Statistical Mechanics : Entropy and Conservation of Information.

- Shoaib Akhtar.

** You can make your prediction with maximum precision
... maximal predictibility.. if you know
- starting point (Inial conditions)
- Laws of evolution of system.

If you have closed system (which is either everything or it is sufficiently isolated from everything else that other things in the system dont influence it)

;- if you know initial condition & you know laws of Evolution of system.
↳ Then you have complete predictability.

* In many cases that total predictability would be useless, example; having a list of position & velocity of every particle in a room would not be very useful to us.. the list would be too long.
↳ and subject to rather quick change is a matter of fact

⇒ So you can see; "While basic laws of physics are very powerful in their predictability, they also in many cases can be totally useless for actually analyzing what is goin on"

⟹ Statistical Mechanics or Probability Theory is then used.

[it is just basically probability theory as applied to physical system *]

↳ it is applied when you dont know the initial condition with complete perfection.
→ It also may be applied if you dont know laws of motion with infinite precision.
↳ It is also applied when the system under investigation is not a closed system.

* In just those situations where ideal predictability is impossible
↳ Then we resort to probabilities.

- but, for example; no. of molecules in the room is so large; and Probabilites tend to become very very precise predictors when laws of large numbers are applicable.

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↳ Statistical mechanics Here can be highly predictable, but not for everything.

example you have a box of gas (isolated)
- has some energy in it.
- particles rattle around.

↳ If you know Temperature, then you can predict Energy, Pressure ~~some things~~ (These things are highly predictable)

↳ but; you cant predict position of ~~one~~ every molecules
- you cant predict when there might be fluctuations of thing which happen which dont really violate probability theory...

(to many of them to keep track off.)

"If you know something about the system, you can predict other things with great precision; but there are some things which you cant predict.

↳ You can predict probability for a fluctuation ; but you cant predict when the fluctuation is going to happen.

example flip a coin billion times
- you can bet approximately half of them come tails, & other heads. within some margin of error.
- but there will also be fluctuations
  ↳ there might come thousands heads in a row
  - can you predict when that thousands heads will come up. NO
  ↳ (but you can predict how often a thousand heads will come ~~up~~ up ... yes .. answer: not very often)

Question: Why probability works?
- The first answer will be it does not always work. (there are exception) 'when it does not .... rarely ... how rarely, every so often)

↳ This we are not going to explain.
↳ Actually nobody could explain why Probability works.

Calculus of Probability / Mathematical Theories of Probabilities.

- now; we will take Probability to take a premitive concept. and we will suppose there is some sort of space of possibilities.

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* Space of possibility can be
  - Space of outcomes of experiments
  - or " " states of system.

Space of state can sometime be outcome space; if the experiment consits of determining the state of system, ~~then space of st~~
↳ Then the state of system is outcome.

so; we have space; & lets lable the elements of that space by "i".

- and if we are ignorant (Statistics always has to do with ignorance) you dont know everything so you assign probabilities to outcomes.

$P(i)$ to i^{th} outcome.

...(in the begining, lets imagine that "i" ~~innumerat~~ innumerates some discrete finite collections of possibilies
↳ later on we can have ∞ no. of possibilities
(we can actually have a continuously ∞ no. of possibilities) so; here; $i = 1, 2, \ldots, N$

* what are the rules $P(i)$ has to satisfy?

Rules
① $P(i) \geq 0$ (we dont like negative probabilities ↳ we dont know what they mean)

② $\sum_i P(i) = 1$ (Total probability should be one) (you should certain get some result of experiment)

③ Its a kind of hypothesis.. The Law of Large numbers.

That; if you either make many replicas of same system or do the same experiment over & over very large no. of times ....and take all of the experiments which gave you i^{th} outcome;
that is some number; let; $N(i)$ denotes numbers of time that the experiment turned up i^{th} possibility.
2 let; N be total number of trials; note; $N = \sum_i N(i)$

its a physical hypothesis; $\lim_{N \to \infty} \frac{N(i)}{N} = P(i)$ ie; $\frac{N(i)}{N} \xrightarrow[N \to \infty]{} P(i)$
(large N)
(in the limit of large N)

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lets suppose there is a quantity $F(i)$ associated with i^{th} state.

example; we could assign; $F(H) = +1$; & $F(T) = -1$ ..

- F is some function of state; it's also a thing which we could imagine measuring; → it could be • energy of state.
  or • momentum " "

Then; Average of $F(i)$ .. denoted by $\langle F(i) \rangle$
(averaged over probability distribution)

defination; $$\langle F(i) \rangle = \sum_i F(i)\, P(i)$$

- Average may or may not be any possible experimental output.

also; you can write it in another way; $$\langle F(i) \rangle = \frac{\sum_i F(i)\, N(i)}{N}$$ in the limit of large N.

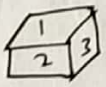
We are also making assumption that states are mutually exclusive.

☆ It is the symmetry of coin which tells that therefore probability of getting (ignoring tiny bias) head or tail is usually deemed to be $1/2$.

- Heads and Tails are symmetrical w.r.t. each other,

↪ so; Symmetry quite often (actually always in some deeper sense) in many cases dictates probabilities.

☆ Probabilities are usually taken to be equal for configuration which are related to each other by some symmetry.

☆ example; dice 

∴ We use the principle of symmetry to tell us that $P(i)$ are all equal
& hence; $P(i) = \frac{1}{6}$.

You may be able to use some deeper underlying theory & to use some concept of symmetry from deeper underlying theory .... but in absense of those things .. you have to get $P(i)$ from experiments.

assume that $\frac{N(i)}{N} \xrightarrow{\text{converge to}} P(i)$; and this way you measure probabilities. (and you can thereafter use them if you want.)

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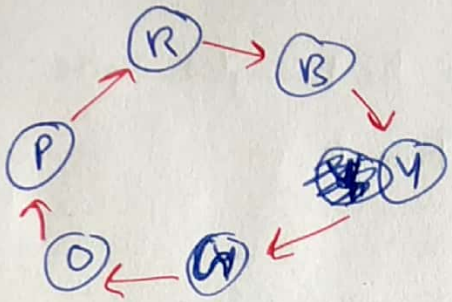
example ; Assume law of ~~motion~~ motion is
(rule of updating configurations)

dice

R → B
B → Y
Y → G
G → O
O → P
P → R

≡



making the assumption now:

that there is a discreate time interval between such events of changing configurations.

~~Here may not be symmetry.~~

↳ now; if this is rule to go from one configuration to other

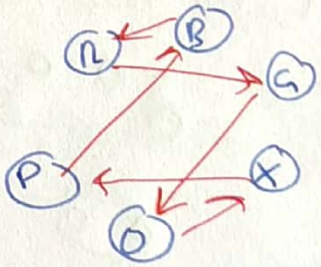
⇒ and my job is now to catch the dice at a particular instant & ask what the colour is.
(I dont know from where it started)

↳ but we can still tell probability of each one of them is 1/6

• it does not have to do with symmetry structure of the die.
↳ it would just be the fact that as it passes through these sequence of states it spends 1/6th of its time in each configuration.

Note here ; the 1/6th does not here depend on detailed law;

for example, the law could have been different ;



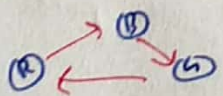
(but this new law shares with the previous law that there is closed cycle of events in which you pass through each colour once before you cycle around)

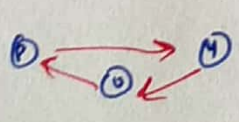
here also; all P(i) = 1/6

So; here ; this prediction of 1/6th does not depend on knowing about starting point and also not on knowing law of physics

↳ but ; it is important to know that there is particular kind of law.

lets write another law.





notice in this case ; if you are in one of the cycle ; you stay there forever.

• if you knew you would started on upper cycle. somewhere; (does not matter where you exactly start)

then you would know; $P(R) = P(B) = P(G) = \frac{1}{3}$ & $P(P) = P(O) = P(Y) = 0$

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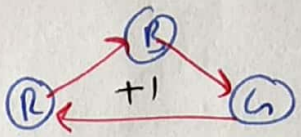
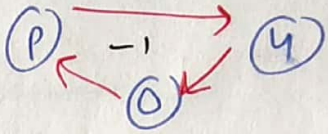
↳ More General Case.

that; you know with some probability that you start on upper triangle
& with some other " " " " " lower " .

infact: lets call give the triangles name;

let; upper triangle be +1 triangle.
lower " " -1 " .





so; you have; $P(+1)$, $P(-1)$ } ⇒ They are probabilities for individual cycles.

This case here is what we call having a conservation Law.

↳ Here; Conservation Law would just be conservation of these numbers +1 or -1.

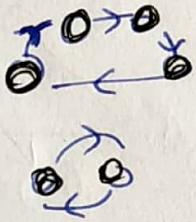
... these assigned +1 or -1 could be analogous or actually could be energy say.
(lets think of it as energy)

maths; $P(B) = P(R) = P(G) = P(+1) * \frac{1}{3}$

$P(P) = P(Y) = P(O) = P(-1) * \frac{1}{3}$

* A conservation law is that configuration space divides up in cycles like this.
(cycles need not have equal size)

example



* Someone has to supply to you some idea about relative probabilities of cycles (where that comes from?
... is actually part of steady of Statistical Mechanics)

↳ and the other part of the steady ~~is that~~ has to do with thing that if I know I am on some cycle; then how much time do I spend with each particular configuration.

This is what determines Probabilities in Statistical Mechanics.

⇒ some apriori probabilities from somewhere that tells you prob. for different conserved quantities
& cycling through the system.

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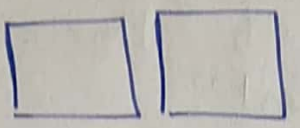
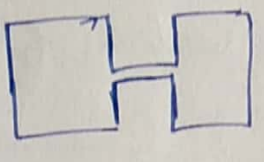
If we have a closed system

it has energy. The energy is some function of the state of the system.

now; lets; have two closed system. 

→ if they are both closed system; there will be ~~two~~ conserved quantities.
∴ energy of both the systems.
(and they are both separately conserved)
↳ because they dont interact with each other (we had assumed this here)

now; lets suppose they are connected. 

; then there is only one conserved quantity, The Total Energy
(and it is sort of distributed between two of them)

→ You can ask; ~~###~~
Given total amount of energy; what is the probability that energy of one subsystem is one thing and energy of other subsystem is other.

- This is a circumstance; where; may be; giving the probability you ran (we are talking about cycles of one of the systems here) may be determined by thinking about system as a part of bigger system.

Conservation of Information.
Its a rule that you can keep track of system both forward and backward.

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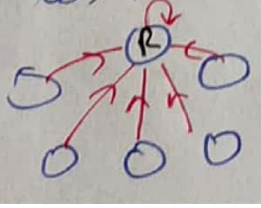
example lets take a bad law. ; Rule is wherever you are you go to Red.



* This law has a feature, that it is not reversible. (in the sense that you can go from Blue to Red; but not from Red to Blue)

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• You can predict the future ; but not the past.

→ It is a bad law ; because you looses track where you started.

☆ It is the most basic law of physics... you may call it minus first of Physics.

that ; " Information is never lost "

↳ i.e; distinctions or differences between states propagates with time ... and you never loose track in principle

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☆ Good law : Every state has one incoming arrow & one outgoing arrow.

• incomming arrow to tell from where you came from.
& • outgoing arrow " " where you will be going.

(In Continuum Classical mechanics ... there is a version of this law ... Liouville's Theorem.)

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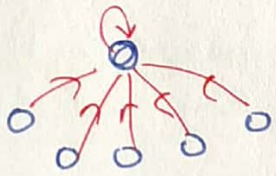
counterexample ; Friction ... wherever you start you come to rest

(its like )

⇒ This seems to be violation that distinction is not preserved.

→ but ; it is not violating actually ;

If when it sliding & friction is heating ; the surface will get heated up ... and if you keep track of every molecule ... you will find out that distinction between starting point is recorded. ∎

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example ; Lets imagine a fundamental law ;

$$\frac{d^2 x_n}{dt^2} = -\gamma \frac{dx_n}{dt}$$

it represents viscous drag.

→ for n^{th} particle

... same problem as above example.

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↳ it also looks a violation of Second Law of Thermodynamics ; that things get simpler..

↳ you start with random bunch of particle moving in random direction ... and you let it run ... and it all comes to rest.

... what you end up with is simpler... and requires less information to describe than what you started with..

There is another way of saying one arrow in & one arrow out.

- Suppose we have collection of states & we assign them probabilities for some subsets of them (and all others we assign zero)

let; you have N states all together. - N ⇒ Total no. of states.

now; we look at M (M<N) ... & we say probabilities for those M state is $P = \frac{1}{M}$ & zero for all the others.

↳ Than number of states which have non-zero probability will remain constant ; and probabilities will remain equal the 1/M. (or be the same)

...(The states may be shuffled ... but the no. of non-zero probabilities will remain fixed)

↳ This is characterization of Information conserving laws.

★ For Information non-conserving law.

... you may start with probability distribution ~~for five states, P, O, Y~~

$\frac{1}{5}$ for each - R, C, P, O, & Y → and than later there is only one state that has probability .. and ~~that's~~ thats R.

~~It's the case of quantifying~~.

We can quantify

let M be no. of states (under the assumption that they all have equal probabilities)

let M be the no. of occupied ~~states~~ states (or) states which have non-zero probabilities. with equal probabilities.

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- M is characterizing our ignorance ; large M ... large ignorance.
  ... if M = N .. maximal ignorance.

- Minimum amount of ignorance you can have ; when you know precisely in what state it is in . ; then M = 1

↘ M is the measure of ignorance
  ↳ and associated to it there is a concept of ignorance.

Note Entropy is comming before everything
(before Temperature, Energy, etc)

↳ Entropy is more fundamental in certain sense than any of them.

$S = \log M$ .... This entropy is conserved.
(all that happens is that states which are occupied are reshuffled, but there always be M of them with prob. $1/M$)

↳ and that's Conservation of Entropy ; if we can follow the system in detail.

⇒ But in reality we may be lazy .. loose track of system
... and we may wind up with little knowledge
(although we started with lot of knowledge)

↳ and this is not because Equations of motion caused information to be lost ; but because we were not just careful.

(perhaps we can't be careful .. there are too many degrees of freedom to keep track of off)

↳ So ; when this happens ; Entropy increases.
(but it simply increases because our ignorance is gone up ... not because anything has really happened in the system)

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- If we could follow it ⇒ we will find that entropy is conserved.

Note: Entropy can't decrease.

- because good laws or equation of motion will never create extra information
  (and there is no way we would get extra information)
  ↳ And certainly we are not just going to add information whatever we like (that will be cheating)

* minimum ignorance corresponds to some 1 in some sense here
  so; $S = \log(1) = 0$; (still it is not negative)

- There is limit to minimum ignorance. (has lower bound)
  ↳ and this in turn bounds entropy (entropy has lower bound)
  ⇒ and it is not going to decrease.

* Entropy approximately measures no. of states which have non-zero probability.
  .... the Bigger it is .. the less you know.

Maximum value of S,
  it is $\log N$; now of course N could be as large as possible (it could be infinite)
  ↳ you might have infinite no. of states.
  (and if you have; then there is no upper bound to the amount of ignorance you can have)

↳ We said that entropy is deep and fundamental ... and so it is but, there is also an aspect to it which makes it in certain sense less fundamental.
↳ "Entropy is not just property of the system;
It is property of system & your state of knowledge of the system"

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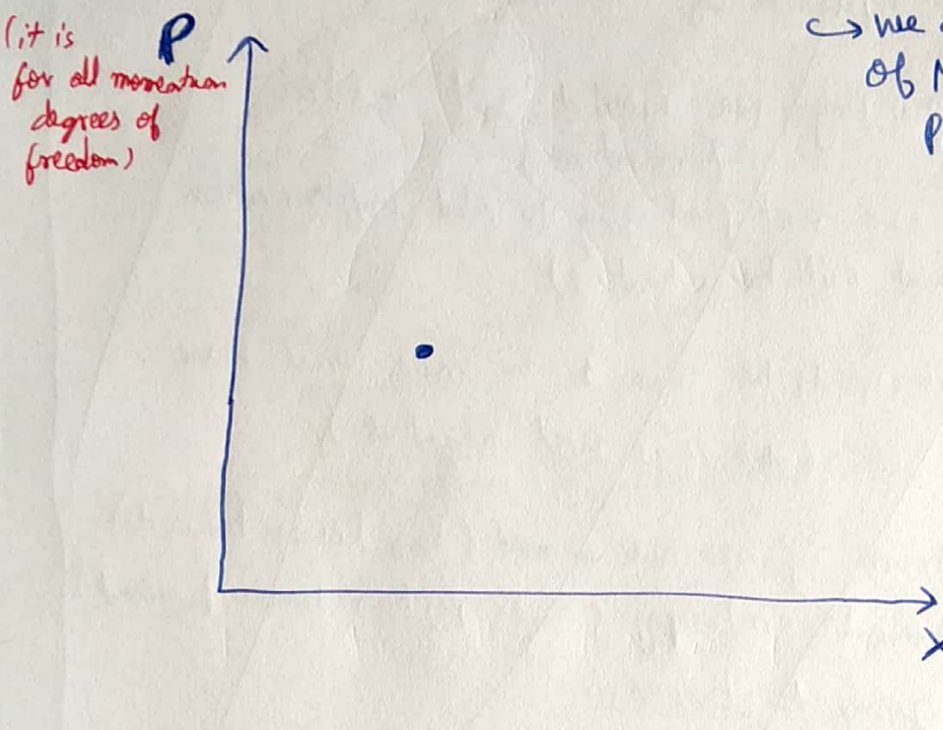
Entropy depends on
- Characteristic of system.
- ~~Your~~ state of knowledge of system.

Continuous mechanical system.

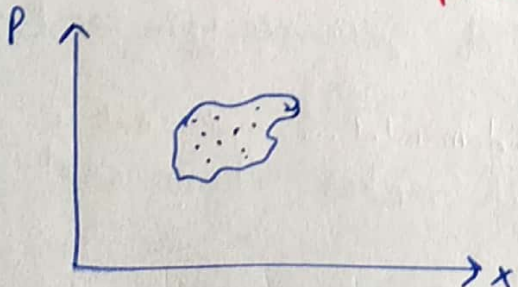
* mechanics of particles moving around.
... with continuous positions & velocities.
↳ we describe the space of ~~states~~ states of Mechanical system as points in Phase space.



lets start with the analogue of probability distribution which is zero for some set of states & constant (or the same) for some other sets.

we can represent that by drawing a patch in phase space
(a sub region in phase space)

↳ and say that; in that sub region, there is equal probability that the system is at any point in there. and zero probability outside.



example • you know all particles are in the room .. puts boundary in space ; ie ; ✱

• you ~~know~~ may know all particles have momentum within some range that confines p ; ie ; p

so: patch bound.

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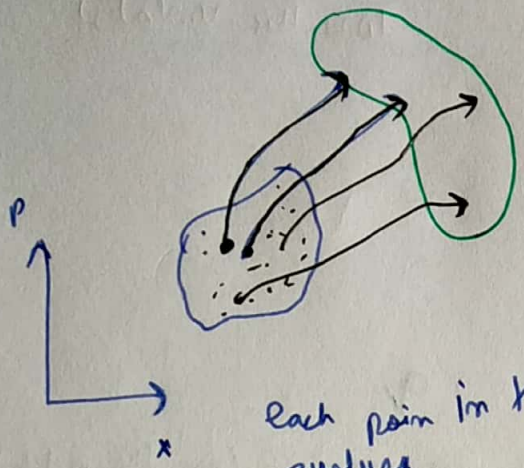
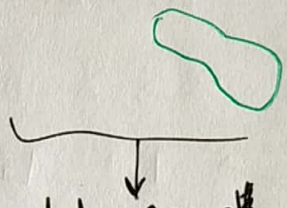
* Now; what happens if system evolves;
.. x & p change.



motion of system with time is almost like fluid flowing in phase space.

each point in the patch evolves.

↳ after certain time; the occupied patch becomes some other patch.



and has equal prob. ~~than~~ to be anywhere in there.

~~and Liouville's Theorem says that~~ that

and Liouville's Theorem says that ; ~~volume~~
↳ whatever the occupied state evolves into,
it evolves into something of the same volume.

↳ In other words; roughly speaking... Same number of states.

(It is the immediate analogue of discreate situation;
where if you start with M state & follow the system according to equation of motion, you will occupy same no. of states afterward as you started with)
↳ Different states... but it preserve the number of them.
& the probabilities will remain equal.

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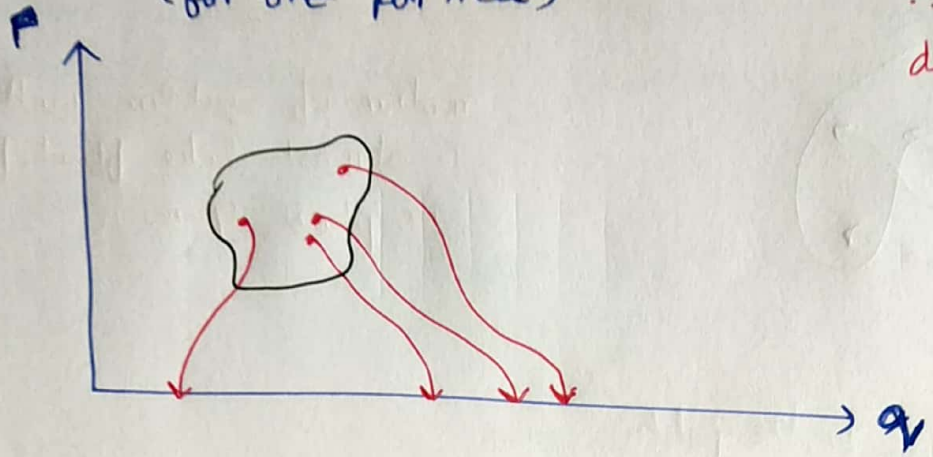
example; imagine that from wherever you started... you ended up $p = 0$. (for one particle)

(this can't happen ... but lets see what does this violates)



⇒ it would then mean that the entire ~~region~~ region (or the patch) would get mapped to one dimensional region.

↳ & one dimensional region has zero area.

↳ but Liouville's Theorem prevents this... so this can't happen.

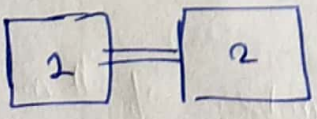
First Law of Thermodynamics.

(First of all, there is a conserved quantity, ... that quantity is called Energy ... but right now the name is not important)

lets, just say that there is Energy conservation. (whatever this energy is ... we will find later)

$$\frac{dE}{dt} = 0 \quad \Rightarrow \text{Law of Energy Conservation for closed system.}$$

* if a system consists of more than one part in interaction with each other then of course any one of the parts can have changing energy ... but the sum total of all of the parts will conserve energy.



so; $\frac{dE_1}{dt} = -\frac{dE_2}{dt}$ (actually; $\frac{dE_1}{dt} + \frac{dE_2}{dt} = 0$)

* here; we have assumed that if a system is composed of two parts, then the Energy is the sum of two parts. (this is really not generally true)

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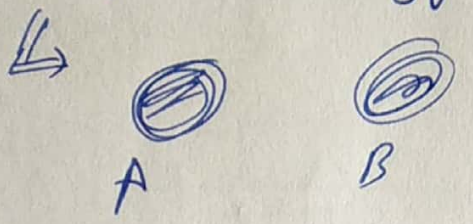
example:

we have two systems & they interact with each other

↳ there may be forces between two parts... There might be potential energy that is function of both the coordinates.



$$E_{Total} = K_A + K_B + V_{AB}$$

K_A: Kinetic energy of A

K_B: Kinetic energy of B

V_{AB}: This term does not belong to either particle... it belongs to both of them in a sense; and its the potential energy of interaction between them.

↳ In this context you can't really say that energy of one thing plus the energy of other thing.

but; ★ Energy conservation is still true.

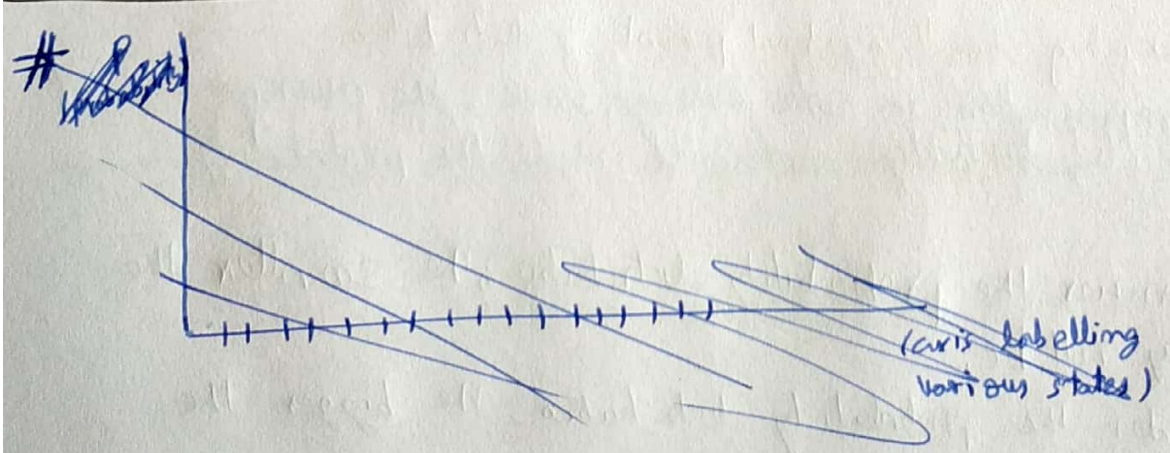
★ Energy is not always additive because ★ in general their might be an interaction term.

NOTICE!! Temperature is a highly derived quantity.

i.e; we mean that despite the fact that the thing which you feel, so it makes it feels that it is something intuitive;

it is actually ฿ mathematically derived concept.

↳ and is less primitive or fundamental than energy or entropy.



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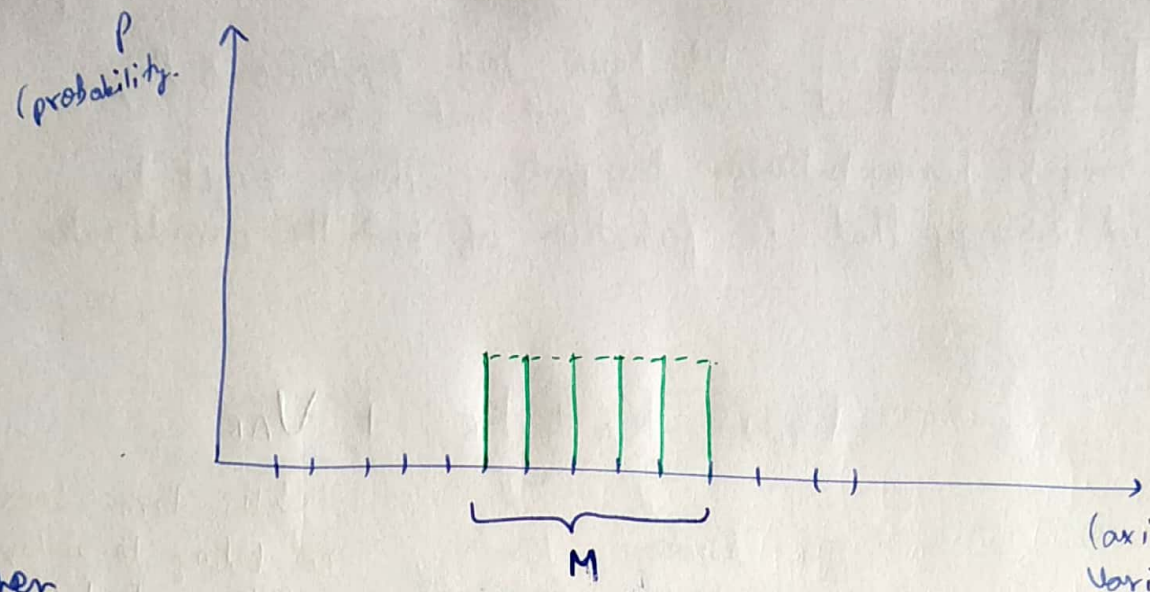
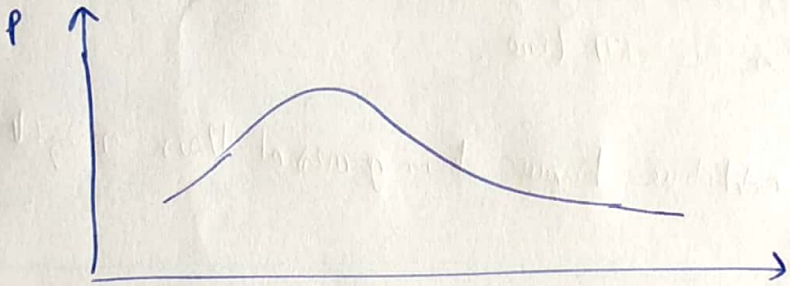


then

$$S = \log(M)$$

↳ but generally speaking we don't have positive distribution like this.
↳ they are in general more complicated.



