Introduction to Statistical Mechanics
Prof. Girish S Setlur
Department of Physics
Indian Institute of Technology – Guwahati

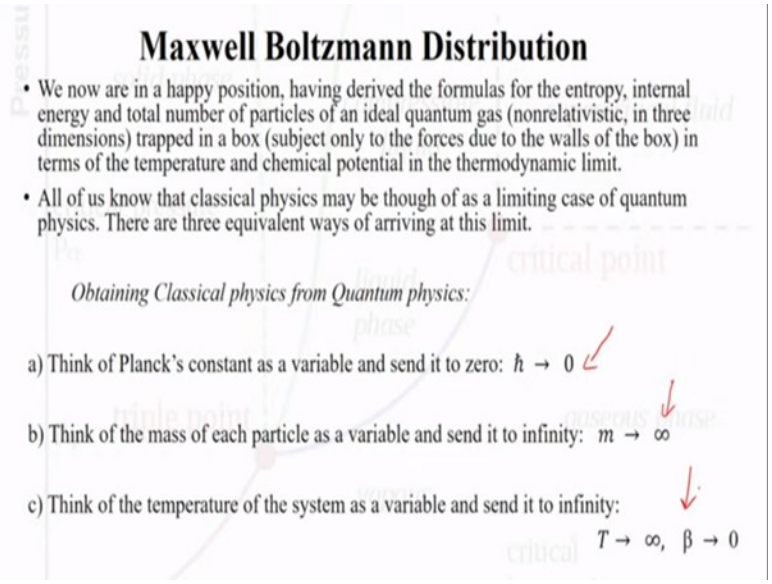
Module No # 1
Lecture No # 5
Maxwell Boltzmann Distribution

Ok, so let us continue, so the goal of this hour of lecture is to see if we can understand the distribution of velocities of molecules of a classical gas. So it is called Maxwell Boltzmann distribution. So historically of course this was derived first and the quantum gases where derived later. So, but we have actually done the logically correct way of you know using combinatorics to arrive at what is logically simpler namely that of quantum gases because it quantum mechanics is all about discreteness and counting becomes easier, a combinatorics becomes easier when you are discussing quantum gases.

So naturally we were quite successful in deriving the formulas for entropy, internal energy and total number of particles of an ideal quantum gas . So we are talking about say nonrelativistic so in another words we assume implicitly that the kinetic energy of the molecules or the particles is p^2 /2m. So the E vs p is quadratic and there is also no potential energy. So that is roughly what we have in mind so that is basically an ideal quantum gas as what we have described.

So it could be either bosons or fermions, if its bosons, there is no restrictions on how many particles can occupy at a certain energy level if they all identical fermions then there is a maximum of one fermion per energy level. So now what we want to do is make use of this effort that we have put in and see if we can extract the classical result from the quantum result that we have painstakingly derived. So in another words what I want to do is I want to take the classical limit of a quantum gas.

(Refer Slide Time: 02:37)



Maxwell Boltzmann Distribution

- We now are in a happy position, having derived the formulas for the entropy, internal energy and total number of particles of an ideal quantum gas (nonrelativistic, in three dimensions) trapped in a box (subject only to the forces due to the walls of the box) in terms of the temperature and chemical potential in the thermodynamic limit.
- All of us know that classical physics may be though of as a limiting case of quantum physics. There are three equivalent ways of arriving at this limit.

Obtaining Classical physics from Quantum physics:

a) Think of Planck's constant as a variable and send it to zero: $\hbar \to 0$

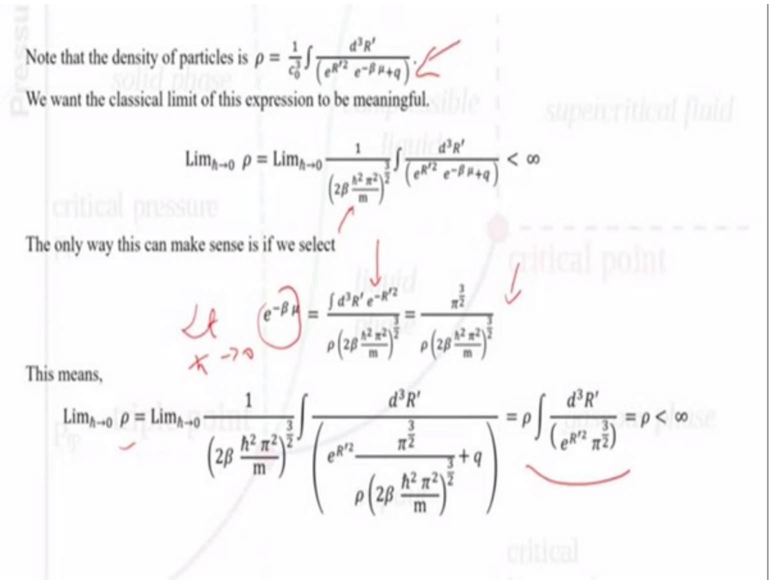
b) Think of the mass of each particle as a variable and send it to infinity: $m \to \infty$

c) Think of the temperature of the system as a variable and send it to infinity:

$T \to \infty, \ \beta \to 0$

So I even described this earlier so I am just repeating myself so the idea is that you can do it in one or several ways. So you either make Planck's constant (h) go to 0 and keep everything else fixed while you do this, so as a result you end up getting the classical limit of a quantum system. Alternatively, you keep everything else fixed and make the mass of each particle tend to infinity or third possibility is again you keep everything else fixed and make the temperature of the system very large. So in either of these three equivalent ways you can send a what is a quantum system to a classical system, so let us make use of this idea.

(Refer Slide Time 03:20)



Note that the density of particles is $\rho = \frac{1}{c_0^3}\int \frac{d^3R'}{\left(e^{R'^2}\, e^{-\beta\mu} + q\right)}$.

We want the classical limit of this expression to be meaningful.

$$\text{Lim}_{\hbar\to 0}\ \rho = \text{Lim}_{\hbar\to 0} \frac{1}{\left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{3}{2}}} \int \frac{d^3R'}{\left(e^{R'^2}\, e^{-\beta\mu} + q\right)} < \infty$$

The only way this can make sense is if we select

Lt

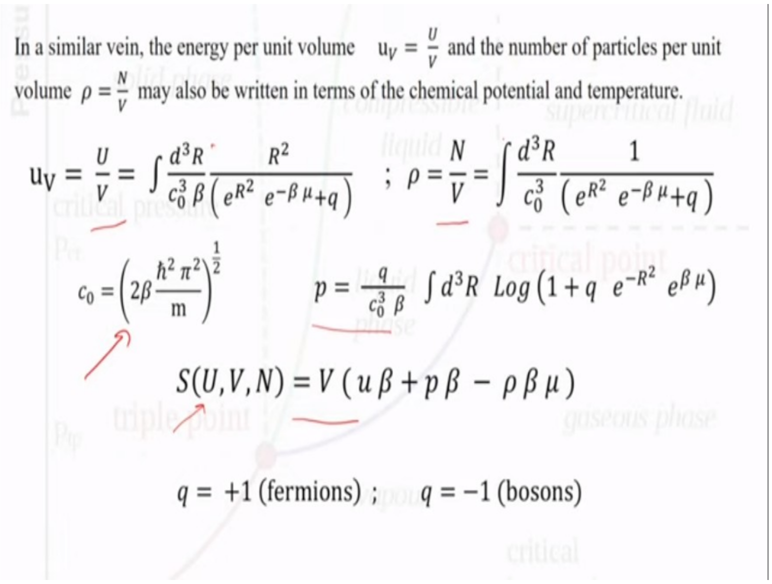
$\hbar \to 0$

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

This means,

$$\text{Lim}_{\hbar\to 0}\ \rho = \text{Lim}_{\hbar\to 0} \frac{1}{\left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{3}{2}}} \int \frac{d^3R'}{\left(e^{R'^2} \frac{\pi^{\frac{3}{2}}}{\rho\left(2\beta \frac{\hbar^2 \pi^2}{m}\right)^{\frac{3}{2}}} + q\right)} = \rho \int \frac{d^3R'}{\left(e^{R'^2}\, \pi^{\frac{3}{2}}\right)} = \rho < \infty$$

So recall that in the quantum case that we had derived the density of particles and expression for the density of the particles in terms of the temperature and chemical potential in this fashion. So if you recall we had a formula for c_0 which I have described earlier so maybe I can refresh your memory and go back here so this was my c_0.



