# Statistical Mechanics
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## Lecture – 34
## Problem solving demo – part 1

This would be the last lecture of our course where, I would like to make some quick announcements. So, we are now in the position of evaluating the entire course by an end semester exam so, just to sort of give you guys a feeling of what is expected in the end semester exam.

So, we will ask questions spanning across the course on you know various chapters and the weight age would be roughly 60 percent from the final exam. And, this will be a 3 hour exam where we will give some descriptive questions pen and paper calculations where you will be asked discretely what is required in a problem, so you to work out the various steps and give us the answer

And if you have done the assignments carefully or invested time in the assignments and you have done you have attended all the classes then there should not be any problem at all. So, there will be about 6 descriptive questions in a total of 3 hours and today the task is to just get a flavor of the type of problems that you can expect. And, one should know at the end of any statistical mechanics course introductory statement course the student is expected to know a few basic things.

So, we will sort of do some problems not indicating that this is these are the only problems you will encounter. But, these are the type of problems you are supposed to solve with very simple calculations.

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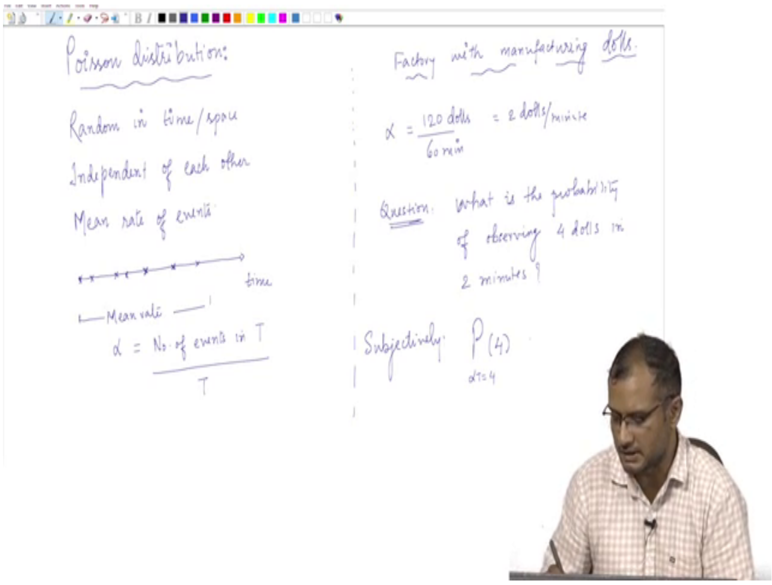

Poisson distribution:

Random in time/space

Independent of each other

Mean rate of events

Mean rate

$\alpha = \frac{\text{No. of events in } T}{T}$

Factory with manufacturing dolls.

$\alpha = \frac{120 \text{ dolls}}{60 \text{ min}} = 2 \text{ dolls/minute}$

Question: what is the probability of observing 4 dolls in 2 minutes?

Subjectively: $P_{\alpha T = 4}(4)$

So, we shall do that now and so, I am going to title this particular lecture as Problem solving demo, if that is a meaningful name right. So, we will start with the Poisson distribution a very important distribution in statistical mechanics and how about we do a simple problem here?

So, if you recall this process of Poisson statistics is applicable to completely random you know processes in time or in space and they are completely independent of each other, the processes are the events are independent of each other. So, and under such a setting the only rate only thing known to us is basically the mean rate of events, which means if you start your window of observation this is the time axis, then you may see processes happening very randomly ok.

So, when the processor are random, all you can basically comment reliably is what is the mean rate? So, mean rate is given as some number of events that are happening in some interval in some interval T divided by the length of the interval ok. So, for instance the example that comes to my mind is let us say you go to a factory where, but basically which is involved in manufacturing dolls.

Now, in such a condition if you happen to visit such a factory which is manufacturing large number of dolls, if you stay there for a minute you may see a doll coming out of the you know whatever their manufacturing process; if you stay for another minute you will say maybe 2 dolls coming out.

So, if you stay there for let us say 60 minutes and you observe for a 120 dolls then you can say that the average manufacturing rate, which is alpha its basically 2 dolls per minute. That is not to say that if you stay there exactly minute you will say 2 dolls you may see more than 2, you may see 3 dolls, even 4 dolls or you may see 1 or nothing; because the dolls that are coming from the conveyor belt are basically these random crosses in time you may see 1 or you may see nothing or you may see more than 2.

So, what is known for sure is that the average rate of the manufacturing of dolls is 2 dolls per minute. Now the question you can ask interesting questions that you can ask is what is a probability of observing or the manufactory, manufacturing 4 dolls in 4 minutes 4 dolls in 2 minutes?

So, the average rate is basically 2 dolls per minute and stay there for 2 minutes what is the probability that you will see 4 dolls? By this question I mean that objectively I mean that if you collect 30 volunteers and these volunteers could be your friends. And, you ask them to go to this factory at random times and ask each one of them to stay there for 2 minutes; and count the number of dolls they see coming out of the conveyor belt.

Most of them will say that they observed 4 dolls because that is what the average see a rate seems to convey, because the average rate is 2 dolls per minute. So, most of them will say I saw 4 dolls because I stayed there for 2 minutes 2 times 2 is 4, so that is the answer. But some of them will say I saw 5 dolls and some of them will say I saw 3 dolls some will even say I saw 1 doll or I saw nothing because dolls are a random variable in this problem.

So, eventually what you will do at the end is you will just add up the guys you got 4 dolls and divide by the total number of volunteers, that would give to you the probability of observing 4 dolls in 2 minutes that is how you would do it the problem objectively. Subjectively you can compute this from Poisson statistics which is basically saying what is the probability of seeing 4 dolls when the average number of dolls is actually 4, you may be tempted to say that this says 100 percent, but it is not it will not come out to be 100 percent.

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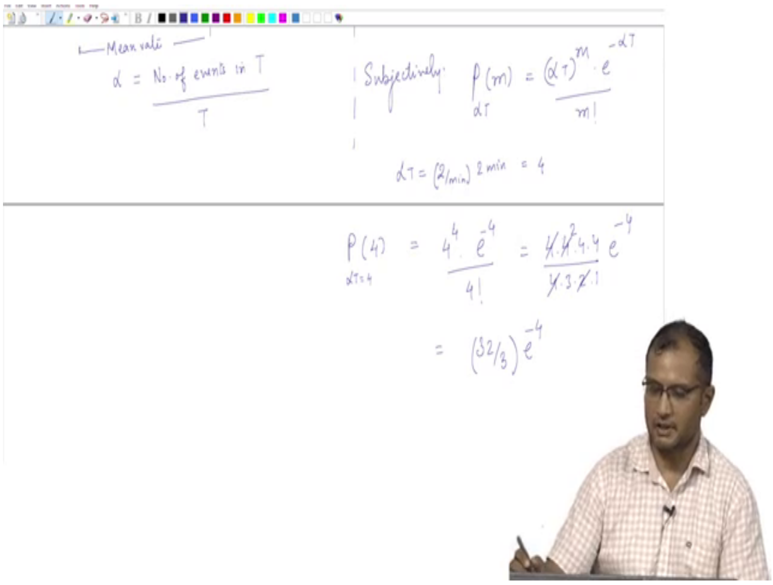

Mean vali

$$\alpha = \frac{\text{No. of events in } T}{T}$$

Subjectively

$$P_{\alpha T}(m) = \frac{(\alpha T)^m \cdot e^{-\alpha T}}{m!}$$

$$\alpha T = (2/\text{min})\, 2\,\text{min} = 4$$

$$P_{\alpha T=4}(4) = \frac{4^4 \cdot e^{-4}}{4!} = \frac{\cancel{4}\cdot\overset{2}{\cancel{4}}\cdot 4\cdot 4}{\cancel{4}\cdot 3\cdot\cancel{2}\cdot 1}\, e^{-4}$$

$$= (32/3)\, e^{-4}$$

So, if you recall your formulas the probability let me write down the formula first. From Poisson statistics the probability of seeing m events when the average number of events is alpha T is alpha T to the power m into e raised to minus alpha T over m factorial. So, in this case our alpha T is basically 2 per minutes which is the rate and the observation time capital T is 2 minutes ok.

