THERMODYNAMICS
&
STATISTICAL MECHANICS

Around 1600 AD: Notion of heat & temp. widely accepted & associated with the motion of microscopic constituents of matter. (During that time the concept of atoms was not developed)

1700 – 1840:- Heat was instead a fluid like substance started becoming more popular

1850 – Joules & others experimentally shows that heat is a form of energy.

Sadi Carnot had explained the relation between heat & energy.

1850:- Rudolf Clausius & William Thompson formulated the First law which is the idea that total energy is conserved. The Second Law of Thermodynamics which is the idea that heat cannot be completely converted to work was also formulated

1860:- James Clark Maxwell derived the expected distribution of molecular speeds in a gas by taking into account molecular collisions.

1872: Ludwig Boltzmann constructed an eq. to describe time evolution of a gas regardless of whether it was in equilibrium or not.

1860:- Clausius introduced entropy as a ratio of heat to temp & had stated the II Law in terms of the increase of this quantity

1900:- Gibbs introduced ensemble which is a collection of many possible states of a system, each assigned a certain possibility. He argued that if the time evolution of a single state were to visit all other states in the ensemble - the so called ergodic hypothesis - then averaged over a sufficiently long time a single state behave in a way that was typical of the ensemble.

So we can divide closely related state into ensembles with ~~defini~~ some probabilities. This practice is called ~~Coarse~~- Coarse-Graining.

Gibbs gave an argument that entropy would increase with time if states of a systems were to be identified by coarse-graining in which nearby states were not distinguished.

Zeroth Law:- If A & B are in equilibrium with a third C, they are also in equilibrium with one another.

Equilibrium:- A system is said to be in eq. if its (eq) macro-properties do not change appreciably over time.

A macroscopic system in eq. is characterized by a no. of thermodynamic coordinates or state functions (pressure & volume) (tension, length) (Electric field & polarization)

First Law:- The work required to change the state of an isolated system depends only on initial & final states & not on the intermediate states through which the system passes.

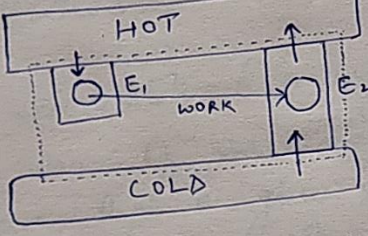
(Something similar in Classical Mechanics !!)

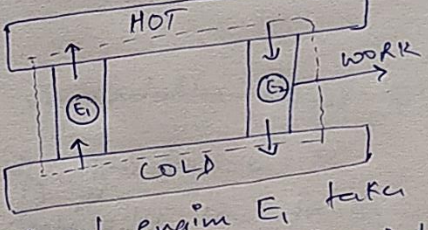
The above process is called "adiabatic" which means - no heat flows in or out of a system & no mass enters or ~~exits~~ exits the system.

<u>Second Law</u> :- → No process is possible whose sole result is the transfer of heat from a colder to a hotter body. (Clausius Statement)

→ No process is possible which involves converting heat completely into work (Kelvin statement)

EQUIVALENCE OF KELVIN & CLAUSIUS STATEMENTS





Let the illegal engine E_1 takes heat from HOT and converted completely into work (violation of Kelvin)

The legal engine E_2 takes heat from COLD & dumping into HOT by utilising WORK. (just like refregirator)

The combined effect of E_1 & E_2 can be summarized in a dashed rectangle. i.e heat moves from COLD to HOT (violation of CLAUCIUS)

Let illegal engine E_1 takes heat from COLD & dumps into HOT (violation of CLAUCIUS)

The legal engine E_2 takes heat from HOT & dumps into COLD but does some <u>work</u> as well.

Combined effect of E_1 & E_2 is Heat is completely converted into WORK (violation of KELVIN)

MICROSTATES AND MACROSTATES

Every thermodynamic system is made of subatomic constituents that participate in the dynamics & dictate the behaviour of the bulk system

Statistical mechanics is an attempt to link the dynamics of the microscopic constituents to the behaviour of the bulk through a function known as entropy

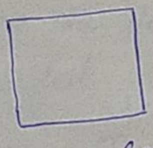
A macrostate is a collection of variables that describe the bulk system such as total internal energy, volume & no. of particles if we are talking about a gas. It could also describe related concepts which we will encounter later such as temp, pressure & chemical potential.

A microstate is a huge collection of variables equal to the no. of microscopic degree of freedoms in the system. Thus a given macrostate typically corresponds to a huge no. of microstates. i.e different microstates can correspond to the same macrostate.

ENTROPY :- According to Boltzmann, entropy is the logarithm of a no. of microstates of a thermodynamic system which corresponds to a given macrostate

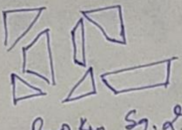
Is Entropy a measure of disorder in a system?

The notion of ordered microstates is human biased or very subjective.

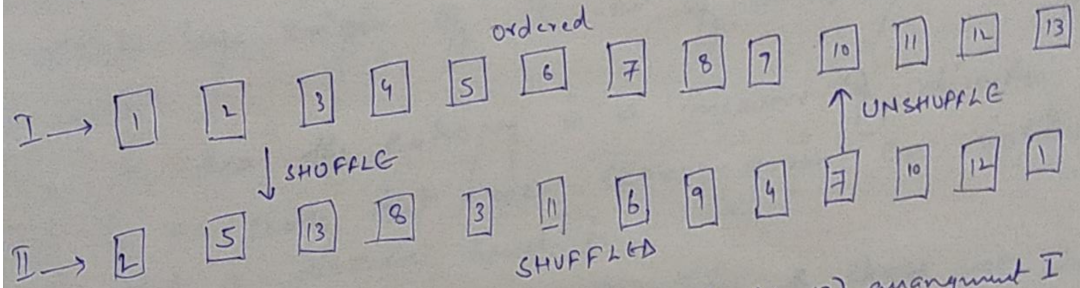


Ordered Sq.

Broken Sq. 1
or
Ordered Sq. 1



Broken Sq. 2
or
Ordered Sq. 2



Lets consider ordered or unshuffled cards (1–13) arrangement I. Now, we shuffle it to get shuffled card arrangement II as shown above.

Now, which arrangement of cards I OR II is more likely to happen.

i.e the I → II after shuffling

OR II → I after unshuffling.

The obvious answer would be I → II after shuffling

However, both the cases is highly <u>unprobable</u>. because both the arrangements are unique.

So in terms of statistical mechanics, we do coarse-graining by selecting a state (or set of states) and consider it ordered And any state (or set of states) which does not resemble with it will be considered disordered.

Now, if we can designate arrangement II (set of all possible arrangement) as shuffled, then it seems that it is more likely for to happen $\mathrm{I} \longrightarrow \mathrm{II}$ then $\mathrm{II} \longrightarrow \mathrm{I}$

Hence an irreversibility is introduced.

Which lays origin of IInd Law of thermodynamics by Gibb's.

So the idea the entropy is a measure of disorder is in a sense that we coarse-grain our notion of what a disorder hand is.

If we take a ensemble of states & choose not to distinguish between them, then it is true that an ordered state is more likely to become unordered state then the reverse to happen. i.e disorder increases.

So according to Gibb's, for an isolated system entropy of a system with time either remains same or it increases. Because we choose to define entropy in a coarse-grain sense & purposely ignore ~~diff~~ variation in microstates between different possibilities & collectively called it a disordered state

Quantify Entropy

A deck of cards has 26 cards of equal Black & Red cards.

Suppose in a hand, I have N cards of $N_1 \rightarrow$ Black & $N-N_1 \rightarrow$ Red cards.

So, No. of ways to get N_1 Black cards are $C(26, N_1)$

$$= \frac{26!}{(26-N_1)!\, N_1!}$$

No. of ways to get $(N-N_1)$ Red cards are $C(26, N-N_1)$

$$= \frac{26!}{(26+N_1-N)!\, (N-N_1)!}$$

Thus the entropy of the system is

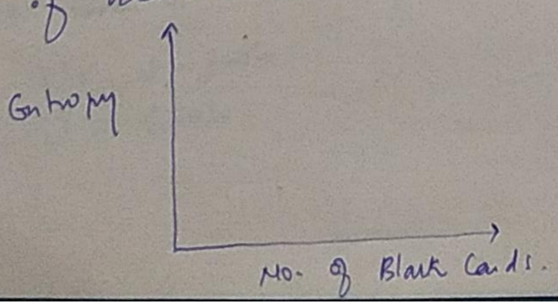
$$S(N, N_1) = \log\left[C(26, N_1)\, C(26, N-N_1)\right]$$

$$= \log\Bigg[\frac{26!}{(26-N_1)!\, N_1!} \times \frac{26!}{(26+N_1-N)!\,(N-N_1)!}$$

NOTE

The entropy $S(N, N_1)$ is a function of the macrostates described by the two ~~macrostates~~ macroscopic quantities N, N_1. These macrostates corresponds to many possible microstates.