In a similar vein, the energy per unit volume $u_V = \frac{U}{V}$ and the number of particles per unit volume $\rho = \frac{N}{V}$ may also be written in terms of the chemical potential and temperature.

$$u_V = \frac{U}{V} = \int \frac{d^3R}{c_0^3\,\beta} \frac{R^2}{\left(e^{R^2}\ e^{-\beta\mu} + q\right)} \quad ; \quad \rho = \frac{N}{V} = \int \frac{d^3R}{c_0^3} \frac{1}{\left(e^{R^2}\ e^{-\beta\mu} + q\right)}$$

$$c_0 = \left(2\beta \frac{\hbar^2\pi^2}{m}\right)^{\frac{1}{2}} \qquad p = \frac{q}{c_0^3\,\beta} \int d^3R\ Log\left(1 + q\ e^{-R^2}\ e^{\beta\mu}\right)$$

$$S(U,V,N) = V\,(u\,\beta + p\,\beta - \rho\,\beta\,\mu)$$

$$q = +1 \text{ (fermions)} \ ; \quad q = -1 \text{ (bosons)}$$

(Refer Slide Time 3:45)

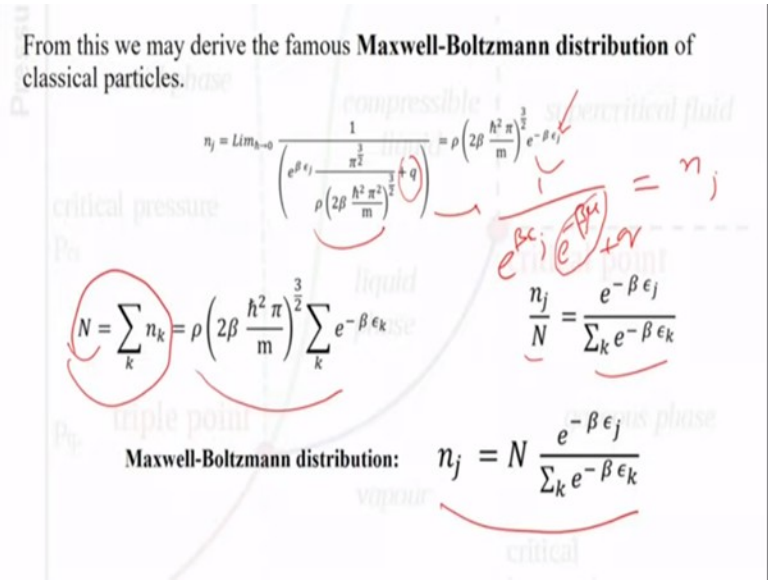
I have derived so this is the energy density that I have derived then the number density and the equation of state was this and this was the entropy. So everything is all linked up in terms of the chemical potential and temperature and if you do not like that you can always invert these two relations and you can always express the chemical potential and temperature in terms of the energy and number of particles in the system and you can express the entropy in terms of its legitimate independent variables namely entropy, number of particles and volume.

So given the that was the c_0 and this the density of particles N / V so what I want to do is I want to take the first point of U that is a I think of the classical system as $\hbar \to 0$ limit of the quantum system. So in order to that I have to explicitly display all the location where $\hbar$ appears. So one of the places where it appears is here and so you see that it explicitly appears there so as I make $\hbar \to 0$ this whole thing is going to become infinity unless well we know that the density of particle is fixed.

So I do not want it to become infinity, so only way to achieve to make sure that it does not become infinity is to do the following, so you select this quantity such that it becomes huge. So as a result when it becomes huge this quantity becomes very small and it is being divided by a very small quantity so the ratio kind becomes a constant so that is the idea. As ħ → 0 so limit ħ → 0 , I select my $e^{-\beta\mu}$ to be this quantity.

So I am going to make this selection that it is for small ħ I want it to be this. So now I am going to substitute that here and you will see that by design I recover ρ again. So this choice when ħ is small so when I am discussing classical system by choice I am only you know I am kind of getting an identity which I should. Ok so that the density of the particles is not being un-physically large.

(Refer Time Slide 06:06)



From this we may derive the famous **Maxwell-Boltzmann distribution** of classical particles.

$$n_j = Lim_{\hbar\to 0} \frac{1}{\left(e^{\beta\epsilon_j} \frac{\pi^{\frac{3}{2}}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{\frac{3}{2}}} + q\right)} = \rho\left(2\beta\frac{\hbar^2\pi}{m}\right)^{\frac{3}{2}} e^{-\beta\epsilon_j}$$

$$\frac{1}{e^{\beta\epsilon_j} e^{-\beta\mu} + q} = n_j$$

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

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

Maxwell-Boltzmann distribution: $n_j = N\frac{e^{-\beta\epsilon_j}}{\sum_k e^{-\beta\epsilon_k}}$

So now we can use this idea to derive Maxwell Boltzmann distribution immediately, so this is nothing but

$$n_j = 1/(e^{\beta\varepsilon_j} e^{-\beta\mu} + q)$$

So this was the quantum version of the you know occupation probability or the number of particles occupying ,average number of particles occupying energy level ε_j . So this is what we had derived for the quantum case.

Now in the classical case all we are doing is that taking this quantity and replacing it with our classical limit namely $e^{-\mu}$ as this classical limit and then keep in mind that $\hbar$ is very small so in which case this term is going to dominate a lot. And so as a result this q becomes irrelevant. So remember that when q was + 1 we were talking about fermions when it was – 1 we were talking about bosons. So now when $\hbar$ is very small this whole thing becomes insensitive to what q is.

So you end up getting a distribution which is of this form which is what is called the Boltzmann distribution. So what Boltzmann had suggested and Maxwell had derived later was that the number of particles of a classical ideal gas was you know in contact with the thermal reservoir and so on is proportional to the exponential of the energy at divided by the absolute temperature which it falls exponentially as you increase energy when the temperature is fixed.

So this is the famous Maxwell Boltzmann distribution and you can of course get rid of this normalization you know that the total number of particle has to be fixed. So you kind of handle that this way and then you fix it by just dividing up by the number of particles and then you get this. This is just the convenient normalization and then I am able to derive the Maxwell Boltzmann distribution like this.