So, that is the capital T which is my observation time and this is basically 4. So, I can write down for P 4, when the average number is also 4 probability of observing 4 dolls and the average number of dolls that you expect is also 4, as basically 4 times 4 into e raised to minus 4 over 4 factorial, so this would be 4. So you can knock this off and this will give you 32 over 3 into e raised to minus 4. So, this is the probability of observing 4 dolls when the average number of dolls expected is 4.

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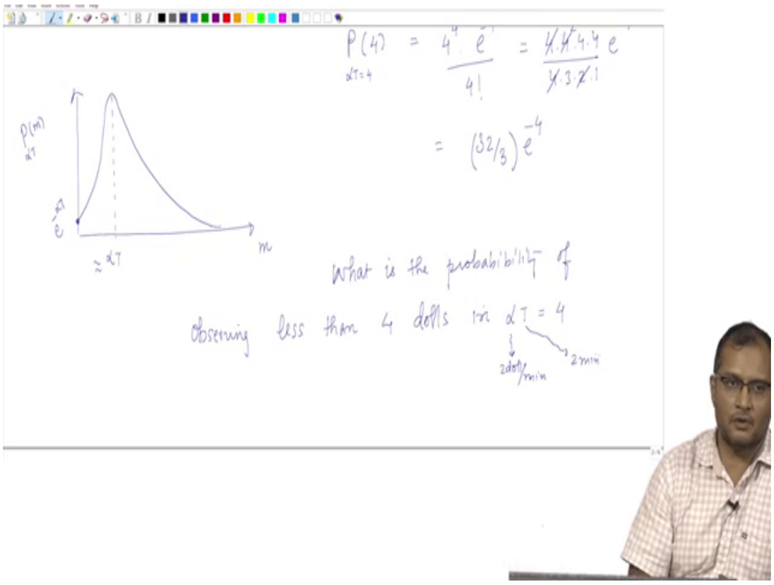

$$\underset{\alpha T=4}{P(4)} = \frac{4^4 \cdot e}{4!} = \frac{\cancel{4}\cdot\cancel{4}\cdot 4\cdot 4}{\cancel{4}\cdot 3\cdot\cancel{2}\cdot 1} e$$

$$= \left(32/3\right) e^{-4}$$

What is the probability of observing less than 4 dolls in $\alpha T = 4$

And this should not surprise you because you already know the graph of the Poisson statistics, which says that if I am asking what is the probability of seeing m events in a time interval that the mean number of events is alpha T; this should have a maximum near the mean and it should then go to 0 as intuitively ok.

So, this is basically the behavior of the this value is very close to alpha T and this value is basically e raised to minus alpha T. So, for large observation time the curve will hit devices at 0 (Refer Time: 11:15) and that completes the problem for the probability of finding exactly 4 dolls.

So, you may also ask in connection to this as what is the probability of observing less than 4 dolls, in the same interval of 2 minutes where alpha T becomes 4. So, this rate is 2 dolls per minute and my observation time is 2 minutes. So, my average number of dolls that I expect its still 4, but I want to see what is the probability of getting less than 4 dolls because many observers either 30 volunteers that you brought in did also some of them also saw less than 4 dollars some of them saw 2 dolls, 3 dolls M 1 doll and nothing.

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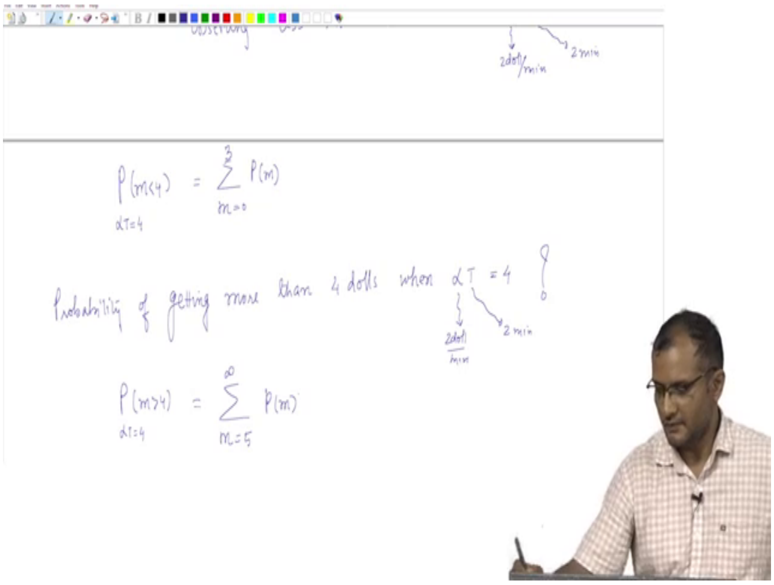

2doll/min

2 min

$$\underset{\alpha T=4}{P(m<4)} = \sum_{m=0}^{3} P(m)$$

Probability of getting more than 4 dolls when $\alpha T = 4$ ?

2doll/min

2 min

$$\underset{\alpha T=4}{P(m>4)} = \sum_{m=5}^{\infty} P(m)$$

So, the probability of seeing less than 3 dolls, when the average number of dolls that you were expecting to see was 4 is basically sum over all the values 0 to correct. So, you can compute P 0, P 1 and P 3 and that should be the answer you can also ask: what is the probability of getting more than 4 dolls, when the average number of dolls that you expect is 4.

So, we are not changing the average so our rate is still 2 dolls per minute and my observation time is also 2 minutes. So, I expect 4 dolls as the average, but now I am asking, what is the probability of getting more than 4 dolls; because some of these volunteers who you chose will see more than 4 dolls ok.

So, so then you will basically ask what is P m greater than 4 when the mean number of dolls was 4. So, then this is basically all the probabilities m equal to 5, 6 all the way to infinity. So, you need to just sum over all the probabilities now this is tricky, because you have now infinite terms here.

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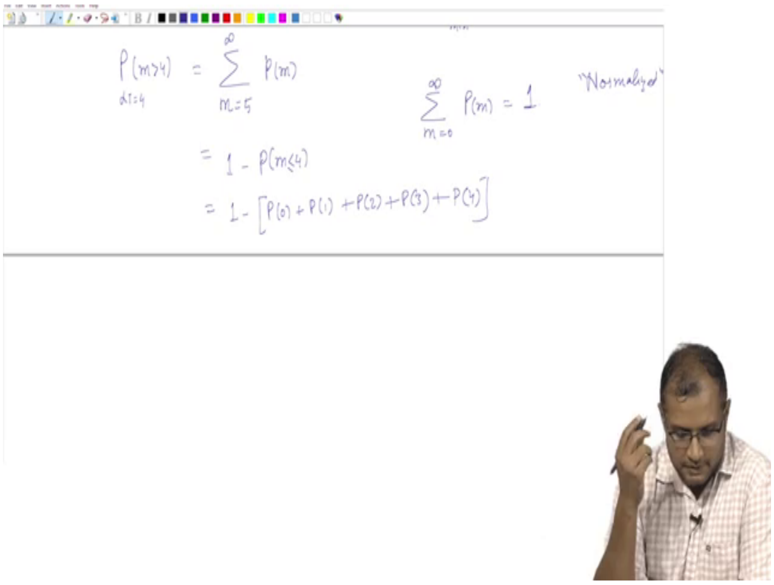

$$P(m>4) = \sum_{m=5}^{\infty} P(m)$$

dt=4

$$\sum_{m=0}^{\infty} P(m) = 1$$

"Normalized"

$$= 1 - P(m\leq 4)$$

$$= 1 - \left[P(0) + P(1) + P(2) + P(3) + P(4)\right]$$

So, the best way to do this is just use the axiomatic definition of probability that we know that you know there is a condition that this probability must be normalized. So, if we have this summation m going from 0 to infinity P of m which is unity right this is normalized probability ok.