So; How we define Entropy in more general context.

$$S = -\sum_i P(i) \cdot \log P(i)$$

$\log P(i) \equiv \log_e (P(i))$
↳ the base is "e"

↳ it is representing something about probability distribution.

it is representing in some average sense, the average no. of states which are importantly contained inside the probability distribution

- The narrower the probability distribution; the smaller the entropy will be.
- The broader the probability distribution; the bigger the entropy will be.

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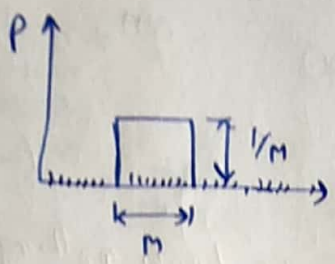
~~Pg 16~~ (Pg 17)

Note!! From the defination of entropy you can also see that it is average of $-\log(P(i))$

i.e. $S = -\sum_i P(i) \log(P(i)) \Rightarrow \boxed{S = -\langle \log P(i) \rangle}$

Example



$$S = -\sum_i P(i) \log(P(i))$$

$$= \underbrace{-\sum P(i) \log(P(i))}_{\text{Terms having non zero } P(i)} + \underbrace{\sum P(i) \log(P(i))}_{\text{terms having } P(i) = 0}$$

So;

$$S = -\sum \frac{1}{M} \log(1/M) + 0$$

$$\Rightarrow S = +M \times \left(\frac{-1}{M} \log(1/M)\right)$$

$$= -\log(1/M) = \log(M)$$

(Reduced to the initial trivial defination)

$\therefore$ ~~$\log(x) \cdot x$~~

note:

$$\lim_{x \to 0} x \cdot \log x = 0$$

↳ so; this implies ... contribution from states with very very small probability will be very-very small.

NOTICE!! Entropy is associated with probability distribution.

↳ Its not a thing like energy which is only property of system.

↳ It is the think which has to do with specific probability distribution on space of possible states.

☆ The defination Entropy has to do with both ~~of~~

- the system
- & your state of knowledge about the system.

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Example: System of lot of coins.

O O O O O O O O O O

we have N coins

case I: Each one can be Head or Tail.

under circumstances when all prob. are equal

~~... so; $S = \log(2^N)$~~

2^N is total number of states

So; $S = \log(M) = \log(2^n)$ So: $M = 2^n$ (actually here $M = N$)

$S = n \log(2)$

↳ entropy when we know nothing (complete ignorance ...) (maximum entropy)

Here we see an example of the fact that entropy is proportional to no. of degrees of freedom in this case. (no. of degrees of freedom here is n)

- and we also discover a unit of entropy;

Unit of entropy is called Bit.

★ Bit is basic unit of entropy for system which has only two states.

So; log 2 plays a fundamental role in information theory as unit of entropy.

(in general it does not mean that entropy is always an integral multiple of log 2)

★case II: Suppose we know state completely

So; in that case; $M = 1 < N$; so; $S = \log(M) = 0$

↝ so; absolute knowledge corresponds to zero entropy.

(perfect or complete knowledge)

"The more you know, the smaller is the entropy"

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☆ Case III Suppose we know; it contains (n-1) heads & 1 tail.

So; What is Entropy;

So; there are ${}^{n}C_1 = n$ states with non zero probability.

So; $M = n < N$; So; $S = \log(n)$

"In general entropy is not integral multiple of $\log 2$; nevertheless $\log(2)$ is basic unit of entropy ; its called as bit."

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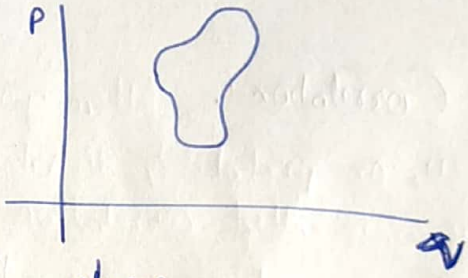
in Defination of Entropy in Phase space.

- Continuously infinite system.

$$S = \log V_{PH}$$



; V_{PH} is phase space volume.
(The volume of the region which is occupied and has non zero probability distribution)

→ This is the closest analogue that we can think of to $\log(M)$ where M represents no. of equally probable states of discreate system.

☆ now; if we have some arbitrary probability distribution. P
P will be function of all of the coordinates & all of momenta (basically, all of the independent variables of phase space)

$P(p, q)$

~~or say; $P(p_i, q_i)$~~

So; incidently; obviously $\sum P(p,q) = 1$ ...will not make sense
(you cant sum over infinitely set of variables)

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it becomes integral ; $\int P(p_i, q_i) \cdot d^D p\, d^D q = 1$

where; 2D is dimensionality of phase space.

So; we expect entropy to be ... & it is.

$$S = -\int d^D p\, d^D q \cdot P(p_i, q_i) \cdot \log\left(P(p_i, q_i)\right)$$

$$S = -\sum_i P(i) \log(P(i))$$

☆ Correlation : When you measure something, you learn something new, or probability distribution for the other thing is modified. This is called correlation

- For complete ignorance, there is no correlation.
- For any other kind of configuration in general, there is very likely to be some (not necessarily) correlation.

ex: Complete ignorance ○ ○ ○ ○ ○ ○ → n coins.

⇒ If you measure one coin to be Head ... you dont know anything about other. (uncorrelated.)

---

ex (n-1) is head; & one tail (It is correlated)

case I If you measured one Head; so; new probability that one of the other one is tails is $\frac{1}{n-1}$ (initially it was $1/n$)

↳ it changes probability distribution.

case II : If you measured one Tail; ⇒ Then you know all others are Head.

↳ gives complete knowledge .... (Like Entanglement)

☆ Entropy is additive whenever there is no correlation. (uncorrelated systems have additive entropies) ex complete ignorance: $S = n \cdot \log 2$

$$= \sum_{i=1}^{n} \log 2$$

ex (n-1) tail & one tail is correlated

So; Entropy is not additive here; its $S = \log(n)$

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Boltzmann factor ; speed of light ..... many constants in physics are conversion factor.

Speed of light ⇒ conversion factor from distance to time.

★ Kelvin understood that the natural units that temperature has to do with is energy.

eg: Temp. of gas determines kinetic energy of molecules.

★ Natural unit of temperature is Energy.

eg Joule can be a unit of temperature (it is rather large unit)

↳ The conversion factor from human units of temperature to basic units of energy would be some small or large (reciprocal of the small) number.

↓

like; Celcius; etc.

$$E = \frac{3}{2} \times k_B \times t_K$$

; 3 ⇒ has to do with dimension of space.

$\frac{1}{2}$ ⇒ just a glitch of defination

E = kinetic energy of molecule in dilute gas

k_B = conversion factor ↳ i.e; Boltzmann Constant

t_K = human scale of temperature (in Kelvin here)

$$k_B = 1.4 \times 10^{-23} \frac{J}{K}$$

(it is not an accident that Avagadro number is roughly $\sim 10^{23}$)

★ In all of fundamental physics : temperature always comes in with k_B multiplied to it.

(In all fundamental formulas of physics)

↳ And that's because ; the fundamental quantity is really energy.

★★ We will define a new unit of temperature "T" i.e; $T \equiv k_B t_K$ ⇒ once we do this ; we will get rid of k_B in all equations.

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S_{CARNOT} ; Carnot had a quantity which he called Entropy. (or say "steam engine units")

$E = t \cdot s$

Joules per Kelvin was Carnot's unit of entropy.

⇒ In modern physics; we think of entropy as being measured in bits (A fundamental unit of entropy is log 2 for example)

There is a conversion from Scarnot to Statistical defination of entropy.

$$\underbrace{S = -\sum p_i \log(p_i)}_{\text{Boltzman Entropy}}$$

(statistical defination... "modern")

⇒ This is dimension-less.

$$S = -\sum p_i \cdot \log(P_i) = \frac{1}{k_B} \cdot S_{CARNOT}$$

S_{carnot} ; Kelvin ⇒ can be thought off as human units (convinient for humans to have a measure)

S ; T ⇒ are fundamental or natural units.

---

* Boltzman never knew precise value of his constant (he had rough idea ; and he knew it was related with Avagadro number)
* Newton also did not know the value of his constant.

Boltzman did understand that only if he could measured the properties of atoms ; that energy would be related to temperature through his constant.

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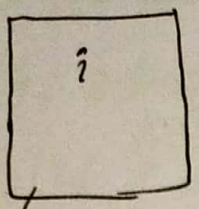

Environment

↳ System with many degrees of freedom

: System has collection of states; lets label it by i.

↳ & each state has energy E_i

When a system comes to equilibrium; it does not come to a particular state. It may interact with its environment. Energy may go back & forth.

↳ But on the average; in equilibrium: there is some probabilistic ideas that system is in i^{th} state; $P(i)$ with energy E_i.

∴ Rules on $P(i)$

$$\sum_i P(i) = 1$$

$$\sum_i P(i) \cdot E(i) = \langle E \rangle \} \Rightarrow$$

when we say average; what we really have in mind is that the energy is constantly changing. It fluctuates. Goes back & comes in from the environment - but over short times; it averages.

---

* $P(i)$ depends on the average energy of system.
* Average energy may depend on nature of environment. (hotter, colder...)

↳ Average energy can be thought off as a parameter. (you can heat it, put on stove ... cool environment ...)

so you can change the average energy; and in that sense;

$P(i)$ depends on average energy: let $E = \langle E \rangle$

$\Rightarrow P(i, E)$

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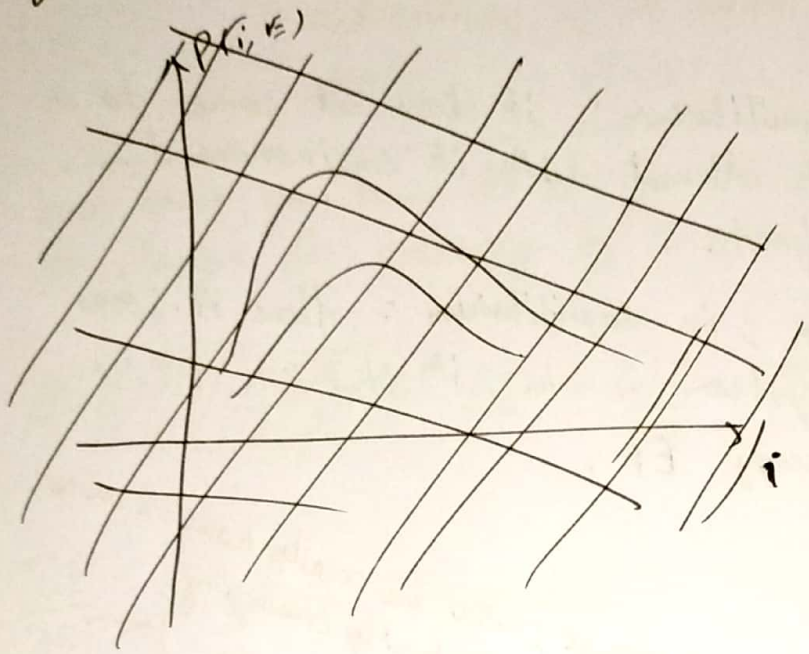
* If you increase $\bar{E}$; then you tilt the probability distribution towards larger energy values of E;

(L) this means that there is not a single probability distribution that you call equilibrium : There is a family of them for each value of $\bar{E}$.

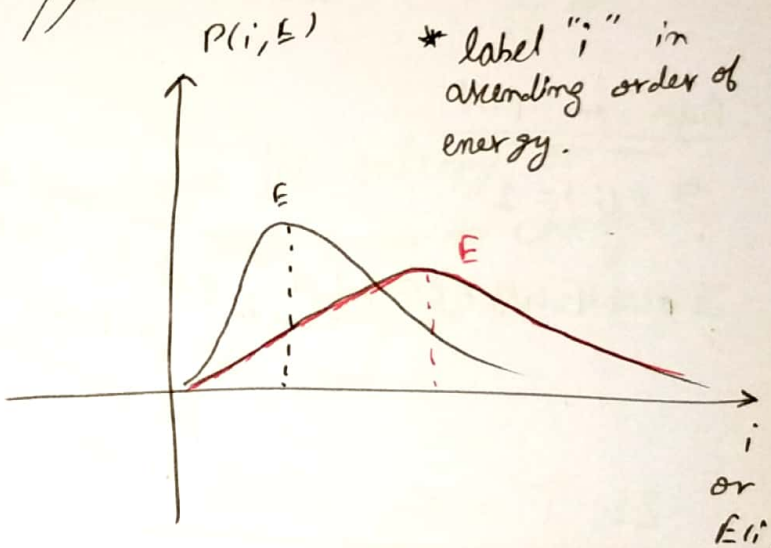


~~* For energy~~

* For every value of energy ; there is a probability distribution.

$$\sum_i P(i,E) = 1$$

$$\sum_i P(i,E)\, E(i) = \bar{E}$$



* label "i" in ascending order of energy.

The area under curve must be the same

$\therefore$ $\bar{E} > E$ (curve peaked to the right has more E)

There is one parameter of family of equilibrium distribution like this. ...
(we can take the parameter to be $\bar{E}$ (as we took here for analysis))

⇒ We are now doing just a mathematical exercise : There is one parameter family of ~~each~~ probability distributions parametrized by the average energy. No two of them has same average energy by assumption. And higher the $\bar{E}$ is ; the broader the probability ~~dist.~~ distribution is likely to be.

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for each value of E; there is entropy.

∴ So; entropy now becomes a function of E.

$$S(E) = -\sum_i P(i,E) \log\left(P(i,E)\right)$$

~~so i~~ so; we see that there is connection between average energy and entropy if we know this one parameter ~~family~~ family. $P(i,E)$...

How much you have to change the average energy in order to change the entropy by 1 bit ;i.; $\log 2$.

$$\Delta E = \frac{\partial E}{\partial S} \cdot \Delta S \quad ; \text{or} \quad \Delta S = \frac{1}{\frac{\partial E}{\partial S}} \cdot \Delta E$$

$$= \frac{\partial S}{\partial E} \Delta E$$

$\frac{\partial E}{\partial S}$ is called Temperature

↳ Tells how much you have to change the entropy or; how much you have to change energy in order to change the entropy by a certain amount. ... as long as the change is small.

∴ defination of Temperature is such that; $dE = T \cdot dS$

note; $dE = T \cdot dS$

$= t_k \, dS_{carnot}$ (Boltzman constant gets cancelled)

★ It is typical for normal physical system that Entropy & Energy are monotonic ... that is; when you increase the energy you usually increase the width of probability distribution; and in so doing increase the entropy.

★★

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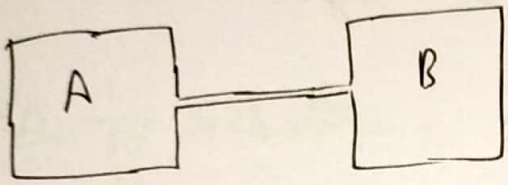
So; we are going to assume; Energy and Entropy are monotonically increasing functions of each other; singled valued.
We can come later & ask if that is always true.
No. But when it is not true .. they are unusual situations.

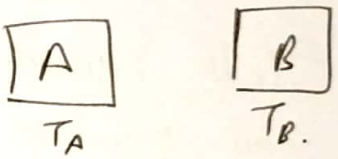
$\Rightarrow$ T is positive $\quad \frac{\partial E}{\partial S} > 0$ (assumption for the moment)

Lets have two systems A & B.

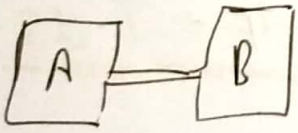


A & B are connected by a thin pipe.
This pipe means that they can exchange energy with each other but weakly.

Initially A & B are not connected. Each of them are at equilibrium but at different temperature



Now allow them to exchange energy ... connect them.



Which way the energy flows?

↳ This is the most basic concept of temperature ... Heat (or energy) will flow from ~~higher~~ hotter (or system of higher temperature) to the System of lower temperature.

when $T_A = T_B$; heat does not flow either way on the average.

∴ ~~Assume~~ ~~Proof without loss of generality~~ ; $T_A > T_B$

Second Law of Thermodynamics : When you allow the systems to come to thermal eqm ; when you allow A & B to equilibriate : the entropy increases.

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$S = S_A + S_B$ (why entropy is additive ... because it is logarithm of something .. & probability is multiplied $P_A P_B$ ... & when you take log .. it adds)

"Entropy is additive"

First Law of Thermodynamics : when system equilibriates by changing energy ; the total energy is conserved.

$dE_A = -dE_B$

if energy of A increases; the energy of B decreases by same amount.

Second Law of Thermodynamics

(we will justify this later)

$dS_A + dS_B > 0$

$\therefore dE_A = T_A dS_A$

$dE_B = T_B \cdot dS_B$

Definition of Temperature.

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(Pg 28)

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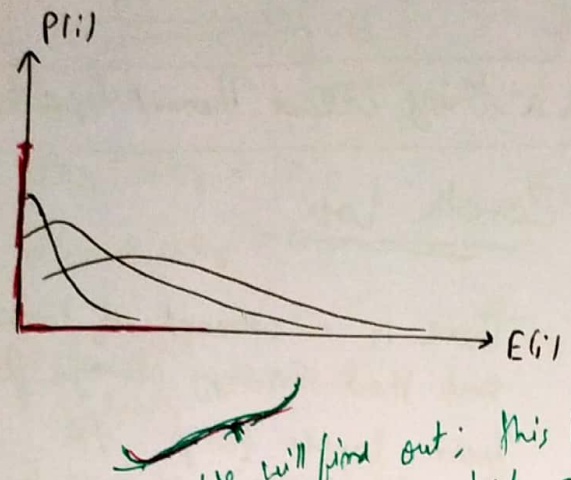
 Statistical Mechanics : Maximizing Entropy —Shoaib Akhtar

$S = -\sum_i P(i) \log P(i)$ definition

$P(i)$; $\sum P(i) = 1$

$E(i)$; $\sum P(i) E(i) = \langle E \rangle$



We will find out; this is exactly the picture which governs the probability distributions of states in thermal equilibrium.

We can invent a probability distribution which gets narrower as it moves to the right (as $E \uparrow$) but as we will see the probability distributions that govern thermal eqm are not like that

~~Thermal equilibri~~

Thermal equilibrium can be characterized by temperature (or) by Average Energy.

In thermal eqm ; heat tends not to flow.

The probability distribution for given average energy do in fact tend to broaden as energy goes up so that entropy is monotonically increasing function of energy .. average energy - E.

When people were axiomatizing thermodynamics ; the Zeroth law came in before almost anything else.

... today we think Zeroth law as a consequence of first law & second law in a sense.

He will prove ... If you have a probability distribution & you allow it to evolve being a little bit careless (called coarse graining)

we will find probability distribution always broadens.

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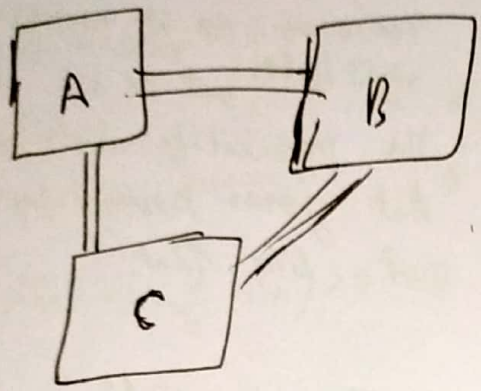
If you have large system. And it is difficult to keep track of everything ... so you loose track of things; so the probability distribution tends to broden; and this is the increase of entropy with time.

Zeroth law asserts that there is such a thing called Thermal Equilibrium.



Zeroth Law

There is a concept of temperature such that Energy always flows from larger temp. to smaller temp. if the system is not in equilibrium.

... untill they equilibriate
i.e. Temperature becomes equal.

$A \overset{eqm}{\sim} B$ & $B \overset{eqm}{\sim} C$

$T_A = T_B$ $\quad T_B = T_C$

$\Rightarrow A \overset{eqm}{\sim} C$

$T_A = T_C$

Zeroth Law

(i) There is a notion of temperature.
(ii) Energy flow from higher temp. to lower temp.
(iii) In thermal equilibrium; the temperature of all parts of the system is same.

(if the temp. was not the same in all parts of the system, then energy will flow untill it became the same)

existence of Temperature function which tells which way energy flows.

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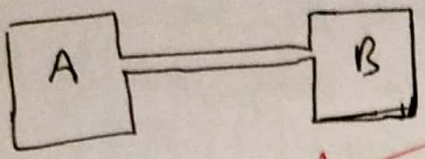
What does the defination "$\tau = \frac{\partial E}{\partial S}$" has to do with the idea of flow of heat?

$T_B > T_A$ without loss of generality.



→ First Law: Energy conservation

$dE_A + dE_B = 0$

$dS_A + dS_B > 0$ → Second Law: Entropy Increases.

we have; $dE_A = T_A dS_A$

$dE_B = T_B dS_B$

$\Rightarrow \quad T_A dS_A + T_B \cdot dS_B = 0$

$\Rightarrow \quad dS_B = -\frac{T_A}{T_B} \cdot dS_A$

$\therefore \quad dS_A + \left(-\frac{T_A}{T_B} dS_A\right) > 0 \quad \Rightarrow \quad \left(1 - \frac{T_A}{T_B}\right) dS_A > 0$

$\Rightarrow \quad T_B \cdot dS_A - T_A dS_A > 0$

$\Rightarrow \quad (T_B - T_A) dS_A > 0$

we will assume; Temperatures are positive unless otherwise there are situations where it can be negative

$\therefore$ since $T_B > T_A \Rightarrow \underline{dS_A > 0}$

$\therefore$ if $T_A > T_B \Rightarrow \underline{dS_A < 0}$

$T_A dS_A > 0$

$\Rightarrow \underline{dE_A > 0}$

it follows: $dE_B < 0$

⇓

Energy (or heat) has flowed from B to A.

so; The defination of temperature as given "$dE = TdS$"; that the temperature is such that it defines a direction of ~~Heat~~ heat flows.

☆ There is no flow of energy when $T_A = T_B$.

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Zeroth law of thermodynamics; i.e. Temperature determines the direction of heat flow.

When heat flow stops because the system comes to eqm; it must be that the temperature is same in every part of the system.
Conversely; if the temp. is not the same in every part of the system; heat will flow untill it becomes the same.

A state means; as much as you can possibly know about the system if you had infinite precision.

↪ There may limits that have to do with fundamental rules of physics such as Quantum Mechanics .... but still; a state means as much as can be known about a system by an infinitely precise observer. (powerful observer)

Imagine your system is not closed; but in contact with outside world & can exchange energy with it.

* Think of the system as being embedded in huge reservior (the environment)

of much larger degrees of freedom ... that provide a Heat Bath; which allows energy to flow back and forth untill the system in question comes to thermal equilibrium with the big heat bath.

The heat bath is so big that even a little bit of energy flows from into the subsystem, the temperature does not change much.

↪ we can imagine that the big system is at some Temperature; and simply wait untill the small system is in equilibrium with the big system.

Particularly convinient choice of heat bath; is just to imagine that the system in question is one of a very large number of identical systems which are connected together by little pipes which allow heat to flow back and forth.

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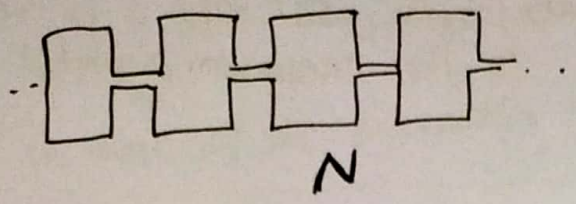
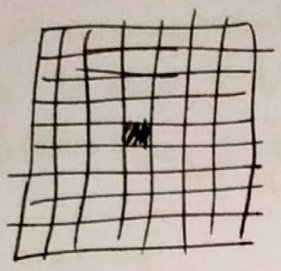


one of them is the system that we are studying; the rest of them simply provide the heat bath.

(or)



"This is a useful trick to pretend that the heat bath is just a ~~repeating~~ repeatation of same system over and over again"

States labelled by i

Occupation Number is the number of systems occupying the i^{th} state.

n_i ⟹ these are no. of replicas of the system which are found in i^{th} state.

How many ways are there for redistributing the systems among the states for given sets of n_i.

$n_i = \{n_1, n_2, n_3, \ldots\}$

Given the occupation no.; how many ways are there of redistributing the states so as to create that set of occupation number.

↳ Obviously this will be closely connected with probabilities for the state "i".

"The more ways there are of distributing the system into a given set of occupation numbers; the more likely that set of occupation number is. This is symmetry argument. of all possible ways of redistributing things are symmetric w.r.t. each other & equally likely; than the most probable configuration (which means the

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most probable set of occupation numbers) is the set of occupation numbers which gives rise to the maximum number of ways of redistributing things.

There are constraints.

① $n_1 + n_2 + n_3 + \ldots = \sum_i n_i = N$ ⇓ Total no. of systems.

② $n_1 E_1 + n_2 E_2 + \ldots = \sum n_i E_i =$ Total energy.

Lets assume that Total energy is proportional to N;
we are going to study the system making more & more replicas .... it is clear; as we double no. of replicas the total energy is doubled if at least we want to keep things fixed within a given box.)

we can expect; $\boxed{\text{Total energy} = NE}$

E is average energy per subsystem.

So; Total energy is $\underline{NE}$

$$\Rightarrow \sum_i n_i E_i = NE$$

∴ lets define; probability $P(i)$; that any one of the subsystem is in state i to be

$$P(i) \equiv \frac{n_i}{N}$$

⇝ now; rewriting the constraints in terms of $P(i)$

$$\sum_i n_i = N \implies \sum_i P(i) = 1$$

$$\sum_i n_i E_i = NE \implies \sum_i P(i) E(i) = E$$

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assume ; N is finite (very large although) & there are infinite no. of energy levels.

⇒ sb: most of the occupation numbers are going to be zero.

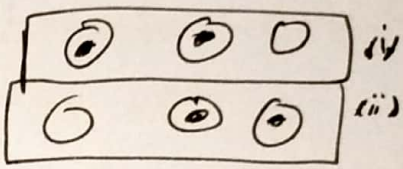
No. of arrangements in order to keep the set of occupation no. fixed $= \frac{N!}{n_1!\, n_2!\, n_3! \cdots} = \frac{N!}{\prod_i n_i!}$

→ with no regard whether the constraints are satisfied.

note: $0! = 1! = 2$

example $n_i = (N, 0, 0, \ldots) \Rightarrow$ Ans 1

example $n_i = (1, 1, 0)$ $N = 2$ $\Rightarrow$ Ans $\frac{2!}{1!\,1!\,0!} = 2$.



Approximate factorials $N!$ when N is very big.

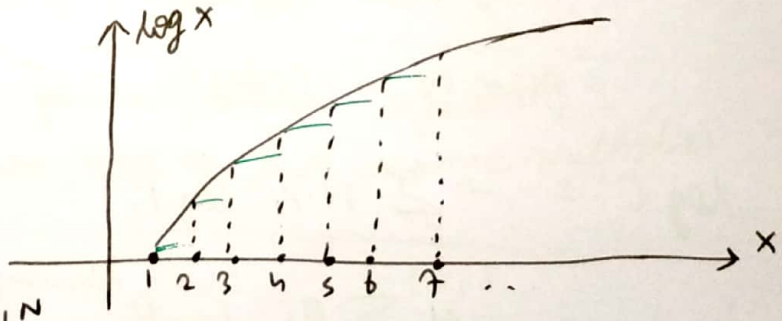
We allow N to go bigger & bigger; & so all the n_i gets bigger & bigger :⟹ we will assume; all the n's are very big.

Standard Approximation for Factorials

Stirling Approximation $\quad N! = N^N \cdot e^{-N}$ (for large N)

∴ proof $\quad \log N! = \sum_{n=1}^{N} \log(n)$

$$\approx \int_{x=1}^{N} dx \cdot \log x$$



$$\Rightarrow \log N! \approx (x \log x - x)\Big|_{x=1}^{N}$$

$$= N \log N - N \quad \text{(neglect "+1" here)}$$

$$\Rightarrow N! \approx N^N \cdot e^{-N}$$

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we will look for set $\{n_i\}$ which will maximize

$$C := \frac{N!}{\prod n_i!}$$; but subject to two constraints.

$$\sum n_i = N$$

$$\sum n_i E_i = E_T$$

∴ maximizing a function is same as maximizing its logarithm.