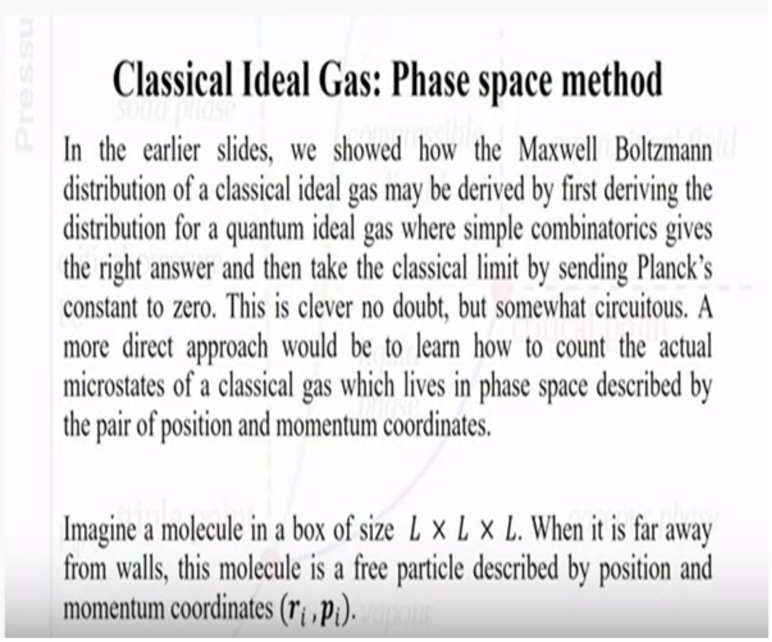
So this normalization ensures that this is respected, there is a total number of particles as it what it should be. So you see its quite beautiful we have successfully derived the number of particles in a classical ideal gas purely using quantum ideas which were motivated by combinatorics. That was easy for us to do because after all we use the simple counting arguments to directly write down the partition function and other physical quantities of quantum gases.

But then doing this same for classical gas is likely to be difficult because that the discreteness is lost in a classical gas and it is not easy to count you know the number of microstates of a classical gas. So it is useful to first do it in a quantum sense where we can count easily and then take the classical limit so which is what we have done successfully. But now we also want to do the harder thing which is not start from a quantum gas rather do the hard problems of explicitly counting the number of states, the number of microstates of a classical gas directly.

Of course, that is how people did it in the beginning when you know that the subject of statistical mechanic predates quantum mechanics. So it is people did not know about quantum gases at all.

So they first derive the classical expressions directly by learning how to count microstates of a classical gas where the discreteness feature is not present.

(Refer Slide Time 09:53)



Classical Ideal Gas: Phase space method

In the earlier slides, we showed how the Maxwell Boltzmann distribution of a classical ideal gas may be derived by first deriving the distribution for a quantum ideal gas where simple combinatorics gives the right answer and then take the classical limit by sending Planck's constant to zero. This is clever no doubt, but somewhat circuitous. A more direct approach would be to learn how to count the actual microstates of a classical gas which lives in phase space described by the pair of position and momentum coordinates.

Imagine a molecule in a box of size $L \times L \times L$. When it is far away from walls, this molecule is a free particle described by position and momentum coordinates $(\boldsymbol{r}_i, \boldsymbol{p}_i)$.

So all right, how do we do that? So that the way to do that is use what is called as a phase space method. So if you remember that the phase space in classical mechanics we are talking about the collection of the positions and momenta of the various particles, so that is called the phase space of the system. But what we have to do is that each molecule has a state which is basically a point in phase space so in another words if you have a molecule which occupies a certain position in space.

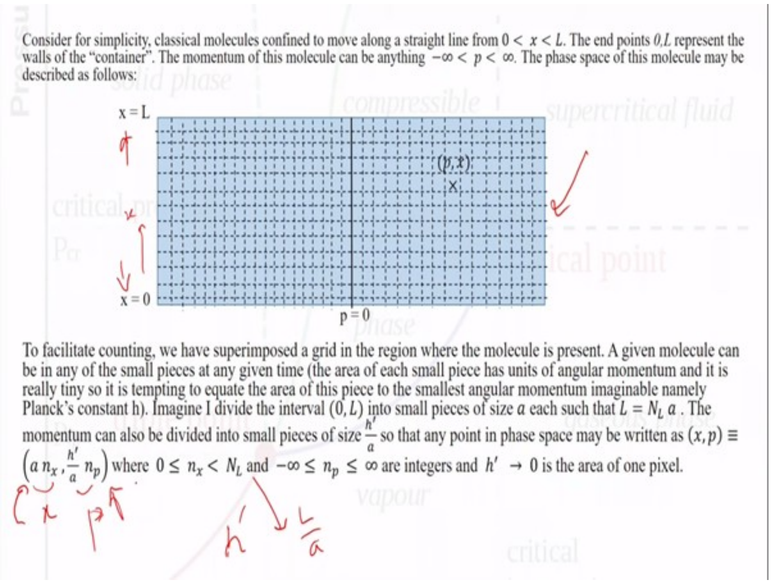
So as a result it is described by three components of the position vector and then it also has three components of the momentum vector so put together ther are 6 real numbers which describes as a coordinates of a particle in phase space. So now what we have to do is we have to populate that phase space by all the n classical molecules that we have in our position. In such a way that we force those molecules to occupy a certain restricted volume say we talk about the cubical box of side L.

So you have a cubical box of side L by L by L and I force my molecules to be present only in that box. And I also make sure that importantly the other constraint is that I have to make sure that the total energy of all the molecules put together is some fixed quantity. So notice that when

I talk about energy I only talk about kinetic energy because I am talking about ideal classical gas so they do not interact with each other expect you know perhaps with the walls of the container so until they hit the walls of the container no forces act on them.

So within the walls of the container so it is just kinetic energy of the particles, so just by forcing myself to only consider particles that live inside the container I can make sure I am not making a mistake. So how do I count when the object that I want to count is not discrete but some continuous.

(Refer Slide Time 11:57)



Consider for simplicity, classical molecules confined to move along a straight line from $0 < x < L$. The end points *0,L* represent the walls of the "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 where the molecule is present. A given molecule can be in any of the small pieces at any given time (the area of each small piece has units of angular momentum and it is really tiny so it is tempting to equate the area of this piece to the smallest angular momentum imaginable namely Planck's constant h). Imagine I divide the interval $(0, L)$ into small pieces of size a each such that $L = N_L\, a$. The momentum can also be divided into small pieces of size $\frac{h'}{a}$ so that any point in phase space may be written as $(x, p) \equiv \left(a\, n_x, \frac{h'}{a}\, n_p\right)$ where $0 \le n_x < N_L$ and $-\infty \le n_p \le \infty$ are integers and $h' \rightarrow 0$ is the area of one pixel.

So it is somewhat like you know if somebody asks you to count the number of water droplets in the ocean you would probably laugh at that person and say that the ocean is just one continuous body of fluid I cannot really count the number of what does that even mean. So that is the problem we are confronted with right now because we are being called upon to count the number of you know points as it where in the phase space.

When in fact the phase space itself is described by the position and momentum and the components of the position in a momentum which are all continuous and so there is no way of counting a priori. So what we do in order to facilitate this is that we discretize the artificially divide up the phase space into small pixels. So it is similar to what you have on your computer screen your computer screen does look granular so it looks rather smooth and continuous by then if you look under microscope or lens you will see that it is actually made of pixels.

So, pixels are small squares and each square has a uniform intensity of a certain color. So we are going to do the same thing here, so we are going to take this phase space out here so I have purposely restricted myself to molecules moving in one dimension so in another words my molecules are forced to live between x = 0 and x = L. And however, they are not restricted to any particular momentum they can have any positive momentum however large or any negative momentum implying that they are moving opposite direction, also however large.