So, which means I can write down this particular sum from probability greater than 4 as simply 1 minus the probability of m less than 4 fine. So, that is basically 1 minus P 0 plus P 1 plus P 2 this is the answer right. So, then we come to the closure of this problem.

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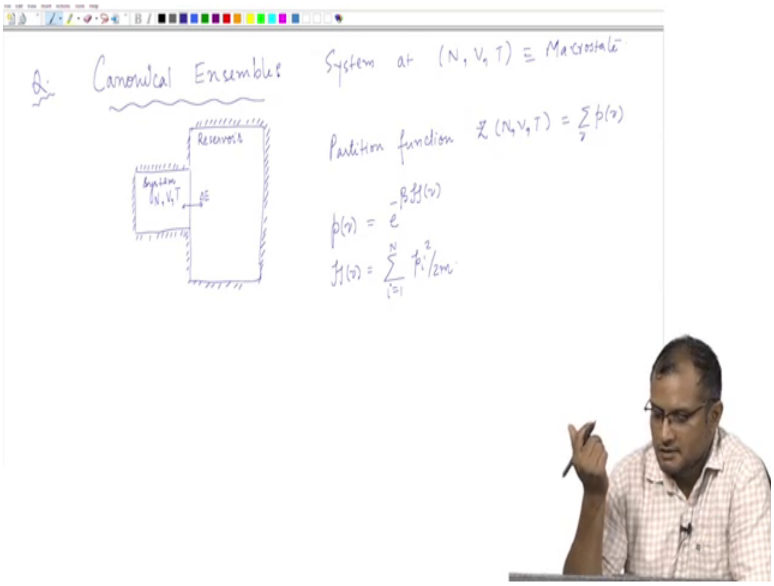

Q. Canonical Ensemble

System at $(N, V, T) \equiv$ Macrostate

Partition function $Z(N,V,T) = \sum_{\nu} p(\nu)$

$$p(\nu) = e^{-\beta \mathcal{H}(\nu)}$$

$$\mathcal{H}(\nu) = \sum_{i=1}^{N} p_i^2/2m$$

So, we can pick up some problems from statistical mechanics the basic postulates so, I will start with the canonical ensemble so right. So, in the canonical ensemble we know that the system under consideration is at constant, if I take an ideal gas as a working system it is maintained constant N comma, V comma, T. So, suppose if I ask you to compute let us say to compute the equation of state, now this is a problem that we have done in the class, but let me just concoct a question that is of relevance from the point of view of stability of matter.

Let us say if I ask you to prove that free energy is a negative quantity, which means if I allow the gas which is in contact with the reservoir, thermal reservoir and if I allow the gas to expand by removing the walls the particles are thermo started coupled to the reservoir. Now, there is no constraint on them to stay inside a fixed volume I simply remove the walls.

So, the particles will in occupy a larger volume and they will keep on occupying larger volume, until the volume becomes infinity which is something that we expect by intuition. If you want to show that this is what happens in reality and you want to give a rigorous argument you want to provide a rigorous argument, you would want to show that the infinite volume state is a stable thermodynamic state, either you show that or you show that infinite volume state is the maximum of entropy.

So, this is the disorder argument the first argument was basically to show that the infinite volume state is a minimum of free energy. So, either you show its a minimum of free energy or the maximum of entropy both arguments would show that the infinite volume state is a stable state. So, for that you know we must first obtain the free energy and then comment on stability of gas.

So, if you recall a canonical ensemble, so this is like a working material or a or an ideal gas. Let us say for example, this is basically a system under contact with the reservoir and the joint system is isolated. So, the system plus reservoir is under micro canonical ensemble it is isolated from the surroundings ok. So, the this is the insulation complete both mechanical isolation and thermal isolation is indicated here.

So, the system is maintained at constant temperature by allowing energy interactions and it is maintained at constant volume by simply keeping fixed walls and maintained at constant number of particles by not allowing particles to escape, so, the walls are not poorest. So, now, under such a setting we have already computed the partition function of the gas right. So, this partition function is nothing, but as discussed already its a function of the microstate. So, this is your microstate and the partition function is nothing, but the norm of your probability distribution.

So, the probability to find my system in some microstate nu, if I sum over all the probabilities then basically I get my partition function. So, for the ideal gas the probability of finding a microstate nu is e raised to simply the Boltzmann factor beta H nu where, H nu is simply you know the Hamiltonian of a microstate and for an ideal gas it is purely kinetic right, which means I must compute the partition function by using integral.

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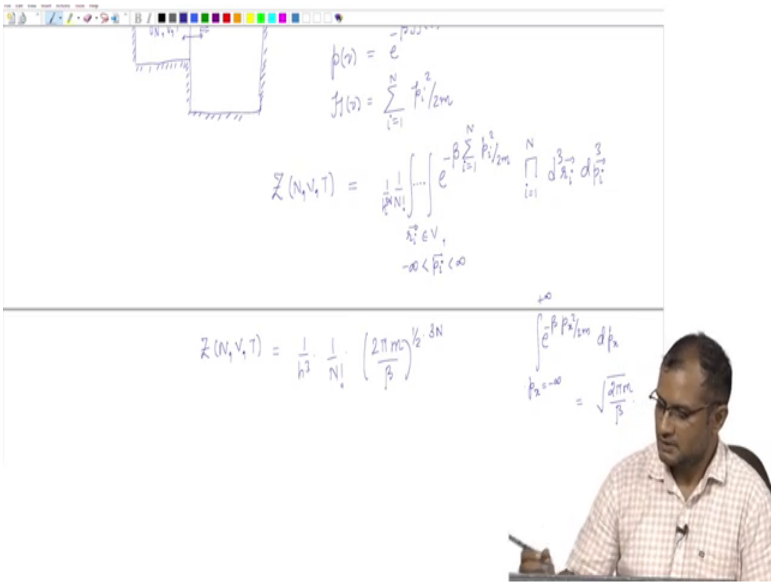

$p(\nu) = e^{-\beta}$

$\mathcal{H}(\nu) = \sum_{i=1}^{N} p_i^2/2m$

$$Z(N,V,T) = \frac{1}{h^{3N}}\frac{1}{N!}\underset{\substack{\vec{r}_i \in V,\\ -\infty < \vec{p}_i < \infty}}{\int\cdots\int} e^{-\beta\sum_{i=1}^{N} p_i^2/2m} \prod_{i=1}^{N} d^3\vec{r}_i\, d^3\vec{p}_i$$

$$Z(N,V,T) = \frac{1}{h^3}\cdot\frac{1}{N!}\cdot\left(\frac{2\pi m}{\beta}\right)^{1/2\cdot 3N}$$

$$\int_{p_x=-\infty}^{+\infty} e^{-\beta p_x^2/2m}\, dp_x = \sqrt{\frac{2\pi m}{\beta}}$$

Here summation over microstates is not possible because the variables of the microstate are the momentum particle momentous which are continuous random variables. So, when you are dealing with continuous random variables you have to basically remove exchange the summation with an integral over the entire phase space. So, if I refer the phase space to be something like gamma and basically p of gamma is basically, now the probability density at the face point face space point gamma and g of gamma is nothing, but the density of space phase space density.

So, then I have to compute the partition function by a continuous representation and under such a setting, the phase space integral that I am just talking about here is basically this quantity d gamma which is the phase space volume. So, I will write down my probability density which is e to the power minus beta summation I going from 1 to N p i square by 2 m and this has to be integrated over the entire phase space volume ok.

And what I am going to do is basically write down, this phase space volume element in 6 N dimensions as the product of these d cube r i and p is so, it is a 6 dimensional phase space volume. And I am going to integrate it over the entire coordinate. So, basically here each position belongs to my volume v and the momentous are basically going from minus infinity to plus infinity ok.

