Statistical Mechanics
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Lecture - 36
MicroCanonical to Canonical - Part I

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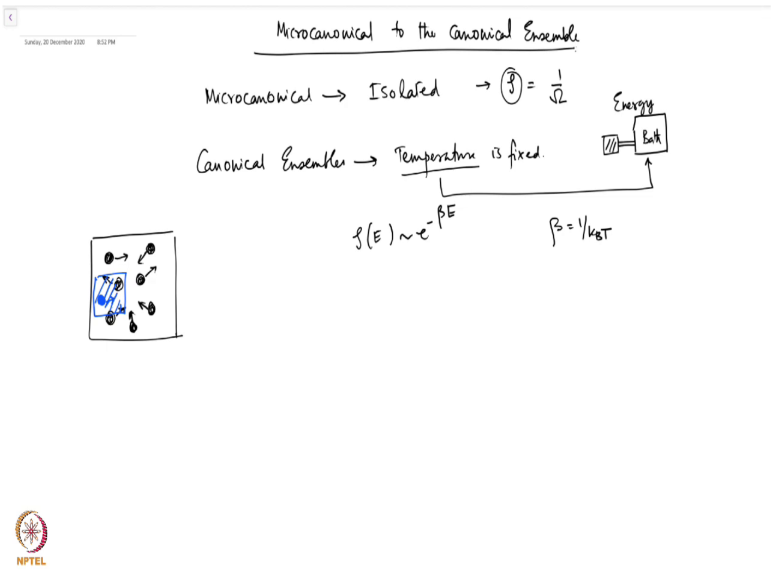

Welcome back. So, today our topic of discussion is going from the MicroCanonical to the Canonical ensemble. Now, it should be mentioned over here that in the thermodynamic limit both of them should give you the same result. So, in the microcanonical ensemble what we had seen was this particular ensemble, means that the system is completely isolated there is no environment or a path.

In contrast the canonical ensemble means the temperature is fixed. So, that essentially this means that you have a system which is connected to a big large path. You have allowed energy exchange with this path and that essentially means that the energy can fluctuate, but the temperature is held constant and that this temperature (Refer Time: 01:29) on the system is the temperature of the path.

Here of course, we show that the probability density of a microstate is equal to 1 over omega, where omega is the total number of microstates available. In this particular case we saw that the probability density, for a system to be in an microstate with energy E is poses e to the power minus beta E where beta is equal to 1 over K B T.

Now, the idea is now to being to build the connection between these two ensembles. For example, if you consider an ideal gas which essentially in our picture the model system is n particles contained within the volume v and they are moving around right.

Now, if that is the only system that is available to us we will say that the system is isolated and we will apply microcanonical formalism to the system, determine the total number of microstate and therefore, the rho and from there we calculate the entropy and we move and we calculate the rest of the thermodynamic quantities from this entropy.

However, you can also argue look I have this big volume where I have all these particles which are moving around randomly there is an underlying molecular chaos to this system and I have treated the system in a microcanonical using a microcanonical approach, because I do not have any additional information. Just an ideal gas, but then if I zoom into the system let us say, I can consider this particle the blue particle which if I zoom out is part of the ideal gas, but if I zoom into the system I can see this blue particle is in a path of other particles.

Therefore I can I mean although it is a single particle that we will be talking about and statistical mechanics essentially you single particle level is difficult, but we can still say that look, but this particle is in a path of the other particle. So, in principle you can say that look I can have pick up a sub system sufficiently large enough which is in a path of the whole system rest of the system.

So, the idea is that there is a relation between the microcanonical and canonical and we are going to explode that. Unfortunately, though we need to know to establish this connection we have to know the explicit form of the Hamiltonian. So, we will do it case by case we will take three examples and try to do it.