So I have this rectangularish looking phase space and I want to populate this phase space with my molecules. But before I do that, I have to in order to facilitate counting I am going to discretize this phase space by imposing a certain grid on it which is basically same as dividing it up into a whole bunch of pixels. So how do I do that? I say that imagine that the position which is this axis I should have flipped these two coordinates, so I am talking about the position here.

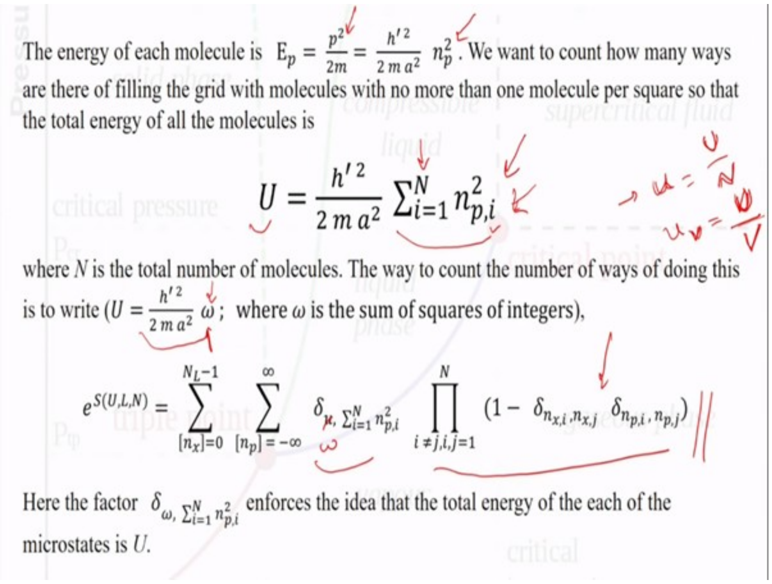
So the position is this is x, so I am going to call nx I have defined $n_x = x / a$. In another words I am going to say that x is some kind of a multiple of a small number called a in another word I am dividing up this interval from x = 0 to x = L into a whole bunch of pieces and each piece has a size or length a. So and n_x would be the number of steps I have to move in this direction in order to reach x. So similarly, I do the same thing with p except that I want to make sure that my size of my pixels is some quantity I called ħ.

So right now, it has no special significance, later you will see that it is indeed very special so we going to discuss that later. Right now, it is just a you know the area of my pixel which I have mandated or by fiat I have chosen it to be ħ it is just a notation for a pixel of a small size. So because the pixel area ħ I will be forced to express my momentum in terms of discrete multiples of ħ/ a.

So that if I take the product of the length and the breadth of the pixel, I get ħ. And n_p is an integer which can be as negative or as positive as it wants. And how ever n_x because my x's are all positive from 0 to L and force to choose my n_x to be between 0 and a maximum value determined by of course this N_L would be nothing but L over a where L is my there is size of my system a physical size of my system divided by this size of each pixel in a x size of each pixel.

So of course, I mean you might be wondering what gives me the right to do this because after all it is a very contrived and artificial thing to do. And of course the implication is that towards the end I am going to make the pixel size tends to 0, so I am going to make the pixels go away and everything becomes nice and smooth and hopefully I will be able to extract meaningful physical quantities even in that limit.

(Refer Slide Time 16:51)



The energy of each molecule is $E_p = \frac{p^2}{2m} = \frac{h'^2}{2\,m\,a^2}\, n_p^2$. 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

$$U = \frac{h'^2}{2\,m\,a^2} \underbrace{\sum_{i=1}^{N} n_{p,i}^2}$$

$\to u = \frac{U}{N}$

$u_v = \frac{U}{V}$

where N is the total number of molecules. The way to count the number of ways of doing this is to write ($U = \underbrace{\frac{h'^2}{2\,m\,a^2}}\, \omega$; where ω is the sum of squares of integers),

$$e^{S(U,L,N)} = \sum_{[n_x]=0}^{N_L-1} \sum_{[n_p]=-\infty}^{\infty} \delta_{\underset{\omega}{\cancel{\mu}},\, \sum_{i=1}^{N} n_{p,i}^2} \underbrace{\prod_{i\neq j, i,j=1}^{N} \left(1 - \delta_{n_{x,i}, n_{x,j}}\, \delta_{n_{p,i}, n_{p,j}}\right)} \,\Big\|$$

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.

So now, so let me go ahead and start re-expressing all my physical quantities in terms of these number called n_x and n_p. Okay so how do I achieve that? So I simply know that the energy of each molecule with momentum p is $p^2 / 2m$. So I can rewrite p in terms of n_p here and so if I do that I get a quantity here so the energy of the each molecule is proportional to that square of that integer. So notice that I have to ensure in addition to of course ensuring that the particle does not exit my system in other words its position is locked between x = 0 to x = L.

I have to make sure that it also, all the molecules put together should not have any energy other than U. So in other word its total energy of all the molecules put together is forced to be U. So notice that this index i are refer to the index which tells you which molecule I am looking at. So if i = 1 I am looking at the first molecule if I am looking at i = 2 it is the second molecule and so on and so an N is the total number of molecules.

So when I do this ,if I fix U so as usual I have a kind of Diaphantine type of system here so where I am being forced to find out all the different u's possible which ensure that the total energy is U. So naturally I attempted to rescale or redefine my U in terms of this dimensional less energy called ω. So it happens to be integers because so after all it is just the sum of the squares of the integers so this also be better be an integers not only that it is the sum of squares of certain class certain set of integers ok.

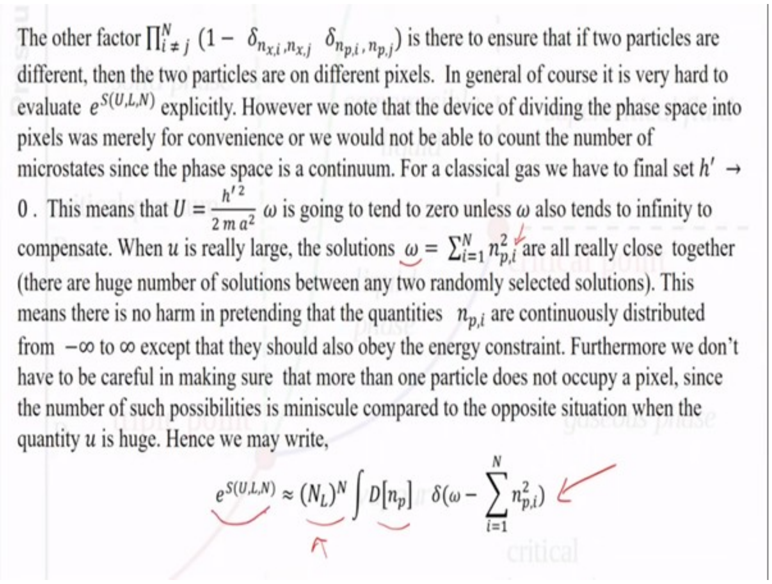
I had to recall this U not U but ω I called it ω because notice that I have reserved the symbol u for U / N and because of that I was forced to call U / V as using a different name. So I was forced to call U / V as u_V . So I do not want to confuse my listener so I am going to make these conventions standard right now. So this small case u is nothing but total energy per particle and this small case u_V is the energy density that means total energy per unit volume.

However, this ω is some integer which happens to be related to the total energy. So as usual the constraint is going to be this that I am forced to make sure that sum of the squares of this integer is ω. Then there this is nasty looking constrain which just tells me that only one molecule can occupy given pixel. So that means remember that the phase space so I you know it is not like the fermions anything.