So, this is both volume and position integration and to account for in distinguish ability I will use the N factorial which is basically to account for the fact that I do not want to over compute my microstates these are the N factorial projections in the phase space that result into a degenerate Hamiltonian.

So, they have to be sort of removed and that removal is basically the division by this N factorial my density of space states g of gamma is also coming here in the fact of a normalization constant which is h to the power 3, this also exists to non dimensionalized my partition function.

And finally, if I compute this partition function, then I will observe that I get this very simple expression. So, basically each momentum coordinate when integrated will give me 2 pi m over beta to the power half and since, I have 3 N of them I should get a factor of I should get another power of 3 N ok.

So, this p square by 2 m so if you want to compute over so basically this means that, this you write it as beta p x square by 2 m, the p x p x going from minus infinity to plus infinity this will give you square root of 2 pi m by beta ok. So, since you have a triple integral it raised 2 it gives you a power of 2 pi m over beta to the power 3 half and there are N such integrals so, you get 3 N by 2.

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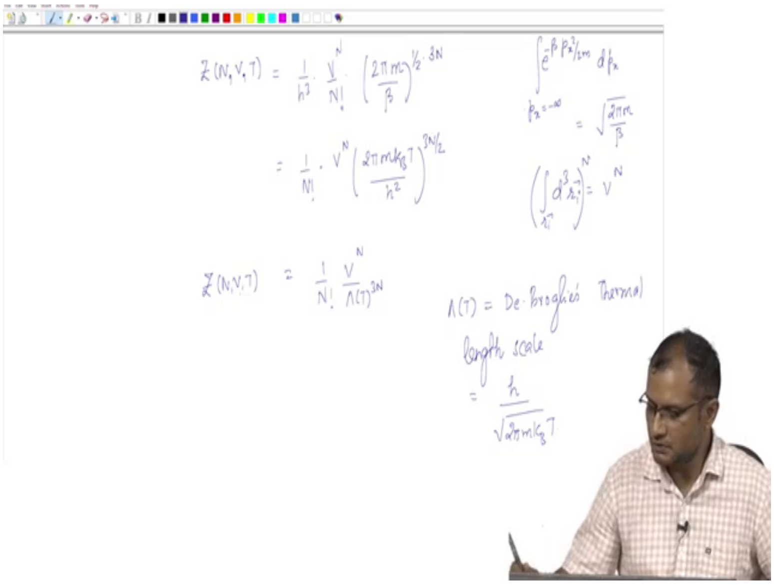

$$Z(N,V,T) = \frac{1}{h^3} \cdot \frac{V^N}{N!} \cdot \left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}\cdot 3N}$$

$$= \frac{1}{N!} \cdot V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

$$Z(N,V,T) = \frac{1}{N!} \frac{V^N}{\Lambda(T)^{3N}}$$

$$\int_{p_x=-\infty} e^{-\beta p_x^2/2m}\, dp_x = \sqrt{\frac{2\pi m}{\beta}}$$

$$\left(\int_{\vec{r}_i} d^3 \vec{r}_i\right)^N = V^N$$

$\Lambda(T)$ = De Broglie's Thermal length scale $= \frac{h}{\sqrt{2\pi m k_B T}}$

So, then what you have is basically a simple integral here which is, I can rewrite it as 1 upon you are also missing a factor of V to the power, because that is the integral and so, if there are N such integrals it will give you V raise to, so, that is why we have V raise to N.

So, now I have 1 over N factorial into V raise to N into 2 pi m k B T over h square to the power 3 N by 2 and this, if I define the de Broglie wavelength as lambda becomes nothing. But where I have defined the De Broglie wavelength thermal wavelength or De Broglie thermal length scale, as h over square root of 2 pi m k B T ok. So, then we can write this as a it is lambda 2 power 3 alright.

So, this is my partition function and now the idea was to show the free energy is negative and the infinite volume state is a minimum of free energy. So, let us compute a free energy.

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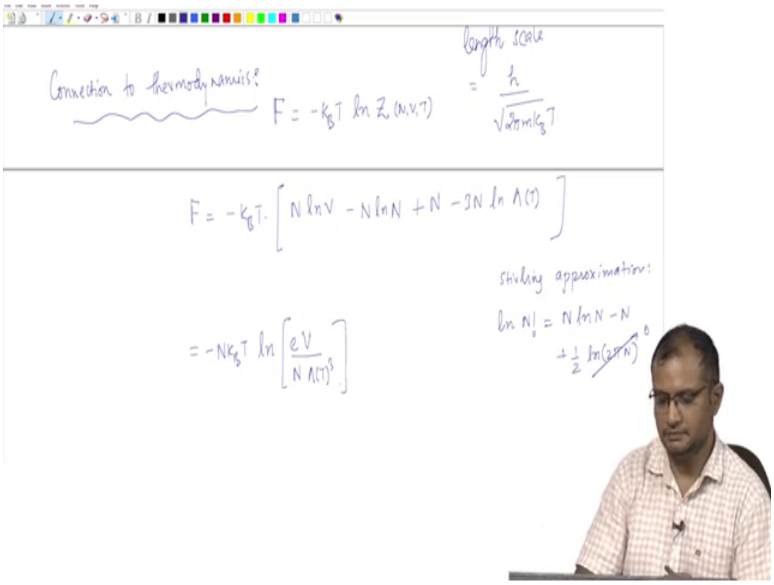

Connection to thermodynamics?

$F = -k_B T \ln Z_{(N,V,T)}$

length scale $= \frac{h}{\sqrt{2\pi m k_B T}}$

$F = -k_B T \cdot \left[ N \ln V - N \ln N + N - 3N \ln \Lambda(T) \right]$

stirling approximation:

$\ln N! = N \ln N - N + \frac{1}{2} \cancel{\ln(2\pi N)}^{0}$

$= -N k_B T \ln \left[ \frac{eV}{N \Lambda(T)^3} \right]$

So, we know from the connection to stat mech has already been discussed or connection to thermodynamics, you are already in stat mech. So, we need to go to thermodynamics is provided by this beautiful law or beautiful relationship that the energy scale is related to minus k B T ln of Z. And so, since we have these Z in front of us we can simply compute the free energy as minus k B T into ln Z.

So, this would be simply N and ln V and if you use a sterling from formula for N factorial we get, using sterling approximation where plus basically, if you use the good studying approximation they have an ln of 2 pi N, but since ln N is much smaller than N ln in and N we are going to drop this ok. Because ln N is much smaller than, also N log N; so, then if you rearrange all the terms by pulling N out what do we get we get ln of V over ok.

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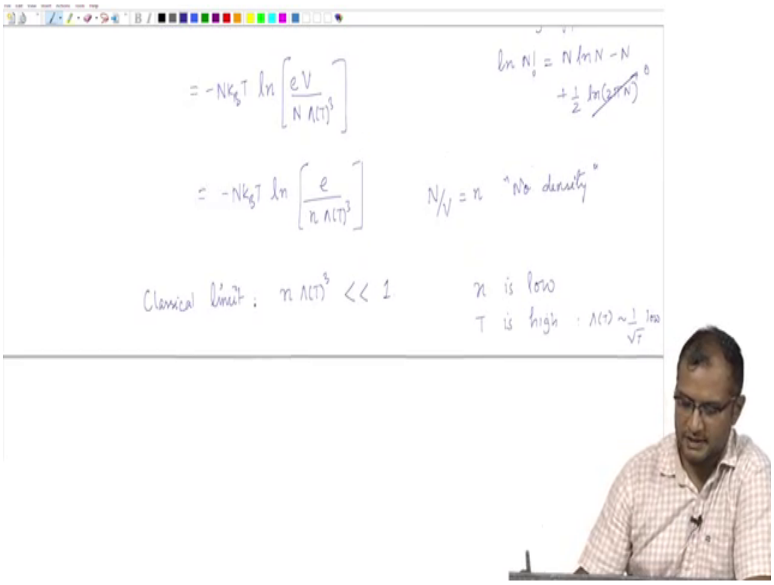

$$= -Nk_BT \ln\left[\frac{eV}{N\Lambda(T)^3}\right]$$

$$\ln N! = N\ln N - N + \cancel{\tfrac{1}{2}\ln(2\pi N)}^{\,0}$$

$$= -Nk_BT \ln\left[\frac{e}{n\Lambda(T)^3}\right]$$

$N/V = n$ "No density"

Classical limit : $n\Lambda(T)^3 << 1$

$n$ is low

$T$ is high : $\Lambda(T) \sim \frac{1}{\sqrt{T}}$ low

And then I can write it as minus N k B T ln of e over small n lambda cube; where this small n is nothing, but number density ok. And so, in the classical limit, which is basically the limit where we work the classical gas is in the classical limit the classical limit is when you have high temperature and low density.