~~$\log\left(\frac{N!}{\prod n_i!}\right) \neq \log N! - \log \prod n_i!$~~

lets use stirling approximation. $\therefore \frac{N!}{\prod n_i!} = \frac{N^N \cdot e^{-N}}{n_1^{n_1} n_2^{n_2} \cdots \cdot e^{-n_1 - n_2 - n_3 - \cdots}}$

$$= \frac{N^N}{\prod (n_i)^{n_i}}$$

$P(i)$ is probability for a given system to be in the state "i".

$$\log(C) = N \log N - \sum_i n_i \cdot \log n_i$$

we know; $P(i) = \frac{n_i}{N}$

$\Rightarrow n_i = N P(i)$

$$\Rightarrow \log(C) = N \log N - \sum_i N P(i) \log(N \cdot P(i))$$

$$= N \log N - \sum_i N P_i (\log N + \log P_i)$$

$$= N \log N - \sum_i N \log N P_i - \sum_i N P_i \cdot \log P_i$$

$$= N \log N - N \log N - \sum_i N P_i \log P_i$$

$$\Rightarrow \log C = -\sum_i N \cdot P_i \cdot \log P_i$$

$$= -N \sum_i P_i \cdot \log P_i$$

$$= +N \cdot S$$

; where; S is entropy of any one of the system.

so; Maximizing $C \Rightarrow$ Maximizing $\log C \Rightarrow$ Maximizing Entropy.

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The occupation no. which maximizes the no. of ways that you can rearrange the system (keeping the occupation no. fixed) simply corresponds to maximizing the entropy.

∴ Now ; maximize entropy subject to constraints

$$\Sigma P(i) = 1$$
$$\Sigma P(i)\, E(i) = E.$$

maximize $\log C$ or entropy with respect to choice of occupation numbers $\{n_i\}$; which translates into maximizing entropy w.r.t. probability distribution.

"The most probable distribution of occupation numbers $\{n_i\}$ corresponds to probabilities which maximizes the entropy"

★ it is the constraint $\Sigma P_i E_i = E$ which breaks the symmetry between different states.

Mathematical Problem

Find $\{P_i\}$; which gives maximum value for $-\Sigma P_i \cdot \log P_i$

given that $\Sigma P_i = 1$ & $\Sigma P_i E_i = E$

We need the mathematical concept of Lagrange multipliers.

"We will find that many of the thermodynamical quantity ; such as Temperature ; are nothing but Lagrange multiplier."

---

given a function of set of coordinates $\{x_i\}$: $F(x_i)$

∴ find $\{x_i\}$ which make F maximum.

↳ we solve $\frac{\partial f}{\partial x_i} = 0 \quad \forall\ i$

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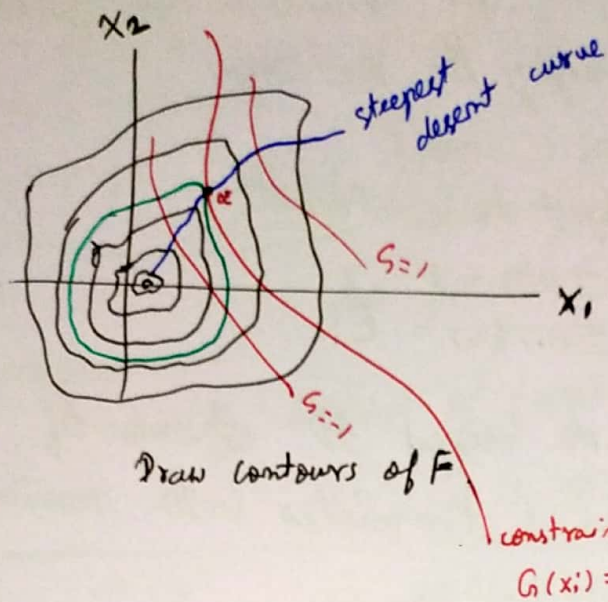
ex x_1, x_2 ; $F(x_1, x_2)$



Draw contours of F.

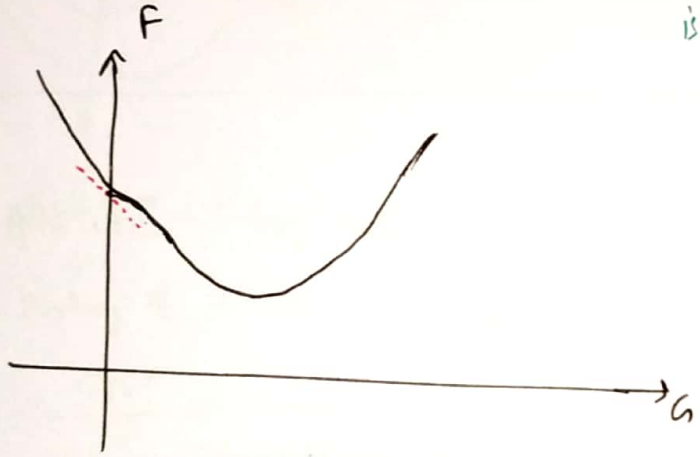
constraint $G(x_i) = 0$

Lets here ; add a constraint : $G(x_i) = 0$

and we are looking for F along the curve $G=0$.

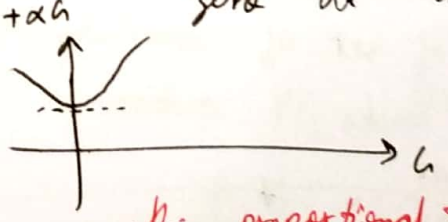
; and ask where F is maximum along the constraint surface.

↳ you can see that it happens at the point where level surface is tangent to $G=0$.



(move along steepest descent curve)

Add to F something proportional to G. ⇒ so; you can make derivative zero at $G=0$



↳ so by appropriate choice of adding something proportional to G you can actually make the point ($G=0$, F level tangent to $G=0$) a minimum of the new function.

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The new function $(F)' = F + \lambda G$.

[λ is a number chosen to make the derivative flat at $G=0$]

$F(x_i) + \lambda G$ — There is some "λ" which will make this whole function here stationary at the point "α" we are looking for.

Method of Lagrange multiplier

λ is called Lagrange multiplier.

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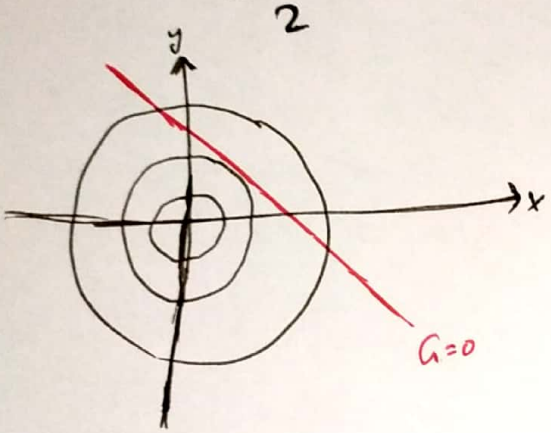
example $F = \frac{x^2+y^2}{2}$ minimize F given that $x + y = 1$



$G = x+y-1 = 0$

$F = \frac{x^2+y^2}{2}$

$\therefore$ rule; $(F)' = \left(\frac{x^2+y^2}{2}\right) + \lambda (x+y-1)$

thinking of λ as known thing $\Rightarrow$ minimize $(F)'$

$$\frac{\partial (F)'}{\partial x} = 0 \quad \& \quad \frac{\partial (F)'}{\partial y} = 0$$

$\therefore \frac{\partial (F)'}{\partial x} = x + \lambda \quad \therefore \frac{\partial (F)'}{\partial y} = y + \lambda \Rightarrow x + \lambda = 0$ and $y + \lambda = 0$

$\Rightarrow x = -\lambda$ & $y = -\lambda$

$G=0$

$\Rightarrow x+y=1 \Rightarrow -\lambda - \lambda = 1 \Rightarrow \boxed{\lambda = -1/2}$

$\Rightarrow x = 1/2, \; y = 1/2$

If we have more variables & more constraints $G, H,$

So; $(F)' = F + \lambda G + \mu H + \ldots$

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ex $F = \frac{x^2+y^2-z^2}{2}$; $G_1 : (x+y) = 2$

$G_2 :$ ~~$(y^2$~~ $(z+x) = 2$

we want to find min (F) subject to constraints G_1 & G_2.

$(F') = F + \lambda_1 G_1 + \lambda_2 G_2)$

minimize (F') ; $\frac{\partial F'}{\partial x^i} = 0$ & $G_1 = 0$ & $G_2 = 0$

$F(P_i)$
(or better say $S(P_i)$) ; Constraints $G_1 : (\sum_i P_i) - 1 = 0$

$G_2 : (\sum P_i E_i) - E = 0$

maximize F as a function of all of probability

⟺ it will give probability distribution as a function of "i" that corresponds to the most likely possible value for the occupation number.
(The occupation number tends to cluster around this value)

$S(P_i) = -\sum_i P_i \cdot \log P_i$ } ⇒ You are going to shift around P_i's to maximize S.

" Vary the probability distribution until you find that probability distribution $\{P_i\}$ which maximizes the entropy (S) "

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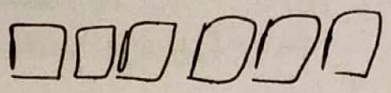
 Statistical Mechanics: The Boltzmann distribution — Shoaib Akhtar.

$S = -\sum_i P_i \cdot \log P_i$; $S(\{P_i\}) = -\sum P_i \log P_i$

constraints 1) $\sum P_i = 1$ 2) $\sum P_i E_i = E$ Total energy is NE.

E is average energy per box.



$\Rightarrow -S = +\sum_i P_i \cdot \log P_i$; we will talk about minimizing "$-S$" rather than maximizing "S" (They are same thing)

↳ It is our linguistic habit of talking about minimizing something.

∴ so; we talk about minimizing "$-S$" subject to constraints.

$\therefore F(P_i) := -S(P_i) = \sum_i P_i \cdot \log P_i$; constraint equations

$\sum P_i - 1 = 0$

$\sum P_i E_i - E = 0$

$\therefore$

$$(F)' = F + \alpha\left[\sum_i P_i - 1\right] + \beta\left[\sum_i E_i P_i - E\right]$$

we will have two lagrange multiplier α & β for each of two constraints equations

E is a fixed constant that is determined once and for all by the energy supplied for the whole collection of identical systems.

when we differentiate; 1 & E dont give any contribution.

(they are constants)

↳ So we can throw them away & have the following $(F)'$

$$\Rightarrow F' = F + \alpha \cdot \sum_i P_i + \beta \sum_i E_i P_i$$

$$\Rightarrow F' = \sum_i P_i \log P_i + \alpha \sum_i P_i + \beta \sum_i E_i P_i$$

It is very fortunate that each term is a sum; each term of which contains only one of the P's !

$$\Rightarrow F' = \sum_i \left(P_i \log P_i + \alpha P_i + \beta E_i P_i \right)$$

$$\Rightarrow \frac{\partial F'}{\partial P_i} = \log P_i + P_i \cdot \frac{1}{P_i} + \alpha + \beta E_i$$

$$\Rightarrow \boxed{\frac{\partial F'}{\partial P_i} = \log P_i + 1 + \alpha + \beta E_i}$$

now; $\frac{\partial F'}{\partial P_i} = 0$

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$\Rightarrow \log P_i = -(1+\alpha) - \beta E_i$

$\Rightarrow P_i = e^{-(1+\alpha)} \cdot e^{-\beta E_i}$

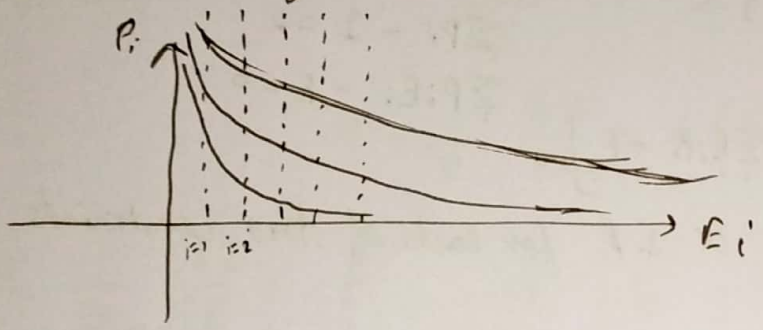
$\Rightarrow \boxed{P_i = \frac{e^{-\beta E_i}}{Z}}$

standard name of $e^{(1+\alpha)}$ is called Z in statistical mechanics

$Z := e^{(1+\alpha)}$

Relative probability of different states is $e^{-\beta E_i}$.

note!! β must have some physical significance. It is the only variable in here that has any chance of telling us what the average ~~en~~ energy is.



Bigger the β
$\Rightarrow$ Faster the P_E falls off.
(and vice versa)

What are these different curves going to be parametrized by? It is going to be parametrized by β; but it can also be parametrized by average energy

$\therefore$ It is quite clear: ~~The~~ The further out the curve is
; i.e; for bigger β ; ~~bigger~~ smaller the average energy is.
; for smaller β ; larger the E

$\Rightarrow$ so; "β" has something to do with energy.
It is the thing which you tune to change the average energy.

$\therefore$ ~~Partition~~ $\sum_i \left(\frac{1}{z} \cdot e^{-\beta E_i}\right) = 1$

From where do the E_i come from?
* There are some laws of physics that had to do whatever is inside the box that tells you what are possible energy level.

We will take this to be known.
↳ Someone has calculated all the energy levels for us.

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$\Rightarrow \boxed{\sum_i e^{-\beta E_i} = Z}$ $\quad ; Z(\beta) := \sum_i e^{-\beta E_i}$

Sum over all states

Partition Function.

"It fits in the probability distribution as a kind of normalization constant which makes sure that total probabilities add up to 1"

$\therefore \sum_i \frac{1}{Z} \cdot e^{-\beta E_i} \cdot E_i = E$ $\Rightarrow$ This is an equation β in terms of average energy E.

$Z = \sum_i e^{-\beta E_i} \Rightarrow \frac{\partial Z(\beta)}{\partial \beta} = -\sum_i E_i \cdot e^{-\beta E_i}$ differentiate the definition of $Z(\beta)$

$\Rightarrow \frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\left(\sum_i E_i \cdot \frac{e^{-\beta E_i}}{Z} \right)$

$\Rightarrow \frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -E \quad \Rightarrow \quad \boxed{E = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta}}$

energy as a function of β

$\Rightarrow$ ~~$\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\frac{\partial (\log Z)}{\partial \beta}$~~

$\boxed{E = -\frac{\partial (\log Z)}{\partial \beta}}$

All the parameters which define the system such as the volume, shape of the box; all the other thing which you could imagine varying are kept fixed. These are called Control Parameters

---

★ note It is much easier to measure Temperature than to Energy.

$S = -\sum_i P_i \log P_i$

Entropy logically comes before energy. or anything else.

$\Rightarrow S = -\sum_i \frac{1}{Z} \cdot e^{-\beta E_i} [-\beta E_i - \log Z]$

$\Rightarrow S = \beta \sum_i \frac{e^{-\beta E_i}}{Z} \cdot E_i + \sum_i \frac{1}{Z} \cdot e^{-\beta E_i} \cdot \log Z$

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$\Rightarrow \boxed{S = \beta E + \log Z}$ note $\log Z$ comes over & over again.

$S = \beta \cdot E + \log Z$ where; E is average energy.

If we can calculate entropy & energy ; then we can calculate Temperature.

∴ defination of Temperature (change in energy when you change the entropy by one unit is called Temperature)

$dE = T \cdot dS$

$\Rightarrow \boxed{T = \frac{dE}{dS}}$ rate of change of energy w.r.t. entropy.

$\Rightarrow \frac{1}{T} = \frac{dS}{dE}$ E & β depend on each other.

$\Rightarrow \frac{1}{T} = \beta + E \cdot \frac{d\beta}{dE} + \frac{d}{dE}(\log Z)$

Better approach

$dS = \beta dE + E \cdot d\beta + \frac{\partial \log Z}{\partial \beta} d\beta$

$\Rightarrow dS = \beta dE + E\,d\beta - E\,d\beta \Rightarrow \boxed{dS = \beta dE}$

remember $E = -\frac{\partial \log Z}{\partial \beta}$

defination of Temperature has $dE = TdS$

$\Rightarrow dE = \frac{1}{\beta} dS \Rightarrow \boxed{T = \frac{1}{\beta}}$

β started out simply as a Lagrange multiplier. We manipulated it, used calculation ... and find that β is related to Temperature.

∴ $T = k_B t_k \Rightarrow \boxed{\beta = \frac{1}{k_B t}}$ in laboratory units.

In theorist units where temperature has units of energy:

$\beta = 1/T$

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$$P_i = \frac{1}{Z} \cdot e^{-\beta E_i} \quad ; \quad Z = \sum_i e^{-\beta E_i} \quad ; \quad E = -\frac{\partial}{\partial \beta} \log Z \; ; \; T = \frac{1}{\beta}$$

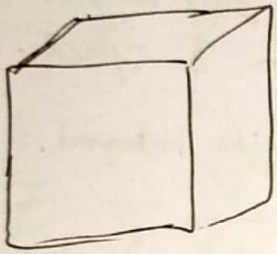
$$S = \beta E + \log Z$$

---

example Ideal gas. (A gas of molecule in a box where each molecule is a point molecule; and molecules are weakly interacting so we ignore interaction between them (or) we can say that the gas is so dilute that probability of two molecules being close enough together to interact is negligible.)

The approximation is that molecules do not interact at all.

→ here; Energy is just sum of kinetic energy of molecules inside the box.



V, N
↓ volume
↓ no. of molecules

$\frac{N}{V}$ ⇒ density of molecules (ρ) ; $\rho = \frac{N}{V}$

The states are the collection of values of position & momentum for each molecule.
(This is how we label the states)

2 → a state is collection of
$(x_1, x_2, \ldots x_{3N})$ 3N coordinates
& $(p_1, \ldots, p_{3N})$ 3N coordinates.

⟹ State of system is just a point in the 6N dimensional space.

Set of values of $\{x_i\}$ & $\{p_i\}$ label a point.

∴ Here sum over state is replaced by integral over x_s & p_s.

$$Z = \int_{\text{All state}} d^{3N}x \, d^{3N}p \cdot e^{-\beta \cdot E_{\text{state}}}$$

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Energy of a state = Kinetic energy (Total) = $\frac{1}{2m}[p_1^2 + p_2^2 + p_3^2] + \ldots$ (Pg 46)

$\Rightarrow E_{state} = \frac{1}{2m}\sum_{n=1}^{3N} p_n^2$

"n" labels which coordinate we are talking about

ii;

$$E_{state} = \frac{1}{2m}\sum_{n=1}^{3N} p_n^2$$

take masses of all molecules or constituents of gas to be equal.

$$Z = \int_{-\infty}^{+\infty} d^{3N}x\, d^{3N}p\; e^{-\frac{\beta}{2m}\sum_{n=1}^{3N} p_n^2}$$

→ integral over all possible momentum & space.

→ It is a definite integral.

momentum integration factorize.

$$Z = \int d^{3N}x \left(\int dp_1 \cdot e^{-\frac{\beta}{2m}p_1^2} \cdot \int dp_2 \cdot e^{-\frac{\beta p_2^2}{2m}} \cdots \right)$$

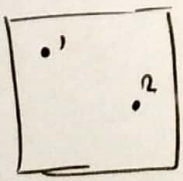
$$\Rightarrow Z = \int d^{3N}x \cdot \left(\int dp \cdot e^{-\frac{\beta}{2m}p^2} \right)^{3N}$$

$$\Rightarrow Z = \left(\int_{-\infty}^{+\infty} dp \cdot e^{-\frac{\beta}{2m}p^2} \right)^{3N} \left(\int d^{3N}x \right)$$

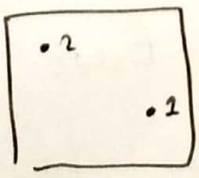
$$\Rightarrow Z = \left(\int_{-\infty}^{+\infty} dp \cdot e^{-\frac{\beta p^2}{2m}} \right)^{3N} \left(\int dx_1 dx_2 dx_3 \right)^{N}$$

$$\Rightarrow Z = V^N \cdot \left(\int_{-\infty}^{+\infty} dp \cdot e^{-\frac{\beta p^2}{2m}} \right)^{3N}$$

note



State I



State II

Are state I & II same state?

Ans Do particles carry label with names attached to them.

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In Classical Physics it does not matter ! In quantum mechanics it does matter)

In quantum mechanics; particles do not carry names.

(so; have divide by $N!$

i.e; $Z = \frac{1}{N!} \cdot \int d^{3N}x\, d^{3N}p \cdot e^{-\frac{\beta}{2m}\sum_{n=1}^{3N} p_n^2}$)

It does not matter to put $N!$. At the end it will not make any difference in the formula.

↳ its a common practice to divide by $N!$: i.e: $\frac{V^N}{N!}$

and to say that we over counted everything by a factor of $1/N!$.

$$Z = \frac{V^N}{N!} \cdot \left(\int_{-\infty}^{+\infty} dp \cdot e^{-\frac{\beta}{2m} p^2} \right)^{3N}$$

; let; $\frac{\beta}{2m} p^2 = q^2$

$$\int_{-\infty}^{+\infty} dp\, e^{-\frac{\beta}{2m} p^2} = \int_{-\infty}^{+\infty} \sqrt{\frac{2m}{\beta}} \cdot dq \; e^{-q^2}$$

$$= \sqrt{\frac{2m}{\beta}} \int_{-\infty}^{+\infty} dq \cdot e^{-q^2}$$

$$= \sqrt{\frac{2m}{\beta}} \cdot \sqrt{\pi}$$

$$\Rightarrow \int_{-\infty}^{+\infty} dp \cdot e^{-\frac{\beta}{2m} p^2} = \sqrt{\frac{2m\pi}{\beta}}$$

$$\Rightarrow \boxed{Z = \frac{V^N}{N!} \cdot \left(\sqrt{\frac{2m\pi}{\beta}} \right)^{3N}}$$ Partition function for ideal gas.

$$Z = \frac{V^N}{N!} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}}$$

∴ N is of the order of 10^{23} (Avogadro...) ⇒ we can here approximate $N!$ by stirling formula.

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$$Z = \frac{V^N}{N^N \cdot e^{-N}} \cdot \left(\frac{2m\pi}{\beta}\right)^{3N/2} \Rightarrow Z = \left(\frac{e \cdot V}{N}\right)^N \cdot \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}$$

(here e is exponential)

$\therefore$ density of particles ; $\rho = \frac{N}{V}$

$$\Rightarrow Z = \left(\frac{e}{\rho}\right)^N \cdot \left(\frac{2m\pi}{\beta}\right)^{3N/2}$$

$$\boxed{Z = \left(\frac{e}{\rho}\right)^N \cdot \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}}$$

$$\log Z = N\left\{\frac{3}{2}\log\left(\frac{2m\pi}{\beta}\right) + \log\left(\frac{e}{\rho}\right)\right\}$$

$$\Rightarrow \log Z = N\left\{\frac{3}{2}\log\left(\frac{2m\pi}{\beta}\right) - \log\left(\frac{\rho}{e}\right)\right\}$$

$$\Rightarrow \log Z = N\left\{\frac{3}{2}\log\left(\frac{2m\pi}{\beta}\right) - \log\rho + 1\right\}$$

; ρ is also constant for a given amount of gas in a box.

$$\Rightarrow \log z = N\left\{-\frac{3}{2}\log\beta + \text{constants} + \dots\right\}$$

since; $E = -\frac{\partial(\log z)}{\partial\beta}$

$$\Rightarrow E = N \cdot \frac{3}{2} \cdot \frac{1}{\beta} \Rightarrow \boxed{E = N\left(\frac{3}{2} \cdot \frac{1}{\beta}\right)}$$

$$\Rightarrow \boxed{E = N \cdot \left(\frac{3}{2} \cdot T\right)}$$

$$\boxed{E = \frac{3N}{2} \cdot T}$$

- 3 came from 3-dimensional space
- 1/2 came from gaussian integral
- N came from no. of constituents in the gas. (particles)

For an ideal gas; it is good approximation to say that energy per particle $\left(\frac{E}{N}\right)$ is $\frac{3}{2} \cdot T$

ie:

$$\boxed{\frac{E}{N} = \frac{3}{2}T}$$

$$\boxed{\frac{E}{N} = \frac{3}{2}k_B t_k}$$

This is the idea that particles move around with the kinetic energy which is proportional to Temperature

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Since; Kinetic energy is sum of three terms $\frac{p_x^2}{2m}, \frac{p_y^2}{2m}, \frac{p_z^2}{2m}$

You can say that for each direction of space the energy stored in momentum in that direction is $\frac{1}{2}T$ per particle.
(Translation kinetic energy)

The numerical factor in Z makes no difference; because it log makes that a additive constant & when we differentiate it gives zero.

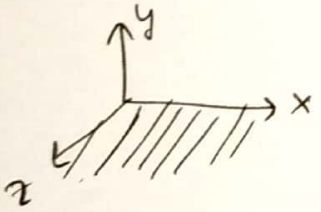
* In Classical Physics; there is no content to $1/N!$
* In Quantum Mechanics; $\frac{1}{N!}$ is important.

---

ex Including potential; $E_{state} = \frac{1}{2m}\sum_{n=1}^{3N} p_n^2 + \sum_{n=1}^{N} m.g y_n$

$$d^{3N}x = (dx_1 dx_2 \dots dx_N)(dy_1 dy_2 \dots dy_N)(dz_1 dz_2 dz_3 \dots dz_N)$$

∴



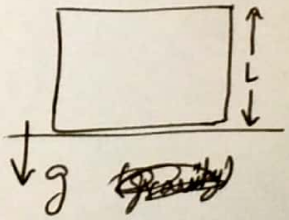
$$; Z = \frac{1}{N!}\int d^{3N}x\, d^{3N}p \cdot e^{-\frac{\beta}{2m}\sum_{n=1}^{3N} p_n^2} \cdot e^{-\beta\sum_{n=1}^{N} mgy_n}$$

$$\Rightarrow Z = \frac{A^N}{N!}\cdot\left(\int_{-\infty}^{+\infty} dp \cdot e^{\frac{-\beta}{2m}p^2}\right)^{3N}\cdot\left(\int_0^{BL} e^{-mgy\cdot\beta}\cdot dy\right)^N$$

A is area of base of the box

$(\int dx_1 dz_1) = A$; b is height of the box

∴ A is area of the box
L is height of the box.



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$$Z = \frac{A^N}{N!} \cdot \left[\int_{-\infty}^{+\infty} dp \cdot e^{\frac{-\beta p^2}{2m}}\right]^{3N} \left[\int_0^L e^{-mgy\cdot\beta} dy\right]^N$$

(Partition function for box of gas in Gravitational field)

∴ ~~This simplifies~~

∴ To simplify : let the box be infinitely high.
(This is litterarily problem of atmosphere between earth surface & infinity)

$$Z = \frac{A^N}{N!}\left[\sqrt{\frac{2m\pi}{\beta}}\right]^{3N} \cdot \left(\frac{1}{\beta mg}\right)^N$$

$$\Rightarrow Z = \frac{A^N}{N!}\left(\frac{2m\pi}{\beta}\right)^{3N/2}\left(\frac{1}{\beta mg}\right)^N$$

$$\Rightarrow \log Z = -\frac{3N}{2}\log\beta - N\log\beta + (\text{constants}).$$

$$\Rightarrow \frac{\partial \log Z}{\partial \beta} = -\frac{5N}{2}\cdot\frac{1}{\beta} \Rightarrow E = \frac{5}{2}N\cdot\frac{1}{\beta}$$

$$\Rightarrow \boxed{E = N\left(\frac{5}{2}T\right)}$$

Calculate entropy ; $S = \beta E + \log Z$ & entropy per particle $\left(\frac{S}{N}\right)$.

Boltzmann distribution : $P_i = \frac{e^{-\beta E_i}}{Z}$

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 Statistical Mechanics : Pressure of an ideal gas and fluctuations

— Shoaib Akhtar

"Foundations of Statistical Mechanics are very mathematical"

Lets say, a room is filled with molecules which are moving with velocity

$\frac{1}{2}mv^2$; i.e; $\frac{1}{2}mv^2 = \frac{3}{2}T$

↳ if we know now velocity of every molecule ; we can then compute the force on the wall by asking how many molecules per unit time hit the wall ; if indeed they are distributed uniformly (which we dont know for sure till now) : and if we know that direction of velocity is isotropic

↳ We can calculate no. of collisions on the wall per unit time.

" " " momentum delivered by each particle to the wall.

" " " force (it is rate of change of momentum) on the wall.

" " " pressure (force per unit area)

(You will get right answer in the case where molecules are completely free)

We want something called the "Equation of State"

↳ We want to calculate what Pressure is, as a function of Temperature, Volume, no. of molecules

$S = -\Sigma P_i \log P_i$; for Boltzman distribution : $P_i = \frac{e^{-\beta E_i}}{Z}$; $\beta = 1/T$

$S = \beta E + \log Z$; where ; E is average energy.