It is just that the phase space I am going to divide by phase space into smaller and smaller pieces in such a way that I will end up with a situation where precisely one molecule is sitting in a given pixel or no molecules at all. So in other words , suppose two molecules are sitting in a given pixel I divided up in grid even finer. So I will make the grid even finer until I reach a state where precisely one molecule is sitting there or no molecule is sitting there at all.

So if I mean there is no molecule to begin with no matter how fine I divided molecule would not appear of nowhere. So if it was if two molecule sitting I'll divide into two further pieces so as a result I will end up with a grid with either no molecules or one molecule. So that is basically what this is but this is kind of looks very scary this whole expression looks very scary and it is, this is how you would actually count if you are serious about counting something which is intrinsically smooth and continuous and you wanted to discretize it and count anyway.

(Refer Slide Time 21:19)



The other factor $\prod_{i \neq j}^{N} (1 - \delta_{n_{x,i}, n_{x,j}} \ \delta_{n_{p,i}, n_{p,j}})$ is there to ensure that if two particles are different, then the two particles are on different pixels. In general of course it is very hard to evaluate $e^{S(U,L,N)}$ explicitly. However we note that the device of dividing the phase space into pixels was merely for convenience or we would not be able to count the number of microstates since the phase space is a continuum. For a classical gas we have to final set $h' \rightarrow 0$. This means that $U = \frac{h'^2}{2\,m\,a^2}\,\omega$ is going to tend to zero unless ω also tends to infinity to compensate. When u is really large, the solutions $\underline{\omega} = \sum_{i=1}^{N} n_{p,i}^2$ are all really close together (there are huge number of solutions between any two randomly selected solutions). This means there is no harm in pretending that the quantities $n_{p,i}$ are continuously distributed from $-\infty$ to ∞ except that they should also obey the energy constraint. Furthermore we don't have to be careful in making sure that more than one particle does not occupy a pixel, since the number of such possibilities is miniscule compared to the opposite situation when the quantity u is huge. Hence we may write,

$$\underline{e^{S(U,L,N)}} \approx \underline{(N_L)^N} \int \underline{D[n_p]} \;\; \delta(\omega - \sum_{i=1}^{N} n_{p,i}^2)$$

But fortunately, we are saved by this limit that we are going to employ which I have already mentioned earlier and that is called as thermodynamic limit. See in the thermodynamic limit the idea is that the total energy of the system is enormous, in fact its scales with the size of the system. So idea is that the total energy tends to infinity, volumes tends to infinity in such a way that the ratio is fixed. So I am going to imagine a situation where the total energy of my system is enormous.

So as a result the implication then is that the ω which is an integer is an enormous huge integer. So when it is a huge integer you can see that there will be a huge number of solutions of this, so if a certain set of integer n_{p1} , n_{p2} , …., n_{pn} is an integer then you know there will be a whole bunch of possible solution very close to that selected sequence of number. So there will be a whole bunch of closely clustered solutions which are also acceptable because of the hugeness of ω.

So as a result there is no penalty to be paid in the thermodynamic limit by replacing summation the discrete summation over these integers by an integration. So I am not going to be rigorous here and try and prove this rigorously. I did something similar earlier if you recall when I was trying to explain to you how to convert a discrete sum into a integration in the context of a thermodynamic limit but here well this is similar not quite the same.

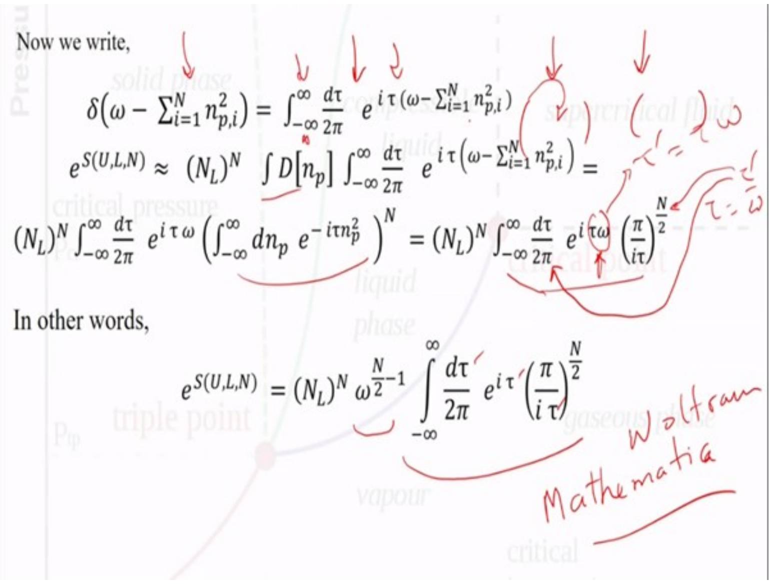
But as a result, I will either differ the proof to may be an exercise or may be those of who are interested can ask me later. In anyway also the restriction that no two molecules should occupy the same pixel is also superfluous here. Because in the thermodynamic limit the number of ways in which that can happen is miniscule compared to the number of way which, the total number of ways in which you can arrange your molecules in these pixels.

So it is kind of hugely suppressed, the number of ways in which you can populate pixel with two or more molecules is significantly less compared to the number of ways in which you can populate molecules in general, that is if ω is huge ok. So that is also something that I will leave you to think about and you know to come to an agreement with.

So as I said now I am in this happy situation of having replaced my summation over this n_p 's by integrations and notice that here what I have here is that it is simply sum over all these discrete number of n's in n_x's which is it just counts how many steps there are in the x direction. So because I have divided up my length of the box from 0 to L into N_L steps. So of course, you know for each particle the answer is N_L and because I have N particles it is $(N_L)^2$.

Remember that I am counting a number of ways which I can do things, so the number of ways is product of number of ways doing it for 1, 2, 3 ,…., N particles its instead of one particle raise to the number of particles. And of course according to Boltzmann that is precisely the exponential of the entropy of the system.

(Refer Slide Time 24:57)



Now we write,

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

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

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

$\tau' = \tau\omega$

$\tau = \frac{\tau'}{\omega}$

In other words,

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

Wolfram Mathematia

So now I am going to use my usual trick which is to rewrite my Dirac delta function of course it is notice that it is not the Kronecker delta function. If it was Kronecker delta I remember I had used angle between 0 and 2 π. But because the Dirac delta I have to use a Fourier transform so where the limits are -∞ to ∞. So I am just going to go ahead and substitute this way of writing a Dirac delta function here and then I am going to do the same integral over the p's, n_p's .

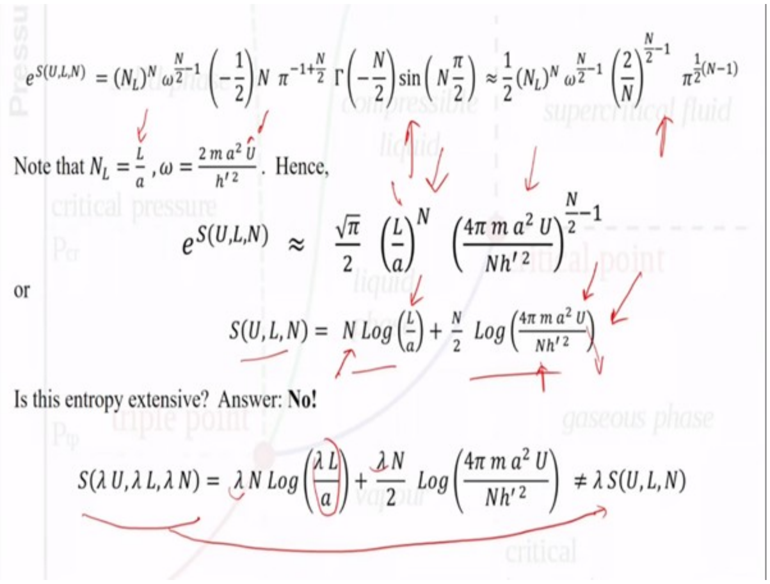
So when I do this I end up with this expression and so I can extract so you see I am now called up to do this integration. But I really do not care about this integration in its entirety all I want to know is how this depends on ω which is my you know if you recall ω is just that energy divided by some constant, the total energy of the system is huge. So I just care about how this whole thing depends on total energy which is related to ω.