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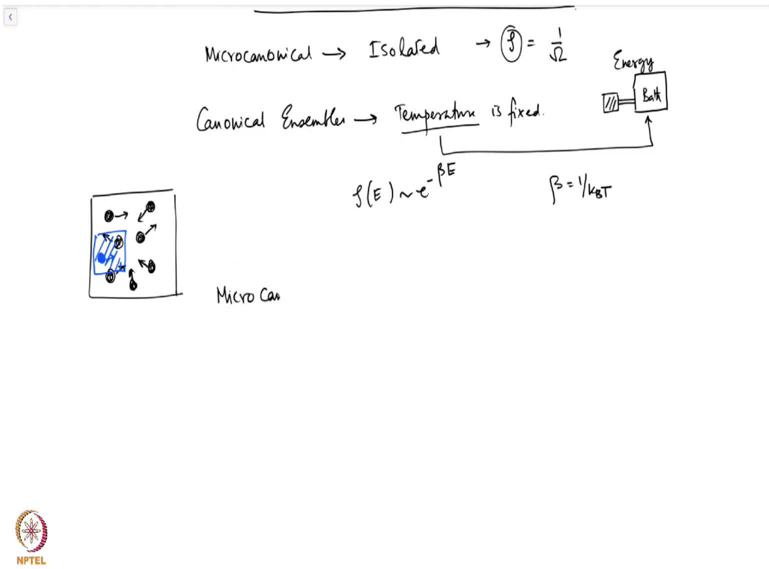

So, now microcanonical ensemble.

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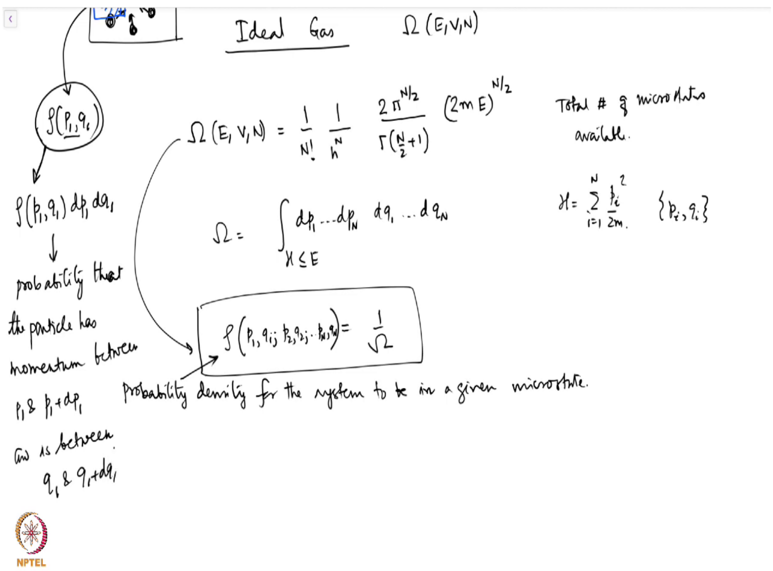

So, we will talk, we will start with the ideal gas example ideal gas here I have to determine omega of E V N and this we have already done in a previous lecture. The total number of microstates that is available is 1 over h to the power N I am just considering in a 1 dimensional system. So, that it is easier to handle I mean its very easy to generalize such a thing, and then I have 2 pi N to the N by 2 gamma of N by 2 plus 1 and then I had twice m E raised to the power N by 2.

So, this was the total number of micro states which were available. So, total number of microstates available. And essentially this was integration of H the Hamiltonian dp 1, dp N, dq 1, dq N and our Hamiltonian for this ideal gas system was i equal to 1 to N p i square over twice m right. So, therefore, from this omega now, I can calculate this joint probability distribution which is rho of so, we will just write down this is equal to 1 over omega.

And this was a probability for the system to be in a microstate. This probability density this is the probability density for the system to be in a given microstate and essentially this statement is this equation is telling me that all the microstates are equally probable because I do not have any at other additional information. So, the micro state is now defined by the set p i q i. So, therefore, you have a joint probability distribution p 1 q 1 p 2 q 2 all the way up to p N q N is given by this.

Now, from this joint probability distribution when you say look I would not want to figure out this blue particle is in the path of the other particle. So, essentially you are asking what is the probability density of finding the blue particle with a momentum p 1 and at q 1. So, rho p 1 not so, ok. So, not that so, what is the probability density for the blue particle to be in a microstate with p 1 q 1.

So, therefore, essentially this means that rho p 1, q 1, dp 1, dq 1 is the probability that the particle is well has momentum between p 1 and p 1 plus dp 1 and is at or not at that is between q 1 and q 1 plus dq 1. This is the standard interpretation of problem density and our task is to figure this out. So, clearly I can now integrate out this joint probability distribution.