$\Rightarrow S = \frac{E}{T} + \log Z$

$\Rightarrow E - TS = -T \cdot \log Z$

A (called Helmholtz Free energy)

Helmholtz Free Energy (A) is now another Thermodynamic variable like E, S, T.

- Things are given names if they occur over and over again.

Control Parameters : they are the parameters which we as an experimentalist can easily change.

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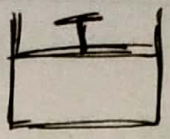
Control Parameters are macroscopic ; they are not going to change details of one molecule at a time.

ex Volume of container of gas.



ex Magnetic & Electric field on the system.

(Variables usually come in pairs ;
one is called Control Parameter ;
and the other is usually called the Conjugate Thermodynamical variable)

* Pressure & Volume are closely connected ; & they are conjugate pairs.

Theorem|| suppose you have two functions of two variables.

E , S these are functions of two independent variables in the problem ; ie: T, V ie; $E = E(T, V)$

$S = S(T, V)$

$\left.\frac{\partial E}{\partial V}\right|_S$

⇓

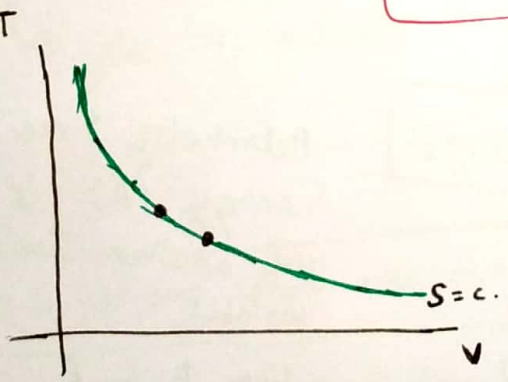
differentiating E w.r.t. V keeping S fixed ;

∴ Theorem is

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left(\left.\frac{\partial E}{\partial S}\right|_V\right)\left(\left.\frac{\partial S}{\partial V}\right|_T\right)$$

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left(\left.\frac{\partial E}{\partial S}\right|_V\right)\left(\left.\frac{\partial S}{\partial V}\right|_T\right)$$

Proof||



draw contour line of S
(here we will draw only one line)

"$\left.\frac{\partial E}{\partial V}\right|_S$" means rate of change of E w.r.t. V along a line of constant S.

∴ [illegible]

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$\left.\frac{\Delta E}{\Delta V}\right|_S$; here; δE & ΔV are actually differentials
↳ but we are writing here as ΔE .. or ΔV to remind that $\frac{dE}{dV}$ is ratio of small differences.

$$\Delta E = \left.\frac{\partial E}{\partial V}\right|_T \cdot \Delta V + \left.\frac{\partial E}{\partial T}\right|_V \cdot \Delta T$$

$$= \left.\frac{\partial E}{\partial V}\right|_T \Delta V + \left.\frac{\partial E}{\partial S}\right|_V \cdot \left.\frac{\partial S}{\partial T}\right|_V \cdot \Delta T$$

$$\Rightarrow \frac{\Delta E}{\Delta V} = \left.\frac{\partial E}{\partial V}\right|_T + \left.\frac{\partial E}{\partial S}\right|_V \cdot \left.\frac{\partial S}{\partial T}\right|_V \cdot \frac{\Delta T}{\Delta V}$$

(till now we have not used the fact that we are moving along the line of constant S)

condition for moving along line of constant S
$\Rightarrow$ i.e; $dS = 0 \Rightarrow \left.\frac{\partial S}{\partial V}\right|_T \cdot \Delta V + \left.\frac{\partial S}{\partial T}\right|_V \cdot \Delta T = 0$

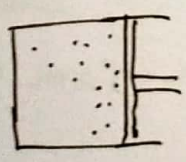
$$\Rightarrow -\left(\left.\frac{\partial S}{\partial V}\right|_T\right) \Big/ \left(\left.\frac{\partial S}{\partial T}\right|_V\right) = \frac{\Delta T}{\Delta V}$$

$$\Rightarrow \frac{\Delta E}{\Delta V} = \left.\frac{\partial E}{\partial V}\right|_T - \frac{\left(\left.\frac{\partial S}{\partial T}\right|_V\right)\left(\left.\frac{\partial E}{\partial S}\right|_V\right)\left(\left.\frac{\partial S}{\partial V}\right|_T\right)}{\left(\left.\frac{\partial S}{\partial T}\right|_V\right)}$$

$$\Rightarrow \frac{\Delta E}{\Delta V} = \left.\frac{\partial E}{\partial V}\right|_T - \left(\left.\frac{\partial E}{\partial S}\right|_V\right)\left(\left.\frac{\partial S}{\partial V}\right|_T\right)$$

↳ this is actually $\left.\frac{\partial E}{\partial V}\right|_S$ since we had used $\frac{\Delta T}{\Delta V}$ for the case $dS = 0$.

Pressure is just one special case of a response to a control parameter.

\# 

The work done on piston is negative of change in energy of inside gas molecules.

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dE

If you move the system Adiabatically; then change in energy of the gas dE is;

$$dE = -dW$$

where; dW is work done on the piston by the gas.

$$dW = (PA) \cdot dx$$

(Force, displacement)

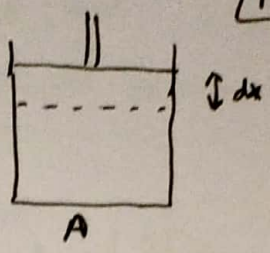
$$\Rightarrow dE = -PAdx$$

$Adx = dV$ (change in volume)

$$\Rightarrow \boxed{dE = -PdV} \Longrightarrow \text{This defines Pressure}$$

$$P = -\frac{\partial E}{\partial V}$$

Defination of Pressure under the circumstances that we do the operation adiabatically.



note!! piston is moved slowly.
; and make sure no energy comes from outside ; ie; insulate walls of the system.

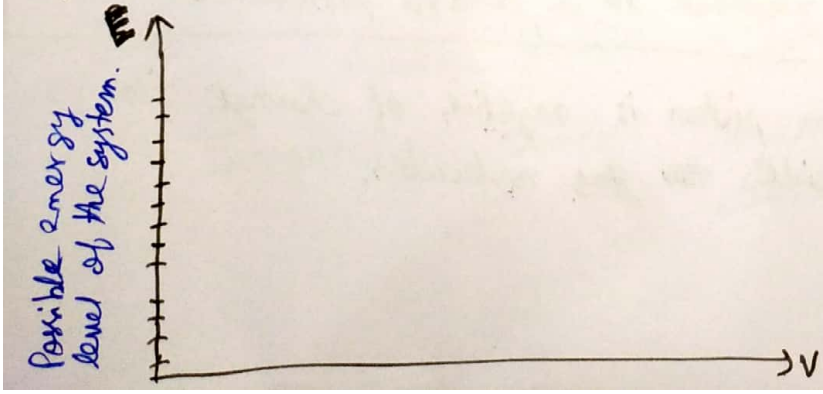
Adiabatic: means slowly & no heats comes into or flow out of the system.

Second law of Thermodynamics

Entropy always increases or stays the same $dS \geq 0$

· when entropy stays the same (when it does not increase)
ie; $dS = 0$ $\Longrightarrow$ These are Adiabatic processes.

Quantum Mechanical explanation (use that energy levels are discreate)



we change the volume
↳ does energy level stays the same?

A No

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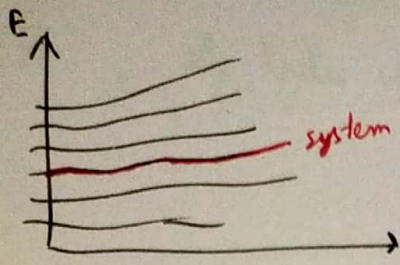

Quantum Mechanical Theorem

Adiabatic Theorem.

"If a system has a definite energy & you slowly change the parameter (whatever control parameters happen to be)

slow with no added & subtracted heat ⇐

↳ The system will stay & simply ride along the energy level

↳ keeping not the same energy, but it won't jump from one energy level to another"

⇒ If you change the system rapidly; you can have jump from one energy level to another.

P_i labelling probability for different energy levels.

∴ P_i stay the same

∴ The value of energy may shift ; but the probabilities dont change.

& since entropy is made up of P_i

i.e; $S = -\sum P_i \cdot \log P_i$ ⇒ so entropy also stays the same

⇒ so; Adiabatic process is sometime called Isentropic process (meaning to say that entropy does not change)

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so; in the defination of $P = -\frac{\partial E}{\partial V}$ we now know what to keep fixed ; it is entropy.

so;

$$P = -\left.\frac{\partial E}{\partial V}\right|_S$$

note!! easy thing to usually calculate is how things vary with temperature or at a given temperature ⇒ just because Temperature is the thing which directly appears in Boltzmann Distribution.

⟹ so; it is always easier to work as a function of Temperature ; than as a function of anything else.

---

so; $P = -\left.\frac{\partial E}{\partial V}\right|_S = \left(\left.\frac{\partial E}{\partial S}\right|_V\right)\left(\left.\frac{\partial S}{\partial V}\right|_T\right) - \left.\frac{\partial E}{\partial V}\right|_T$

$\therefore \left.\frac{\partial E}{\partial S}\right|_V$ is Temperature ;

(holding the volume fixed means you ~~are not~~ are holding the system fixed ⇒ you are not changing the control parameters.)

↳ It is just the original system with fixed energy levels & you are holding that fixed

↳ so; $\frac{\partial E}{\partial S}$ under those circumstances is just Temperature.

(remember ; $dE = T\,dS$)

$$\Rightarrow P = T\cdot\left(\left.\frac{\partial S}{\partial V}\right|_T\right) - \left.\frac{\partial E}{\partial V}\right|_T$$

↳ now only derivatives which appear is w.r.t. Volume at fixed temperature.

↳ this is good. Volume & Temperature can be thought off as independent variables.

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$$\Rightarrow P = -\frac{\partial}{\partial V}(E - TS)\Big|_T$$

$$\frac{\partial}{\partial V}(TS) = \frac{\partial T}{\partial V}\cdot S + T\frac{\partial S}{\partial V}$$

$$\therefore \frac{\partial T}{\partial V} = 0$$

$$\Rightarrow P = -\frac{\partial}{\partial V}(E - TS)\Big|_T$$

$$\Rightarrow \boxed{P = -\frac{\partial A}{\partial V}\Big|_T}$$

remember

$E - TS$ is Helmholtz Free Energy

$$A = E - TS$$

↳ Helmholtz Free Energy

we know: $A = -T \log Z$

$$\Rightarrow P = \frac{\partial}{\partial V}(T \cdot \log Z)\Big|_T \Rightarrow \boxed{P = T \cdot \frac{\partial}{\partial V}\log Z\Big|_T}$$

↳ All that we have done is completely general. It will not matter whether it is liquid, gas, plasma or solid.

---

for any control parameter q: there is always derivative of energy E w.r.t. this parameter q at fixed entropy.

↳ That is called the Conjugate Thermodynamical Variable.

ex Volume & Pressure are conjugate variable's Thermodynamically.

The question of exactly what time scales constitute slow, is the one which can depend on details.

↳ The question of what happens when you move sufficiently slowly : do not depend on details.

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* When you calculate the partition function; it is the partition function as a function of other variables at fixed ~~temp~~ temperature.

Ideal Gas

$$\therefore Z = \int d^{3N}x\, d^{3N}p \cdot e^{\frac{-\beta}{2m}\sum_{n=1}^{3N} p_n^2}$$

$\int d^{3N}x$ gives you volume if there is one particle ie; $N=1$

↳ & if there are N particles; it gives volume to the N^{th} power; ie; $\int d^{3N}x = V^N$

$$\Rightarrow Z = f(\beta)\cdot \frac{V^N}{N!}$$

$\therefore$ (we may or may not put in the factor $\frac{1}{N!}$ ... it will not make any difference)

$$\Rightarrow \log Z = N\log V - \log(N!) + \log(f(\beta))$$

↳ because we have to work with $\log Z$.

$$\Rightarrow \log Z = N\log V - \log(N!) + \log(f(\beta))$$

↳ this term depends on volume; and it came from the fact that we have to integrate the position of particle over the whole volume.

$$\frac{\partial}{\partial V}(\log Z) = \frac{N}{V}$$

~~it is in by definition; $\frac{N}{V} \Rightarrow \rho$~~

notice; $\frac{N}{V}$ is density ρ

$$\Rightarrow T\cdot\frac{\partial}{\partial V}(\log Z) = T\cdot\frac{N}{V}$$

$$\Rightarrow \boxed{P = T\cdot\frac{N}{V}} \Rightarrow \boxed{PV = NT} \longrightarrow$$ Here; N is no. of particles.

$$\Rightarrow \boxed{P = \rho T}$$

$PV = NT$ (or) $P = \rho\cdot T$ } This is equation of State of Ideal Gas.

Ideal Gas.

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Fluctuations

(it measures the width of distribution ... how broad is the distribution is)

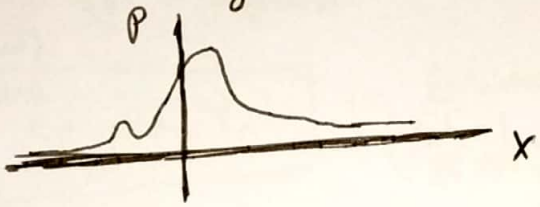
The fact that energy fluctuates in certain ways is ~~not~~ evidence that the system is really made up of molecules or so forth.

If you look in a box of gas & it is in equilibrium with another system so that it is exchanging energy with it
↳ The energy won't be a definite value. → The thing we have been calling Energy "E" is the average energy.

Energy will fluctuate.

Defination ||

lets begin with a quantity whose average is zero



average of x is zero. ; but average of x^2 is not zero

↳ it is measure of the width of distribution.

So; fluctuation; usually called Δx or uncertainity in x

is; $$\Delta X = \sqrt{\langle x^2 \rangle}$$

$\therefore (\Delta X)^2 = \langle x^2 \rangle$ } ⇒ mean square fluctuation.

In the general case when $\langle x \rangle \neq 0$

$\therefore$ define a new variable : $x - \langle x \rangle$

$\therefore$ note; $\langle x - \langle x \rangle \rangle = 0$

$$\Rightarrow \quad (\Delta(\langle x - \langle x \rangle \rangle))^2 = \langle (x - \langle x \rangle)^2 \rangle$$

$$= \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle$$

$$= \langle x^2 \rangle - 2\langle x\langle x \rangle \rangle + \langle \langle x \rangle^2 \rangle$$

$$= \langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2$$

$$(\Delta(\langle x - \langle x \rangle \rangle))^2 = \langle x^2 \rangle - \langle x \rangle^2$$

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$(\langle x^2\rangle - \langle x\rangle^2)$ is variance ; i.e., fluctuation away from the norm (away from the average)

So; $\boxed{(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2}$ Definations of fluctuation.

---

lets calculate fluctuation in Energy in terms of Partition Function

"Energy in a box fluctuates if it is in eqm with heat bath".

$\therefore (\Delta E)^2 = \langle E^2\rangle - \langle E\rangle^2$; $\langle E\rangle = -\frac{\partial}{\partial\beta}(\log Z)$

↳ Average energy.

(here ; $\langle E\rangle$ denotes average energy .. not just E)

$\therefore \langle E\rangle = \sum \frac{1}{Z}\cdot e^{-\beta E_i}\cdot E_i = \frac{1}{Z}\cdot\left(-\frac{\partial Z}{\partial\beta}\right)$

$\therefore \langle E^2\rangle = \sum \frac{1}{Z}\cdot e^{-\beta E_i}\cdot E_i^2 = \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial\beta^2}$

$\therefore \boxed{(\Delta E)^2 = \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2}$ $\boxed{(\Delta E)^2 = \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\cdot\left(\frac{\partial Z}{\partial\beta}\right)^2}$

$\therefore$ lets see; $\frac{\partial^2}{\partial\beta^2}(\log Z) = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta}\right) = (\Delta E)^2$

$\therefore$ $\boxed{(\Delta E)^2 = \frac{\partial^2}{\partial\beta^2}(\log Z)}$

(or) $(\Delta E)^2 = -\frac{\partial}{\partial\beta}\langle E\rangle$

$\therefore (\Delta E)^2 = -\frac{\partial}{\partial T}(\langle E\rangle)\cdot\frac{\partial T}{\partial\beta}$;

$\Rightarrow (\Delta E)^2 = \frac{1}{\beta^2}\cdot\frac{\partial}{\partial T}(\langle E\rangle)$

$\Rightarrow (\Delta E)^2 = T^2\cdot\frac{\partial}{\partial T}(\langle E\rangle)$

$T = \frac{1}{\beta}$

$\Rightarrow \frac{\partial T}{\partial\beta} = -\frac{1}{\beta^2}$

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$$(\Delta E)^2 = T^2 \cdot \frac{\partial}{\partial T}\langle E\rangle$$

$\frac{\partial \langle E\rangle}{\partial T}$ is Heat Capacity. ~~specific heat~~

$$\Rightarrow \boxed{(\Delta E)^2 = C_v \cdot T^2}$$

$$C_v = \frac{\partial \langle E\rangle}{\partial T}$$

note; C_v is a function of temperature.

* fluctuation is also a function of temperature.

Rate of change of average energy w.r.t. Temperature; keeping volume constant. (Heat Capacity)

Heat Capacity. ~~Specific heat~~ at constant volume (in general; constant control parameters)

$$\therefore C_v = \frac{\partial}{\partial T}\langle E\rangle = \frac{1}{k_B} \cdot \frac{\partial \langle E\rangle}{\partial t_k}$$

$$\therefore \boxed{(\Delta E)^2 = k_B \cdot C_v \cdot t_k^2}$$

in laboratory units

$\Rightarrow$ presence of k_B implies that fluctuations are small.

(k_B is a small number, Boltzman Constant)

This formula is not specific to any particular system. This is very general.

This goes beyond thermodynamics; whenever you actually see at the end of formula like this ; a k_B $\Rightarrow$ it really does depend on the fact that systems are made up of molecules.

.. Avagadro no. ... k_B is closely related to Avagadro number.

$\therefore C_v = m \cdot \underline{c_v}$; $m \Rightarrow$ mass of the sample.

C_v = Heat Capacity.

c_v → Specific heat (rate of change of energy per unit temperature; per unit mass)

$$\boxed{(\Delta E)^2 = k_B \cdot m\, c_v \cdot t_k^2}$$

Heat Capacity depends on mass $\Rightarrow$ it is proportional to no. of molecules.

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$\frac{1}{m} \cdot \frac{\partial \langle E \rangle}{\partial T}$ } ⇒ Specific Heat ; $\frac{\partial \langle E \rangle}{\partial t}$ } ⇒ Heat Capacity

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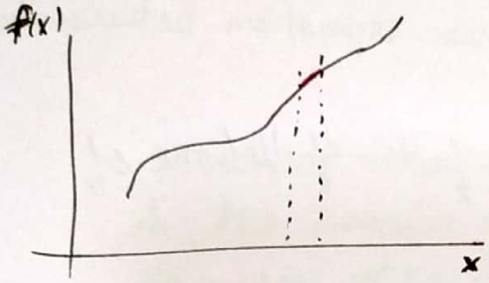
Lec-6 Statistical Mechanics : Weakly interacting gases, heat and work.

— Shoaib Akhtar.

normaly ; you have some quantity which you can measure in the laboratory easily : it could be length of stretched spring (or) height of mercury and you ask what could the quantity in question depends on.

☆ any function which is smooth ; over a limitted range will be linear.



: If it is linear ; then we can say : over that limitted range ; variations in the quantity that we are measuring are proportional to variations in whatever the independent variable is.

A gas of weakly interacting particles.

* weakly interacting because it is dilute.

Assumptions : The range of forces is small by comparison with distance between the particles. The potential energy between particles (or the forces) are small.

$$E = \sum_n \frac{p_n^2}{2M} + \sum_{n>m} U(|x_n - x_m|)$$

$\sum_{n>m}$ ⇓ sum over pairs

"n" stands for which molecule we are talking about.

p_n ⇒ stands for sums of components of momentum.

: $(x_n - x_m)$ means the vector from n^{th} position to m^{th} position.

i.e;

$$E = \sum_n \frac{p_n^2}{2M} + \sum_{n>m} U(|x_n - x_m|)$$

"U" is potential energy. It has been assumed to be smaller as compared to Kinetic Energy between molecules.

---

consider two particles 1 & 2 ; and consider the following integral.

notation : $dx_1 \equiv d^3x_1 \equiv dx_1\,dy_1\,dz_1$

$dx_2 \equiv d^3x_2 \equiv dx_2\,dy_2\,dz_2$

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$$\int d^3x_1 \cdot d^3x_2 \; U(|x_1 - x_2|)$$

Steps to integrate over two coordinates.

(i) Integrate over one of the coordinates keeping seperation with the other one fixed

⇓ Then

(iii) Integrate over seperation between them.

Here we will get a factor of Volume of space.

☆ other way to integrate.

(i) First holding particle 2 fixed ; and integrating over the position of other particle.

This gives $\int d^3x \; U(|x|)$

This quantity is combination of how strong the potential is and how wide spread it is distributed.

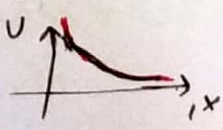
∴ give it name U_0 ; $\boxed{U_0 \equiv \int d^3x \; U(|x|)}$

(iii) Now; lets integrate the position of the first molecule : which means move the pair around.

↳ This will give another factor of Volume of space ... here; Volume of Gas.

so; $\boxed{\int d^3x_1 \, d^3x_2 \; U(|x_1 - x_2|) = V \cdot U_0}$

not all we dont expect a ∝ factor of Volume in U_0 ⇒ because we are assuming $U(|x|)$ goes to Zero for large $|x|$



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V_0 is qualitatively equal to height of the function $U(1x1)$; let that be U ; times the volume "v" over which the function $U(x1)$ is significant.

$$V_0 \sim U \cdot v$$

This volume is roughly equal to couple a times of volume of a molecule.

"The forces between molecules or potential energy between molecules is only significant when the two molecules are within a couple of molecular diameters of each other."

$\therefore$ V is volume of whole sample (whole box of gas)

* the small volume v is absorbed in V_0. (we will not worry about it anymore)

as combination of small molecular size volume times the strength of the potential energy between the molecules.

Note|| There is always boundary effect here.

Is we are here assuming: that for large volume : the volume is much bigger than the area.

(so got neglected the boundary effect)

when you move the molecule near the box of the wall (during the integral of the position of first molecule in step (ii)) by assuming the other molecule can be anywhere around it.

But it can be anywhere around it ; but not banging into the wall.

"If the box is much bigger than the molecular volume;
i.e: $V >> v$ $\Rightarrow$ Then the error made is very small"

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The unit (dimensions) of $\int d^3x_1 d^3x_2 V(|x_1 - x_2|)$ are units of (Volume)^2 (Energy) $\Rightarrow$ but $\int d^3x_1 d^3x_2 V(|x_1 - x_2|) \propto V$ ✓

not $\int d^3x_1 d^3x_2 V(|x_1 - x_1|) \propto V^2$ ✗

In Thermodynamics & in Statistical Mechanics : in general; we often ignore surface things.

Note// In this formalism; we dont have to think about things like Collission, or following the particles.

The existence of potential energy will do our job. The derivative of Potential Energy is force ... and force creats collisions.

This is beauty of Statistical Mechanics.

↳ You loose all intuition about what is really going on ; but you have set of mechanical rules ... follow the rules ... and you get answer in completely rigorous way.

✱ There could be terms in the energy which could depend on three particles at a time.

The energy between two particles concievably could depend on the presence of nearby third particle.

so; we have made an assumption when we have used potential energy can be written as sum of pairs.

↳ Why is it good approximation?

Good approximation when probability of the particles being close enough together to feel each other is small.

When gas is dilute ; particles spend most of the time being far enough away that they simply dont feel each other.

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Some fraction of the time; two particles get close enough together to feel each other; i.e; to be within molecular range distance; i.e; to be in the little "v" volume distance $\Rightarrow$ and that's when forces between molecules become important.

$\Rightarrow$ The probability that given three molecules will be within molecular diameter of each other is much smaller than the probability of two of them being near each other.

"Three body simultaneous collision is rare"

$\Rightarrow$ So; if there were three body forces; they will be less important, not because they were weaker but because on the average the probability of finding three particles in the neighbourhood of each other for dilute gas is very small.

Lets calculate partition function.

$$Z = \int \frac{d^{3N}p \cdot d^{3N}x}{N!} \cdot e^{-\beta\left(\sum_{n}^{N} \frac{p_n^2}{2M} + \sum_{n>m}^{N} U(|x_n - x_m|)\right)}$$

note: dp & dx stand for high dimensional multiple integral.

dp → momentum integral; dx → space integral.

$dp \equiv d^{3N}p$; N is no. of particles.

$dx \equiv d^{3N}x$

$\therefore d^{3N}x \longrightarrow \frac{d^{3N}x}{N!}$

(because of N particles....)

↳ although it will not matter in the final answer.

notation

$\frac{p^2}{2M}$ stands for $\sum_{n}^{N} \frac{p_n^2}{2M}$

$\sum_{n>m}^{N} U(|x_n - x_m|) \equiv U(x)$

↳ stands for function of all positions.

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So; in our simplified notations.

$$Z = \frac{\int dp\, dx}{N!} \cdot e^{-\beta \cdot \frac{p^2}{2M}} \cdot e^{-\beta U(x)}$$

$$= \left(\int dp \cdot e^{-\beta \cdot \frac{p^2}{2M}} \right) \left(\frac{1}{N!} \right) \left(\int dx \cdot e^{-\beta \cdot U(x)} \right)$$

remember $\int dp \cdot e^{-\beta \cdot \frac{p^2}{2m}} = \left(\sqrt{\frac{2\pi M}{\beta}} \right)^{3N}$

$$\Rightarrow Z = \left(\int dp \cdot e^{-\beta \cdot \frac{p^2}{2m}} \right) \left(\frac{V^N}{N!} \right) \cdot \left(\int dx \cdot e^{-\beta U(x)} \cdot \frac{1}{V^N} \right)$$

$$\Rightarrow Z = \left(\int dp \cdot e^{-\beta \cdot \frac{p^2}{2m}} \cdot \frac{V^N}{N!} \right) \left(\int dx \cdot e^{-\beta U(x)} \cdot \frac{1}{V^N} \right)$$

We recognise this as partition function for ideal gas.
Lets call it Z_0.

$\therefore Z_0$ corresponds to $U(x) = 0$

ie; Z_0 is ideal gas partition function.

$$\Rightarrow Z = Z_0(\beta) \cdot \int dx \cdot e^{-\beta U(x)} \cdot \frac{1}{V^N}$$

$\because \int \frac{dx}{V^N} \cdot e^{-\beta \cdot U(x)} =: I$; $U(x)$ is small quantity by assumption.

$\therefore e^{-\beta \cdot U(x)} = 1 - \beta \cdot U(x) + O\left(U(x)^2\right)$ Taylor expansion.

$$\Rightarrow I = \int \frac{dx}{V^N} (1 - \beta U(x)) = \int \frac{dx}{V^N} - \beta \int \frac{dx}{V^N} \cdot U(x) = 1 - \frac{\beta}{V^N} \int dx\, U(x)$$

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$$\Rightarrow I = 1 - \beta \int \frac{d^{3N}x}{V^N} \sum_{n>m} U(|x_n - x_m|)$$

; note
each sum gives the same answer
; because their is nothing distinguishable

$$\Rightarrow I = 1 - \beta \cdot {}^{N}C_2 \int \frac{d^3x_1 \cdot d^3x_2 \; U(|x_2 - x_1|)}{V^N} \cdot d^3x_3 d^3x_4 \ldots d^3x_N$$

$$\Rightarrow I = 1 - \beta \cdot \frac{N(N-1)}{2} \int \frac{d^3x_1 \cdot d^3x_2 \; U(|x_2 - x_1|)}{V^N} \cdot \int d^3x_3 \cdot d^3x_4 \cdot d^3x_5 \ldots d^3x_N$$

$$\Rightarrow I = 1 - \beta \cdot \frac{N(N-1)}{2} \cdot \frac{1}{V^N} \cdot V \cdot U_0 \cdot V^{(N-2)}$$

$$\Rightarrow \boxed{I = 1 - \frac{\beta \cdot N \cdot (N-1)}{2} \cdot \frac{U_0}{V}}$$

remember

$$\int dx_1 \cdot dx_2 \cdot U(|x_1 - x_2|) = V U_0$$

since N is large ; $N(N-1) \simeq N^2$

$$\Rightarrow I = 1 - \frac{\beta N^2}{2} \cdot \frac{U_0}{V}$$

$$\Rightarrow \boxed{Z(\beta) = Z_0(\beta) \left[1 - \frac{\beta N^2}{2} \cdot \frac{U_0}{V} \right]}$$ Partition function.

$$\Rightarrow \log Z(\beta) = \log Z_0(\beta) + \log \left(1 - \frac{\beta N^2}{2V} U_0 \right)$$

↳ correction term

Taylor Series expansion

for small x ; $\log(1-x) \sim -x$;

i.e; $\log(1-x) = -x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} - \frac{x^5}{5} + \ldots$

$$\Rightarrow \log(1-x) = -x + O(x^2)$$

so; $$\log Z = \log Z_0 - \frac{\beta N^2}{2V} U_0$$

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$$\log Z = \log Z_0 - \frac{\beta N^2}{2V} U_0$$

$$\therefore E = -\frac{\partial}{\partial \beta}(\log Z) = -\frac{\partial \log Z_0}{\partial \beta} + \frac{N^2}{2V} U_0$$

$$\Rightarrow \boxed{E = E_0 + \frac{N^2}{2V} U_0} \qquad -\frac{\partial \log Z_0}{\partial \beta} = E_0 = \frac{3}{2} NT$$

$$\Rightarrow \boxed{E = \frac{3}{2} NT + \frac{N^2}{2V} U_0}$$

$$\therefore \frac{N}{V} = \rho$$

$$E = N\left(\frac{3T}{2} + \frac{1}{2} U_0 \cdot \frac{N}{V}\right)$$

$$\Rightarrow \boxed{E = N\left(\frac{3T}{2} + \frac{1}{2} U_0 \rho\right)}$$ ⟹ Energy is proportional to no. of particles.