So in order to do this what I am going to do is I am just going to rename this variable as something else may be τ'. So in which case I am going to rewrite this as τω and then τ itself will become τ'/ω. So when I substitute that here and also there and then I do my integrations so actually I will get τ' all over the place so I have been lazy and called the τ again but you know what I mean.

So basically I end up extracting ω out of my integrations which is all I care about. So I care about the omega dependence only and this is just some constant and of course this also is interesting because it depends on the number of particle which is also of interest in some sense.

So but nevertheless this is the answer and I can now go ahead and use my tables or you know some software. My preferred software is called Mathematica well I am not a spokesperson for this company Wolfram Mathematica. I just happened to use it you know I do not have shares in this company so I am not advertising it there are other products that I used also that equally useful MATLAB and so many other similar software symbolic algebra packages.

(Refer Slide Time 27:38)



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

Note that $N_L = \frac{L}{a}, \omega = \frac{2 m a^2 U}{h'^2}$. Hence,

$$e^{S(U,L,N)} \approx \frac{\sqrt{\pi}}{2} \left(\frac{L}{a}\right)^N \left(\frac{4\pi m a^2 U}{N h'^2}\right)^{\frac{N}{2}-1}$$

or

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

Is this entropy extensive? Answer: **No!**

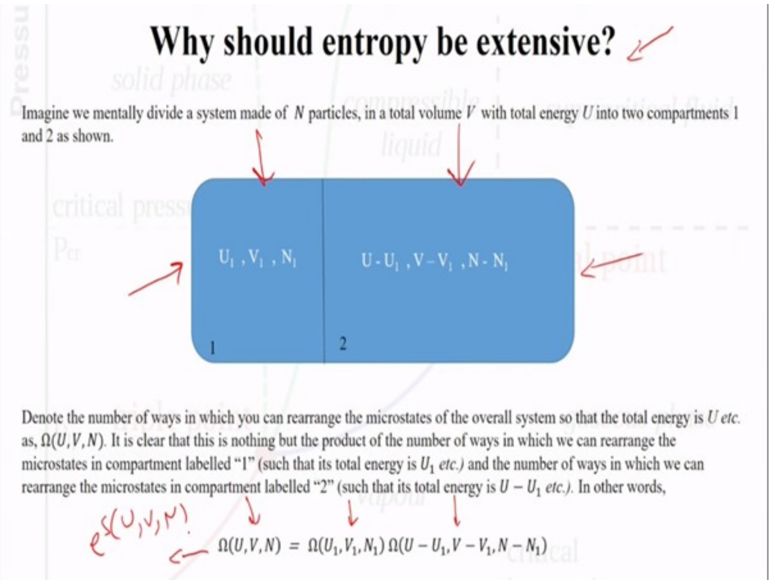
$$S(\lambda U, \lambda L, \lambda N) = \lambda N \, Log\left(\frac{\lambda L}{a}\right) + \frac{\lambda N}{2} \, Log\left(\frac{4\pi m a^2 U}{N h'^2}\right) \neq \lambda S(U,L,N)$$

So you can go ahead and use that and perform this integration and you end up getting something like this and the end result is this. So now I am going to go ahead and bring back the quantities that I was started off with, namely the length of the system and also the total energy of the system. So let me bring that back, so when I bring that back the exponential of the entropy is going to start looking familiar. So it involves total internal energy, number of particles and the size of the system L, ok.

So now I take the logarithm of this and I end up getting this. So now the important question that I ask myself is , is this entropy function that I have derived which is that function of the total energy U, the length of the system L and the number of particle N ,is it extensive? So recall that N extensive function is one which has this property namely if you take S(U, L, N) and I balloon each of these quantities by a factor λ.

So as a result my U is replaced by λ U, L is replaced by λL and N is replaced by λ N and if S were extensive it should become λ S(U, L, N). So if that if S were extensive but now let me stare at this answer and ask myself does this obey at this property of extensivity. The answer is no because of this reason that of course this λ comes outside here and there but then it goes away here because if I scale U by λ, if I scale N by λ then λ cancels out as it should. But however there is nothing here to cancel the λ so there is a λ that remains in the log.

(Refer Slide Time 29:47)



Why should entropy be extensive?

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

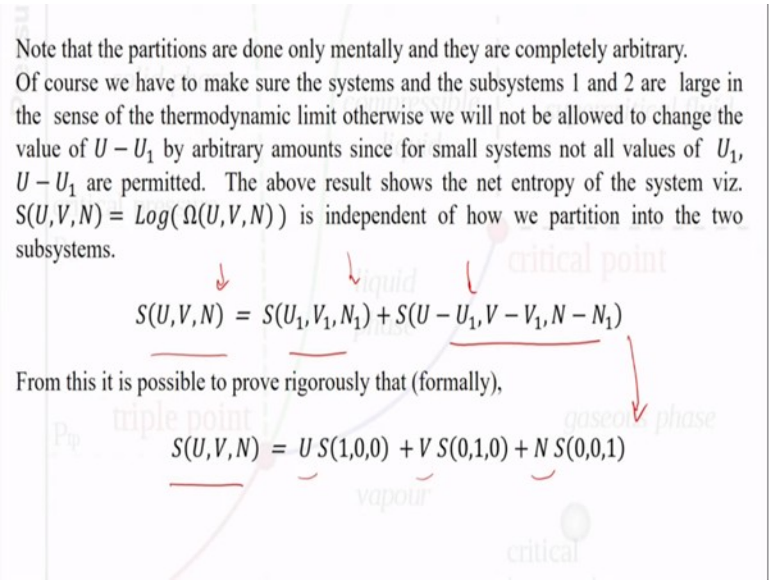
Denote the number of ways in which you can rearrange the microstates of the overall system so that the total energy is U *etc.* as, $\Omega(U,V,N)$. It is clear that this is nothing but the product of the number of ways in which we can rearrange the microstates in compartment labelled "1" (such that its total energy is U_1 *etc.*) and the number of ways in which we can rearrange the microstates in compartment labelled "2" (such that its total energy is $U - U_1$ *etc.*). In other words,

$$e^{S(U,V,N)} \leftarrow \Omega(U,V,N) = \Omega(U_1,V_1,N_1)\,\Omega(U-U_1,V-V_1,N-N_1)$$

Ok so this is annoying because I want entropy to be extensive. So that the question now is why should the entropy be extensive? So let me try an answer that question so this is important. So the reason why entropy should be extensive is if it is not extensive it kind of leads to an uncomfortable paradox. So imagine that there is a huge system of say let us talk about a gas right now so which has a total internal energy of U and total volume of V and total number of particles N.

So imagine I kind of mentally partition this into two pieces, one piece has a U1, N1 number of particles and V1 volume and other has a remaining energy, volume and number of particles. So clearly the number of ways I can rearrange the microstates of the combined system is simply the product of the number of ways in which I can rearrange the microstates so of this mentally partition subsystem and the way in which I can rearrange the microstates of the second partition. So that is what I have written here. So I expect this to be the case.