So, the De Broglie wavelength which goes as proportional to inverse square root of temperature is also very very small. So, these are basically the limit of quantum mechanics where the wave function of a particle is very is highly deal is highly localized its highly localized. So, which means you do not need a wave picture for a particle, you need particles are treated as distinct objects with deterministic dynamics.

So, the classical limit is when you have density very low or de Broglie wavelength has very large very very low. So, n lambda cube which is a beautiful dimensions dimensionless number it tells it is basically much much smaller than 1. So, as we have already seen in quantum statistics when this dimensionless number is of the order of one that is the onset of quantum mechanics and when it is much larger than one you are definitely quantum mechanical.

But here n lambda cube is much smaller than 1, because our n is very low and the temperature is high ok. So, if temperature is high they were De Broglie wavelength which goes as 1 upon square root of T is also very low ok. So, the product of 2 low numbers is much lower than 1 right.

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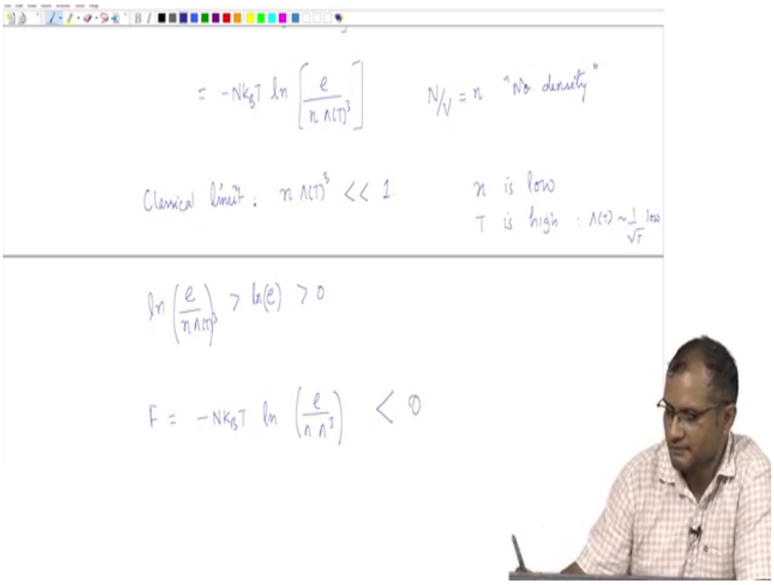

$= -Nk_BT \ln\left[\frac{e}{n\Lambda(T)^3}\right]$  $N/V = n$ "No density"

Classical limit : $n\Lambda(T)^3 << 1$  $n$ is low

T is high : $\Lambda(T) \sim \frac{1}{\sqrt{T}}$ low

$\ln\left(\frac{e}{n\Lambda(T)^3}\right) > \ln(e) > 0$

$F = -Nk_BT \ln\left(\frac{e}{n\Lambda^3}\right) < 0$

So, then if this is the case then I can always say that e over n lambda T cube is much much greater than e if that is the case, I can say that ln of this is much much greater than ln of e, but at least greater than ln of e. I know that ln e is positive, so which means my free energy which is negative NKBT into ln of e over n lambda cube must be negative so that shows my free energy should be negative.

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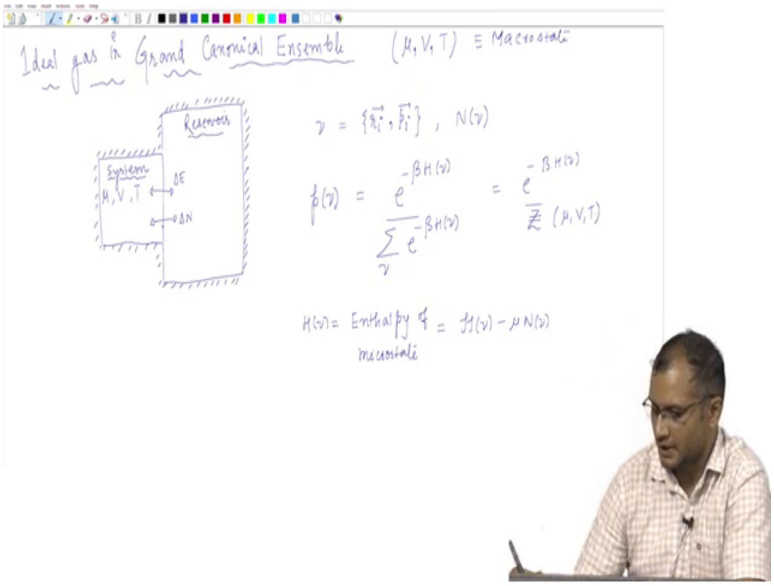

Ideal gas in Grand Canonical Ensemble  $(\mu, V, T) \equiv$ Macrostate

$\nu = \{\vec{q_i}, \vec{p_i}\}$ , $N(\nu)$

$$\rho(\nu) = \frac{e^{-\beta H(\nu)}}{\sum_{\nu} e^{-\beta H(\nu)}} = \frac{e^{-\beta H(\nu)}}{\mathcal{Z}(\mu, V, T)}$$

$H(\nu) =$ Enthalpy of microstate $= \mathcal{H}(\nu) - \mu N(\nu)$

So, we will now talk about the grand canonical ensemble. This is the ensemble where you maintain a system at constant volume constant chemical potential constant volume and constant temperature.

So, we are looking at for instance an ideal gas, in the grand canonical ensemble. So, this is like if you draw small schematic then this is my system and I have kept it in contact with the reservoir, which has a twofold task of constraining the temperature at temperature T by allowing energy exchange and keeping a chemical potential mu by allowing for particle exchange and we keep the volume to the constant by imposing fixed walls.

So, this is my system and that is my reservoir and the joint system now is both mechanically and thermally shielded from the universe. So, the joint system exists in micro canonical ensemble, in the sense that there cannot be any exchange of particles, energy with the universe.

And certainly under such a setting the microstate label, so this is the macro state label a typical microstate in the grand canonical ensemble will have the label of particle coordinates both momentum and position coordinates and also the volume of the microstate.

Because volume is also sorry, I am so sorry I should have mentioned the number of particles. So, the number of particles is also variable of the microstate which means, if I want to identify the probability of finding my system in a microstate nu then this is nothing, but e to the minus beta some energy scale which is the enthalpy scale divided by summing over all the microstates e to the power minus beta H nu; where H nu is an enthalpy of the microstate keep in mind that in the grand canonical ensemble the energy scale is not the internal, energy because the internal energy along with the chemical energy which is nu N is the random variable of the problem.

So, the enthalpy is basically the internal energy or I will call this internal energy as the internal Hamiltonian of the microstate minus this chemical energy mu N nu ok, so this is the energy scale of the problem. So, then one can write down this thing as the partition function ok.