⟺ Energy per particle is $\left[\frac{3T}{2} + \frac{1}{2} \rho . U_0\right]$

U_0 is potential energy between pairs of particles.

a factor of density "ρ" appears with U_0 as "ρU_0" ⇒ because if density of particles increases, chances of their interaction increases
↳ so there should be more contribution of U_0's.
↳ so; density term appears multiplied to U_0.

---

notice; $\frac{1}{2} U_0 \rho$ does not depend on Temperature.

$$A = -T \log Z$$

$$P = -\left.\frac{\partial A}{\partial V}\right|_T = T \cdot \left.\frac{\partial \log Z}{\partial V}\right|_T$$

$$= \frac{NT}{V} + \frac{T}{2} \cdot \beta \cdot \frac{N^2}{V^2} U_0$$

$$\boxed{P = \rho T + \frac{1}{2} \rho^2 U_0}$$

ideal gas solution

$$PV = NT$$
$$\Rightarrow P = \frac{NT}{V}$$
$$\Rightarrow P = \rho T$$

$$\Rightarrow P = \rho T + \beta T \cdot \frac{\rho^2}{2} U_0 \Rightarrow \boxed{P = \rho T + \frac{\rho^2}{2} U_0}$$

$$\boxed{P = \rho T + \frac{\rho^2 U_0}{2}}$$

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$\frac{1}{2}\rho^2 U_0$ is first correction the dilute gas for pressure.

$\therefore \quad P = \rho \cdot T + \frac{1}{2}\rho^2 U_0$

good approximation to keep ideal gas assumption is: $P = \rho T$

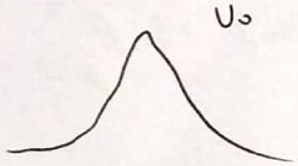
when $\rho^2 U_0 \ll \rho T$

$\Rightarrow$

$\rho U_0 \ll T$

* ρU_0 is potential energy per particle.
* T is measure of Kinetic energy per particle.

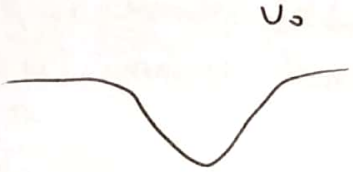
so; Ideal gas approximation is a good approximation when Potential Energy per particle is much less than the Kinetic energy per particle.



repulsive

$(U_0 > 0)$

extra pressure



attractive

$(U_0 < 0)$

less pressure.

Getting the formula for energy is not a problem of Statistical Mechanics.
(or say potential energy)

↳ It is prolem of Quantum Mechanics, or say Molecular Structure or Atomic physics.

↳ The formulas are our starting point for thinking about Statistical Mechanics.

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The ~~second~~ correction term in P is ~~$\frac{1}{2}B_2 V_0$~~ $\frac{1}{2}\rho^2 V_0$

↳ factor of ρ^2 appears here (not ρ)

↳ because it has to do with the probability that three particles come together.

∴ PT requires only one particle. ~~Only~~ ; particle is either there or not there ; it does not matter whether other particles are nearby.

∴ Probability of finding a particle in little volume (molecular volume) is ρ.

~~Finding one particle in a unit small volume is ρ~~

~~" two " " " same small volume ρ^2~~

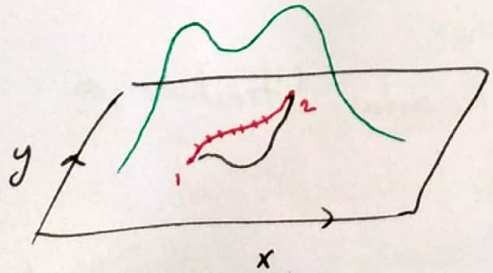
~~" three " " " " "~~

" "

* Finding one particle in a unit volume is ρ.
* " two " " " small volume (same region) is ρ^2
* " three " " " " " " ρ^3
* .
* :
* " n " " " " " " " ρ^n.

☆ Notion of Exact & Non-exact differentials.

∴ let ; F be a function of two variable. $F(x, y)$



$$dF = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$$

$$\boxed{dF = F_x\,dx + F_y\,dy}$$

↳ differential "dF".

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$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ } a theorem of calculus .. for continuous & ~~differentiable~~ differentiable functions.

$\Rightarrow$ $\boxed{\frac{\partial F_y}{\partial x} = \frac{\partial F_x}{\partial y}}$ restrictions on F_x & F_y $\Rightarrow$ so that dF is really a small change.

F_x & F_y form components of gradient vector.

$\Rightarrow$ $\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0$ } $\Rightarrow$ curl of something. ; ... actually curl of gradient of F.

$\Delta F = \int_1^2 F_x dx + F_y dy$ (through any path ..)

↳ The line integral is independent of path.
(it is not true in general for any F_x and F_y.

↳ equivalent of saying this is : integral over close loop should be zero ; $\oint F_x dx + F_y dy = 0$

Ex Change in fuel as you go from point "1" to say point "2" ....

↳ obviously when you go in close loop : some fuel is lost.

$\Rightarrow$ change in fuel can also be written as differential ; but it is not the differential of some function.
(If it was differential of well defined function, if you go around in a loop ; the change has to be zero)

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"You can always define a differential ; but that differential is not necessarily the differential of a function"

$$dF = F_x\,dx + F_y\,dy$$

ib "$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0$" is true; The vector field (F_x, F_y) are called Exact.

$\Rightarrow$ when not true; it is called In-exact.

∴ when the differential is differential of a function; it is called Exact ; when it is not, it is called In-exact.

Inexact differential usually have to do with the thing that depend not only end points of trajectory ; but depend on the whole trajectory.

---

ex $F_x = y$; $F_y = x$ $\quad \frac{\partial F_x}{\partial y} = 1$; $\frac{\partial F_y}{\partial x} = 1 \Rightarrow \frac{\partial F_x}{\partial y} - \frac{\partial F_y}{\partial x} = 0$

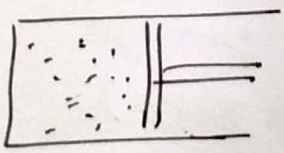
So; This is exact.

∴ take ; $F = xy$; $y = \frac{\partial}{\partial x}(F)$; $x = \frac{\partial F}{\partial y}$

ex $F_x = y$; $F_y = -x \Rightarrow \frac{\partial F_x}{\partial y} = 1$; $\frac{\partial F_y}{\partial x} = -1$; $1 - (-1) \neq 0$

↳ This is a perfectly good rule for differentials; but it is inexact.

Heat and Work. (have to do with changes in energy)



There are two independent variables here.
↳ one can take them to be Temperature (T) and Volume (V)

↳ (or) you can take it to be Entropy of the box (S) and Volume (V)

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~~* We will take E & V to be independent variable.~~

* We will take S & V to be independent variable.

(any two things will do by the way :) ...)

↳ This is here enough to determine the Thermodynamic state of the gas.

$dE = -P \cdot dV$

↓↓

change in energy of gas if you don't change the entropy

$\therefore \left.\frac{\partial E}{\partial V}\right|_S$ } ⇒ This is essentially ~~definition~~ defination of Pressure (with negative sign)

$dE = T \cdot dS$

↳ change in energy keeping volume fixed.

$\therefore \left.\frac{\partial E}{\partial S}\right|_V$ } ⇒ This is essentially the defination of Temperature.

$\therefore \quad dE = -P \cdot dV + T \cdot dS$

↓↓ change volume little bit ⇒ Then ⇒ Put little bit of heat

↳ make small change of both volume & entropy.

(We are doing here the most general process)

⇒ $\boxed{dE = -P \cdot dV + T \cdot dS}$ First Law of Thermodynamics

(just expresses energy conservation)

$\therefore$ Work done (W) ; $dW = -P \cdot dV$

(~~work done by the gas ...~~)

$\therefore$ Q stands for heat ; $dQ = T \cdot dS$ } ⇒ This is the defination of the heat you put in

⇒ $\boxed{dE = dW + dQ}$

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$P \cdot dV$ is the work done by the gas on the piston

$-P \cdot dV$ " " " " " " piston " " gas.

$\therefore dW \equiv -P \cdot dV \Longrightarrow$ is the work done on the gas.

The question is ;

that is dQ an exact differential.

(is there such a thing ; the Heat . . .)

$\Rightarrow$ i.e; is the total amount of heat Q that you put in is zero if you move is a closed path in Entropy - Volume ; i.e; S - V space. ?

$\hookrightarrow$ it depends on path (we will prove this)

i.; dQ is not an exact differential ; neither is dW

.; dQ & dW are inexact differential.

$\hookrightarrow$ but ; dE is exact differential.

$\therefore dQ = dE + P \cdot dV$ (change indepent. Variable from S, V to E & V)

dQ : Assume Q is an exact differential

$\hookrightarrow$ this would mean ;

$$\left.\frac{\partial Q}{\partial E}\right|_V = 1 \quad \& \quad \left.\frac{\partial Q}{\partial V}\right|_E = P$$

Test the Curl

$$; \frac{\partial^2 Q}{\partial V \partial E} = 0 \quad ; \frac{\partial^2 Q}{\partial E \partial V} = \frac{\partial P}{\partial E}$$

$\therefore$ if dQ is exact ; then $\frac{\partial P}{\partial E} = 0.$

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will you believe that if you have a box of gas and you change energy in the box of gas; then pressure does not change.

⇒ No ofcourse it change.

↳ lets check for ideal gas

$P = \frac{NT}{V}$; $E = \frac{3}{2}NT \Rightarrow \frac{2E}{3} = NT$

$\Rightarrow \boxed{P = \frac{2}{3} \cdot \frac{1}{V} \cdot E}$ $\Rightarrow \frac{\partial P}{\partial E} = \frac{2}{3V}$

⇒ so; it is not true that $\frac{\partial P}{\partial E}$ is always zero.

↳ so; curl test fails ⇒ indicating that there is no such thing as Q being a function of what the state of the system is
↳ It depends on how you move from one place to another.

↳ i.e: Amount of heat that you have to put into the system in order to change it from one state to another state; depends on the path that we take.

↳ This is why; Heat is not a good description of the State of the System.

→ Both Heat & Work are like that;
dQ & dW are inexact.
↳ Only the combination of two of them "dW + dQ" is really the function of State of the System.

"Heat is not a property of the system"

- "Your state of tired-ness is a property of you; but it is not the property of landscape where you are moving."

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Pg 78

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 Statistical Mechanics: Entropy V/s Reversibility

-Shoaib Akhtar.

In thermal eqm at temperature "T" in a dilute gas; every molecule has a energy equals to $\frac{3}{2}k_B t_k$.

↳ from here you can see; Temperature goes to zero when Energy goes to zero.

Ideal gas has only Kinetic Energy.

$\therefore \frac{3}{2}k_B t_k = \frac{1}{2}m v^2$ ← This tells what average velocity is.

$\Rightarrow \boxed{\frac{3k_B \cdot t_k}{m} = v^2}$ → Actually it is velocity of molecule.

→ This we might expect is more or less the speed of sound in a gas. (it is wrong by a factor of $\sqrt{3}$ ... order of magnitude is essentially correct.

We also have a better formula ... for speed of sound.

$\therefore$ let; c denote the speed of sound.

$$c^2 = \frac{\partial P}{\partial(\sigma)}$$

↳ Very General Formula.

where; σ is mass density.

$\therefore$ remember; $\rho = \frac{N}{V}$

$\Rightarrow \boxed{\sigma = m\rho}$

σ: mass density.

ρ: Particle density

$$\Rightarrow \boxed{c^2 = \frac{\partial P}{m\,\partial \rho}}$$

$\therefore$ For ideal gas $PV = Nk_B t \Rightarrow P = \frac{N}{V}k_B T \Rightarrow \boxed{P = \rho k_B t}$

$\Rightarrow \frac{\partial P}{\partial \rho} = k_B t$

$\Rightarrow c^2 = \frac{1}{m} \cdot k_B \cdot t_k$

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For air $k_B = 1.3 \times 10^{-23}$

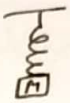
$m = 30 \times$ (mass of proton)
$= 4 \times 10^{-26}$ kg (mostly made up of Nitrogen; N_2 .)

$(t_K)_{\text{Room temperature}} = 300$ K.

$\frac{1}{2}mc^2 \Rightarrow c = 500$ m/s → This is little big

(The correct answer is around 300 m/s)

A harmonic oscillator in a system.
(treat the rest of the system as Heat Bath)

Harmonic oscillator here can be –
i) mass attached to spring 
(or)
ii) electromagnetic wave in a cavity.
(or)
.... almost anything oscillating.

} Harmonic Oscillator covers large group of possible system.

★ lets do Statistical Mechanics of Harmonic Oscillator.

"Oscillating System in a Heat Bath"

$$E = \frac{m\dot{x}^2}{2} + \frac{k \cdot x^2}{2}$$

$$= \frac{p^2}{2} + \frac{kx^2}{2}$$

Energy.

★ Boltzmann distribution; for the system.

note!! The Heat Bath determines the temperature.

$$\therefore \; e^{-\beta \cdot \frac{p^2}{2m}} \cdot e^{-\beta \frac{kx^2}{2}}$$

$$\therefore Z = \int dp\, dx \cdot e^{-\beta \cdot \frac{p^2}{2m}} \cdot e^{-\beta \cdot \frac{kx^2}{2}}$$

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$$Z = \left(\sqrt{\frac{2\pi m}{\beta}}\right)\cdot\left[\frac{1}{2}\sqrt{\frac{2\pi}{k\beta}}\right]$$

$$\Rightarrow \boxed{Z = 2\pi\sqrt{\frac{m}{k}}\cdot\frac{1}{\beta}} \Rightarrow \boxed{Z = 2\pi\sqrt{\frac{m}{k}}\cdot T}$$

$\therefore$ angular frequency of oscillator is: $\omega = \sqrt{\frac{k}{m}}$

$$\Rightarrow \boxed{Z = \frac{2\pi}{\omega}\cdot\frac{1}{\beta}}$$

$$\therefore \log Z = \log\left(\frac{2\pi}{\omega}\right) + \log(\beta) \Rightarrow \frac{\partial}{\partial\beta}(\log Z) = -\frac{1}{\beta}$$

$$\Rightarrow E = -\frac{\partial}{\partial\beta}(\log Z) = \frac{1}{\beta} \Rightarrow \boxed{E = T} \text{ (or) } \boxed{E = 1/\beta}$$

→ it is not so different from note $\frac{3}{2}T$ of particle in a gass.

* why no 3 : because it is one dimensional oscillator.

* why no $\frac{1}{2}$: The last two integral ... which gave us $\frac{1}{2}(\beta)^{-1}$ ... so we had $(\beta)^{-1}$

→ if we had more degrees of freedom ... we would have got $\frac{1}{2}\cdot\frac{1}{\beta}$ for each of them.

ie: $\frac{1}{2}\log\beta$ in $\log Z$ for each of them.

* Average Kinetic energy & Average Potential Energy are infact equal ~~... how they~~ in Harmonic oscillator ; here they are $\frac{1}{2}\cdot T$.

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Note The energy does not depend on mass of particle; it only depends on Temperature.

↳ This means the same case in particles in gas.

Also energy is also independent of constant k.

∴ think for $k \to \infty$.

i.e; under circumstances ... it is just a constraint thing that it has fix length (perhaps, the length being zero) which cannot be changed.

↳ Under those circumstances ... we will say that we cant excite it ... we can't give it energy ... There is no way to start it vibrating.

↳ You can't give it Kinetic energy because it is absolutely locked in place.

↳ " " " " Potential " " you can't pull it away.

↳ yet the formula "$E = T$" does not seem to care.

(There also seems to be Energy T; no matter how hard it is to get that oscillator going)

There is something wrong. We have actually ignored one crucial feature of nature.

- We have not ignored anything about Classical Mechanics. (actually it is correct Classical Mechanical conclusion)

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We are doing something wrong : missing some ingredient to physics here which tends to keep the oscillator (or having this much energy "E = T".

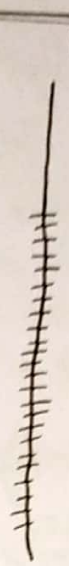
↳ That ingredient is of course Quantum Mechanics.

Quantum Mechanical Harmonic oscillator.

$n \cdot \hbar\omega$

"Quantum Harmonic oscillator is discreate set of states.. all equally ~~sta~~ spaced "

Energy of single Harmonic oscillator comes in discreate integer multiple of $\hbar\omega$.



↳ lets calculate ; Partition function for Quantum Mechanical Oscillator.

$$Z = \sum_{n=0}^{\infty} e^{-\beta \cdot n\hbar\omega}$$

$$\Rightarrow Z = \sum_{n=0}^{\infty} \left(e^{-\beta\cdot\hbar\omega}\right)^n = 1 + x + x^2 + x^3 + \ldots \infty$$

$$= \frac{1}{1-x}$$

where : $x = e^{-\beta\hbar\omega}$

$$\Rightarrow \boxed{Z = \frac{1}{1 - e^{-\beta\hbar\omega}}}$$

$$\because E = \frac{-1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\frac{\partial Z}{\partial \beta} = \frac{-1}{(1 - e^{-\beta\hbar\omega})^2} \left(\because (-\hbar\omega) \cdot e^{-\beta\hbar\omega}\right)$$

$$\Rightarrow \frac{\partial Z}{\partial \beta} = \frac{-\hbar\omega \cdot e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$

$$\Rightarrow \frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = \frac{-\hbar\omega \cdot e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})}$$

$$\Rightarrow E = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

$$\Rightarrow \boxed{E = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}}$$

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"High temperature, is a situation where classical theory is good".

↳ each one little quanta of energy is thought as very small.

* A classical spring is great many units of energy. In that sense; classical system in quantum units has lot of energy. This must mean that it must have high temperature in some quantum sense.

"Quantum Systems become Classical when temperature is very high."

When temperature is high; there is lot of energy

↳ Then Quantization of energy becomes un-important.

So; let work in high Temperature range

$\therefore$ T large $\Rightarrow \beta$ is small.

$$E = \frac{\hbar\omega \cdot e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})}$$

$$E = \frac{\hbar\omega \left(\lim_{\beta\to 0} e^{-\beta\hbar\omega}\right)}{1 - 1 + \beta\hbar\omega + O(\beta^2)}$$

$$\Rightarrow E = \frac{\hbar\omega}{\beta\hbar\omega} \Rightarrow \boxed{E = \frac{1}{\beta}}$$ This is the same Classical Energy.

"We see that in high Temperature situation; it just reproduces just the Classical Physics"

What happens at low temperature (large β)

$$E = \frac{\hbar\omega \cdot e^{-\beta\hbar\omega}}{(1 - \lim_{\beta\to\infty} e^{-\beta\hbar\omega})} \Rightarrow \boxed{E = \hbar\omega \cdot e^{-\beta\hbar\omega}}$$

$\Rightarrow$ we get something which is exponentially small.

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We find that Quantum Mechanics tends to supress the energy of oscillator when temperature is low enough.

* At very low temp. ; it does not behave like a classical oscillator : it has much less energy than the corresponding Classical oscillator would have.

☆ Where is the crossover — Where does it go from being Quantum to Classical?

The crossover is where the exponential goes from being small to being large.

(In formulas like $E = \frac{\hbar\omega \cdot e^{-\beta\hbar\omega}}{1 - e^{-\hbar\beta\omega}} = f(e^{-\beta\hbar\omega})$

↳ The crossover between high temp. & low temp. behavior is when what's in the exponential here is about 1

i.e; $\beta\hbar\omega \simeq 1$

⇒ The exponential controls whether the discreatness of energy level is important or not.

● Cross-over means transition from Quantum Behavior to Classical Behavior.

$\beta\hbar\omega = 1 \Rightarrow T = \hbar\omega$

$\beta\hbar\omega > 1$: Quantum

$\beta\hbar\omega < 1$: Classical.

The crossover is when the energy of the oscillator classically is equal to one Quantum worths of Quantum Mechanical Energy. (if you try to make T low than that, the oscillators have less than one Quantum worths of energy)

It does not want to have less than one Quantum worths of energy ; & so expression of energy is also almost zero for low T.

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Topology : Module 1 : Set Theory — Shocib Akhtar

Set : A set is a collection of well defined distinct object.

Notation : capital letters A, B, X, Y denotes set ; and lowercase a, b, x, y denote elements belonging to these sets.

$x \in A$ (x belongs to A)

$x \notin A$ (x does not belong to A)

When the temperature is too low, we are deep in the Quantum regime ; and so the oscillator has exponentially small energy compared to what it would be Classically.

↓

When Temperature goes up ; at some point, T will get larger than $\hbar\omega$ ⇒ and that is the point where you begin to activate the oscillator.

You can't activate the Quantum oscillator unless the T is such that it corresponds to more than one quantum worth of energy.

↳⟹ so ; at low temperature (upto some temperature) ; the diatomic molecules behaves like a monoatomic molecule.

(you donot stop vibrations going)

↳ when you raise T enough ; so that T is bigger than a quantum of energy ; the diatomic molecule starts to behave like a diatomic molecule (i.e. it gets it vibrational degree of freedom)

☆ Stiffer the oscillator ; larger is the frequency. ; $\omega \propto \sqrt{k}$

so ; stiffer the oscillator ; ~~higher is the~~

higher is the cross-over temperature.

Molecules are pretty stiff on the scale of a rubberband. And the T at which molecules goes from looking like a monoatomic molecule to being a diatomic molecule ; is fairly high.

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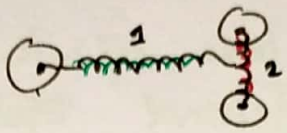
When you heat even more ⇒ atoms themselves start to vibrate ⇒ ~~[illegible]~~ eventually they will get ionized.

"As you heat a system you start to discover that it has more & more degrees of freedom"

~~mmmm~~ is stiff.

≡ A crazy molecule



} is very stiff.

At low temp., there is not enough T to overcome the ~~Quantum threshold~~ Quantum threshold for oscillator to start oscillating. So, it behaves like a point.

↳ you heat to such T; where you activate the oscillator "1" but not still enough to oscillate "2". (it behaves like a diatomic molecule)

"1" is strong stiff spring

"2" is supper dooper ~~stro~~ strong stiff spring.

↳ You heat it more ⇒ it activates "2" ⇒ it starts to behave as if three molecules connected by spring.

"As you heat the system, more and more degrees of freedom become ~~acti~~ activated and you start to discover complexity of things"

(you dont discover complexity of things at low temperature ⇒ you discover the Quantum behavior of things.)

"As you increase T; degrees of freedom unfreeze themselves from Quantum constraint & start behaving classically"

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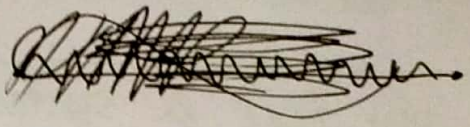
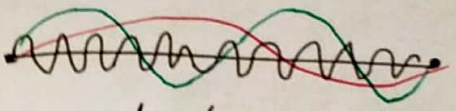
* A vibrating oscillator is infinite no. of Harmonic Oscillator. → The infinite no. becomes shorter & shorter wavelengths



↳ if each one of these oscillators have had energy equal to T (classically) & there are infinite no. of them



↳ so the string will have infinite amount of energy when it will come to Thermal ~~eq~~ equilibrium.

(A classical paradox) ⟹ solved by Quantum mechanics.

Solution: Most of these oscillators have very high frequency (shorter wavelength ⇒ higher frequency of the oscillator)

↳ & therefore most of the oscillator at any given temperature are frozen out by ~~Quantum~~ Quantum mechanics...

... not free to oscillate.

---

* Adding a constant to every energy level is equivalent to multiplying the partition function by a constant; and the result is no. change in anything ~~of~~ interesting.

The second law of thermodynamics is a puzzle; because it says that the world is irreversible & that there is something called Entropy which always increases. or stays the same.

on the other hand; Newton's eqn are completely reversible. ⇒ Anything which can happen in one direction of time can happen in the opposite direction of time.

↳ There is tension between reversibility on one hand of the fundamental equations and irreversibility of the observational properties of complicated systems.

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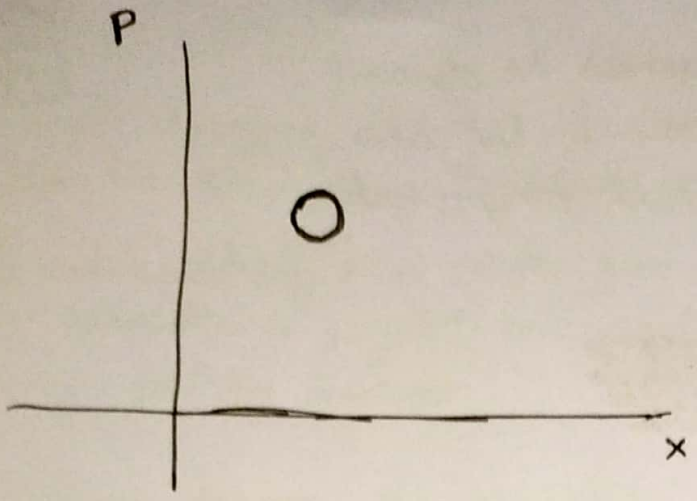

We start out with some probability distribution.

∴ constant probability inside the blob ○. & zero outside.

"Probability density is constant within the blob".

entropy of this system has to do with the size of the blob.

"The more you know corresponds to the volume of the blob being smaller".

Liouville's Theorem

⇒ volume stays the same as time goes on ⇒ entropy stays the same.

Prob. distribution may change because the states which are occupied become different ⇒ but entropy does not change.

↳ This is correct view of what is called micro-entropy.

⇒ but: there is another concept of entropy which does increase. and it has to do with something called coarse graining.

Typically, our experiments are such that we cannot resolve points in phase space.... There is some resolution of states.

⟺ in Quantum Mechanics, it turns out that, that resolution is naturally built in. and the smallest uncertainity is given by the plank's constant.

"Instead of talking about points in phase space; we will now talk about coarse-grained points in phase space".

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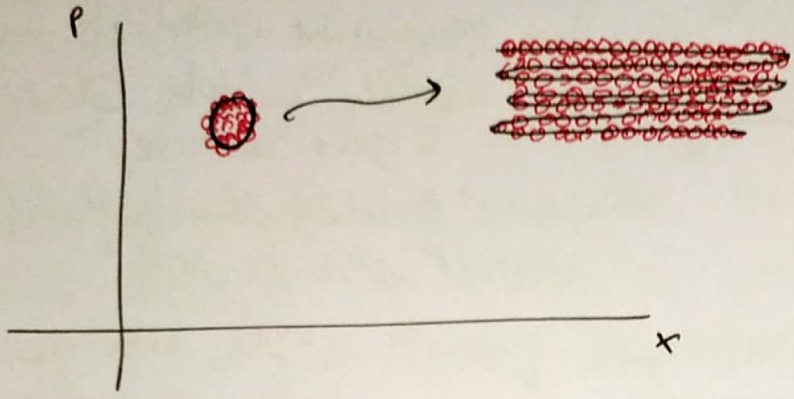
☆ make up a dynamics which preserves the dynamic..
...preserves area on the plane .. but takes the phase volume & turns it into long snake.



because of our limited resolution powers, we cannot tell a phase space from a neighbouring phase space.

↳ so; we take these phase points & blobbafy them.
we think of them instead of ~~points in~~ as being points in the phase space; as blobs.