(Refer Slide Time 31:29)



Note that the partitions are done only mentally and they are completely arbitrary. Of course we have to make sure the systems and the subsystems 1 and 2 are large in the sense of the thermodynamic limit otherwise we will not be allowed to change the value of $U - U_1$ by arbitrary amounts since for small systems not all values of U_1, $U - U_1$ are permitted. The above result shows the net entropy of the system viz. $S(U,V,N) = Log(\Omega(U,V,N))$ is independent of how we partition into the two subsystems.

$$\underline{S(U,V,N)} = S(U_1,\underline{V_1,N_1}) + S(\underline{U-U_1,V-V_1,N-N_1})$$

From this it is possible to prove rigorously that (formally),

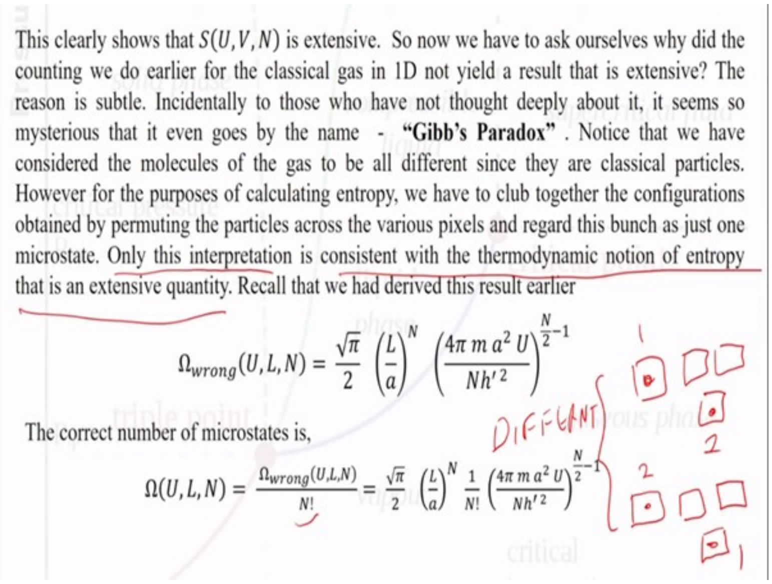
$$\underline{S(U,V,N)} = U\,S(1,0,0) + V\,S(0,1,0) + N\,S(0,0,1)$$

Now I can show you that this is nothing but the statement of extensivity of entropy because I can remember that Ω is nothing but the exponential of the entropy of the system so as I said I take logarithm on both sides and end up with this equation, ok. So now you can show will probably relegate this to some tutorial or some other exercises so you can show that the only answer that is consistent with this equation, remember that I can partition this there is no restriction on U1 V1 and N1.

Of course the only restriction is that these U's and V's have to be very huge otherwise I cannot really, strictly speaking if U and V and N or not huge then I do not have any right to kind of mentally partition in it some random arbitrary way because you know then I would not be able to have the solution of those Diophantine equation you know willingly. So I have only certain kind of partitioning will allow solution and certain other kind of partitioning will give me no solution at all.

However, if these U's and V's are huge then I am kind of at liberty to partition it anyway I want. So you can convince yourself in the exercises that the only solution consistent with this equation is the solution which makes S extensive so that means it is linear in U, linear in V and linear in N. So now the uncomfortable paradox that we have in front of us is that we seem to have done this correctly we have counted the number of microstates by partitioning the phase space into small grains, small pixels and yet we are unable to come up with an expression which is extensive.

(Refer Slide Time 33:11)



This clearly shows that $S(U,V,N)$ is extensive. So now we have to ask ourselves why did the counting we do earlier for the classical gas in 1D not yield a result that is extensive? The reason is subtle. Incidentally to those who have not thought deeply about it, it seems so mysterious that it even goes by the name - **"Gibb's Paradox"** . Notice that we have considered the molecules of the gas to be all different since they are classical particles. However for the purposes of calculating entropy, we have to club together the configurations obtained by permuting the particles across the various pixels and regard this bunch as just one microstate. Only this interpretation is consistent with the thermodynamic notion of entropy that is an extensive quantity. Recall that we had derived this result earlier

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

The correct number of microstates is,

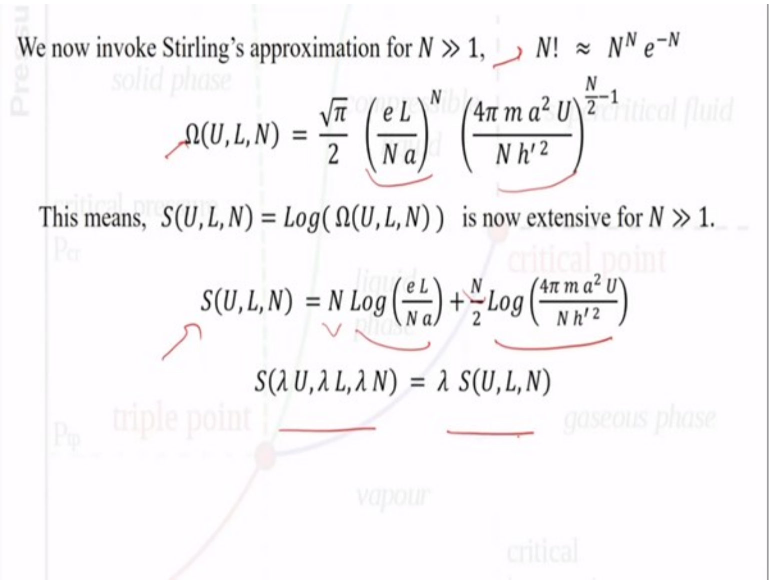
$$\Omega(U,L,N) = \frac{\Omega_{wrong}(U,L,N)}{N!} = \frac{\sqrt{\pi}}{2}\left(\frac{L}{a}\right)^{N}\frac{1}{N!}\left(\frac{4\pi\, m\, a^2\, U}{N h'^2}\right)^{\frac{N}{2}-1}$$

So this is known as Gibbs' paradox. So Gibbs not only stated the paradox but also gave us solution. So instinctively what we have done basically is we have thought of all the molecules as being different. So strictly speaking what we should do is that if I take say suppose that there is a one molecule occupying this pixel and then there is a empty pixel and empty pixel then there is another molecule occupying this pixel so I called this what I have done instinctively is that I have called this molecule 1 and molecule 2 and I have I have considered these two states as being different.

Ok what I have done is so I have considered these two to be different while counting. So just think about it so that is what I have done. But what this paradox is suggesting is that I really should not have done this. So in other words its telling me that I had better not considered these two configuration has been different so if the molecules are all identical I am compelled by thermodynamic necessity to divide by certain factor of N ! which is basically the number of ways in which I can permute all the molecules which are occupying these pixels.

So this is the only interpretation that is consistent with the thermodynamic notion of entropy that is an extensive quantity. So I won't really try and you know derive this in any more convincing way. Because I do not think there is such a derivation it is just so happens that if you do this you get an entropy that is extensive.

(Refer Slide Time 34:59)



We now invoke Stirling's approximation for $N \gg 1$, $N! \approx N^N e^{-N}$

$$\Omega(U,L,N) = \frac{\sqrt{\pi}}{2}\left(\frac{e\,L}{N\,a}\right)^N \left(\frac{4\pi\,m\,a^2\,U}{N\,h'^2}\right)^{\frac{N}{2}-1}$$

This means, $S(U,L,N) = Log(\,\Omega(U,L,N)\,)$ is now extensive for $N \gg 1$.