Now take $N = 10$, Calculate the entropy & plot entropy Vs the no. of black cards.



Staircase Example:-

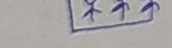
Consider a staircase of M steps, with n_1 people standing on first step, n_2 people standing on 2nd step, n_3 people standing on third step & so on....

So, total no. of people $n_1+n_2+n_3 \dots + n_M = N$

Potential energy will be (of the microstate)

$$whn_1 + 2whn_2 + \dots + Mwhn_M = U$$

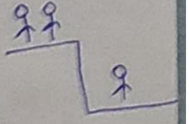
where w is weight of one person & h is height of one step



Now let $M=2$, $N=3$ ~~$= n_1+n_2$~~

CASE I → All three peoples on first step

$U = 3wh$

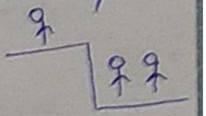


CASE II → one on step one, two on second step

$U = wh + 2 \cdot 2wh$

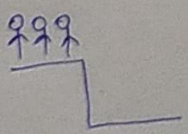
$U = 5wh$

CASE III → two people on first step, one on second step



$U = 2 \cdot 2wh + 2wh$

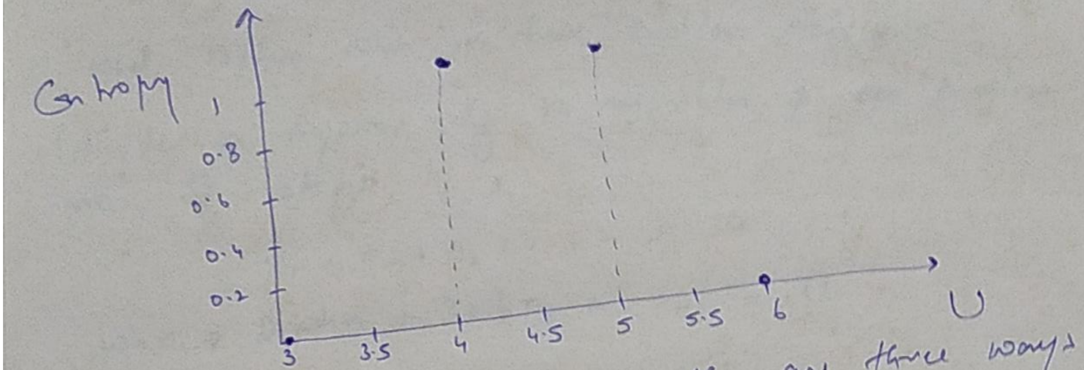
$U = 4wh$



CASE IV → All three on second step

$U = 2 \cdot 3wh$

$U = 6wh$



As three people are distinct, so there are three ways to get P.E 4wh & 5wh

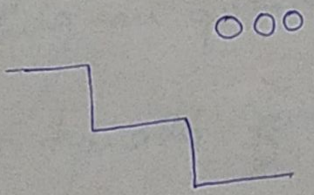
CASE I :- there is only one way of getting 3wh so $\log 1 = 0 =$ entropy

CASE II & CASE III → there is three ways of getting P.E 5wh & 4wh

∴ entropy $= \log 3 \approx 1$

CASE IV → there is only one way of getting P.E 6wh

∴ entropy $= \log 1 = 0$



Marbles Example
3 → Marbles, 3 → steps.

List the cases & plot the graph of entropy vs. U.

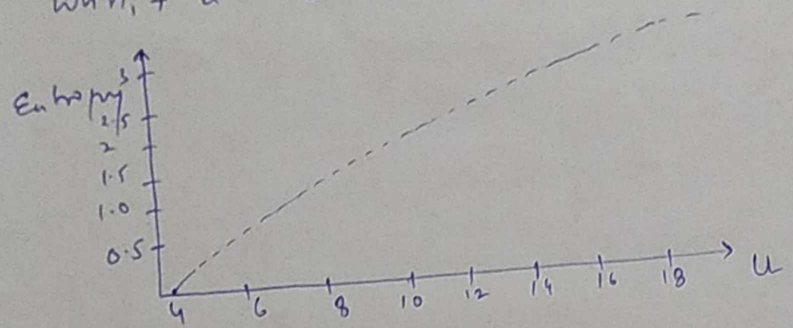
Important :- the entropy reaches zero at the end because we have fixed no. of steps.

What happen when we have endless staircase ?

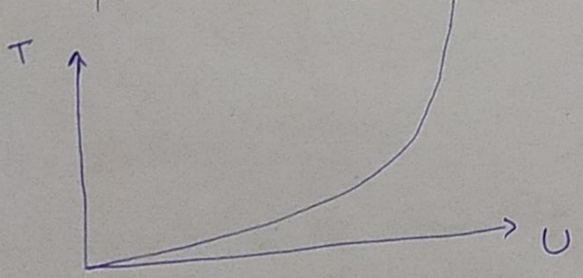
Consider a system of 10 marbles & an endless no. of steps.

$$n_1 + n_2 + n_3 + \dots = 10$$

$$\omega h n_1 + 2 \omega h n_2 + 3 \omega h n_3 + \dots = U$$



Also temperature $T = \dfrac{1}{\partial S(U,N)/\partial U}$



What if these marbles we are calling are quantum objects?

Now quantum objects or particles are typically fermions or bosons.

if they are fermions then we have to add a restriction that there cannot be more than one fermion on a given step of the staircase.

Q = Take 2 fermions & 2 steps, plot entropy Vs U.

Generating Function Method (to count no. of microstates)

It is an analytical method for counting the no. of solutions of Diophantine Eqs. without actually listing all the possible solutions explicitly.

Bosons: Imagine first the situation of identical marbles on an infinite staircase.

Define a function of variables $x_1, x_2 - - -$

$$G[x] = \sum_{[n]=0}^{\infty} Z[n] \prod_{j=1}^{\infty} x_j^{n_j}$$

$$Z[n] = \delta_{U-\sum_{j=1}^{\infty} j n_j, 0} \; \delta_{N-\sum_{j=1}^{\infty} n_j, 0}$$

$$\boxed{\delta_{m,0} = \begin{cases} 1 & m=0 \\ 0 & m\neq 0 \end{cases} \quad \text{(Kronecker Delta)}}$$

Note that the term $e^{S(U,N)} = \sum_{[n]=0}^{\infty} Z[n]$ represents the total no. of ways in which marbles can be arranged on an infinite staircase such that the total no. of marbles is N & the total no energy is U.

Now $$\sum_{[n]=0}^{\infty} Z[n] = G[x=1]$$

Hence it is sufficient to calculate $G[x]$ to obtain the entropy of the system. $G[x]$ is called the generating function of the "microcanonical partition function" $Z[n]$

Microcanonical: "micro" means taking into account the detailed distribution of the no of individual marbles on each step, "Canonical" means natural or conforming to a set of rules i.e "canon".

Partition fn :- "partition" is a way of writing an integer as the sum of small integers Eg $10 = 2+3+4+1$

In order to calculate the generating fn $G[x]$, we write the Kronecker deltas in a form resembling a generating fn. itself. If k is an integer

$$\delta_{k,0} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta k} = \begin{cases} \\ \\ \end{cases}$$

this means.

$$Z[n] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta(U - \sum_{j=1}^{\infty} j n_j)} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi(N - \sum_{j=1}^{\infty} n_j)}$$

$$G[x] = \sum_{[n]=0}^{\infty} \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta(U - \sum_{j=1}^{\infty} j n_j)} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi[N - \sum_{j=1} n_j)} \prod_{j=1}^{\infty} x_j^{n_j}$$

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \sum_{[n]=0} (e^{-i\theta j} e^{-i\phi} x_j)^{n_j}$$

Sum of products $= \sum_{n=0}^{\infty} y_1^{n_1} y_2^{n_2} y_3^{n_3} \cdots = \frac{1}{1-y_1} \frac{1}{1-y_2} \frac{1}{1-y_3} \cdots$

Product of Sum $= \prod_{j=1}^{\infty} \sum_{n_j=0}^{\infty} y_j^{n_j} = \prod_{j=1}^{\infty} \frac{1}{1-y_j} = \frac{1}{1-y_1} \frac{1}{1-y_2} \frac{1}{1-y_3} \cdots$

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \frac{1}{1-(e^{-i\theta j} e^{-i\phi} x_j)}$$

If the height of the steps are uneven - say ϵ_j instead of j; $j=1,2,3\ldots$

the $$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \frac{1}{(1-e^{-i\theta\epsilon_j} e^{-i\phi} x_j)}$$

The no. of microstates with total energy & total no. of particles fixed can be obtained from $G[x]$ by setting all the x-values to unity

$$e^{S(U,N)} \equiv G[x=1] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \frac{1}{1-(e^{-i\theta\epsilon_j} e^{-i\phi})}$$

Above eq. represents a general answer to the question that what is the entropy of the system of N identical bosons distributed over energy levels ϵ_j in such a way that the total energy of the system is U. But this is hard to compute analytically.