↳ The blobs cover more area in future.

"It is not violating Liouville, we are just loosing information because we can't keep track of this fine structure".
(Actual true dynamics is such that the snake here has same area as blob ... & Liouville theorem holds true)

☆ If we could follow phase points with infinite precision & define probability density with infinite precision, the volume would not change.

↳ But in every real situation we can't distinguish one state from a nearby state. So we do this process of Coarse ~~Graining~~ Graining.

Coarse Graining is replacing points of phase space by blobs of phase space.

↳ If we do this ≠ volume increases

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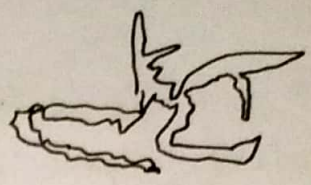
without changing the evolved snake may grow some fibres, which in turn may grow smaller fibres. (Chaos)

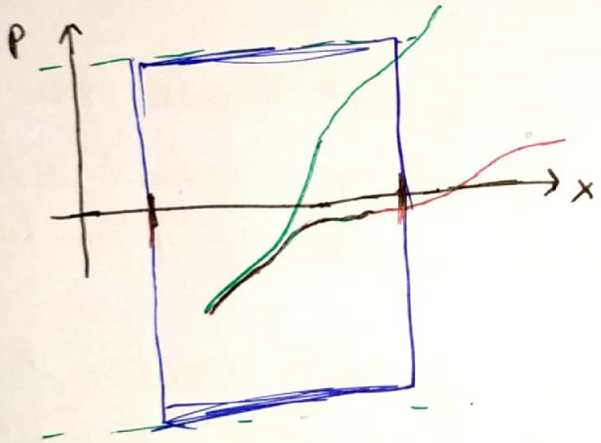
↳ and eventually, no matter how good your resolution is, you will start seeing entropy increases.



∴ whatever degree of resolution we have; we will see that ~~volume in~~ the volume in consideration will increasing ⇒ resulting in increase in entropy. ... This is the second law of Thermodynamics.

∴ Lets; think of a gas of large no. of particles in a box.

↳ if it is in a box ⇒ this means x's are bounded.



(two nearby points may evolve to to points which may be very far apart)

∴ Can the momentum be anything?

And Usually the energy constraints how much the maximum momentum can be.

↳ so; even if all the energy of the system went into one particle, that particle will still itself have finite energy.

↳ The effective region of phase space which is available to us is some big area shape ... but it is finite (it does not ~~extend to~~ extend to infinity in any direction).

If we are truly off by a truly tiny amount (i.e; nearby phase points); the difference in the trajectory ~~of~~ of the whole system will be small for a while ... but sooner or later it is gonna start

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increasing. Errors compound & so sooner or later the nearby trajectory is going to deviate. This is the character of what is called Chaotic System.

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↪ So; no matter how close you start together, you will eventually depart and fill up a lot of phase space if you are not infinitely precise ..... so; nearby close phase points seem to spread out even though the volume of phase space strictly speaking stays the same.

"Not that the entropy always increases; but given any configuration it is most probable that the next configuration will have more entropy.

↪ Entropy probably increases".

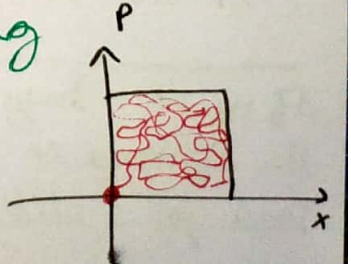
Chaotic means that nearby phase trajectory tends to seperate after a long enough time.

↳ It is the phenomenon of close by points in phase space following each other for a while & then departing by huge amount so that the system becomes effectively unpredictable if we have finite resolution .....

↪ Situation in which predictability effectively breakes down in order to predict the system for a length of time "t" your precision with initial conditions & knowledge of evolution of the system has to get better & better as the time over which you want predictability is more.

... when trajectories deviate far apart.. and due to coarse graining after a long time it will eventually cover the whole phase space ... ⇒ thus leading to minimum knowledge ... that probability become constant over whole phase space

⟹ It corresponds to reaching maximum entropy.



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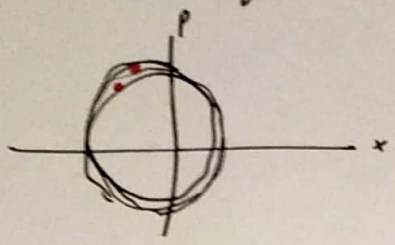
ex Non-Chaotic System

Harmonic oscillator



~~If~~ Close by phase points in this case never get far from each other.

"You need to know initial condition and laws of motion with high precision to ~~overcome~~ overcome chaos."

ex Ordinary pendulum is not chaotic.. it is very very predictable.

ex Double pendulum is very chaotic

"Given any length of time that you want to predict.. there exists a tolerance (or say a precision) Σ that will allow you to predict for that later time"

↳ given t, there exist Σ .. such that and so forth...

LYPNOV coefficient is the exponential growth of the separation of trajectories.

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Poincarré Recurrance ... evacuate the room air in one side of the room ... and stick the air in other side of the room ... i.e; Start with initial condition where all the air is in left side of the room.

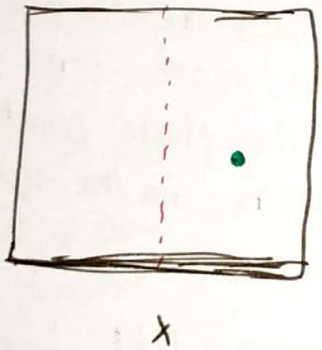
↳ Now let it go . ↳ comes the thermal eqm → fills the room pretty much uniformly

↳ Entropy increases

∴ what if you sit there & wait for long.
Sooner or later the unlikely event will happen ; where by accident or just waiting long enough in time ..all of the air reapper on the left side of the room. ... This is called Poincarré Recurrance.

How long do you have to wait ?

∴ start with idea of phase space ($6N$ dimensional space ; $3N + 3N$ (space + moment))



∴ P is bounded because of energy.

We start with phase point (as initial condition) on right side of the room.

↳ & see how it evolves.

∴ now; Phase point moves Chaotically.

∴ The phase point moves in a complicated way & pretty much fills up the phase space; in a sense that if you coarse grain it & fuzzy-lize a little bit , it will look like it pretty much fill up the phase space.

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What percentage of time do you expect that the phase point resides such that the particles are all in one of the room.

↳ it looks half the time

(that's crazy... we don't expect this ~~clearly~~ intuitively)

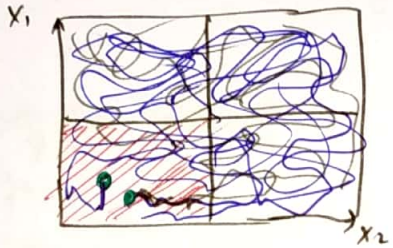
↳↳ The mistake what we are making is that we are just drawing the picture in 2-dimensions.

↳ What happens if we have ~~N pair~~ N particles and thus $6N$ coordinates.

... remember.. we are not ~~as~~ talking about the part of the phase space where one particle is on the right hand side.. but talking about all of them being on ~~right~~ right hand side.

↳ ex lets check for two partiles

2) lets forget momentum & look at only space.



To say that both of the particles are on one half of the room ; is to say that the phase point is somewhere in the quarter.

∴ ~~1/4 percentage~~

$\frac{1}{4}$ fraction of time both particles are on the left hand side (or at ~~as~~ right hand side) of the room.

⟹ If there are N particles ; then $\left(\frac{1}{2}\right)^N$.

fraction of time all the particles like in one half of ~~the~~ the room.

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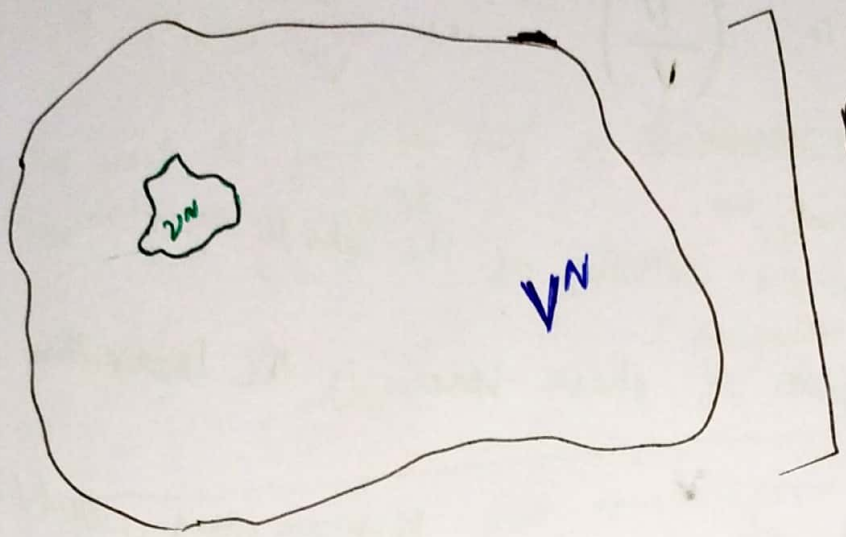
Lets take the phase space and identify a sub-region of it (the sub-region which we are interested in ... i.e; an interesting configuration that is very unlikely)



phase space excluding momentum.

v => Volume of little region

V => Volume of the box.

∴ What is the volume of phase space if there are N particles?
(for momentum now,.. they are not important here)

↳ it is (Volume of Box)^N i.e; V^N

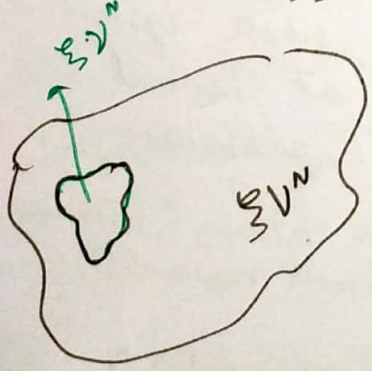
~~...~~.

↳ roughly say that volume of the whole phase space V^N
(This is same V^N which we discovered when we calculated the partition function & integrated over the position)

note!! V is the volume of the box.
v " " " of the region where we want all particles to be there.

note!! If including both momentum & space.

Then; volume of whole phase space is $\xi \cdot V^N$
(where ξ is some constant)
and ξ is the same constant which appears in the volume of little sub region; i.e. ξv^N



★ ξ is determined by energy
(finite ness of energy)

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What percentage of time will you expect phase point be in $\xi . v^N$ over there?

i.e; $\frac{\xi . v^N}{\xi . V^N}$ i.e; $\left(\frac{v}{V}\right)^N$ i.e; $\frac{v^N}{V^N}$

$\therefore$ v^N could be a small no.

$\therefore$ V^N is proportional to the entropy of the whole system.

The entropy of a region of phase space is the logarithm of the volume of that region.

$\therefore$ v^N is exponential of entropy that a gas would have if it was in the little region. (all the particles)

$\therefore$ Lets take that little region to be pretty small ... that's just a number.

$\therefore$ V^N is exponential of entropy of the whole gas in thermal equilibrium.

$$S = \log V^N \Rightarrow V^N = e^S$$

$\Rightarrow$ so; this tells that likelihood of finding a system within a tiny volume of phase space is always proportional to

e^{-} (Entropy of Thermal equilibrium state)

i.e; $P = \frac{e^{+S_0}}{e^{+S_T}}$

$\Rightarrow P = e^{(S_0 - S_T)}$

$\therefore S_T >> S_0$

$\Rightarrow S_0 - S_T \simeq -S_T$

$\Rightarrow \boxed{P \simeq e^{-S_T}}$

$S_T \Rightarrow$ Entropy of whole system at thermal equilibrium.

$S_0 \Rightarrow$ entropy within small region.

$\Rightarrow$ it is same as $\left(\frac{1}{2}\right)^N$ that we got ... (i.e $v = V/2$ ... but an approximation ...)

$\hookrightarrow$ Very improbable .....

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$P = e^{-S_T}$ ⟹ it is a sort of approximation for $P = \left(\frac{1}{2}\right)^N$

[if we want to select v to be half of V

i.e.; $v = V/2$]

∴ if we want to find in half of ~~the room~~ the room

then; $P = \left(\frac{1}{2}\right)^{10^{23}}$ because N is of the order of 10^{23}

(Avagadro ~~number~~ number.....)

(multiple of avagadro number)

.... roughly you can say $P = \left(\frac{1}{2}\right)^{10^{30}}$

↳ He did the exercise just to understand in what sense systems are reversible. i.e.; If you wait long enough they will reverse themselves

If you study the system over sufficiently long time, you will discover that the ~~entropy goes~~ unlikely address goes up & down in completely time symmetric way.

⟹ What is not time symmetric ; is that if you knowingly start in a very odd configuration, i.e. in a tiny volume of phase space; ~~then most likely~~ the next thing is to find yourself out of that volume.

so; if you start in an odd situation with all molecules in a corner of the room, you expect the next thing to find that the molecules spread out. Infact, you find that the next, and the next thing is to pretty much spread out uniformly. ⟹ This sounds like it violates the reversibility of physical laws.

Infact; if you would to wait long enough, you will find reversing itself and doing everything imaginable for a closed system.

Future Reference: There is Quantum version of Poincarre recurrence Theorem.

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It is a deep conceptual point that helped Boltzman resolve puzzle of the apparent one-way-ness of time and the two-way-ness of the laws of motion.

↳ Ofcourse what it requires to make sense out of it is that we eventually would have to understand why the universe started in a little corner of phase space... that's a seperate issue.

→ still an open question.

If you watch a close system long enough, you will find that the measure of localization of the particles would decrease (if you started in a corner) ⇒ Then pretty delocalized for a long time and then pop-up ⇒ and then go back down ⇒ and then pop up ⇒ go back down ⇒ ....

but the time scale to discover this reversibility that what goes up must come down so as to speak is this $2^{10^{30}}$.

Every now and then you would find the molecules in exactly the right configuration : i.e; to shish into the corner pretty much the same way they shished out of the corner.

...write Susskind say on Universe... & then conclude that Universe must be Open System as per Susskind.
(earlier people thought Universe to be a closed system)

If the universe was a closed box ; & then you ask what is the most likely configuration to find a planet with life on it.

↳ You will discover that the most likely possibility is to have uniform gas everywhere except the smallest amount of possible gas necessary to make up a planet, having condensed into a planet.

The chances that you see one planet is very very small. " " " " " two " are vastly more negligible than that.

So; if we ask what an astronomer would see (given that they exist somehow) ~~& don't disturb the evolution of universe~~ i.e; the conditional probability that there is a planet and on that planet there are astronomers & they do

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have astronomical observations; what is the most likely thing they will see.

... The most likely thing they will see is nothing or some gas out there (but not condensed into another planet)

↳ What is the probability that you will see universe full of stars?

Absolutely negligible.. unless you know that in fairly recent past that you started with very exceptional & unusual starting point: then the flow out from that starting point is likely to have certain kind of structure that a random fluctuation would not have.

... it is called problem of Boltzman Brain.

It is a problem of using statistics to understand the world, the way it is. And it is always the conditional question; i.e: given that we are here on earth, that set of all various things what is the probability that we see something say "X".

↳ And the probability in a closed universe that we see X would be much higher than to see only X and not something other, say "Y".

↳ so; it is not a good theory to think that we are result of random fluctuations. If we were; then we would have no explanation of the coherence of history.

Why history looks like it had coherence past; and why there is consistency to historical evidence; if the planet just materialized in a random fluctuations with us sitting here today.

The probability of formation of Boltzman Brain in a room of gas with random fluctuation is extremly small. Boltzman will not be surprised to find himself because if assumes the theory of random fluctuation then he will see that I was about to form at some point and this is the time when I am formed.

Now, lets ask what is the probability that Boltzman life

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will be seen in the room given the Boltzman Brain has formed is even more smaller than the probability of formation of Boltzman Brain.

So, the chance of Boltzman Brain in the room discovering Boltzman wife is extremely - extremly small.

↳ But if Boltzman Brain finds his wife, children & other people ... then we would be sure that it could not be just the result of random fluctuations.

"Boltzman Brain problem suggest that Universe may not be a closed system"

"If you have a system with a flow moving through it ; then it can create interesting structures. "

ex flow of water through pipe can create vortices.
(These vortices have little structure)
... eddy currents

ex eddy currents ...

↳ If you stop the flow by sealing off the ends of the pipe ; then what happens is that the eddy currents disappears and the liquid just returns to a quiescent, dull, boaring equilibrium.

"Even in this flow situation, entropy is increasing."

---

what is the flow in the case of life that allows this kind of apparent violation?

The same thing is true on earth, the flow is the flow of energy from the Sun. .... life is a kind of little eddy.. vortices that appear in the moving fluid

↳ The fluid being energy from the sun.

When we talk about Magnets in statistical mechanics, we are usually not talking about pieces of iron. We are usually talking about Mathematical models of certain kind of system that has certain feature which resemble magnetism.

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* Ordinary magnet is made up of lots of little magnets.
(could be small as single atoms (or) could be little crystal grains)

Experimental facts

and typically at very high temperature those little magnets are randomly oriented in such a way that the net sample does not have net orientation. The orientation is random. Not just the orientation of whole thing is random, but the relative orientation of the parts of it are random & so there is no net magnitization; i.e. you dont see a macroscopic field from it.

If you cool it down, and the energies stored in pairs of these little magnets is such that the magnets like to line up in the same direction ⇒ Then you will find that groups (lumps) of the little magnets tend to be in alignment, but other like groups of magnet will also tend to be in alignment, but in other directions. And you find sort of domains. Domains which are magnetized, which means they tend to point in the same direction, but these domains are still fairly small.

As you cool it down more and more; the energy consideration that things like to be in the same direction (like means that energy is lowered if magnets are parallel..); then as you suck energy out of the system more & more of them would want to come into alignment; and these domains will start to grow. Eventually you may or may not hit a point at finite temperature; (non-zero)

at which all of a sudden these domains become infinitely big so that the magnet tends to be somewhat lined up everywhere in the same direction.

↳ This is called Ferromagnetic transition.

(its a phase transition)

* certainly at zero temperature, you will expect them to be all lined up; because at zero temp. the only state of importance in Boltzman distribution is the lowest energy state.

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And the lowest energy state is that all the microscopic magnets line up.

↳ which direction they line up may be random.

→ and this itself called Spontaneous Symmetry Breaking.

note!! ↳ just one little elementary atom being in a magnetic field which tends to line up little bit may govern the whole thing about the way, the whole system lines up.

↳ There is a symmetry, the symmetry is which way things point. ↳ If they wind up pointing in a direction that symmetry is broken... that is called breaking the symmetry.

but this is spontaneous; there is no magnetic field pushing everything in that direction, it just had to pick up a direction (it may be because of a tiny tiny little stray magnetic field)

The point at which the symmetry is broken (the point at which the magnets tend to line themselves up in some direction) that's a phase transition. And it is called the Magnetic Phase Transition.

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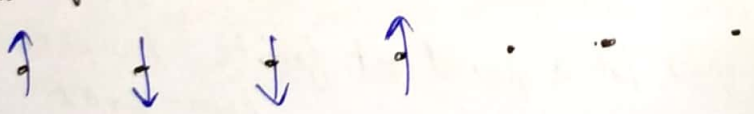
lets think now of an interesting mathematical magnet.

This magnet either points up or down. (a very simple mathematical magnet)

N no. of small ~~magnet~~ magnets.



we will study a very simple version.

(i) There is no interaction between magnets at all.

(ii) But there is a magnetic field. Each atom has a magnet moment, that's just a little number attached to it which tells you how strongly it interacts with the magnetic field.

↳ has magnetic momentum μ. ; has to do with strength of magnetic.

∴ There is magnetic field say H.

So; energy of the small tiny magnet is μH

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The energy of these magnets are different if it is up or down.

∴ in particular; if magnet is up ⇒ give it + energy.
" " " down ⇒ " " − " .

so: let $\sigma_{(i)}$ be a variable for i^{th} magnet.

↑ ↓ ↓ ↑

$\sigma_{(1)}$ $\sigma_{(2)}$

$\sigma_{(1)}$ is for first atom
$\sigma_{(2)}$ " " second " .

& σ is either +1 or −1.

$\sigma_{(i)} \equiv +1 \equiv$ up spin. ⟶ Energy $+\mu H$ of one spin.
$\sigma_{(i)} \equiv -1 \equiv$ down spin ⟶ Energy $-\mu H$ of one spin.

let; n spin up & m spin down
⇒ so; Total energy is equal to $(n-m)\mu H$

i.e; $E = (n-m)\mu H$

∴ remember; $N = n + m$

note// H is the measure of strength of magnetic field imposed from outside

∴ Without asking which one is which, how many configurations are there.
↳ We have N things; and we to group them in two groups.
n & m. ; How many such arrangements are there.

The number of States with a given value of energy $E = (n-m)\mu H$ is $\frac{N!}{n!\,m!}$

↳ lets take one configuration & ask what the Boltzman weigh is,
i.e; $e^{-\beta E}$.
⟶ Indeed find partition function (Partition function is sum over all configurations

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$$Z = \sum_{n,m \text{ (such that } n+m=N)} e^{-\beta \cdot \mu H (n-m)} \cdot \frac{N!}{n!\,m!}$$

↳ for each (n, m) there are these many configurations.

$$\Rightarrow Z = \sum_{n} e^{-\beta \cdot \mu H (2n-N)} \cdot \frac{N!}{n!\,(N-n)!}$$

notations; $X := e^{-\beta \mu H}$; $Y := e^{+\beta \mu H}$

$$\Rightarrow Z = \sum_{n} \frac{N!}{n!\,(N-n)!} e^{-\beta \mu H (2n-N)}$$

$n+m = N$
$n - m = N - 2m$
$m + n = N$
$m = N - n$
$= N - 2(N-m)$
$= 2n - N$

$$\Rightarrow Z = \sum_{n} \frac{N!}{n!\,(N-n)!} X^n \cdot Y^{N-n}$$

$$= (X+Y)^N \Rightarrow Z = \left(e^{\beta \mu H} + e^{-\beta \mu H}\right)^N$$

$$\Rightarrow \boxed{Z = \left(e^{-\beta \mu H} + e^{+\beta \mu H}\right)^N} \Rightarrow Z = \left(\frac{e^{-\beta \mu H} + e^{+\beta \mu H}}{2}\right)^N 2^N$$

$$\Rightarrow Z = 2^N \cdot (\cosh \beta \mu H)^N \Rightarrow \boxed{Z = 2^N \cdot (\cosh \beta \mu H)^N}$$

here: $E \propto \sigma$ (it is not symmetry under $\sigma \to -\sigma$)

Magnetization is the relative percentage of up spins & down spins.

- Magnetization is 0 ⇒ if # (no. of up spin) = (no. of down spin)
- " " positive ⇒ if (— " —) > (— " —)
- " " negative ⇒ if (— " —) < (— " —)

∴ $(n-m)$ is sort of magnetisation; but it is usual to divide by N, so that it becomes magnetisation per magnet.

$$M = \frac{(n-m)\mu H}{N}$$ i.e; $$\boxed{M = \frac{(n-m)}{N}}$$ → defination of Magnetization.

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$E = NM\mu H$

* Magnetization is roughly the probability of being up minus that of being down for a given spin.

note $E_{n,m} = (n-m)\mu H$ is a particular configuration; and we should say that magnetization is average of that $M = \left\langle \frac{n-m}{N} \right\rangle$

↳ Average over the statistical distribution of the Boltzman distribution.

* $E_{n,m} = (n-m)\mu H$ is energy of a particular configuration

& ofcourse $E = \langle (n-m)\mu H \rangle$ is the average energy over Boltzman distribution.

so; $\boxed{\langle E \rangle = N \langle M \rangle \mu H}$

" If something is equal to something, configuration by configuration, then it will also be equal in the average."

↳ usually you dont have to put " $\langle\ \rangle$ " because the defination of magnetization is the average: average over the Boltzman probability distribution.

* at zero temperature ⇒ we expect M to -1
* at ∞ " ⇒ everything is equally probable ⇒ we expect M to be 0. (zero)

so; M goes from -1 to 0.

* and at no point M will be positive; because of the biased down.

$E = -\frac{\partial}{\partial \beta}(\log z)$

$\therefore \log z = N \log 2 + N \log(\cosh \beta\mu H)$

$\frac{\partial \log z}{\partial \beta} = N \cdot \frac{1}{\cosh(\beta\mu H)} \cdot \sinh(\beta\mu H) \cdot \mu H$

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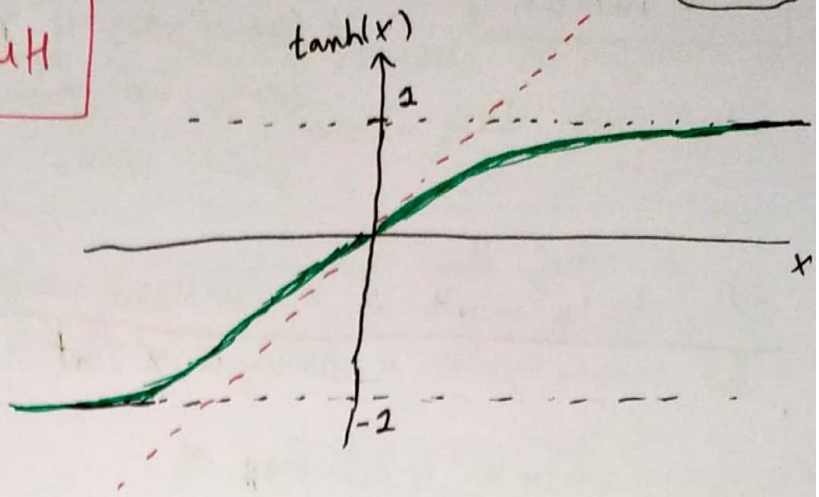
$$E = -N \cdot \tanh(\beta\mu H) \cdot \mu H$$

$$\Rightarrow M = -\tanh(\beta\mu H)$$



∴ Small $T \Rightarrow$ large $\beta \Rightarrow$ $M = -1$

large $T \Rightarrow$ small $\beta \Rightarrow$ $M \simeq 0$

History|| Lezs gave his student Ising a problem whether there was a phase transition in the one dimensional ising model (the name with ~~that~~ which it is now known) .... his student got the wrong answer... he said there was a phase transition ; but actually there was not.

Ising Model :

it is symmetric between up and down. If there is any magnetization, it's because somehow the system has spontaneously broken the symmetry.

- in one dimensional ising model, it does not ~~happen~~ happen.
- in two dimensional ising model, it does happen.

The energy here is not stored particle by particle. Now we have no external field.

So if the little magnets did not interact with each other, there will be no energy. (If there is no energy, then all configurations are equally likely)

In this case ; the magnetic field that each spin sees is due to its neighbours.

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- If both neighbours are up ⇒ it feels magnetic field up.
- If one neighbour is up & one is down ⇒ it feels no magnetic field.
- If both neighbours are down ⇒ it feels magnetic field ~~down~~ down.

↳ so; we are saying that energy is associated with pairs of neighbouring spins; and if the pairs are in the same direction.

~~Now, lets assume~~

~~energy is equal~~

★ Do we want ★ interactions to favour allignment or anti-allignment.

★ Energy is going to be equal for "↑↑" & "↓↓" configuration.
★ " " " " " " " "↑↓" & "↓↑" " .
★ " " " " " unequal for "↑↓" & "↑↑" configuration.

i.e; $E_{\uparrow\uparrow} = E_{\downarrow\downarrow}$ & $E_{\uparrow\downarrow} = E_{\downarrow\uparrow}$ but; $E_{\uparrow\downarrow} \neq E_{\uparrow\uparrow}$.

now, we assume if they are alligned; energy is lowered.
; if they are unaligned, energy is larger.
(Bias situation towards allignment..)

so; lets take E to be just some number usually called J.
J is energy scale of the problem.

$\therefore E = -J \cdot \sigma_{(1)} \cdot \sigma_{(2)}$ (for two neighbouring particles on a lattice)

↳ 1 & 2 are neighbouring sites on the lattice; and this is the energy of the (1)–(2) pair.

note!! ★ if they are anti-alligned ⇒ $\sigma_{(1)}\sigma_{(2)} = -1$
★ " " " alligned ⇒ $\sigma_{(1)}\sigma_{(2)} = 1$

now suppose we have line of them, and each one is interacting with its neighbour, then we can write, $E = -J \sum \sigma_{(n)} \cdot \sigma_{(n+1)}$

~~$E = -J \sigma_{(n)} \sigma_{(n+1)}$~~

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What you expect to happen at infinite temperature.

↳ The general rule is that at infinite temperature just random Chaos.

Everything is equally likely. ⟵ at high temp

* Zero Magnetization. ; every product term in the energy on the ~~average~~ average will be zero

---

* At zero temperature ; all of them will be alligned in the same direction.

↳ but which way? There is two direction ..↑↑↑↑.. (or) ..↓↓↓↓↓..