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$\rho(p_1,q_1)\,dp_1\,dq_1$

$\downarrow$

probability that the particle has momentum between p_1 & p_1+dp_1 as well as between q_1 & q_1+dq_1

$$\Omega = \int_{\mathcal{H}\le E} dp_1 \ldots dp_N \; dq_1 \ldots dq_N$$

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} \qquad \{p_i, q_i\}$$

Joint probability distribution of N variables.

$p_N(x_1, x_2, \ldots x_N)$

$$\boxed{p(x_1) = \int dx_2 \ldots dx_N \; p_N(\{x_i\})}$$

$$\boxed{\rho(p_1, q_1; p_2, q_2; \ldots p_N, q_N) = \frac{1}{\Omega}}$$

Probability density for the system to be in a given microstate.

$$\rho_1(p_1, q_1) = \left(\frac{1}{h}\right) \int_{\mathcal{H}\le E_{N-1}} \frac{dp_2 \ldots dp_N \; dq_2 \ldots dq_N}{(N-1)!\; h^{N-1}} \; \rho_N(p_1, p_2 \ldots p_N; q_1, q_2, \ldots q_N)$$

Dimensionless $\rightarrow \dfrac{\rho_1(p_1,q_1)}{h} \dfrac{(dp_1\,dq_1)}{h}$

N particles with total energy E

(N-1) particles E_{N-1}

Because if you recall if I have a joint probability distribution of N variables this is my joint probability distribution of N variables then essentially the probability distribution of a single variable is dx 2 dx N. We will write down p N to indicate that this is for N variable p N of the set X i.

Starting from this expression that I can determine the probability density of a single variable from the joint probability density of N variables by integrating out the other variables. I can write down the single probability density single particle probability density rho 1 of p 1 q 1 is going to be 1 over h integral dp 2 dp N dq 2 dq N rho N of p 1, p 2, p N, q 1, q 2, q N.

Let me explain few things. I have included the 1 by h factorial purposefully here, because why should this 1 by h factorial be there? The 1 by h factorial is going to be there is because you were interested in after all the probability of finding this particle the blue particle within a momentum range of p 1 and p 1 plus dp 1 and in between q 1 and q 1 plus dq 1 and this probability is p 1, dp 1, dq 1.

But if you notice that if you do not have this 1 by h factorial if you do not have this, then this quantity is dimensionful. So, in order to make everything consistent you have to include the 1 by you have to divide this element by h, but that is unnecessary and is not what we learned in probability. So, we include the 1 by h over here itself and therefore, this 1 by h comes.

By the same argument we are going to have h to the power N minus 1 over here and the indistinguishability of these particles means that I am going to have N minus 1 factorial. Now, this rho N is the rho that we had written down over here which corresponded to this one except that now I have brought in a fact subscript of N just to distinguish it from the fact that the essentially this is an N particle joint probability this density you are looking at.

The question now, is that I am integrating over the momentum of the coordinates of all the rest of the particles, but what are the bounds? The bounds is given by Hamiltonian h is less than E N minus 1. I have N particles which has an so, I have N particles with the total energy E.

Now, I have N minus 1 particles because I have taken care I have taken out one of the particles or I have tagged one of the particles which I am interested in and therefore, the system has an energy E of N minus 1 and I am integrating over all momenta and coordinates which is of the other all the other rest of the particles, over a region which is bounded by this surface which is h less than equal to E N minus 1.

So, let us write this a little bit carefully N minus 1 and I have an N minus 1 factorial. When we did it for the N particle system we had this as h of less than equal to E N which is essentially this one, right. Now let us plug in the value of rho 1.