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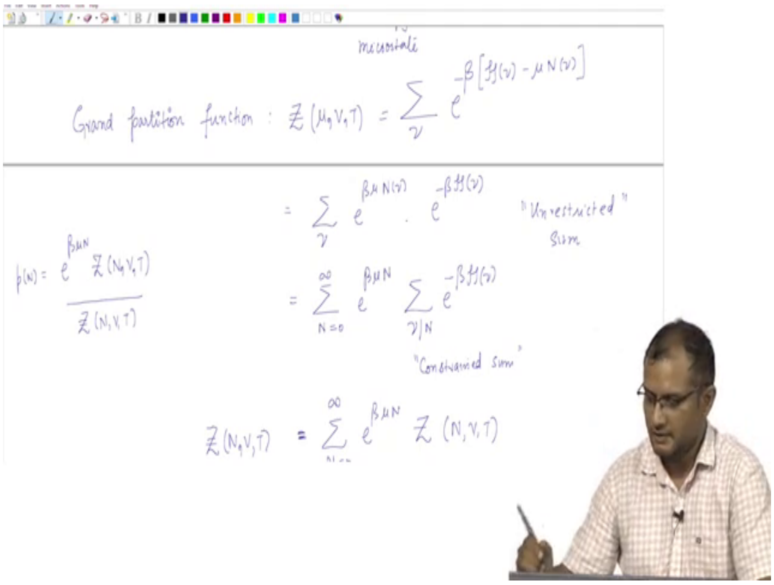

microstate

Grand partition function : $\mathcal{Z}(\mu, V, T) = \sum_{\nu} e^{-\beta[\mathcal{H}(\nu) - \mu N(\nu)]}$

$$= \sum_{\nu} e^{\beta\mu N(\nu)} \cdot e^{-\beta\mathcal{H}(\nu)}$$

"Unrestricted" sum

$$p(N) = \frac{e^{\beta\mu N} \mathcal{Z}(N, V, T)}{\mathcal{Z}(N, V, T)}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\nu | N} e^{-\beta\mathcal{H}(\nu)}$$

"Constrained sum"

$$\mathcal{Z}(N, V, T) = \sum_{N}^{\infty} e^{\beta\mu N} Z(N, V, T)$$

So, now one can write down the grand partition function which was discussed in the class. So, the grand partition function is the norm of your probability distribution, so I will write down as a double you know vertical crosses on the Z just to distinguish from the canonical partition function. So, the grand partition function now this simply becomes the norm of my probability density, which is nothing, but e to the power minus beta into the internal Hamiltonian minus mu and nu ok.

And so this is basically nothing, but I can write it as summation nu and now I can sort of compute this sum easily by interchanging, you know here this is the unrestricted sum; since the microstate label is set up by joint variables which is the particle coordinates and the number of particles.

So, we can decouple them and form a restricted sum in the sense that I can first sum over the number of particles that will go from 0 to infinity and for this, that is set outside in the outside some; I can set up the internal constraints summation and compute the second Boltzmann factor so this is like now the constrained sum.

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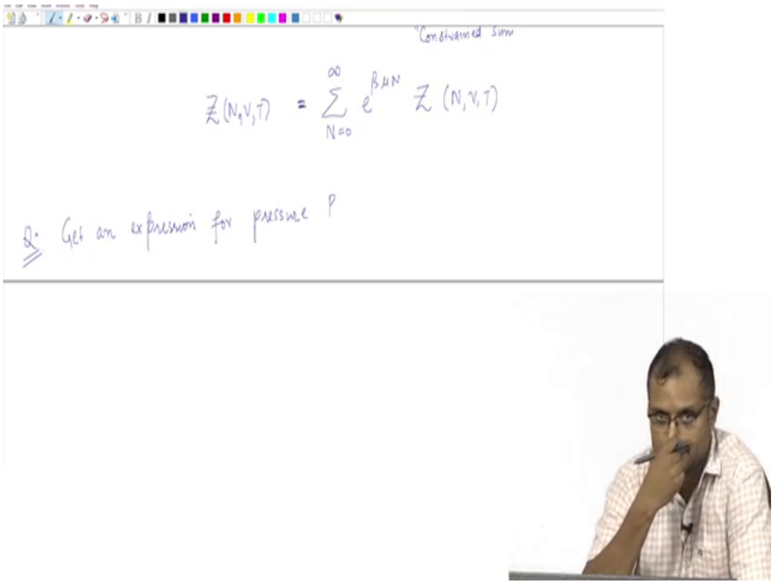

"Constrained Sum

$$\mathbb{Z}(N,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,V,T)$$

Q: Get an expression for pressure P

This is easy to perform and this was computed in the class to be e to the power beta mu N and the canonical partition function. So, this is the left hand side is the grand partition function with a double strike off and the right hand side is the canonical partition function, but suppose we give you in the exam we sort of we will not ask you to do all these derivations in detail.

It will provide you with let us say we provide you with this expression; this was just a recap of the grand canonical ensemble. Suppose you have given the partition functions form and we asked you to prove for instance get an expression for pressure get an expression for pressure P, given this form of partition function ok.

So, you know already by now that between statistics and thermodynamics there always exist a symmetric relationship ok, that comes from partition function so we need that expression here ok. So, for instance I can think of if you know the relationship which is basically the grand potential is minus k B T ln the grand partition function.

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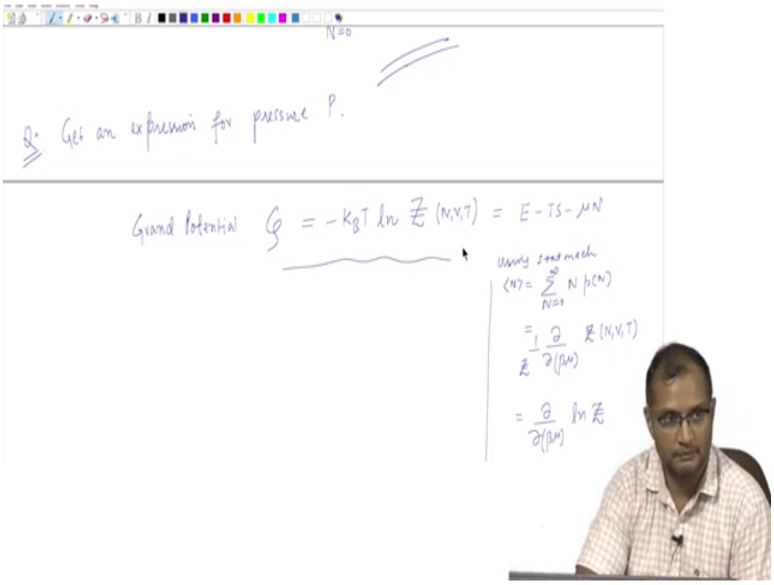

$N=0$

Q: Get an expression for pressure P.

Grand Potential $\mathcal{G} = -K_BT \ln \mathcal{Z}(N,V,T) = E - TS - \mu N$

using stat mech

$\langle N \rangle = \sum_{N=0}^{\infty} N\, p(N)$

$= \frac{1}{\mathcal{Z}} \frac{\partial}{\partial(\beta\mu)} \mathcal{Z}(N,V,T)$

$= \frac{\partial}{\partial(\beta\mu)} \ln \mathcal{Z}$

Then you can straight away do your problems and this grand potential is nothing, but e minus TS minus mu N this may also be provided to you ok. So, if you want to establish this relationship that is also very simple, but suppose this expression is provided to you ok.

Then how do you compute pressure? If you recall I will just be just before we compute the pressure, I just want to establish in your minds that this beautiful bridge that connect stat mech thermodynamics it is very easy to derive you simply measure some observable in both the approaches. So, you measure for instance mean number of particles using stat mech this is an observable mean number of particles N observation. So, using stat mech if you measure and this is nothing, but summation N going from 0 to infinity N sampled in this distribution that is the mean number of.

So, this if you look at the form of your PDF ok. So, somewhere I have written the partition function yeah here the grand partition function. So, you can write down the form of your of your PDF yeah here. So, you can write down the form of your PDF for N as nothing, but e to the power beta mu N into canonical partition function divided by this is a PDF like this.

So, this was the probability to find microstate nu, but if you want to convert into probability of finding number of particles N this is the PDF. So, then you simply measure this and this comes out to be if you want to pull out a beta mu. So, you put out pull out an N. So, you take a derivative with respect to beta mu of your of your ok. So, if you look at the form for the yeah here look at this expression to bring out N you have to take a derivative with respect to beta mu that is what I have done here.