↳ You can't tell off hand.

~~Those~~ There are two ground states.

↳ Both come in with equal probabilities.

* Ground State means state of minimum energy.

⇒ Now if we suppose that there is an external magnetic field which is acting only one one particle; Then there is only one ground state which is in the direction of that little field direction. (even if that magnetic field is small)

↳ At zero temperature, Boltzman distribution favours infineticimally strongly the lowest energy state.

↳ If you were to apply that tiny magnetic field, let the system come to equilibrium at zero temp. ⇒ Then remove the magnetic field. ⇒ The system will then remember it. ⇒ Everybody is holding everybody else in place and the possibility of them all simultaneously jumping to the opposite is remote if there is enough of them. This is called Spontaneous Symmetry Breaking.

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A symmetry is usually represented by mathematical operation on the degrees of freedom: Symmetry is the action which you can do that dont change the energy.

here; what mathematical operation you would do on $\sigma_{(n)}$ to change from up to down?

Ans Multiply by -1.

in the case of one-dimensional ising model; .. ↑ ↑ ↑ ↑ ..

$\sigma_{(i)} \longrightarrow -\sigma_{(i)}$; then the Energy does not change.

↳ This means that we have Symmetry.

↳ This ensures that in some sense there is no bias to up or down.

if the system is going to flop itself all simultaneously into up at zero temperature; this means that it could also flop itself into down.

↳ There is no way to predict in advance unless you know that tiny little stray magnetic field.

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★ Ising actually solved the one-dimensional Ising model correctly given to him by his thesis advisor (Lenz) as a problem. He also realized that there is no phase transition but in the basis of that he believed and wrote in his thesis that Ising Model in any dimension does not have phase transition : and this was wrong.

correct history

★ notations : $J := \mu B$; $E = -\mu B \sigma$

so : $E = -J \cdot \sigma$

(minus sign is just the redefination of what you mean by up and down) ... not changes the physics.

. . . . . .

We have already learnt that you can also think of a subsystem as a system being a small subsystem plus a heat bath.

Just assume a spin is in thermal equilibrium with its environment. The environment being the rest of the magnets :

language: use Spin for a small little magnet here.

$$Z = \sum e^{-\beta(-J \cdot \sigma)}$$

$$\Rightarrow Z = \sum e^{+\beta J \sigma} = e^{\beta J} + e^{-\beta J}$$ } Partition function for just one spin.

Whenever you have independent system (no interaction term here) ↳ we can simply take partition function factors into a factor for each system.

$$\Rightarrow Z = 2 \cdot \cosh(\beta J)$$

... here we are concentrating one spin at a time.

$$E = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\frac{2 \cdot \sinh(\beta J)}{2 \cdot \cosh(\beta J)} \cdot J = -\tanh(\beta J) \cdot J$$

$$\Rightarrow \boxed{E = -J \cdot \tanh(\beta J)}$$ → Average energy of one of the spins.

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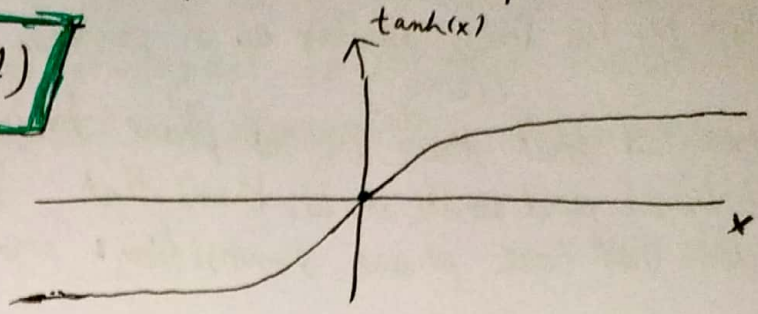
☆ What is the average sigma

$E = -J \cdot \langle \sigma \rangle = -J \cdot \tanh(\beta J)$ } ⇒ Average energy of one particle.

$\Rightarrow \boxed{\langle \sigma \rangle = \tanh(\beta J)}$



take $J > 0$

$\beta \to \infty \Rightarrow T \to 0 \Rightarrow \langle \sigma \rangle \to 1$ (spin will point up with probability very very close to one)

take $J < 0$ (just flip up & down... & the results just flip...)

$\beta \to \infty \Rightarrow T \to 0 \Rightarrow \langle \sigma \rangle \to -1$

∴ origin means $\beta J = 0 \Rightarrow$ very high temperature

Temperature just overcomes any bias for the spin to be up or down. So on the average $\langle \sigma \rangle \to 0$.

One dimensional Ising Model.

. . . ○ ○ ○ ○ ○ ○ ○ ...

$$\boxed{E = -J \sum \sigma_i \cdot \sigma_{i+1}}$$

↳ This is the total energy.

(The minus sign here means that it favours the spin being parallel ↑↑)

$$Z = \sum e^{-J\beta \sum \sigma_i \cdot \sigma_{i+1}}$$

$$\Rightarrow Z = \sum e^{-\beta J \sum \sigma_i \sigma_{i+1}}$$

☆ Knowing that a given ith magnet is up; then what is the probability down the chain here is also up? This is actually called the Correlation function. It is the conditional probability that if we know that a spin at a given point in the lattice is up, then what is the probability that at other place it is also up.

ie; What is the average of the product of spins at two different locations?

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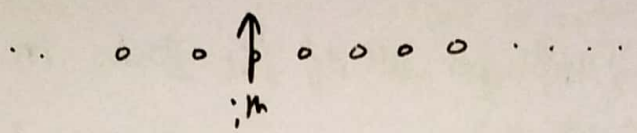
You might think that if you go far enough down the chain, a spin being up at some point will have very little effect farther down the chain. ~~and you might~~ There might be an effect of just having one spin up over here that would propagate all the ways through the system and tell you that there is a net bias throughout the whole sample.



you can diagnoses that by looking at $\langle \sigma_{(i)} \cdot \sigma_{(i+n)} \rangle$

∴ where; n is n units down the chain (average over i)

∋ If there does exist this kind of memory where if the spin is up, it biases the system all the ways to infinity.

* How far down the chain does the signal propagates before it gets lost before it just becomes equally likely far down the chain. .... biasing is some sort of signal.

* Zero temperature is like the perfectly accurate signal, infinite fidelity. That's like the situation where there is no loss whatever, and then everybody just lines up. ... There is perfect correlation.

Let's imagine the chain is finite;
& let the first spin can be either up or down.
↳ lets start by assuming it up. (and later we will put back the configurations towards down)

∴ let; $\mu_1 = \sigma_1 \sigma_2$ (a variable which has to do relationship between first and the second spin)

(assuming $\sigma_1 = 1$)

∴ now $\mu_2 = \sigma_2 \cdot \sigma_3$

if you know σ_1, then μ_1 will give what σ_2 is .. ⇐

.....

Instead of thinking of the spins, think of the links: The link have two possibilities, either parallel or anti-parallel. $\{\mu_i\}$

(This will not tell you anything about the individual spin unless you know that any of the spin's configuration, say the first spin was up)

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if you know: σ_1 & $\mu_1 \& \mu_2$ ⇒ will give what σ_3 is

$\mu_1 = \sigma_1\sigma_2$
$\mu_2 = \sigma_2\sigma_3$ } ⇒ σ_3 .. say if σ_1 is up

$\therefore \quad \sigma_2 = \mu_1$

$\sigma_2\sigma_3 = \mu_2 \Rightarrow (\sigma_2)^2\sigma_3 = \mu_1\mu_2$

$(\sigma_2)^2 = 1 \Rightarrow \sigma_3 = \mu_1\mu_2$

so; if you know $\{\mu_i\}$ for all of the links in between, then you know all the spins.

(say if you knew what the first spin was, say it was $\sigma_1 = +1$)

"There is no redundancy; no double counting as long as you know that the first spin is up; it is equally good to know the μ_s which lives so as to speak on the bonds between the spins. (As it is to know the spin themselves)"

↳ It is useful to use μ_s, i.e; the bond variables: because the energy is just made up out of these bond variables.

(Bond here meaning the relationship between neighbours)

So; we can write;

$$E = \sum_i -J\mu_i$$

notice!! There is one fewer bonds than there are particles.

note!! μ_i just represent individual bonds; and the individual bonds are all independent. There are no relationship between them.

↳ and it is good to know the μ_s as σ_s; as long as you know the configuration of first spin.

↳ so; you can substitute the sum over the spins by the sum over the values of the bonds.

$\mu_i = +1$ (aligned) $\quad$ $\mu_i = -1$ (anti-aligned)

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$$Z = \sum_{\mu} e^{-\beta J \sum \mu_i}$$

This has now reduced to exactly the same problem as

$$Z = \sum e^{+\beta J \sigma}$$

except μ in this here is called σ.

note: $2 \sum_{\mu} e^{-\beta J \sum \mu_i} = \sum_{\sigma} e^{-\beta J \sum \sigma_i \sigma_{i+1}}$

because; we could start with the first point down. (but a constant factor of 2 in partition function will not matter much)

It is sum over un-coupled individual bonds & it has exactly the same form as the partition function for the simpler magnet. (Remember, μ does not stand for a value of magnet, but it stands for relationship between two magnets)

$$Z = 2 \cdot \sum_{\mu} e^{-\beta J \sum \mu_i}$$

So; $Z = 2 \sum_{\mu} e^{-\beta J \sum \mu_i} = (2 \cosh(\beta J)) \cdot 2$ ⇒ for the case of two spins i.e; one bond

↳ if we have N spins ⇒ we have N-1 bonds

⇒ So; we have. $Z = (2 \cdot \cosh(\beta J))^{N-1} \cdot 2$

Better explanation for the factor of 2 | ie; $\sum_{\sigma} e^{-\beta J \sum \sigma_i \sigma_{i+1}} = 2 \sum_{\mu} e^{-\beta J \sum \mu_i}$

$\mu_1 = +1$ → $\sigma_1 = 1, \sigma_2 = 1$ (or) → $\sigma_1 = -1, \sigma_2 = -1$

$\mu_2 = -1$ → $\sigma_1 = 1, \sigma_2 = -1$ or → $\sigma_1 = -1, \sigma_2 = 1$.

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ie; $Z = 2\sum_{\mu} e^{-J\beta \sum_i \mu_i}$

$\Rightarrow Z = 2 \cdot (\cosh(\beta J))^{N-1}$

so; $\langle \mu \rangle = \langle \sigma_i \sigma_{i+1} \rangle = \tanh(\beta J)$ $\Longrightarrow$ taking $J > 0$: the fact that $\langle \mu_i \rangle$ comes to be positive tells us that there is net tendency for i to line up in the same direction as "i+1".

ie; $\langle \mu \rangle = \langle \sigma_i \sigma_{i+1} \rangle = \tanh(\beta J)$

Same as saying ; biased for the μ to be positive

This tells us correlation between neighbours.

☆ lets now go far down the line. Let's find what is the correlation between the i^{th} spin & n units down the chain.

$\langle \sigma_i \cdot \sigma_{i+1} \cdot \sigma_{i+1} \cdot \sigma_{i+2} \cdot \sigma_{i+2} \cdots \sigma_{i+n} \rangle$

ie; $\langle \sigma_i \cdot \sigma_{i+n} \rangle = \langle \sigma_i (\sigma_{i+1} \cdot \sigma_{i+1})(\sigma_{i+2} \cdot \sigma_{i+2}) \cdots (\sigma_{i+n-1} \cdot \sigma_{i+n-1}) \sigma_{i+n} \rangle$

$= \langle \mu_i \mu_{i+1} \cdot \mu_{i+2} \cdots \mu_{i+n-1} \rangle$

$\Rightarrow \langle \sigma_i \cdot \sigma_{i+n} \rangle = \langle \mu_i \cdot \mu_{i+1} \cdot \mu_{i+2} \cdot \mu_{i+3} \cdots \mu_{i+(n-1)} \rangle$

note; since all of the μs are independent $\Rightarrow$ The average factorize.

i.e; $\langle \sigma_i \cdot \sigma_{i+n} \rangle = \langle \mu_i \rangle \langle \mu_{i+1} \rangle \cdots \langle \mu_{i+(n-1)} \rangle$

$= (\tanh(\beta J))^{n-1}$

~~$\tanh < 1$~~

note; $\tanh(\beta J) < 1$

$$\boxed{\langle \sigma_i \cdot \sigma_{i+n} \rangle = (\tanh(\beta J))^{n-1}}$$

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if you go sufficiently far down the chain; the correlation function $\langle \mu_i \cdot \mu_{i+n} \rangle$ becomes arbitrarily small, there will negligible memory at far off points.

↝ Incidently this a pattern; actually a Duality.

In modern physics this could be thought of as first duality, i.e. equivalence of different systems. We found an equivalence between a theory of spin which are connecting nearest neighbours with another theory of just spins which are uncoupled to each other. with a clever change of variables; which basically took sites to bonds. (links)

(Duality between different statistical mechanical systems)

Magnetization can be translated into the statement that there is long range memory $\langle \sigma_{(i)} \sigma_{(i+n)} \rangle$; i.e. say if one spin is up, the others will be biased to be up. (average over i)

↳ it is equivalent to the statement that if you put tiny magnetic field on the system to bias it, it will cause everything to line up.

We found out that for one-dimensional Ising model is that it is never magnetised, except at zero temperature.

(has no phase transition) (it does exactly what you expect to do is that it fades away as you go down the line)

note: There will be long stretches of agreement; and then statistically on average every so often a switch.

↝ Infinite temperature is like you dont get any information from your; so you wind up making a random guess, whatever your neighbour says. ⇒ no correlation between neighbours.

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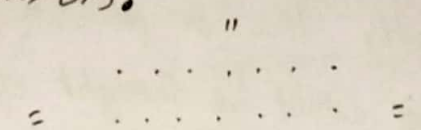
This one dimensional ising model is not much interesting.

In a one dimensional change, when someone makes a mistake, the next fellow does not have any support telling what the right answer is; because it just gets the message from previous person.

What about higher dimensions.

ex two dimensional Ising model



everybody gets four messages from all four neighbour around them.

↳ if one of the messages happens to be wrong, still three of the other messages may be right.

⟺ what the receiving point will do. He will do what the computer Scientists call the error correction.

Error Correction just means that he will take the majority vote.

This works much better. Infact, if the fidelity is good, the bias of initial message will spread throughout and off to infinity.

↳ in fact, we can say; putting a little magnetic field on one spring in two dimensions will bias the whole sample.

meaning

fidelity ⇒ faithfulness to a person, cause, or belief, demonstrated by continuing loyalty and support.

↳ This biasing is very much dimensional dependent.

in one dimension; each point has 2 neighbours.

" two " ; " " " 4 " .

" three " ; " " " 6 " .

in d " ; each point has 2d neighbours.

(in cubical lattice) i.e; in d-dimensional cubical lattice.

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~~If you have~~ ★ even if the fidelity is not so good, if you use weighting procedure such as taking the majority (which will be more good if you have more neighbours ⇒ i.e: indeed higher dimensions) you then do much much better.

---

in one dimensions; only two neighbours ⇒ it does not have much support system.

---

in high dimensions ⇒ have more neighbours ⇒ so; majority will not be wrong very often.

↳ Fluctuations among large no. of variables tend to be very small.

Higher the dimensionality; you have much better shot at being able to propagate the information of a spin throughout the intire lattice.

★ even two dimension is large for the purpose.
★ three dimension is very large.

only the one dimensional ising model does not have a transition

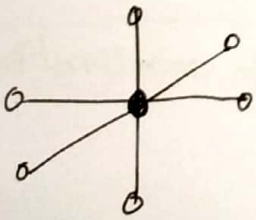
What could be easily predicted?

is that in sufficiently high dimensions is an awfully good argument to say that there is a transition.

---

d- dimensions

: each site surrounded by 2d neighbours.
(we will take d to be very large)



"Because d is very large; we can imagine that all of the neighbours define a field whose fluctuation is much smaller than its average value"

So; the energy of one spin is $E = -J\sigma \sum_{\text{neighbours}} \sigma_{\star}$

(5)

now, lets suppose that there is a bit of bias and so the average of the spins is not zero

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let: $\bar{\sigma}$ denotes the average of the spin throughout the lattice.

since the no. of neighbours is $2d$

$\therefore$ then: $\sum_{\text{neighbours}} \sigma_* \simeq 2d \cdot \bar{\sigma}$ ⟹ mean field approximation

→ pretty good approximation if the no. of neighbours is large.

(larger the no. of neighbours, better is the approximation)

• For large number's as a typical rule we are allowed to average and the fluctuations are small

so: $E = -J\sigma \sum_{\text{neighbours}} \sigma_* = -2dJ \cdot \sigma \cdot \bar{\sigma}$

σ is the particular spin at the given point in consideration.

$\bar{\sigma}$ is the overall average spin.

$E = -2dJ \cdot \sigma \cdot \bar{\sigma}$ ⟹ energy of one particular spin sitting in the bath or say in the field of all the others.

This is called mean field approximation

i.e: $E = -(2dJ\bar{\sigma}) \cdot \sigma$

let: $\bar{\bar{\sigma}}$ denotes the average of the particular spin in consideration.

$$\bar{\bar{\sigma}} = \tanh(2dJ\bar{\sigma} \cdot \beta)$$

σ is moving in the background of all the others & the others constitute a constant field which gives a multiplicative factor contribution in the energy i.e: $2dJ\bar{\sigma}$

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Mean field approximation is sometime also called Self consistent field approximation.

↳ self consisted because the one particular spin which was in consideration is no different from other spins. It is just one of the many spins in the system.

The physical intuition will require that the average of that particular spin $\bar{\bar{\sigma}}$ should be no different from $\bar{\sigma}$ (the average of all the spins)

↳ This has to do with translational invariance.

so; self-consitent field theory is to say that $\bar{\bar{\sigma}} = \bar{\sigma}$

so; we have $\boxed{\bar{\sigma} = \tanh(2dJ\bar{\sigma}\beta)}$

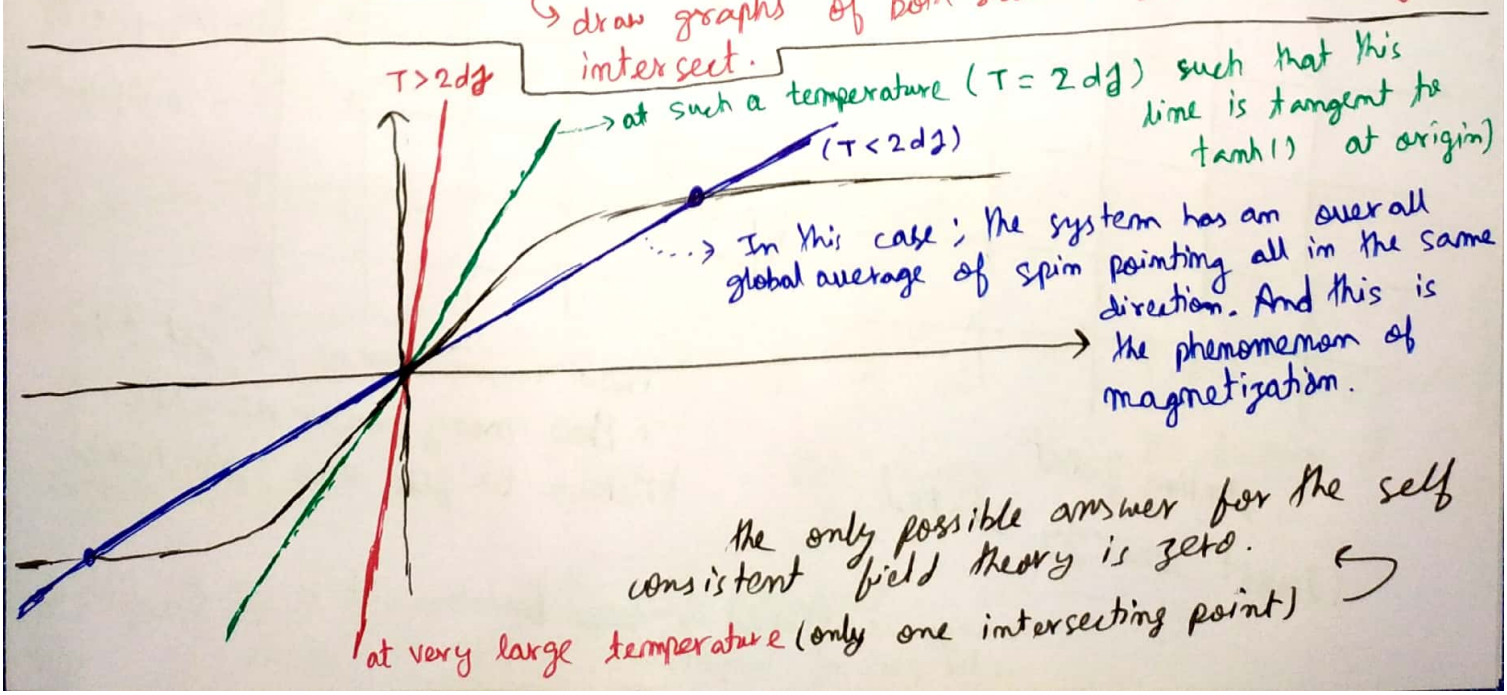
↳ so we have an implicit equation for $\bar{\sigma}$ & we want to solve it.

$\boxed{\bar{\sigma} = \tanh(2\beta dJ \cdot \bar{\sigma})}$

variable change; let: $y = 2\beta dJ\bar{\sigma}$ (because we want to simplify the argument of tanh() function)

so; we have; $\frac{y}{2\beta dJ} = \tanh(y)$

↳ draw graphs of both side & see where they intersect.



at such a temperature ($T = 2dJ$) such that this line is tangent to tanh() at origin)

→ In this case; the system has an overall global average of spin pointing all in the same direction. And this is the phenomenon of magnetization.

the only possible answer for the self consistent field theory is zero.

at very large temperature (only one intersecting point)

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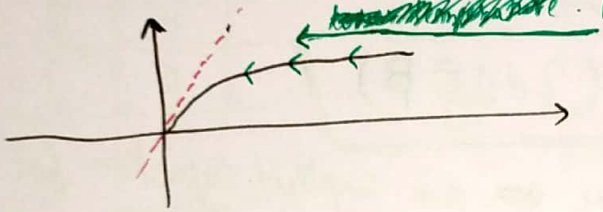
what happens at $T = 2dJ$ is called phase transition. Beyond that point there is some net average magnetization, i.e; an average field that just permeates the whole system.

☆ Why we dont take the origin solution for the case of $T < 2dJ$. (How do I know which solution is right)

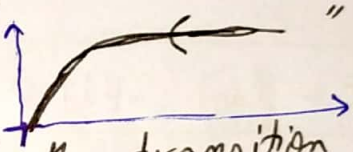
Is we will add tiny little magnetic field that biases the system, and we will discover that the tiniest little magnetic field will tell us to not to be at origin branch of the solution.

⟹ Alternate; go to zero temperature ⇒ There we expect allignment (everything to lock into parallel configuration)

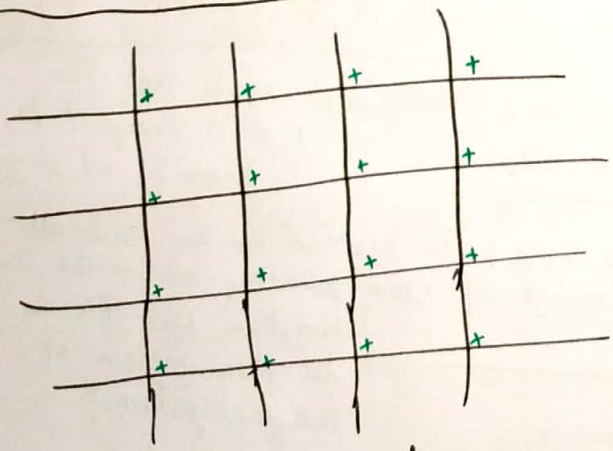
increase temperature.



as you increase the temperature you slide along the line "

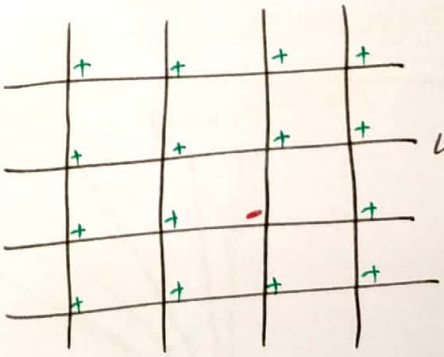


until you get to the transition point ... and beyond the transition temperature ($T > 2dJ$) the only solution is the origin.



starting point (lowest energy state)

flip one spin.



(1st configuration)

(How much energy we get?)
(How many bonds we have broken to flip one spin here)

energy is stored in bonds; it is $\sigma_i \cdot \sigma_{i+1}$ which is the pair of neighbours.

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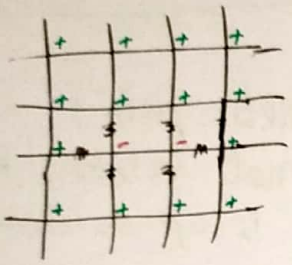
Breaking bonds here means : instead of having parallel we made them antiparallel.

4 bonds broken.

(The no. of places you can ~~break a bond~~ flip one spin is basically the total no. of sites)

↳ This means that the no. of configuration that you can add in with four extra units of energy.

→ now, what is the next configuration.... flip one more spin.



(2nd configuration)

What is the energy of this configuration.

note here (-)—(-) bond is actually not a broken one ... its parallel.

⇝ 6 broken bonds with respect to lowest energy state.

So; we have increased the energy by six units. Each broken bond costs certain amount of energy.

→ We have increased the energy by six broken bonds.

★ If we flip to (-) in some non-adjacent points, then we would have broken 8 bonds.

[each time I flip the spin ⇒ energy goes up]

One-dimensional.

↑ ↑ ↑ ↑ ↑ ↑ ⟹ ↑ ↑ ↓ ↑ ↑ (1st configuration)

Ground State — flip one spin — How many bonds broken?

Ans 2

★ Flipping two spins ⇒ if they are adjacent .... still 2.

★ " three " ⇒ " " " " ... " 3.

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in one-dimension ⇒ you can flip any no. of them & still cost two units of energy. (when you flip adjacents spins...)

↳ We have lot of configuration with same energy.

↳ That is why it is unstable w.r.t. flipping lots & lots of spins.

....and as soon as the temperature is turned on, it costs very little energy to flip whole big loads of them. This is the basic mathematical thing which is going on in one-dimensions.

☆ now, if we turn a little magnetic field.

We imagine the whole system has an external magnetic field; that means that each spin has an extra energy not related to its neighbours, but just from the fact whether it is up or down.

: lets called the magnetic field B. (we will imagine B is eventually very small)

Then energy of a particular spin is $E = -2dJ\bar{\sigma}\sigma - B\sigma$

$\Rightarrow E = -[2dJ\bar{\sigma} + B]\sigma$

This negative favours up spin.