To do it numerically, some approximations are to be made

Lets say the no. of steps are 3 and are equidistant

$$\int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1,2,3} \frac{1}{1-(e^{-i\theta j} e^{-i\phi})} = \frac{(e^{-iN\theta}(-1+e^{-i(N+1)\theta})(-1+e^{-i(N+2)\theta}))}{(-1+e^{-i\theta})^2 (1+e^{-i\theta})}$$

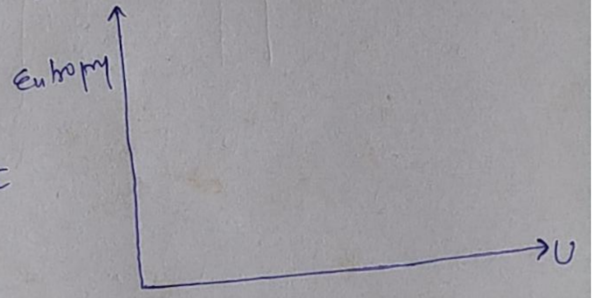
Illy integrate over θ

$$e^{S(U,N)} \equiv \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \frac{(e^{-iN\theta}(-1+e^{-i(N+1)\theta})(-1+e^{-i(N+2)\theta}))}{(-1+e^{-i\theta})^2 (1+e^{-i\theta})}$$

$$\begin{aligned} = \frac{1}{4}(-1)^{-3N}\Big(&-((-1)^{U}+(-1)^{3N}(3+6N-2U))\,\Theta[-3-3N+U] \\ &+(-1)^{N+U}(-\Theta[-2-2N+U]+\Theta[-1-2N+U]+(-1)^{N}\Theta[-N+U]) \\ &+(-1)^{3N}((1+4N-2U)\,\Theta[-2-2N+U]+(-1+4N-2U)\,\Theta[-1-2N+U] \\ &+(3-2N+2U)\,\Theta[-N+U])\Big) \end{aligned}$$

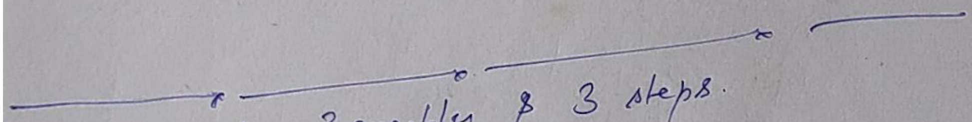
where $\Theta[x<0]=0$ (Heaviside's step function)

$\Theta[x \geq 0]=1$



Plot entropy Vs U

Show the behaviour & comment



Let consider 3 marbles & 3 steps.

Calculate entropy & plot the graph.

GENERATING FUNCTION

Generating fn can be used for abstract representation of infinite series

Defination : Let $A_1, A_2, A_3 \ldots \infty$ be a series of real no.
then a series in power of x, such that

$$g(x) = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + \ldots \infty$$

$$g(x) = \sum_{n=0}^{\infty} A_n x^n$$

is called generating fn of series $A_1, A_2, A_3 \ldots \infty$

→ It can be used to solve counting problems
→ " " " " " " recurrence relations

Example :- Find the generating fn for the following series

$1, -1, 1, -1, 1 \ldots \infty$ ——— ①

Sol. Let the series ① is denoted by $\{A_n\}$.

$g(x) = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + \ldots \infty$ ——— ②

$A_0 = 1, \; A_1 = -1, \; A_2 = 1, \; A_3 = -1 \; \ldots$

$g(x) = 1 - x + x^2 - x^3 \ldots$

EXTENSIVITY OF ENTROPY

Thermodynamic macro-variables such as temprature, total internal energy, volume, entropy, no. of particles, pressure and so on may be classified as being intensive or extensive depending upon how they behave if one doubles, triples or in general, scales by an integer factor the quantities that are manifestly extensive.

(Note: For U, → Only when subsystems don't interact amongst themselves)

The manifestly extensive quantities are total no. of particles, total internal energy (U) & total volume.

Any other quantity that behaves like these three upon "ballooning" the size of the system is called extensive.

Quantities that do not change at all upon scalling the extensive quantities are called intensive.

We know entropy, in terms of total no. of particles N & total internal energy (previous lecture). Now, we can ask, Is entropy also extensive like total internal energy & total no. of particles. This is not easy to answer given the complicated dependence of the entropy on the number of particles & internal energy.

However,

Let us try to answer. For this let us focus on identical marbles on an infinite staircase with uniform heights. And try to plot

$$\frac{S(\lambda U, \lambda N)}{S(U,N)} \quad \text{Vs} \quad \lambda$$

for fixed U, N.

This plot is going to be a straight line if the entropy is extensive. To be sure we expect this to be valid, if at all, only for large values of U, N.

Unfortunately, for large values of U, N it is not possible to list all the solutions and count them so we have to rely on our analytical formula obtained using the generating function method. Hence we now focus on making approximations

We know that,

N Identical bosons:

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \frac{1}{1-e^{-i\theta\epsilon_j} e^{-i\phi}} \qquad ①$$

N Identical fermions:

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} \prod_{j=1}^{\infty} \left(1+e^{-i\theta\epsilon_j} e^{-i\phi}\right) \qquad ②$$

More compactly we may write

N identical quantum particles

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{i\phi N} f_q(\theta,\phi) \quad \text{—— ③}$$

$$\text{where } f_q(\theta,\phi) = \prod_{j=1}^{\infty} \left(1 + q e^{-i\theta \epsilon_j} e^{-i\phi}\right)^q \quad \text{④} \qquad \begin{array}{l} q = +1 \text{ (fermions)} \\ q = -1 \text{ (bosons)} \end{array}$$

$$\text{Now, let } U = N\underline{u} \quad \text{—— ⑤}$$

$$\text{and } h_q(\theta,\phi) = \frac{i}{N} \operatorname{Log}\left[f_q(\theta,\phi)\right] \quad \text{—— ⑥}$$

$$\Rightarrow f_q(\theta,\phi) = e^{-iNh_q(\theta,\phi)} \quad \text{—— ⑦}$$

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{iN(\phi + \theta\underline{u} - h_q(\theta,\phi))} \quad \text{—— ⑧}$$

$$\equiv \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\phi}{2\pi} e^{N\omega_q(\theta,\phi)} \quad \text{—— ⑨}$$

$$\text{where } \omega_q(\theta,\phi) = i\left(\phi + \theta\underline{u} - h_q(\theta,\phi)\right) \quad \text{—— ⑩}$$

We know define the thermodynamic limit

In this limit, $N \to \infty$ even as $0 < h_q(\theta,\phi)$, $\underline{u} < \infty$

Now we have to evaluate an integral of the form

$$R = \int dz\, e^{N g(z)} \quad \text{when } N \to \infty \quad \text{⑪}$$

In thermodynamic limit $U \to \infty$, $N \to \infty$ but $\frac{U}{N} = \underline{u} < \infty$

Here z in eq. ⑪ is of complex nature.

Now in complex variables there is a method called "The Method of Steepest Descents" or the "Saddle Point Method" which says.

$$R \propto e^{N g(z_*)} \; ; \quad \text{where } g'(z_*) = 0 \; (\text{saddle point})$$ ⑫

Hence

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\phi}{2\pi} \, e^{N\omega_q(\theta,\phi)} \propto e^{N\omega_q(\theta_*,\phi_*)}$$ ⑬

Where

$$\frac{\partial}{\partial\theta} \omega_q(\theta,\phi)\Big|_{(\theta,\phi)=(\theta_*,\phi_*)} = \frac{\partial}{\partial\phi} \omega_q(\theta,\phi)\Big|_{(\theta,\phi)=(\theta_*,\phi_*)} = 0$$ ⑭

This means that

$$S(U,N) = S(N\underline{u}, N) = N\omega_q(\theta_*,\phi_*)$$ ⑮

This shows that for large no. of particles in the thermodynamic limit, the entropy of a collection of quantum particles is extensive, provided we can convince ourselves that $\omega_q(\theta_*,\phi_*)$ is intensive in the thermodynamic limit.

Implications of extensivity of entropy

Set $U' = \lambda U$, $V' = \lambda V$, $N' = \lambda N$

$$\Rightarrow \quad S(U',V',N') = \lambda S(U,V,N) \tag{16}$$

$$S(U,V,N) \equiv \frac{d}{d\lambda} S(U',V',N')$$

$$= \frac{dU'}{d\lambda} \frac{\partial S(U',V',N')}{\partial U} + \frac{dV'}{d\lambda} \frac{\partial S(U',V',N')}{\partial V'} + \frac{dN'}{d\lambda} \frac{\partial S(U',V',N')}{\partial N'} \tag{17}$$

Finally, we set $\lambda = 1$ we get

$$S(U,V,N) = U \frac{\partial S(U,V,N)}{\partial U} + V \frac{\partial S(U,V,N)}{\partial V} + N \frac{\partial S(U,V,N)}{\partial N} \tag{18}$$

From thermodynamic limit we know that,

$$\frac{1}{T} = \frac{\partial S}{\partial U} \; ; \; \frac{p}{T} = \frac{\partial S}{\partial V} \; ; \; \frac{-\mu}{T} = \frac{\partial S}{\partial N} \tag{19}$$

(Here we are measuring temp. in unit of energy which is same as setting Boltzmann's constant k_B to unity.)

$$\text{So} \quad S(U,V,N) = U \frac{1}{T} + V \frac{p}{T} - N \frac{\mu}{T} \tag{20}$$

where S, U, V, N are extensive quantities

& p, T, μ are intensive quantities

We have defined our system (previous lecture) as collection of marbles arranged on an infinite staircase. Now, as the marbles are identical we are establishing an analogy with particles (quanta called bosons. Bosons are identical particle and their is no restriction on occupancy of energy level (step of staircase). i.e more than one boson can occupy the same energy level.