So, this is nothing, but d by d beta mu of ln of Z and you can compute N from here, but that is not our target, we want to compute and then you compute N from your thermodynamics also ok. So, you can you can get a relationship, so for instance you can write down your enthalpy H, which is the enthalpy here is e minus mu N and so you can write down the differential and now use ok.

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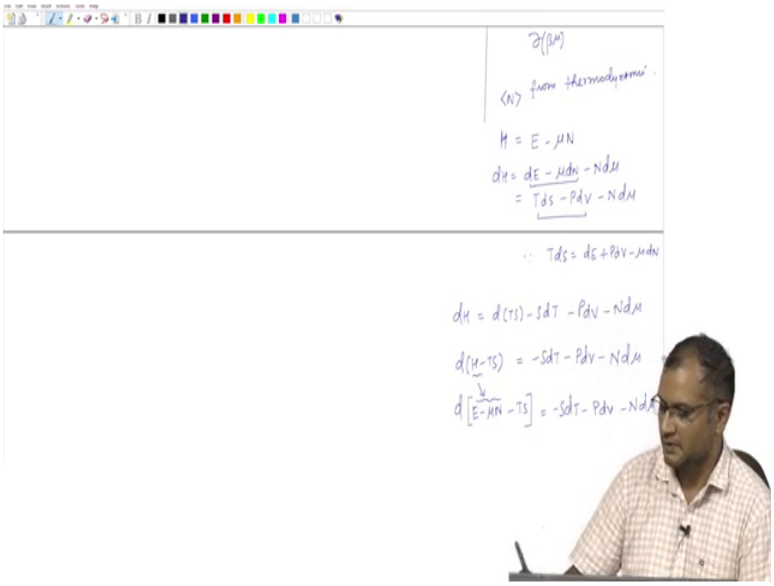

$\partial(\beta\mu)$

$\langle N\rangle$ from thermodynami.

$H = E - \mu N$

$dH = \underbrace{dE - \mu dN} - N d\mu$

$= \underbrace{Tds - Pdv} - N d\mu$

$\because Tds = dE + PdV - \mu dN$

$dH = d(TS) - SdT - Pdv - Nd\mu$

$d(\underset{\sim}{H} - TS) = -SdT - Pdv - Nd\mu$

$d\left[\overset{\searrow}{\widetilde{E - \mu N}} - TS\right] = -SdT - Pdv - Nd$

So, if you use the first law here this becomes T T ds minus P dv because the first law is T ds as correct right. So, I am substituting for d E minus mu d N as T ds minus P dv ok. So, then I can write down this as d H equals to T ds I will write it as d of TS minus S d T minus P dv minus N d mu.

And then this I will write as d of H minus TS which is minus S d T minus P dv minus N d mu ok. And the d of H minus TS is basically E minus mu N that is H and minus TN TS which is equal to minus S d T minus P dv minus N d mu. So, it is very simple so your conjugate variables are back here so mu vd is the ensemble which is constant.

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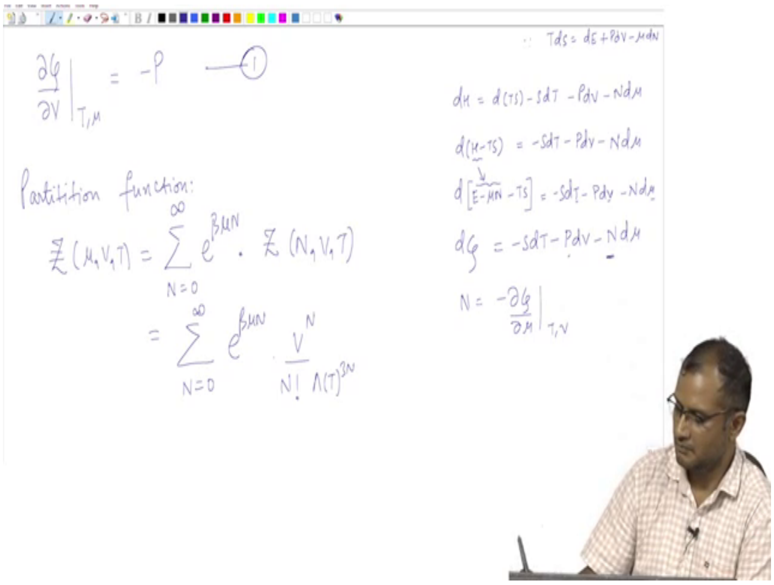

$\because\ TdS = dE + PdV - \mu dN$

$$\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{T,\mu} = -P \quad \text{—①}$$

$$dH = d(TS) - SdT - PdV - Nd\mu$$

$$d(\underset{\sim}{H} - TS) = -SdT - PdV - Nd\mu$$

$$d[\underbrace{E - \mu N} - TS] = -SdT - PdV - Nd\mu$$

$$d\mathcal{G} = -SdT - PdV - Nd\mu$$

$$N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,V}$$

Partition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot Z(N, V, T)$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{V^N}{N!\,\Lambda(T)^{3N}}$$

So, then I can write this as d of sums Xi where Xi is the grand potential; and finally, you can compute for N as its minus d Xi by d mu at constant T comma V. But we will provide some of these relationships you do not have to derive all that, but suppose I give you this relationship and ask you to derive pressure.

So, you just have this connection in front of you so, pressure would be nothing, but pi Xi by d V at constant T comma mu; this would be pressure ok. So, now, you already have Xi in front of you so let us bring down that zai, so Xi is basically minus k B T ln Z ok. So, we need a form for Xi so, let us get that form for Xi so, you will have to obtain your partition function now.

So, we have one relationship with us, so let us get the partition function that is the only step remaining now ok. So, for an ideal gas the partition function the grand partition function, you know if you look at the expression it is nothing, but if you go if you if you recall upstairs it is nothing, but N going from 0 to infinity e raise to beta mu N into the canonical partition function, something that we have derived just now.

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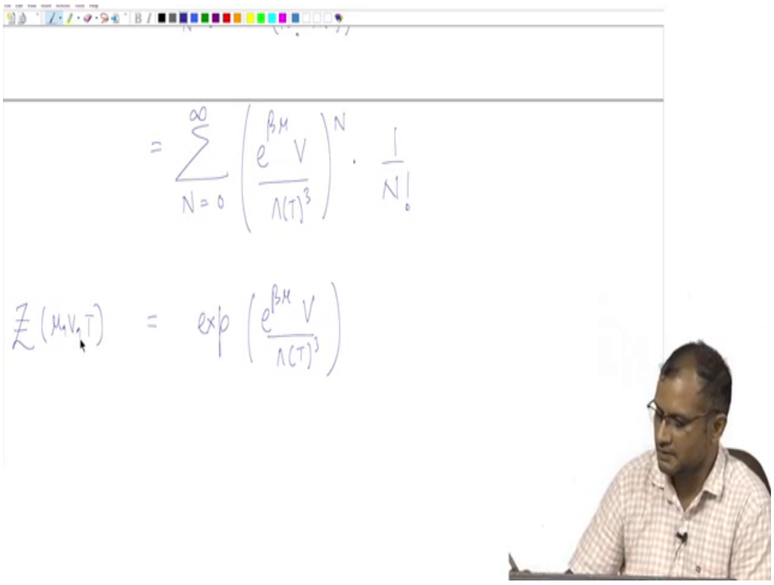

$$= \sum_{N=0}^{\infty} \left(\frac{e^{\beta\mu} V}{\Lambda(T)^3}\right)^N \cdot \frac{1}{N!}$$

$$\mathcal{Z}(\mu, V, T) = \exp\left(\frac{e^{\beta\mu} V}{\Lambda(T)^3}\right)$$

So, why do not we use it straight away? So, this is 0 to N infinity canonical partition function was just derived this is ok, that is the canonical partition function right. And now you can see that this is not looking nothing, but like expansion of an exponential, so I can take this as e to the power beta mu into V over lambda T cube, the whole to the power N into 1 by N factorial. So, this is nothing, but e to the power e raised to be term mu into V by lambda T the whole cube, this is my grand partition function.