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

$$S(\lambda\,U,\lambda\,L,\lambda\,N) = \lambda\,S(U,L,N)$$

So now how do I show that is because you use Stirling's approximation so recall that when N is huge

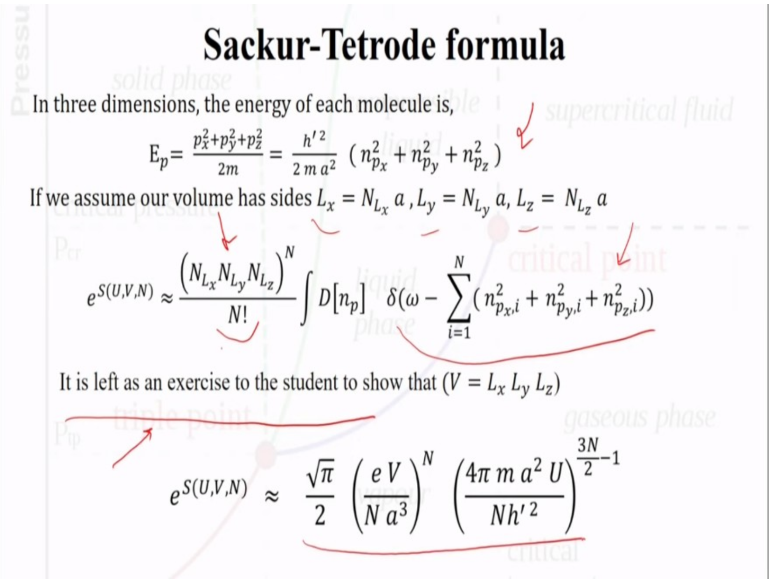
$$N! \approx N^N e^{-N}$$

Again you suppose to know all this from some maths course may be. So just go ahead and substitute that here and low and behold you get an expression of this sort. Where L gets divided by N which is an intensive quantity and this is anyway it was already an intensive quantity raise to N / 2.

So now if I take the Log(Ω) which is my entropy I get a happy result which is proportional to N and proportionality factors are intensive quantities. So now this will certainly obey extensivity and this is what I was looking for. So notice that I have restricted myself till now just for simplicity you know I just wanted to learn how to count phase space when you know by discretizing it into pixels.

So I as a result restricted it to one dimension because I already have two quantities which is momentum and position and I cannot afford to draw a picture on a flat sheet of paper if I go beyond one dimension because I already have two there so I mean position and momentum and then I have if I have more than one position then I will have to immediately go to four dimensions because I will have two position and two momentum components. So that is the reason why I was restricted to look at one dimensional, molecules in one dimension.

(Refer Slide Time: 36:59)



Sackur-Tetrode formula

In three dimensions, the energy of each molecule is,

$$E_p = \frac{p_x^2+p_y^2+p_z^2}{2m} = \frac{h'^2}{2\,m\,a^2}\left(n_{p_x}^2+n_{p_y}^2+n_{p_z}^2\right)$$

If we assume our volume has sides $L_x = N_{L_x}\,a$, $L_y = N_{L_y}\,a$, $L_z = N_{L_z}\,a$

$$e^{S(U,V,N)} \approx \frac{\left(N_{L_x}N_{L_y}N_{L_z}\right)^N}{N!}\int D[n_p]\;\delta\!\left(\omega - \sum_{i=1}^{N}\left(n_{p_x,i}^2+n_{p_y,i}^2+n_{p_z,i}^2\right)\right)$$

It is left as an exercise to the student to show that ($V = L_x\,L_y\,L_z$)

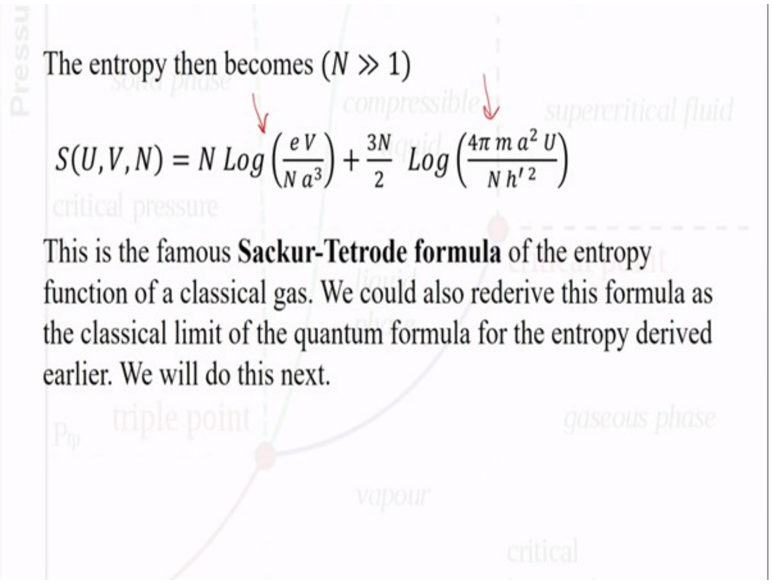
$$e^{S(U,V,N)} \approx \frac{\sqrt{\pi}}{2}\left(\frac{e\,V}{N\,a^3}\right)^N\left(\frac{4\pi\,m\,a^2\,U}{N h'^2}\right)^{\frac{3N}{2}-1}$$

So now let me use my mathematical imagination and see if I can generalize this to what is physically the case which is a three-dimensional classical ideal gas. So in that case I have three components corresponding to x, y and z, so for a given molecule already there going to be three integers n_{px} , n_{py} and n_{pz} . Well this is less important, this is clear what is happening here so it is just the volume so clearly there are three directions.

So what is really interesting is this one so I am going to have to do this carefully this is obvious so you have so in the x direction raise to N, y direction raise to N and z direction raise to N. And of course, this is my Gibb’s factor which prevents the paradox from happening and of course even here if I do not put his I get a paradox which in other words the entropy is not going to be extensive. But what is really important is that I have to learn how to do it in three dimensions.

Well I do not have to learn because I have already done it so all I have to do is repeat this thrice ones, twice, thrice similar thing for n_x , n_y . So I will end up getting you know three copies of the same thing. Ok well slightly more complicated than that there is roughly that ok so I mean it may not be exactly that, that is why written it as left as an exercise to the student so let me leave that instead of trying to explain to you then I will end up doing the whole thing myself, so now I am not going to do that. So its left as an exercise to the students to show that in the end this is what you going to get ,ok.

(Refer Slide Time 38:33)



The entropy then becomes $(N \gg 1)$

$$S(U,V,N) = N\,Log\left(\frac{e\,V}{N\,a^3}\right) + \frac{3N}{2}\;Log\left(\frac{4\pi\,m\,a^2\,U}{N\,h'^2}\right)$$

This is the famous **Sackur-Tetrode formula** of the entropy function of a classical gas. We could also rederive this formula as the classical limit of the quantum formula for the entropy derived earlier. We will do this next.

So when I take the log on both sides I get an expression which is the famous result, it is called Sackur Tetrode formula for the entropy of a classical ideal gas. Ok so I think I stop here so in the next class I am going to see if I can derive this Sackur Tetrode formula also by you know reverting to my original idea of starting with a quantum gas and trying to take the classical limit and see if I can get the same thing.

Because remember we have taken great pains to derive the entropy function also of a quantum ideal gas in addition to pressure and you know various other quantities like energy density and number density and so on. So I am going to relegate this to the next hour so hope you will join me, thank you.