Now we will define an ideal collection of boson gas where energy of a level (step of staircase) is proportional to no. of bosons (marbles) & the proportionality constant is independent of how many bosons (marbles) there are.

Similarly, an ideal fermion gas will be when no more than one particle is allowed on an energy level.

Lets try to evaluate entropy for an ideal Bose gas & an ideal Fermi gas.

we know $\omega_q(\theta,\phi) = i(\phi + \theta\underline{u} - h_q(\theta,\phi))$ —— ⓘ

$$\frac{\partial}{\partial \theta}\bigg|_{\theta=\theta_*} \omega_q(\theta, \phi_*) = \frac{\partial}{\partial \theta}\bigg|_{\theta=\theta_*} i\left(\phi_* + \theta \underline{u} - h_q(\theta, \phi_*)\right)$$

$$= \frac{\partial}{\partial \theta}\bigg|_{\theta=\theta_*} i\left(\phi_* + \theta \underline{u} - \frac{i}{N} \operatorname{Log}[f_q(\theta, \phi_*)]\right)$$

(ii)

$$\frac{\partial}{\partial \cancel{\theta}}\bigg|_{\phi=\phi_*} \omega_q(\theta_*, \phi) = \frac{\partial}{\partial \phi}\bigg|_{\phi=\phi_*} i\left(\phi + \theta_* \underline{u} - h_q(\theta_*, \phi)\right)$$

$$= \frac{\partial}{\partial \phi}\bigg|_{\phi=\phi_*} i\left(\phi + \theta_* \underline{u} - \frac{i}{N} \operatorname{Log}[f_q(\theta_*, \phi)]\right)$$

(iii)

to describe the saddle point set eq. (ii) & (iii) $= 0$

By solving eq. (ii) & (iii) we get

$$U = \sum_j \frac{\epsilon_j}{\left(e^{\beta \epsilon_j} e^{-\beta \mu} + q\right)} \quad \text{(iv)} \qquad N = \sum_j \frac{1}{\left(e^{\beta \epsilon_j} e^{-\beta \mu} + q\right)} \quad \text{(v)}$$

We may relate θ & ϕ, with T & μ as follows.

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial}{\partial U} N \omega_q(\theta_*, \phi_*)$$

$$= \cancel{\frac{\partial}{\partial \phi}}\, iN \frac{\partial}{\partial U}\left(\phi_* + \theta_* \frac{U}{N} - \frac{qi}{N} \sum_j \operatorname{Log}\left(1 + q e^{-i\theta_* \epsilon_j} \cdot e^{-i\phi_*}\right)\right)$$

(vi)

$\Rightarrow$

$$\frac{1}{T} = iN\frac{\partial}{\partial U}\phi_* + iU\frac{\partial}{\partial U}\theta_* + i\theta_* - i\sum_j \frac{\frac{\partial \phi_*}{\partial U}}{(e^{i\theta_* \epsilon_j} e^{i\phi_*}+q)}$$

$$- i\sum_j \frac{\epsilon_j \frac{\partial \theta_*}{\partial U}}{(e^{i\theta_* \epsilon_j} e^{i\phi_*}+q)} \quad \text{— (vii)}$$

$$\Rightarrow \frac{1}{T} = \cancel{iN\frac{\partial}{\partial U}\phi_*} + \cancel{iU\frac{\partial}{\partial U}\theta_*} + i\theta_* - \cancel{i\frac{\partial \phi_*}{\partial U}N}$$

$$- \cancel{i\frac{\partial \theta_*}{\partial U}U} \quad \text{— (viii)}$$

$$\boxed{\frac{1}{T} = i\theta_*} \quad \text{— (ix)}$$

$$\text{||ly } \boxed{-\frac{\mu}{T} = \frac{\partial S}{\partial N}} \longrightarrow \& \ \boxed{i\phi_* = -\frac{\mu}{T}} \quad \text{— (x)}$$

Now, we can write $\beta \equiv \frac{1}{T}$

so our expression in eq. (iv) & (v) becomes by using above discussed relations. where $q=+1$ (fermions) & $q=-1$ (bosons)

Now we can rewrite relations in (iv) & (v) as

$$U = \sum_j \epsilon_j n_j \quad \text{(xi)} \qquad N = \sum_j n_j \quad \text{(xii)} \qquad \text{where } n_j = \frac{1}{e^{\beta\epsilon_j} e^{-\beta\mu}+q} \quad \text{(xiii)}$$

Here n_j has the meaning of the average no. of particle in energy level j.

when $q=1$ (fermions) eq. (xiii) for n_j is called **Fermi-Dirac distribution**

when $q=-1$ (Boson) eq. (xiii) for n_j is called **Bose-Einstein distribution**.

Now, entropy of an ideal Bose & Fermi gas in the thermodynamic limit

$$S(U,N) = N\,\omega_q(\theta_*,\phi_*) = iN\left(\phi_* + \theta_* U - \frac{i}{N}\log[f_q(\theta_*,\phi_*)]\right)$$

$$S(U,N) = -N\beta\mu + \beta U + q\sum_j \log\left(1+q\,e^{-\beta\epsilon_j}e^{\beta\mu}\right) \quad \text{(xiv)}$$

Now, the fundamental relation of thermodynamics is

$$S = -N\beta\mu + \beta U + \beta pV \quad \text{(xv)}$$

comparing eq. (xiv) & (xv) we get

$$\beta pV = q\sum_j \log\left(1+q\,e^{-\beta\epsilon_j}e^{\beta\mu}\right) \quad \text{(xvi)}$$

which is called **Equation of State of an Quantum Gas**

Untill now we have discussed marbles (bosons) arranged on an infinite staircase (energy levels). How could we define such a system confined in a closed space.

Let us consider a system in which ideal quantum particles are confined in a cuboid of size $L \times L \times L$. Since ideal quantum particles don't interact with each other, it is sufficient to treat them as a particle in a box problem.

Since these are quantum particles, they obey wave mechanics of Schrodinger. A wave function of a single particle in such a box is

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \tag{xvii}$$

why n can not be zero or -ive

Quantum no.s.
$(n_x, n_y, n_z = 1, 2, 3 \ldots)$

This wave function corresponds to a well defined energy

$$E = \frac{\hbar^2 k^2}{2m} \tag{xviii}$$

$$\underset{\text{wave vector}}{k = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}}$$

$$k_x = \frac{n_x \pi}{L}$$
$$k_y = \frac{n_y \pi}{L}$$
$$k_z = \frac{n_z \pi}{L}.$$

The sum over the index j is now nothing but the sum over the three integers n_x, n_y, n_z

$$\sum_j (\ldots) = \sum_{n_x, n_y, n_z = 1, 2, 3 \ldots} (\ldots)$$

Remember j represents the height of step which we can
no define by quantum numbers n_x, n_y, n_z

For the case of otherwise free particle trapped in a box,

$$\beta E_j = \beta \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \text{ ——— } \text{(xix)}$$

We want to study this system in thermodynamic limit. To express our system in thermodynamic limit we have to consider that our size of cuboid is very large such that as $N \to \infty$ the density of particles in the cuboid remains fixed.