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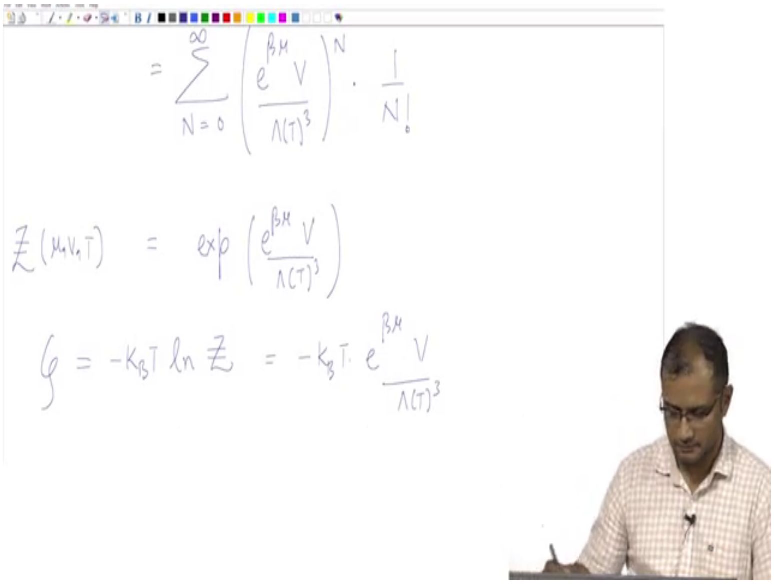

$$= \sum_{N=0}^{\infty} \left(\frac{e^{\beta\mu} V}{\Lambda(T)^3}\right)^N \cdot \frac{1}{N!}$$

$$\mathcal{Z}(\mu, V, T) = \exp\left(\frac{e^{\beta\mu} V}{\Lambda(T)^3}\right)$$

$$\mathcal{G} = -k_B T \ln \mathcal{Z} = -k_B T \cdot \frac{e^{\beta\mu} V}{\Lambda(T)^3}$$

Just take a logarithm and this will give you the grand potential, so just derived grand potential. So, just derived grand potential was minus k B T into ln of the grand partition function, this would be these are symmetric laws there for every one symbol you have something that is an energy scale and connects to the partition function.

So, if you take a logarithm of this is you could just get e to the power of beta mu V by lambda T the whole cube alright. That is the final step you got the grand potential, you have this symmetric relationship which has given you the grand potential now you simply use equation 1. So, I am just going to copy this equation here bring it down.

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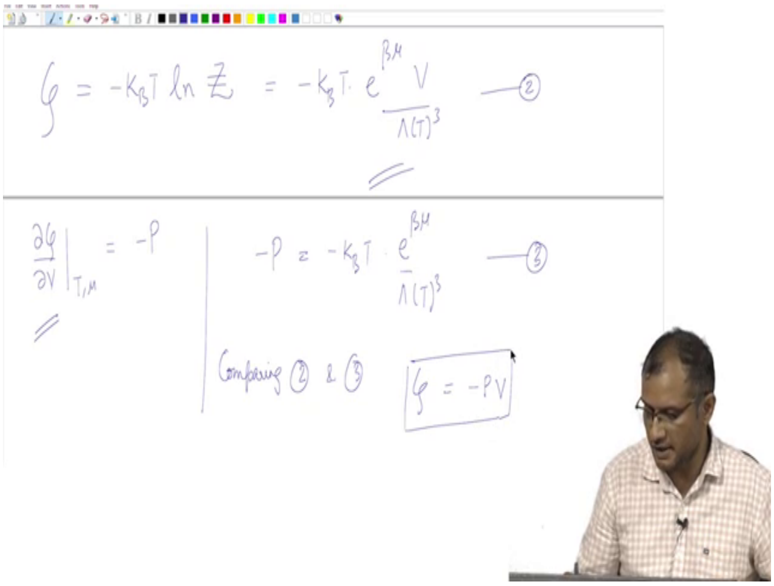

$$\mathcal{G} = -k_BT \ln \mathcal{Z} = -k_BT \cdot \frac{e^{\beta\mu} V}{\Lambda(T)^3} \quad \text{—②}$$

$$\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{T,\mu} = -P$$

$$-P = -k_BT \cdot \frac{e^{\beta\mu}}{\Lambda(T)^3} \quad \text{—③}$$

Comparing ② & ③ $\boxed{\mathcal{G} = -PV}$

So, let us take so you have the grand potential in front of us whose derivative with respect to volume will give me a pressure. So, let us do this, so derivative with respect to volume the constant T and mu will simply give me minus pressure which is minus k B T temperature and chemical potential are constant alright. So, this is the basically develop value of pressure, but suppose I call this as equation 2 and go back to my equation for Xi somewhere I have computed yeah right above right.

So, I have just computed here this underlined expression, so you can clearly see that if I take the ratio of let me call this as equation 3 and then I am actually and call this is equation 2. So, from 3 and 2 you get the relationship between pressure chemical potential and grand potential. So, you can see that the relationship between these 2 is nothing, but Xi is equal to minus P V ok.

So, if I multiply the equation 3 with minus with volume I get equation 2. So, this is the relationship between pressure and chemical potential and the grand potential ok. So, this is one way and similarly you can compute all other quantities in this potential.

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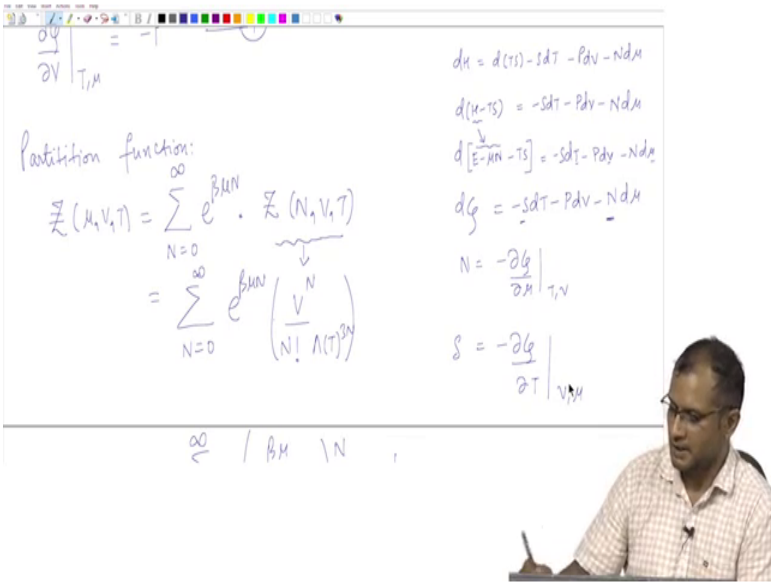

$$\left.\frac{\partial \varphi}{\partial V}\right|_{T,\mu} = -P$$

Partitition function:

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot \underbrace{Z(N, V, T)}_{\downarrow}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} \left(\frac{V^N}{N!\,\Lambda(T)^{3N}}\right)$$

$$dH = d(TS) - SdT - PdV - Nd\mu$$

$$d(H - TS) = -SdT - PdV - Nd\mu$$

$$d[E - \mu N - TS] = -SdT - PdV - Nd\mu$$

$$d\varphi = -SdT - PdV - Nd\mu$$

$$N = -\left.\frac{\partial \varphi}{\partial \mu}\right|_{T,V}$$

$$S = -\left.\frac{\partial \varphi}{\partial T}\right|_{V,\mu}$$

So, like I said here N was determined by taking this derivative, you can determine volume you can determine entropy by simply minus d Xi by d T at constant V comma mu ok. And that ends the discussion on the grand canonical ensemble right.