$\langle\sigma\rangle = \tanh([2dJ\bar{\sigma} + B]\beta)$

assume $B > 0$ here.

mean field approximation gives:

$$\frac{Ty}{2dJ} = \tanh\left[y + \frac{B}{T}\right] \quad \text{or} \quad \frac{y}{2dJ\beta} = \tanh[y + B\cdot\beta]$$

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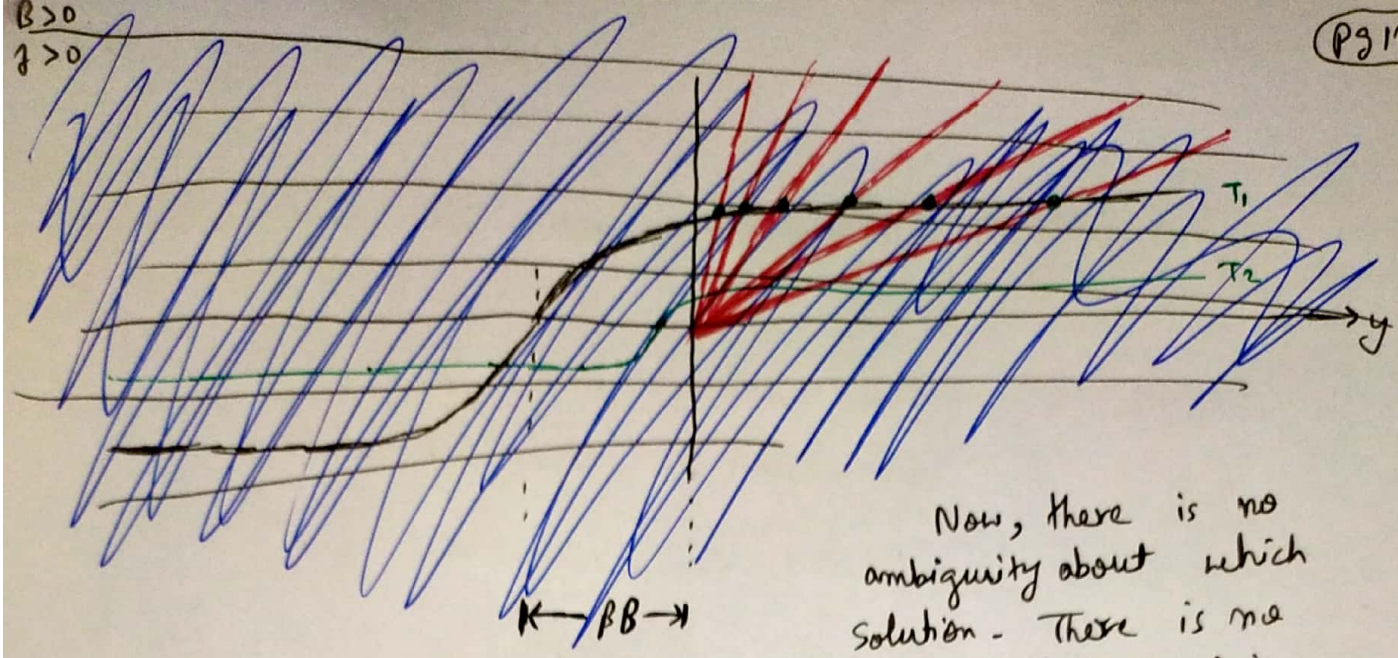
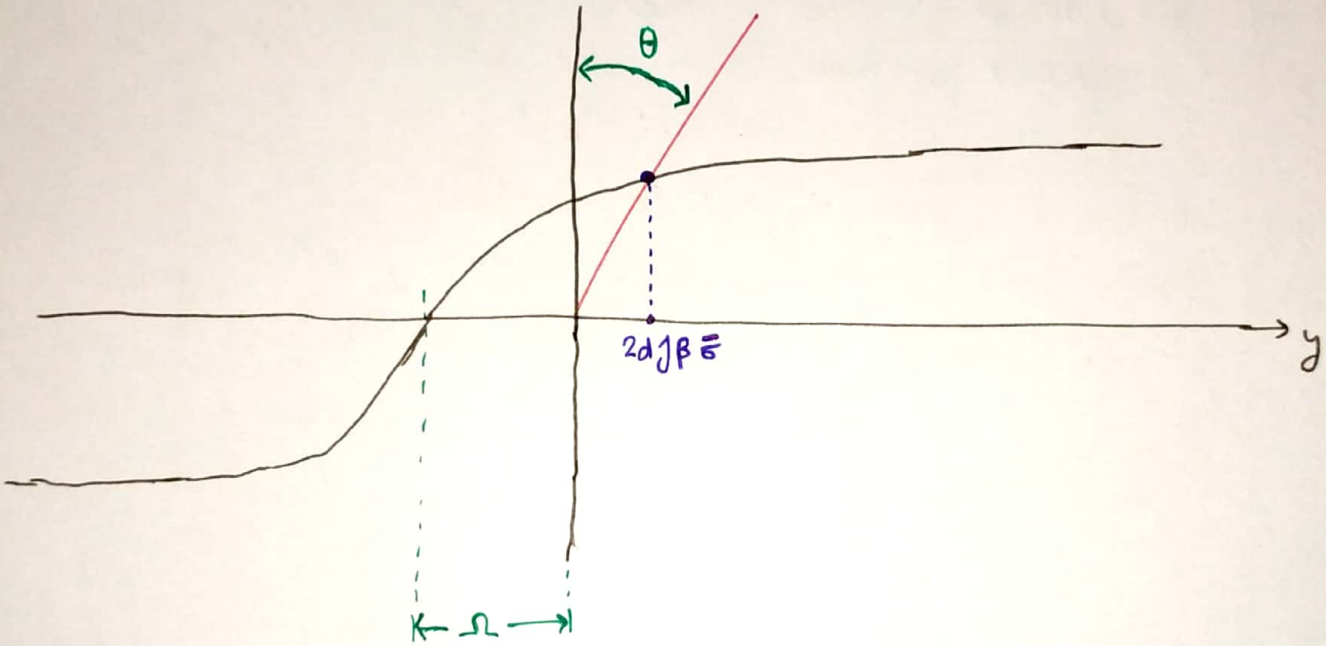


Now, there is no ambiguity about which solution. There is no solution at the origin. And there always exist a solution.

~~T2~~ T1



θ and Ω are parameters of the curve.

$$\frac{y}{2dJ\beta} = \tanh(y + \beta B)$$

$2dJ\beta$ → angular shift parameter of line function.

βB → Shift parameter of tanh( ) function

$$\theta = \tan^{-1}\left(\frac{2dJ}{T}\right)$$

$$\Omega = \frac{B}{T}$$

$$\tan\theta = 2dJ\beta$$

$$\Rightarrow \theta = \tan^{-1}(2dJ\beta)$$

and $\Omega = \beta B$

∴ T increases $\Rightarrow$ θ decreases and Ω decreases.

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as you can easily see ; as $T \to 0$ the solution $\bar{\sigma} \to 0$ ($\bar{\sigma} > 0$)

So; we see that adding a tiny little magnetic field only leaves the magnetized solution.

This is instability $\Rightarrow$ i.e; tiniest-tiniest magnetic field will bias the system upto to magnetised solution.

↳ This is called Spontaneous Symmetry Breaking.

We see that, the solution at which all the spins are equally to be up or down is unstable. (The solution of 50-50 chances of each spin of being up or down)

↳ if you turn on the tiniest magnetic field, the difference in the energy will be enormous. because you will have lots of spins all pointing up after switching magnetic field.

"Tiny pertubation in the magnetic field will bias it".

The configuration to be equally likely in every direction is unstable."

stronger the B ; the more unstable it is.

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 Statistical Mechanics : Liquid - gas Phase transition

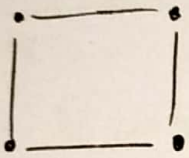
- Shoaib Akhtar.

Ising magnet can also be used as a model for liquid - gas phase transition.

* Mean field approximation always tells you that there is a phase transition. But this happens not to be true in one ~~dimension~~ dimension.
  - ↳ it is true in two and higher dimensions.
  - ↳ by the time you get to three dimensions, every particle in the lattice has enough neighbours that the mean field approximation becomes very good.

$\sigma = \pm 1$

(we are placing a variable at each point on the lattice)



you can think of energy being located in the link between the sites.

language

Energy is low ⟸ • If two neighbours are parallel, we call that unbroken bond.

Energy is high. ⟸ • If two neighbours are anti-parallel we call that broken bond

$$E = -J \sum_{\text{links}} \sigma_{(i)} \cdot \sigma_{(j)} + h \sum_{\text{sites}} \sigma_{(i)}$$

; i & j just means two opposite ends in a link. (They are adjacent)

h is some term proportional to the strength of external field.

$$E = -J \sum_{\text{links}} \sigma_{(i)} \sigma_{(j)} + h \sum_{\text{sites}} \sigma_{(i)}$$

This term tends to want things to lie in same direction

This wants to make them lie down. ($h > 0$)

i.e; $\sigma_{(i)} = -1$

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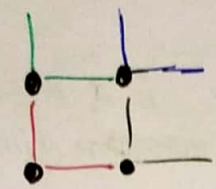
no. of links

2-dimensions



(draw two links from each site and that fills up everything.)

3-dimensions

draw Three links at each site, that will fill up the whole lattice.

Only energy difference are important in statistical mechanics. We can add a constant to energy.

$$Z = \sum e^{-\beta E}$$

we pretend that the average field $\bar{\sigma}$ is just a number & take the statistical mechanical problem of one spin with an energy given by the expression

"$-2dJ\bar{\sigma}\sigma + h\sigma$".

i.e; $E = [-2dJ\bar{\sigma} + h]\sigma$

↳ and we will find $\bar{\bar{\sigma}} = \tanh[(+2dJ\bar{\sigma} + h)\beta]$

Energy of a spin is

$-2dJ\bar{\sigma}\sigma + h\sigma$

↳ average of the particular spin in consideration that we get if all the neighbours happen to be frozen and had the value $\bar{\sigma}$

mean field assumption : $\bar{\bar{\sigma}} = \bar{\sigma}$ (true & more accurate when we have big enough sample and we are in deep interior of it)

i.e; $\bar{\bar{\sigma}} = \tanh[(2dJ\bar{\sigma} - h)\beta]$

$\Rightarrow \bar{\sigma} = \tanh[(2dJ\bar{\sigma} - h)\beta]$ (mean field approximation)

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we got an equation which is

$$\frac{y}{2dJ\beta} = \tanh[y - h\beta]$$

where

$$y = 2dJ\beta\bar{\sigma}$$

This is our mean field equation or consistency equation which tells what y is.

$$\frac{Ty}{2dJ} = \tanh\left[y - \frac{h}{T}\right]$$

$\Rightarrow$ y, indeed the $\bar{\sigma}$: looks like a function of two variables h & T.

* we will take J to be a fixed number.

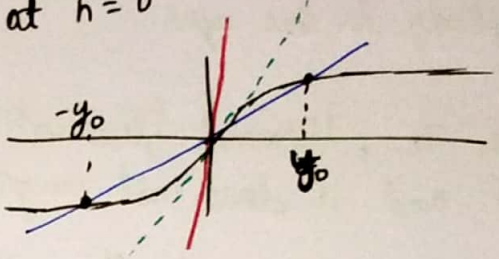
J can be changed by changing the material, also by changing the pressure.

Transition happens at $T = 2dJ$ → called Critical Temperature.

i.e; Slope of line is equal to slope of tanh( ) at origin, i.e; to be 1.

critical point.

at $h = 0$



Slope of hyperbolic tangent at the origin is 1.

$$\frac{d}{dx}(\tanh(x))\Big|_{x=0} = 1$$

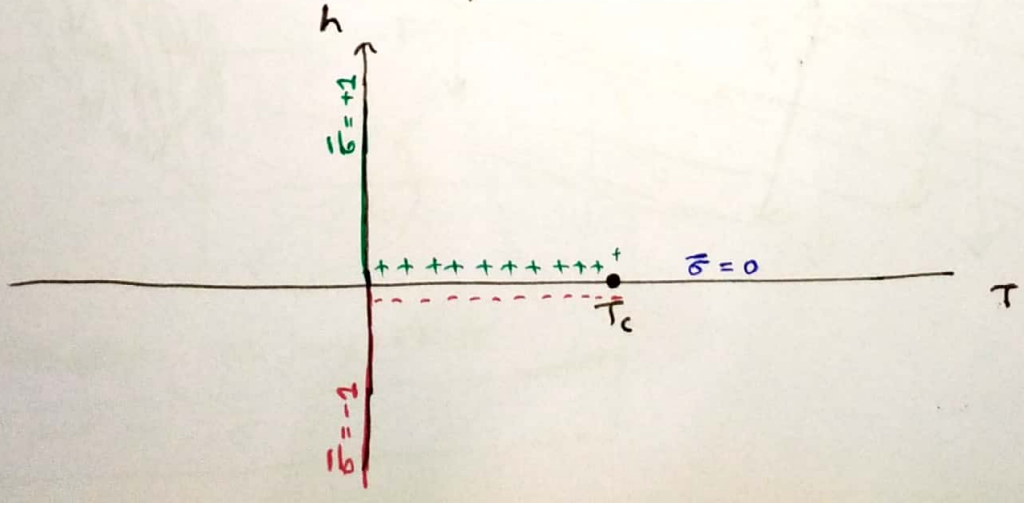
$\therefore$ There is complete symmetry in the problem.. no way to decide whether the solution is y_0 or $-y_0$

symmetry between up's & down's

when $h > 0$ .. only one of the solutions comes into existance.

: physically, we say that the extra magnetic field (even small) has broken the symmetry.

* we can ask what does the magnetization looks like as a function of Temperature and magnetic field.



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$T_c = 2dJ$ is the critical temperature.

∴ below T_c the system is spontaneously magnetised.
~~(there~~ (there is net tendency for everybody to line up)

∴ above T_c, thermal fluctuations wins and it does not magnetised.

* for $d=2$; the numerical results are off by certain amount (although the qualitative answer is correct; but not quite correct ~~for~~ quantatively.

* for $d=3$; the approximation is very good.

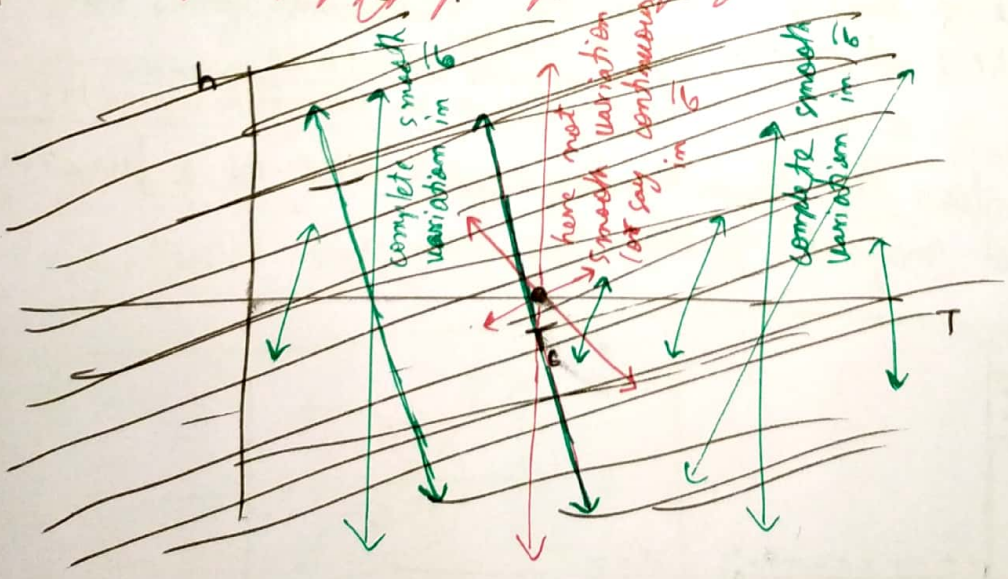
T_c here is actually Curie Temperature

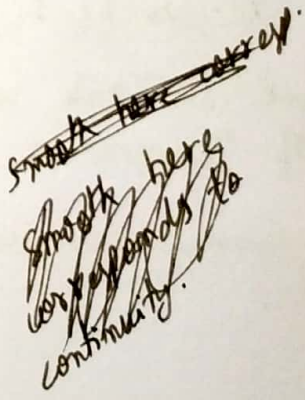
* Curie Temperature is the term ~~used~~ used for magnets strictly.

* If we are talking about general phenomenon of phase transition, we just call ~~it~~ it Critical Temperature.

* at critical temperature; the magnetization is zero
⇒ If you decrease the temperature little bit, it becomes non-zero.

* Magnetization tends to zero in every direction at the critical point ; but once you pass the critical point there is jump in the magnetization.





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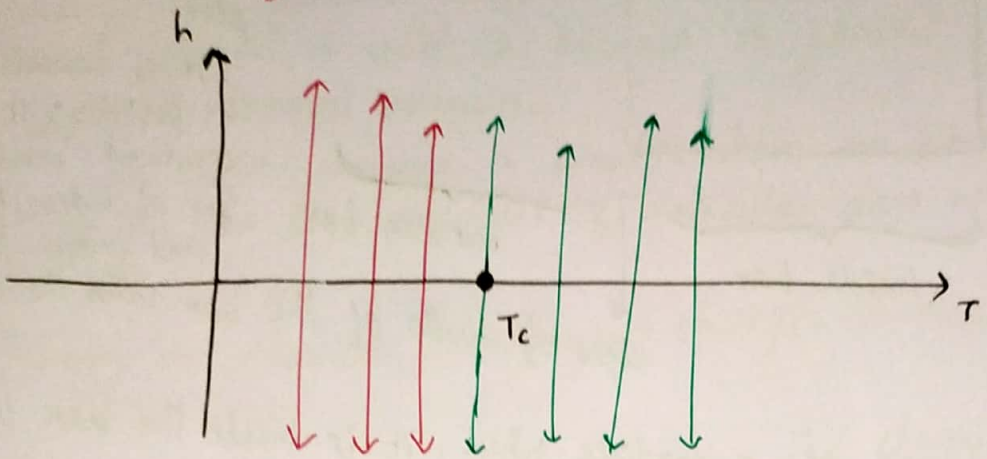
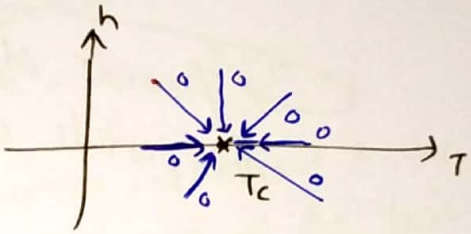
color code

green ⇒ continuous variation in $\bar{\sigma}$

red ⇒ little jump in variation in $\bar{\sigma}$ at * or around $h=0$



☆ magnetization tends to zero in every direction approaching the critical point, at the critical point.

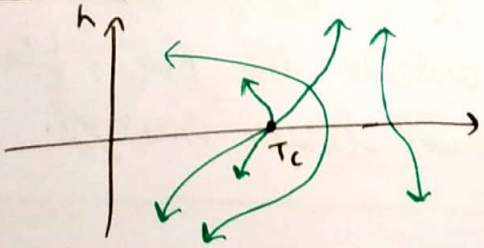


★ once you pass the critical point
ie; for $T < T_c$ (fix this T)
↳ and as you vary the h;
there is jump in magnetization.

∴ a little tiny change in h around $h=0$ which changes the sign of h; flips over the spin & the magnetization changes discontinuously across there.

☆ at $T = T_c$; varying h ⇒ you will find no jump in the magnetization but you will do get from negative to positive.

• note



~~no jump~~ no jump route

no jump in $\bar{\sigma}$.

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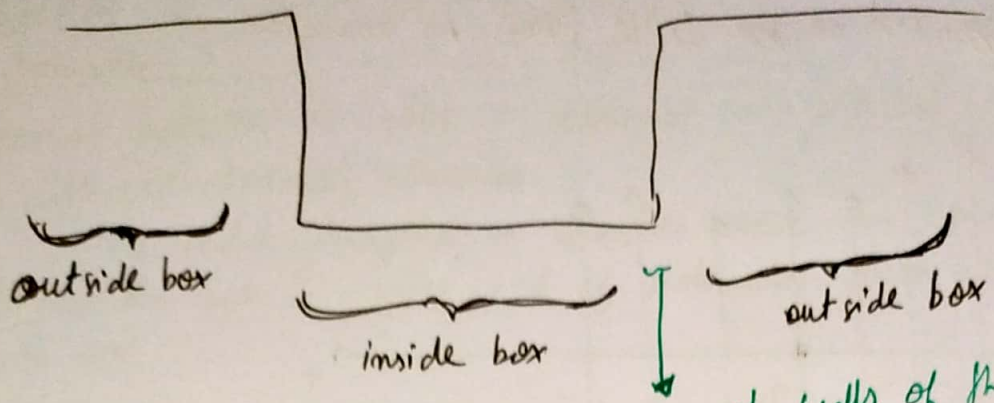
Liquid - Gas phase Transition



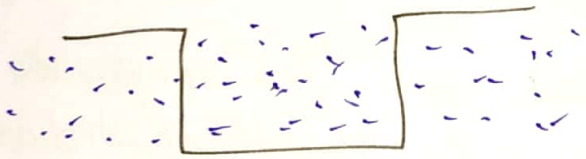
Potential energy plot.
(it is dependent on position; it is constant over box of interest; and jumps as you cross the walls)

* The energy of a particle when it is inside the box is lower when it is outside the box.

(The difference in energy is called Chemical Potential)

→ Amount of energy which it takes to remove the particle out of the box.

Note!! The particles are here all over the place.



We can ask the question; what is the density inside & outside the box.

note!! The walls of the box are permeable. Particles can come in and go out; it can cross the boundary of box.

☆ Energy is low inside the box ⇒ so it is natural that density inside the box will be more than outside the box, because boltzman distribution always favours lower energy.

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☆ We can ask what is the density of fluid as a function of depth of the potential?

Chemical potential is called so because in general it can be different for different chemical molecules.

We could imagine a situation where one kind of molecule prefers to be in the box & other kind of molecules does not prefer to be in the box.

∴ Turning on chemical potentials can change chemical composition in various ways.

"You can tune the density by changing the chemical potential" (ie; change)

Chemical Potential is term in the energy which depends on no. of particles in the box : μ for each particle.

If there are N particles in the box, then $N\mu$.

note!! In our problem N (the no. of particles in the box) is variable because particles can come & go out of the box

↳ This means configuration not only involves position and momentum of every particle ; but also the number of particles inside the box (N). Now since particles can go out & come in the box ?

The part of determining at Thermal equilibrium : is determining how many particles on the average are inside the box.

$$Z = \sum_{P, X, N} e^{-\beta E + N\mu\beta}$$

P : momentum, X : position, N : no. of particles inside the box

☆ Chemical Potential is the thing you adjust if you want to adjust the density of the fluid.

↳ What is liquid - gas transition in this language?

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Take a box ⇒ keep it at a fixed Temperature. ⇒ Then you start varying the Chemical potential.

... so; there is density, which is naturally a function of chemical potential

What happens at transition?
As you vary the chemical potential, all the sudden you hit a point where the density of fluid suddenly changes from being a gas to being a liquid.

"The difference between liquid & vapour is sudden discontinuity in density".

~~What are the things you need~~
What are the conditions that we need to have a liquid-gas phase transition?

(i) A hard core repulsion between molecules. (You cannot stick two molecules at same site; they will repel)

(ii) Little bit of attraction when the molecules are not quite touching.

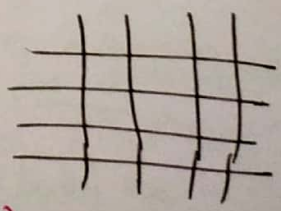
↳ So; we need a potential energy which is big & repulsive when you try to put molecules into each other, and when you seperate a bit, they will attract.
(These is an extremly common feature of molecular interaction)

* Hard Core Repulsion.
* Very short range attraction.

When all little elementary magnets are down; ground state.
↳ lets, call it Empty Space.

"On each site of lattice, you can have the particle or not have the particle. We will make a lattice version of liquid-gas problem."

The particles or molecules live on a lattice



* We can have no particle at a site.
; let's call that down; $\sigma = -1$ (no particle on that site)

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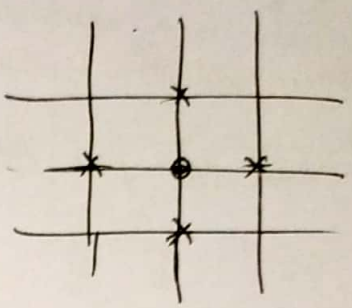
★ $\sigma = +1$ ("yes, particle is there on the site")

i.e. $\sigma = -1$; $\sigma = +1$ → We are trying to model a gas where you can't put two particles on the same site because they have hard core.

★ $$E = \sum_{\text{links}} -J \sigma_i \cdot \sigma_j$$

$E_{\text{Ground State}} = -J \cdot (\text{No. of links})$



★ put 1 particle ; Energy increament 8J
(In 2-dimensions) ⇒ $E = E_{\text{ground state}} + 8J$

★ 2 particles ; energy increament 16J or 12J (when neighbours)

★ 1 particle ⇒ bond broken 4 ⇒ Energy increament 8J

★ 2 " ⇒ bond broken : { 2 particles 8 ⇒ Energy increament 16
2 close particles 6 ⇒ Energy increament 12

(so ; there is potential energy which depends on the position of the particles : and when the particles get within one bond length of each other the energy decreases by 4J : This is like having short range attractive energy)

↳ This is like decreasing potential energy when they are close together (i.e. adjacent) (bring far to adjacent ⇒ then 4J energy decreased)

★ Hard core repulsion taken into account
↳ at one lattice point only one particle
∴ σ can be +1 , −1 ~~but not~~ but not 2, 3, .. etc.

↳ when particles are close together, the energy is negative relative to what it would be when they are far apart.

so ; we have a system now which is mathematically isomorphic to a system of particles on a lattice which have a kind of attractive force between them ; where no. of particles is a variable.

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Chemical potential is the energy stored in just having one particle. It is just the energy having when the particle is present. Just by virtue of having the particle there, i.e; the energy which would not be there if the particle was not there is called the Chemical Potential.

☆ having a particle with no other particles around gives us energy $8J$.
So; There is a chemical potential. Now we would like to vary this Chemical potential (without varying the J)

↳ we can put magnetic field in

i.e; $$E = \sum_{\text{links}} -J\sigma_i\sigma_j + \sum_{\text{sites}} h\sigma_i$$

$2h$ units of energy for every spin flip up. (i.e; every particle you put in gives $2h$ energy)

So; for each isolated particle ... we have $8J + 2h$

(varying Chemical potential is mathematically same thing as varying h)

---

how many particles are there on the average at a particular point?

$\frac{1+\sigma}{2}$

$\sigma = 1$ (yes particle) → $\frac{1+1}{2} = 1$

$\sigma = -1$ (no particle) → $\frac{1-1}{2} = 0$

This is good candidate for no. of particles.

↳ So; the average is $\frac{1+\bar{\sigma}}{2}$

So; $\rho \propto \left(\frac{1+\bar{\sigma}}{2}\right)$; $\rho \Rightarrow$ density of particle. (average no. of particle per lattice cell)

actually; $\rho = \frac{1+\bar{\sigma}}{2}$

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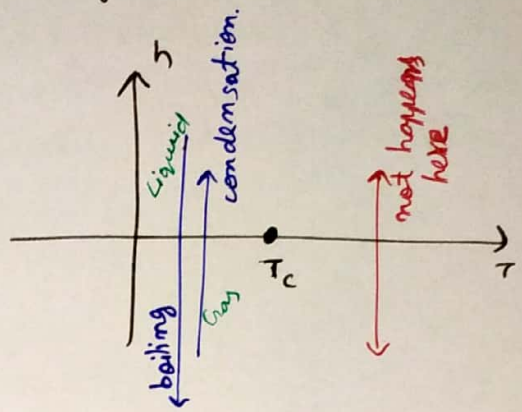
* now: we will vary the chemical potential (actually the h) keeping the temperature fixed.

↳ if we are above or at the critical temperature T_c ; the magnetization varies uniformly & continuously.. no jump
↳ i.e; density does not jump.

↳ below the Critical Temperature ; as you vary h : all the sudden at (around $h=0$) the magnetization jumps. It jumps from negative to positive.

⇒ when it is negative : means density is low
⇒ " " " positive : " " " high.
(i.e. jumps from low density to high density).

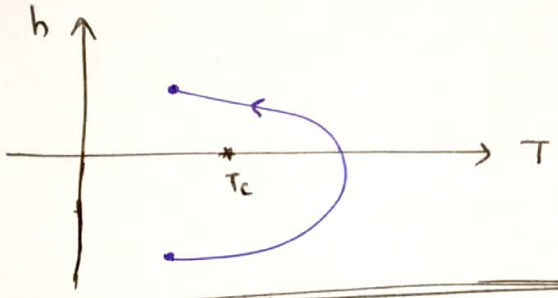


for $T < T_c$

$h > 0$: Liquid
$h < 0$: Gas

density is like magnetization here

notice// you can go from gas to liquid without any jump by going around the critical point (T_c)



As you approach the critical point ; no. of fascinating things happen which are all characterized by Critical Exponents.

Every quantity that you can think of is ~~on~~ interesting, depends on Temperature generally goes as $(T - T_c)^{\gamma}$

∴ This power γ is Critical Exponents. (They of course vary from one kind of phase transition to other).

No. of criticals points are not finite ; but they are discreate.

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Anthropic Principle & fine Tuned Universe

What is the difference being small & being fine tuned?

example!!

Small number

Suppose you are in a light balloon gas. If the density was small; you will rise up to a certain stationary height there & stay there.

Fine tuned

Suppose you are in a submarine inside water. Suppose you can't live in atmosphere, it got poisoned. So, you need to live inside water.

If the density of the submarine is equal to that of water, then the submarine will float (at any level we want)

↳ But if $\rho_{sub} < \rho_{water} \Rightarrow$ it will rise up; atmosphere will kill.

↳ " " $\rho_{sub} > \rho_{water} \Rightarrow$ " " sink; & high pressure will crush.

⇦ So there is a very fine tuning in the composition such that density matches.

(assume density of water is constant)

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* In case of our universe; Cosmological constant is analogous to the density of submarine in the example.

Cosmological Constant in Quantum field Theory gets contribution from every quantum field that exist. Bosons give positive contribution. Fermions " negative " .

and all of the contribution has to balance very finely (exactly the same way as the density of submarine has to balance)

; the mass of the particles associated with those quantum fields shift them little bit & the cosmological constant that results from it shifts little bit.

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