Now at thermodynamic limit, the summation (Σ) over n_x, n_y & n_z is difficult to consider, hence we will convert the summation to integral which is easier (comparatively) to solve

Consider an even function $f(\lambda n)$ of an integer $n = \pm 1, \pm 2$ ----
and a real no. $\lambda > 0$.

i.e $f(-\lambda n) = f(\lambda n)$

Define $J(\lambda) = \lambda \sum_{n=1}^{\infty} f(\lambda n)$ for those $f(\lambda n)$ for which $J(\lambda)$ is finite — (xx)

then $$\lim_{\lambda \to 0} J(\lambda) = \frac{1}{2} \int_{-\infty}^{\infty} f(x)\, dx$$

⇒ Eq. of state can be written as

$$\beta p = q\frac{1}{L}\sum_{n_x=1,2\cdots}\frac{1}{L}\sum_{n_y=1,2\cdots}\frac{1}{L}\sum_{n_z=1,2\cdots}\log\left(1+q\,e^{-\beta\epsilon_j}e^{\beta\mu}\right) \qquad \textcircled{A}$$

Now

$$\beta\epsilon_j = (\alpha n_x)^2 + (\alpha n_y)^2 + (\alpha n_z)^2 \qquad \textcircled{B}$$

where

$$\alpha = \left(\beta\frac{\hbar^2\pi^2}{2mL^2}\right)^{1/2} \equiv \frac{C_0}{2L} \quad \& \quad C_0 = \left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{1/2} \qquad \textcircled{C}$$

∴ Eq. Ⓐ becomes.

$$C_0^3\beta p = q\,2\alpha\sum_{n_x=1,2\cdots}2\alpha\sum_{n_y=1,2\cdots}2\alpha\sum_{n_z=1,2\cdots}\log\left(1+q\,e^{-(\alpha n_x)^2}e^{-(\alpha n_y)^2}e^{-(\alpha n_z)^2}e^{\beta\mu}\right) \qquad \textcircled{D}$$

$\boxed{\text{where } \frac{1}{L} = \frac{2\alpha}{C_0}}$

In the thermodynamic limit, $\alpha \to 0$ since $L \to \infty$. Hence we may replace the discrete summation & by integration

$$C_0^3\beta p = q\int_{-\infty}^{\infty}dX\int_{-\infty}^{\infty}dY\int_{-\infty}^{\infty}dZ\,\log\left(1+q\,e^{-X^2}e^{-Y^2}e^{-Z^2}e^{\beta\mu}\right) \qquad \textcircled{E}$$

$$C_0^3\beta p = q\int d^3R\,\log\left(1+q\,e^{-R^2}e^{\beta\mu}\right) \qquad \textcircled{F}$$

$R = X\hat{x} + Y\hat{y} + Z\hat{z}$

&

$$\boxed{\begin{aligned}\alpha n_x &= X\\ \alpha n_y &= Y\\ \alpha n_z &= Z\end{aligned}}$$

Now, lly the energy per unit volume $u_v = \frac{U}{V}$ & the no. of particles per unit volume $\rho = \frac{N}{V}$ may also be written in terms of chemical potential & temperature

$$u_v = \frac{U}{V} = \int \frac{d^3R}{C_0^3\beta}\frac{R^2}{(e^{R^2}e^{-\beta\mu}+q)} \text{ — } ⓖ$$

$$\rho = \frac{N}{V} = \int \frac{d^3R}{C_0^3}\frac{1}{(e^{R^2}e^{-\beta\mu}+q)} \text{ — } Ⓗ$$

such that $C_0 = \sqrt{2\beta\frac{\hbar^2 Z^2}{m}}$ $\quad p = \frac{q}{C_0^3\beta}\int d^3R \, \mathrm{Log}(1+q e^{-R^2}e^{\beta\mu})$ — Ⓘ

Now we know that

$$S(U,V,N) = \underbrace{V}_{\text{Vol. is extensive}}\underbrace{(u_v\beta + p\beta - \rho\beta\mu)}_{\text{Intensive Quantities}} \text{ — } Ⓙ$$

Fundamental thermodynamic relation where $q=+1$ (fermions) & $q=-1$ (bosons)

Proof of theorem

$$\lim_{\lambda\to 0} J(\lambda) = \frac{1}{2}\int_{-\infty}^{\infty} f(x)\,dx \text{ — } Ⓚ$$

It is easier to prove this by invoking Fourier transform. Any well behaved function (i.e continous for all values of x, and vanishes rapidly at $x=\pm\infty$) can be written in terms of simple function such as trigonometric or exponential functions as follows.

$$f(x) = \int_{-\infty}^{\infty} g(k)\, e^{ikx} \frac{dk}{2\pi} \quad \text{— (L)}$$

And Fourier's theorem guarantees that this way of writing a function is unique where the coefficients $g(k)$ are given by

$$g(k') \equiv \int_{-\infty}^{\infty} f(x')\, e^{-ik'x'}\, dx' \quad \text{— (M)}$$

Hence

$$J(\lambda) = \lambda \sum_{n \geq 1}^{\infty} f(\lambda n) = \lambda \lim_{M \to \infty} \sum_{n=1}^{M} \int_{-\infty}^{\infty} g(k)\, e^{ik\lambda n} \frac{dk}{2\pi} \quad \text{(N)}$$

$$J(\lambda) = \lambda \lim_{M \to \infty} \int_{-\infty}^{\infty} g(k)\, \overbrace{e^{\frac{1}{2}ik(1+M)\lambda} \frac{\sin\left(\frac{kM\lambda}{2}\right)}{\sin\left(\frac{k\lambda}{2}\right)}}^{\text{exponential term}} \frac{dk}{2\pi} \quad \text{(O)}$$

Now $f(-x) = f(x) \Rightarrow g(-k) = g(k)$

$$J(\lambda) = \lambda \lim_{M \to \infty} \int_{\infty}^{\infty} g(k) \cos\left(\tfrac{1}{2}k(1+M)\lambda\right) \frac{\sin\left(\frac{kM\lambda}{2}\right)}{\sin\left(\frac{k\lambda}{2}\right)} \frac{dk}{2\pi} \quad \text{(P)}$$

or

$$J(\lambda) = \lambda \int_{-\infty}^{\infty} g(k) \frac{\pi k\lambda}{2\sin\left(\frac{k\lambda}{2}\right)} \left(\lim_{M \to \infty} \frac{\sin(kM\lambda)}{\pi k\lambda} \right) \frac{dk}{2\pi} \quad \text{(Q)}$$

But $\lim_{M \to \infty} \frac{\sin(kM\lambda)}{\pi k\lambda} = \delta(k\lambda)$ = Dirac Delta Function

$$\lim_{\lambda \to 0} J(\lambda) = \lambda \int_{-\infty}^{\infty} g(k) \frac{\pi k\lambda}{2\sin\left(\frac{k\lambda}{2}\right)} \delta(k\lambda) \frac{dk}{2\pi} = \frac{1}{2} g(0) = \frac{1}{2} \int_{-\infty}^{\infty} f(x)\, dx \quad \text{— (R)}$$

HENCE PROVED

MAXWELL BOLTZMANN DISTRIBUTION

So far we have managed to represent entropy of an ideal quantum gas (fermions or bosons).

Now we also know that classical physics may be thought of as a limiting case of quantum physics.

Now we can migrate to classical regiem from quantum regiem by

a) Think of planck's constant as a variable & send it to zero: $\hbar \longrightarrow 0$

b) Think of the mass of each particle as a variable & send it to infinite: $m \longrightarrow \infty$

c) Think of the temperature of the system as a variable & send it to infinity: $T \longrightarrow \infty,\ \beta \longrightarrow 0$

Now we know from eq. Ⓗ

$$\underset{\text{(density of particles)}}{\rho} = \frac{1}{c_0^3} \int \frac{d^3 k'}{\left(e^{k'^2} e^{-\beta\mu} + q\right)} \qquad \text{——— Ⓢ}$$

So in classical regiem set $h \longrightarrow 0$

$$\lim_{h \to 0} \rho = \lim_{h \to 0} \frac{1}{\left(2\beta \frac{\hbar^2 \pi^2}{2m}\right)^{\frac{3}{2}}} \int \frac{d^3 k'}{\left(e^{k'^2} e^{-\beta\mu} + q\right)} < \infty \quad \text{— Ⓣ}$$

Now, as $h \to 0$ eq. Ⓣ becomes ∞, however we know density of particles (ρ) has ~~to~~ be fixed.

The only way this can make sense is if

$$e^{-\beta\mu} = \frac{\int d^3R' \cdot e^{-R'^2}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{3/2}}$$

The idea is to make $e^{-\beta\mu}$ very huge, so that eq. Ⓣ becomes small & does not approach ∞.

$$= \frac{\pi^{3/2}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{3/2}} \quad \text{——} Ⓤ$$

$$\Rightarrow \lim_{h\to 0} \rho = \lim_{h\to 0} \frac{1}{\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{3/2}} \int \frac{d^3R'}{\left(e^{R'^2}\frac{\pi^{3/2}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{3/2}} + q\right)}$$

$$= \rho \int \frac{d^3R'}{\left(e^{R'^2}\cdot\pi^{3/2}\right)} = \rho < \infty \quad \text{——} Ⓥ$$

So even as $h \to 0$, density of particles remains same

From this we may derive M–B distribution of classical particles

page = 23 eq. xiii

$$n_j = \lim_{h\to 0} = \frac{1}{\left(e^{\beta\epsilon_j}\cdot e^{-\beta\mu} + q\right)} \quad \text{——} Ⓦ$$

$$= \frac{1}{e^{\beta\epsilon_j}\frac{\pi^{3/2}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{3/2}} + q} \quad Ⓧ \equiv \rho\left(2\beta\frac{\hbar^2\pi}{m}\right)^{3/2} e^{-\beta\epsilon_j} \quad (X')$$

As $h \to 0$, the term $\frac{\pi^{3/2}}{\rho\left(\frac{2\beta\hbar^2\pi^2}{m}\right)^{3/2}}$ in eq. Ⓧ becomes very large & q becomes irrelevant

$$N = \sum_k n_k = \rho \left(2\beta \frac{\hbar^2 \pi}{m}\right)^{3/2} \sum_k e^{-\beta \epsilon_k} \quad \text{———} \quad \text{(Y)}$$

So $$\frac{n_j}{N} = \frac{e^{-\beta \epsilon_j}}{\sum_k e^{-\beta \epsilon_k}}$$

$$\boxed{n_j = N \frac{e^{-\beta \epsilon_j}}{\sum_k e^{-\beta \epsilon_k}}} \quad \text{———} \quad \text{(Z)}$$

M-B Distribution

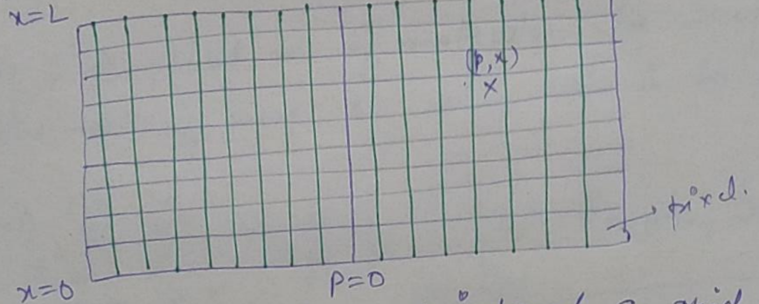
To calculate the no. of microstates in classical system is very difficult. (why?) so we first solved the distribution of particles in quantum gases when it is comparatively easy to calculate no. of microstates & then arrived at distribution of particles in classical systems.

However one can calculate no. of microstates in Ideal classical systems explicitly using Phase-Space methods.

Phase-Space is the collection of position & momenta of various particles in classical mechanics.
(Each position & momentum has three components)

Imagine a molecule in a box of size L×L×L. When it is far away from walls, this molecule is a free particle described by position & momentum co-ordinates (r_i, p_i)

Now, this is a system in which molecules ~~can~~ are continuously varying position & momenta. So, to simplify, we consider classical molecules confined to move along a straight line from $0 < x < L$. These end points $0, L$ represent the wall of container. The momentum of this molecule can be anything $-\infty < p < \infty$. The phase space of this molecule may be described as follows.



To facilitate counting, we have superimposed a grid in the region when the molecules is present. A given molecule can be in any of the small pieces at any given time.

(the size of each piece momentum $\simeq h$)

Imagine $L = N_L a$ & the momentum can also be divided into small pieces of size $\frac{h'}{a}$.

So, any point in phase space may be written as

$$(x, p) \equiv \left(a n_x, \frac{h'}{a} n_p\right) \quad \text{where} \quad 0 \le n_x < N_L, \quad -\infty \le n_p \le \infty$$

are integers & $h' \to 0$ is the area of one pixel

(34)

The energy of each molecule is $E_p = \frac{p^2}{2m} = \frac{\hbar^2}{2ma^2} n_p^2$.

we want to count how many ways are there of filling the grid with molecules with no more than one molecule per square so that the total energy of all the molecules is

$$U = \frac{\hbar'^2}{2ma^2} \sum_{i=1}^{N} n_{p,i}^2 \text{ ——— } ①$$

where N is the total no. of molecules. The way to count the no. of ways of doing this is to write ②

$$e^{S(U,L,N)} = \sum_{n_x=0}^{N_L-1} \sum_{n_p=-\infty}^{\infty} \delta_{\underline{w}, \sum_{i=1}^{N} n_{p,i}^2} \prod_{i\neq j,\ i,j=1}^{N} \left(1 - \delta_{n_{x,i}, n_{x,j}} \delta_{n_{p,i}, n_{p,j}}\right)$$

$$\boxed{U = \frac{\hbar'^2}{2ma^2} \underline{w}}$$

where $\underline{w}$ is the som of squares of integers.

Here the factor $\delta_{\omega, \sum_{i=1}^{N} n_{p,i}^2}$ enforces the idea that the total energy of the each of the microstates is U.

term $\prod_{i\neq j,\ i,j=1}^{N}$ ——— enforces the idea that only one particles occupy one pixel or no— particle in pixel. i.e the size of the pixel is so small that only one particle can occupy.

So by converting summation into integral we can write

$$e^{S(U,L,N)} \cong (N_L)^N \int D(n_p)\, \delta\Big(\omega - \sum_{i=1}^{N} n_{p,i}^2\Big) \quad ③$$

We can write

$$\delta\Big(\omega - \sum_{i=1}^{N} n_{p,i}^2\Big) = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi}\, e^{i\tau(\omega - \sum_{i=1}^{N} n_{p,i}^2)} \quad ④$$

$$e^{S(U,L,N)} \simeq (N_L)^N \int D(n_p) \int_{-\infty}^{\infty} \frac{d\tau}{2\pi}\, e^{i\tau(\omega - \sum_{i=1}^{N} n_{p,i}^2)} \quad ⑤$$

$$(N_L)^N \int_{-\infty}^{\infty} \frac{d\tau}{2\pi}\, e^{i\tau\omega} \left(\int_{-\infty}^{\infty} dn_p\, e^{-i\tau n_p^2}\right)^N = (N_L)^N \int_{-\infty}^{\infty} \frac{d\tau}{2\pi}\, e^{i\tau\omega} \left(\frac{\pi}{i\tau}\right)^{N/2} \quad ⑥$$

In other words,

$$e^{S(U,L,N)} = (N_L)^N\, \omega^{\frac{N}{2}-1} \int_{-\infty}^{\infty} \frac{d\tau'}{2\pi}\, e^{i\tau'} \left(\frac{\pi}{i\tau'}\right)^{\frac{N}{2}} \quad ⑦$$

$$\boxed{\text{where } \tau' = \tau\omega}$$

$$e^{S(U,L,N)} = (N_L)^N\, \omega^{\frac{N}{2}-1} \left(-\frac{1}{2}\right) N\, \pi^{-1+\frac{N}{2}}\, \Gamma\left(-\frac{N}{2}\right) \sin\left(N\frac{\pi}{2}\right)$$

$$\simeq \frac{1}{2} (N_L)^N\, \omega^{\frac{N}{2}-1} \left(\frac{2}{N}\right)^{\frac{N}{2}-1} \pi^{\left(\frac{N-1}{2}\right)} \quad ⑧$$

Note that $N_L = \frac{L}{a}$, $\omega = \frac{2ma^2U}{\hbar^2}$ ⑨

Hence

$$e^{S(U,L,N)} \simeq \frac{\sqrt{\pi}}{2} \left(\frac{L}{a}\right)^N \left(\frac{4\pi m a^2 U}{N\hbar^2}\right)^{\frac{N}{2}-1} \quad ⑩$$

$$S(U,L,N) = N\log\left(\frac{L}{a}\right) + \frac{N}{2}\log\left(\frac{4\pi m a^2 U}{N h'^2}\right) \quad ⑪$$

Is this entropy extensive?

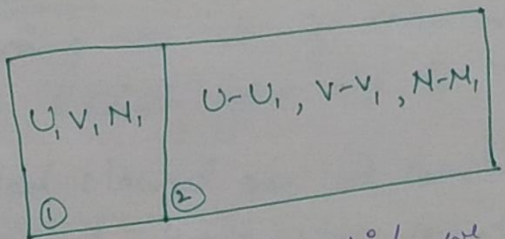
$$S(\lambda U, \lambda L, \lambda N) = \lambda N \log\left(\frac{\lambda L}{a}\right) + \frac{\lambda N}{2}\log\left(\frac{4\pi m a^2 U}{N h'^2}\right)$$

$$\neq \lambda S(U, L, N) \quad ⑫$$

Why Entropy Should be Extensive

Imagine we mentally divide a system made of N particles in a total volume V with total energy U into two components 1 & 2 as shown.

Here U, V, N are in thermodynamic limit



Denote the no. of ways in which we can rearrange the microstates of the overall system so that the total energy is U etc as $\Omega(U,V,N)$. It is clear that this is nothing but the product of the no. of ways in which we can rearrange the microstates of ① & ②.

or $$\Omega(U,V,N) = \Omega(U_1,N_1,V_1)\,\Omega(U-U_1, V-V_1, N-N_1) \quad ⑬$$

take log on b/s

$$\log\Omega(U,V,N) = \log\Omega(U_1,N_1,V_1) + \log\Omega(U-U_1, N-N_1, V-V_1) \quad ⑭$$

$$\Rightarrow \quad S(U,V,N) = S(U_1,V_1,N_1) + S(U-U_1, V-V_1, N-N_1) \quad (15)$$

$$\because \; S = k_B \log \Omega$$

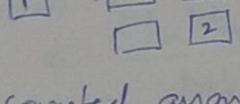
From this it is possible to prove that

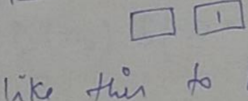
$$S(U,V,N) = U\,S(1,0,0) + V\,S(0,1,0) + N\,S(0,0,1)$$

In above eq. entropy to total system is linear in U, V & N. Which implies that S is extensive

so now in eq. (12) we have represented entropy of an ideal classical gas in 1D, But the entropy is found to be not extensive. This is because we were not careful while counting the no. of rearrangement of particles (molecules) which gave rise to Gibb's Paradox.

Since in ideal classical gas we consider each molecule to be different., Hence, while counting no. of microstates





we counted arrangement like this to be two different rearrangements. Ideally it should be one. Hence to correct rearrangement we will divide the LHS term in our no. of rearrangement eq. ⑩ (page 35) by N!.

$$\Omega(U,L,N) = \frac{\Omega_{\text{wrong}}(U,L,N)}{N!} = \frac{\sqrt{\pi}}{2}\left(\frac{L}{a}\right)^N \frac{1}{N!}\left(\frac{4\pi m a^2 U}{N h^2}\right)^{\frac{N}{2}-1} \quad (16)$$

we know invoke Stirling's approximation for $N>>1$,

i.e $N! \simeq N^N e^{-N}$ —— (17)

$$\Omega(U,L,N) = \frac{\sqrt{\pi}}{2}\left(\frac{eL}{Na}\right)^N \left(\frac{4\pi m a^2 U}{N\hbar^2}\right)^{\frac{N}{2}-1} \text{—— (18)}$$

This means by taking Log on b/s

$$\operatorname{Log}\Omega(U,L,N) = N \operatorname{Log}\left(\frac{eL}{Na}\right) + \frac{N}{2}\operatorname{Log}\left(\frac{4\pi m a^2 U}{N\hbar^2}\right)$$

$\Rightarrow$ $S(U,L,N)$ is linear in N (for $N>>1$) (19)

$\Rightarrow$ S is extensive or

$$S(\lambda U, \lambda L, \lambda N) = \lambda S(U,L,N) \text{—— (20)}$$

In 3D, the energy of each molecule is

$$E_p = \frac{p_x^2+p_y^2+p_z^2}{2m} = \frac{\hbar^2}{2ma^2}\left(n_{px}^2 + n_{py}^2 + n_{pz}^2\right) \text{—— (21)}$$

If we assume our vol. has sides $L_x = N_{Lx}a$, $L_y = N_{Ly}a$, $L_z = N_{Lz}a$

$$e^{S(U,V,N)} \simeq \frac{(N_{Lx}N_{Ly}N_{Lz})^N}{N!}\int D(n_p)\,\delta\left(\omega - \sum_{i=1}^{N} n_{px,i}^2 + n_{py,i}^2 + n_{pz,i}^2\right) \text{ (22)}$$

It is left, as we have already calculated before

$$e^{S(U,V,N)} \simeq \frac{\sqrt{\pi}}{2}\left(\frac{eV}{Na^3}\right)^N\left(\frac{4\pi m a^2 U}{N\hbar^2}\right)^{\frac{3N}{2}-1} \text{—— (23)}$$

Log on b/s

Imp

For $N>>1$

$$S(U,V,N) = N\log\left(\frac{eV}{Na^3}\right) + \frac{3N}{2}\log\left(\frac{4\pi a^2 U m}{N\hbar^2}\right) \text{—— (24)}$$

This is the famous Sackur - Tetrode formula of entropy for an classical ideal gas

The S-T formula can also be obtained by considering classical limit of the quantum entropy.

This can be achieved by setting $h \to 0$

and $$e^{-\beta\mu} = \frac{\pi^{3/2}}{\rho\left(2\beta \frac{\hbar^2\pi^2}{m}\right)^{3/2}} \text{ --- (i)}$$ where fugacity $= \frac{1}{e^{-\beta\mu}}$

Also $$C_0 = \left(2\beta \frac{\hbar^2\pi^2}{m}\right)^{1/2}$$

So $$u_v = \frac{U}{V} = \lim_{h\to 0} \int \frac{d^3R}{C_0^3\beta} \frac{R^2}{(e^{R^2}e^{-\beta\mu}+q)} \text{ --- (ii)}$$

$$= \rho\,\pi^{-\frac{3}{2}} \int \frac{d^3R}{\beta} e^{-R^2}R^2 = \frac{3}{2}\frac{\rho}{\beta} \text{ --- (iii)}$$

$$p = \lim_{h\to 0} \frac{q}{C_0^3\beta} \int d^3R \, \mathrm{Log}\left(1+q\,e^{-R^2}e^{\beta\mu}\right) = \frac{\rho}{\beta} \text{ --- (iv)}$$

$$\beta\mu = \mathrm{Log}\left(\rho\left(2\beta\frac{\hbar^2\pi}{m}\right)^{3/2}\right) = \mathrm{Log}\left(\frac{a^3N}{V}\left(\frac{3N}{U}\frac{\hbar^2\pi}{ma^2}\right)^{3/2}\right) \text{ --- (v)}$$

$$\Rightarrow S(U,V,N) = V\left(u_v\beta + p\beta - \rho\beta\mu\right)$$

$$S(U,V,N) = \left(N\,\mathrm{Log}\left(\frac{eV}{a^3N}\right) + \frac{3N}{2}\mathrm{Log}\left(\frac{U}{N}\frac{mea^2}{3\hbar^2\pi}\right)\right) \text{ --- (vi)}$$

Is the formula for ~~classi~~ quantum ideal gas in classical limits.

Also, $S(U,V,N) = N\log\left(\frac{eV}{Na^3}\right) + \frac{3N}{2}\log\left(\frac{4\pi m a^2 U}{N\hbar'^2}\right)$ — (vii)
(phase-space)

(S-K formula)

Compairing (vi) & (vii)

$$\frac{U}{N}\frac{mea^2}{3\hbar^2\pi} = \frac{4\pi m a^2 U}{N\hbar'^2}$$

$$\text{or} \quad \hbar' = \hbar\sqrt{\frac{3}{c}} \quad \text{— (viii)}$$

⇒ Size of the pixel is proportional to Planck's constant even though we are talking about a classical gas.

Now from eq. (iv) & (iii)

$$p = \frac{\rho}{\beta}, \quad u \equiv \frac{U}{V} = \frac{3}{2}\frac{\rho}{\beta} \quad \text{— (ix)}$$

$$\downarrow \qquad\qquad \downarrow$$

$$\boxed{pV = NT} \qquad \boxed{U = \frac{3}{2}NT} \qquad \because \rho = \frac{N}{V} \ \& \ \beta = \frac{1}{T}$$

Eq. of state of an classical Ideal Gas.

What are temparature, pressure and Chemical potential

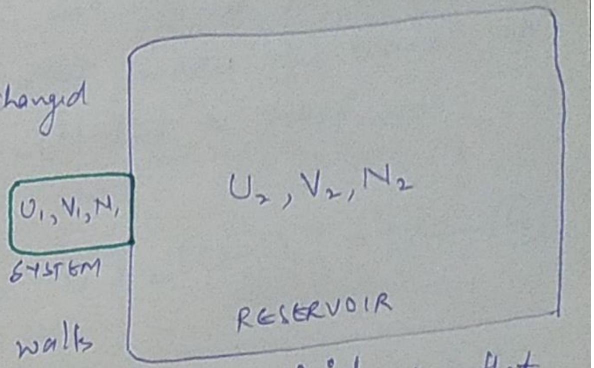
In thermodynamics, temp, pressure & chemical potential is defined as

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} \quad \text{— (A)}$$

$$p = T\left(\frac{\partial S}{\partial V}\right) = \frac{\left(\frac{\partial S}{\partial V}\right)}{\left(\frac{\partial S}{\partial U}\right)} \quad \text{— (B)}$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right) = -\frac{\left(\frac{\partial S}{\partial N}\right)}{\left(\frac{\partial S}{\partial U}\right)} \quad \text{— (C)}$$

Imagine a system, small in size, is in contact with a huge system as shown. such that $U_2 >> U_1$, $V_2 >> V_1$ $N_2 >> N_1$ as shown.



We ~~th~~now allow energy to be exchanged b/w the system & reservoir. However, we forbid the exchange of particles themselves and we also assume that the walls of both the system and reservoir are rigid so that they don't change. Suppressing the other extensive quantities we may write

$\Omega_1(U_1)$ = the no. of ways in which you can rearrange the microstates of the system such that the total energy is U_1, vol. is V_1 & no. of particles is N_1

$\Omega_2(U_2)$: the no. of ways in which you can rearrange the microstates of the reservoir such that the total energy is U_2, vol. is V_2 & no. of particles is N_2.

Because energy can be exchanged b/w the system & reservoir we may write $U_2 = U - U_1$, where the total energy U is fixed.

Hence the net no. of ways in which the microstates can rearrange themselves while also exchanging energy b/w each other can be represented as

$$\Omega_{net}(U) = \sum_{U_1} \Omega_1(U_1)\,\Omega_2(U-U_1) \equiv \sum_{U_1} e^{S_1(U_1)}\, e^{S_2(U-U_1)}$$

Ⓓ

Even though the energy U_1 is not fixed we could find the energy $U_1 = U_1'$ that makes the overall no. of microstates $\Omega_1(U_1)\Omega_2(U-U_1)$ a maximum.

This means

$$\frac{\partial}{\partial U_1}\Big|_{U_1=U_1'} \Omega_1(U_1)\,\Omega_2(U-U_1) = 0 \quad — Ⓔ$$

$$\Rightarrow \quad \frac{1}{T_1} = \frac{\partial S_1}{\partial U_1}\Big|_{U_1=U_1'} = \frac{\partial S_2}{\partial U_2}\Big|_{U_2=U_2'=U-U_1'} = \frac{1}{T_2}$$

Ⓕ

This shows that the most ~~prob~~ probable state i.e the configuration of microstates that has energy U_1' is the one that ensures that the slope of entropy versus internal energy is equal for both the system & the reservoir. This means temp. is that quantity that equalises when a system is in thermal contact with a reservoir which means energy exchange is allowed

Now, suppose the part of the wall that is common to the system and the reservoir is movable, then not only energy U_1 but also the volume V_1 fluctuates since if the partition moves, energy also gets redistributed as work is done.

In this case we have,

$$\Omega_{net}(U,V) = \sum_{U_1,V_1} \Omega_1(U_1,V_1)\,\Omega_2(U-U_1, V-V_1)$$

$$\equiv \sum_{U_1,V_1} e^{S_1(U_1,V_1)}\, e^{S_2(U-U_1,\, V-V_1)} \quad — ⓖ$$

Because energy freely redistributed b/w the system & the reservoir, as usual the temperature of the two become the same. However, now in addition we also see that the slope of the entropy vs volume also becomes the same of the system and the reservoir.

thermodynamics tells us that this quantity is nothing b/w the ratio of the pressure to the temperature.

$$\frac{p_1}{T_1} = \frac{\partial S_1}{\partial V_1}\Big|_{V_1=V_1'} = \frac{\partial S_2}{\partial V_2}\Big|_{V_2=V_2'=V-V_1'} = \frac{p_2}{T_2} \quad — Ⓗ$$

But since the temperature are already equal, this means the pressure on the wall of the system side is the same as the pressure on the wall of the reservoir side.

$$T_1 = T_2 \quad \text{and} \quad p_1 = p_2$$

Now, Given that $U >> U_1$, we may write

$$S_2(U-U_1) \simeq S_2(U) - U_1 S_2'(U) \quad \text{(Taylor series expansion)}$$

$$= S_2(U) - \frac{U_1}{T} \quad — Ⓘ$$

$$\Omega_{net}(U) = \sum_{U_1} e^{S_1(U_1)}\, e^{S_2(U-U_1)} = \sum_{U_1} e^{S_1(U_1)}\, e^{S_2(U) - \frac{U_1}{T}}$$

Ⓙ

Further

$$\Omega_{net}(U) = \sum_{U_1} e^{S_1(U_1)} e^{S_2(U) - \frac{U_1}{T}} \approx e^{S_1(U_1^*)} e^{S_2(U) - \frac{U_1^*}{T}} \text{ —— (K)}$$

Also,

$$\Omega_{net}(U) = e^{S_2(U)} e^{S_1(U_1^*) - \frac{U_1^*}{T}} \text{ —— (L)}$$

Here $S_1(U_1^*) - \frac{U_1^*}{T} = -\beta F$ (M), F = Helmholtz free energy.

$$\Rightarrow \boxed{\Omega_{net}(U) = e^{S_2(U)} e^{-\beta F}} \text{ —— (N)}$$

Also $$\boxed{F = U_1^* - T S_1(U_1^*)} \text{ —— (O)}$$

Free energy is the energy available to be utilized to do work.
During exchange of energy b/w system and reservoir, some of energy is lost as entropy & remaining can is available ~~be used~~ to perform work.

Now, for a system with movable walls.

$$\Omega_{net}(U) = \sum_{U_1, V_1} e^{S_1(U_1)} e^{S_2(U) - \frac{U_1}{T} - \frac{p}{T} V_1} \text{ —— (1)}$$

$$\approx e^{S_1(U_1^*)} e^{S_2(U) - \frac{U_1^*}{T} - \frac{p}{T} V_1^*} \text{ —— (2)}$$

⇒ we can write

$$\Omega_{net}(U) \simeq e^{S_2(U)}\, e^{S_1(U_1^*) - \frac{U_1^*}{T} - \frac{p}{T}V_1^*} \quad \text{———} \quad ③$$

Now we can represent

$$-\beta G = S_1(U_1^*) - \frac{U_1^*}{T} - \frac{p}{T}V_1^* \quad \text{———} \quad ④$$

or

$$\boxed{G = U_1^* + pV_1^* - TS_1(U_1^*)} \quad \text{———} \quad ⑤$$

G is called Gibb's free energy

So when β. we have system of movable walls, the thermodynamics of the system is determined by Gibb's free energy (G)

– where $H = U_1^* + pV_1^*$ ——— ⑥

is known as enthalpy

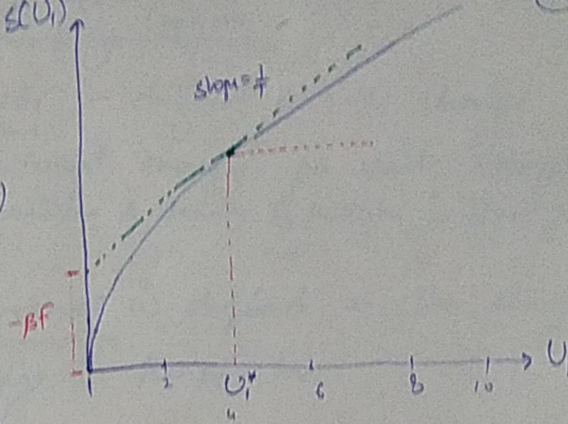
$$\Rightarrow \quad \Omega_{net}(U) \simeq e^{S_2(U)}\, e^{-\beta G} \quad \text{———} \quad ⑦$$

GEOMETRICAL MEANING OF F (free energy)

Consider a plot of entropy versus internal energy as follows. We purposely choose a more general example where the entropy is not extensive. i.e a system which is finite with a large but finite number of particles.

Equation for the tangent to $S(U_1)$ vs U_1 at $U_1 = U_1^*$

$$y(U) = (U - U_1^*)\, S'(U_1^*) + S(U_1^*)$$



we may see that the slope of this straight line by construction is the slope of the curve $S(U_1)$ vs U_1 at $U_1 = U_1^*$

We may also evaluate the y-intercept of this tangent. It is

$$y(0) = (-U_1^*)\, S'(U_1') + S(U_1') = -\beta F$$

The slope of the tangent is the inverse temperature.
The y-intercept of the tangent is the Helmholtz free energy

Thus the function such as Entropy vs Internal energy can either be described as a set of points $(U_1, S(U_1))$ or as a set of slopes and y-intercepts $(\beta_i, -\beta_i F_i)$

In mathematics, this way of describing a curve by a collection of tangents.
collection of tangents rather than a
points that lie on the ~~curve~~ curve is called Legendre
Transformation.

Specific Heat Of Gases

Specific heat at constant vol. is defined as the change in (most probable value of) internal energy per unit change in temperature. (when no. of particles & density of particles is fixed)

Specific heat at constant pressure is defined as the change in enthalpy per unit change in temperature.

Classical Ideal Gas:- Note that internal energy of a classical ideal gas is $\frac{3}{2}NT$. This means specific heat at constant vol. is $C_v = \frac{3}{2}N$.

The enthalpy is $H = U + pV = \frac{3}{2}NT + NT = \frac{5}{2}NT$. This means $C_p = \frac{5}{2}N$. It so happens that while these results are peculiar to an ideal gas, the difference b/w these two is quite generally shown to be N.

In terms of specific heat per particle

$\underline{c}$ = small alphabet

$$\underline{c}_p - \underline{c}_v = 1$$

Quantum Ideal Gases:-

$$u_v = \frac{U}{V} = \int \frac{d^3R}{C_0^3\beta} \frac{R^2}{(e^{R^2}e^{-\beta\mu}+q)} \quad ; \quad \rho = \frac{N}{V} = \int \frac{d^3R}{C_0^3} \frac{1}{(e^{R^2}e^{-\beta\mu}+q)}$$

Solving these two integrals (Poly Log function)

$$\frac{p}{u_v} = \frac{2}{3} \qquad \text{where } p = \frac{q}{C_0^3\beta}\int d^3R \, \mathrm{Log}(1+q e^{-R^2} e^{\beta\mu})$$

or $$\frac{p}{u_v} = \frac{2}{3}$$

$$\boxed{pV = \frac{2}{3} U}$$

This means that for quantum ideal gases (with energy-momentum dispersion being parabolic) the pressure in the thermodynamic limit is related to the total internal energy.