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$h \qquad h \qquad (N-1)$ particles $\quad E_{N-1}$

$$\rho_1(p_1, q_1) = \frac{1}{h} \int_{\mathcal{H} \le E_{N-1}} \frac{dp_2 \cdots dp_N \; dq_2 \cdots dq_N}{(N-1)! \; h^{N-1}} \; \frac{1}{\int_{\mathcal{H} \le E} dp_1 \cdots dp_N \; dq_1 \cdots dq_N}$$

$$= \frac{1}{h} \frac{\int_{\mathcal{H} \le E_{N-1}} dp_2 \cdots dp_N \; dq_2 \cdots dq_N}{\int_{\mathcal{H} \le E} dp_1 \cdots dp_N \; dq_1 \cdots dq_N} = \frac{1}{h} \frac{\Omega(E_{N-1}, V_{N-1}, N-1)}{\Omega(E, V, N)}$$

$$\Omega(E, V, N) = \frac{1}{h^N} \frac{1}{N!} \frac{2\pi^{N/2}}{\Gamma\left(\frac{N}{2}+1\right)} (2mE)^{N/2}$$

So, rho 1 of p 1 q 1 is going to be 1 over h dp 2 dp all the way up to dp N dq 2 dq N divided by N minus 1 factorial h to the power N minus 1. But rho N is 1 over integral h less than equal to E and here I have h less than equal to E of N minus 1 and dp 1 all the momenta and coordinates are the integrated over right. So, which means I have this very nice expression as 1 over h, h less than equal to E N minus 1 dp 2, dp N, dq 2, dq N divided by h less than equal to E dp 1, dp N, dq, 1 dq N.

And this, I can write down as omega total number of microstates with an available energy of E N minus 1 N minus 1 divided by omega E, N. So, if you are careful enough one also has to write down V of N minus 1 N minus 1 and we will write down this as E of V, N. So, let us write down I know the expression for omega E, V, N.

So, we will rewrite it over here omega V, E, V, N was twice by raised to the power N by 2 gamma of N by 2 plus 1 and I had 1 over h to the power N 1 over N factorial and I had twice m E raised to the power N by 2.

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$$= \frac{1}{h} \frac{\mathcal{H} \le E_{N-1}}{\int_{\mathcal{H} \le E} dp_1 \ldots dp_N \, dq_1 \ldots dq_N} = h \, \Omega(E, V, N)$$

$$\Omega(E, V, N) = \frac{1}{h^N} \frac{1}{N!} \frac{2\pi^{N/2}}{\Gamma\left(\frac{N}{2}+1\right)} (2mE)^{N/2} V^N$$

$$\Omega(E_{N-1}, V_{N-1}, (N-1)) = \frac{1}{h^{N-1}} \frac{1}{(N-1)!} \frac{2\pi^{(N-1)/2}}{\Gamma\left(\frac{N-1}{2}+1\right)} (2mE_{N-1})^{\frac{N-1}{2}} V^{N-1}$$

$$\frac{\Omega(E_{N-1}, V_{N-1}, (N-1))}{\Omega(E, V, N)} = \frac{1}{h^{N-1}} \frac{1}{(N-1)!} \frac{2\pi^{(N-1)/2}}{\Gamma\left(\frac{N-1}{2}+1\right)} (2mE_{N-1})^{\frac{N-1}{2}} V^{N-1} \frac{h^N N! \, \Gamma\left(\frac{N}{2}+1\right)}{2\pi^{N/2} (2mE)^{N/2} V^N}$$

It follows that I have omega of E N minus 1 V N minus 1 N minus 1 there has to be a V to the power N here, is going to be 1 over h to the power N minus 1, 1 over N minus 1 factorial twice pi raised to the power N minus 1 by 2 gamma N minus 1 by 2 plus 1 and then I am going to have twice E m E N minus 1 raised to the power N minus 1 by 2 and I am going to have V to the power N minus 1.

Because you are integrating over this momenta q 2 to q n and all of these can individually will give you a value V therefore, you have N minus 1 such variable. So, thus gives you V to the power N minus 1. So, the ratio then becomes E of N minus 1 V of N minus 1 and I have N minus 1 particles to the ratio of to the value of omega of E V N is 1 over h to the power N minus 1 1 over N minus 1 factorial twice pi N minus 1 by 2.

I am sorry there is an alarm which is sounding now and I have no idea why, but please bear with this noise hopefully I am audible over this noise. And then I have twice m E N minus 1 raised to the power N minus 1 by 2 V to the power N minus 1.

Now I have this I have 2 pi N by 2, 2 pi raised to the power N over 2 twice m E raised to the power N by 2 V to the power N and the numerator will have h to the power N 1 over N sorry it is going to be N factorial in the numerator and then I am going to have gamma of N by 2 plus 1.

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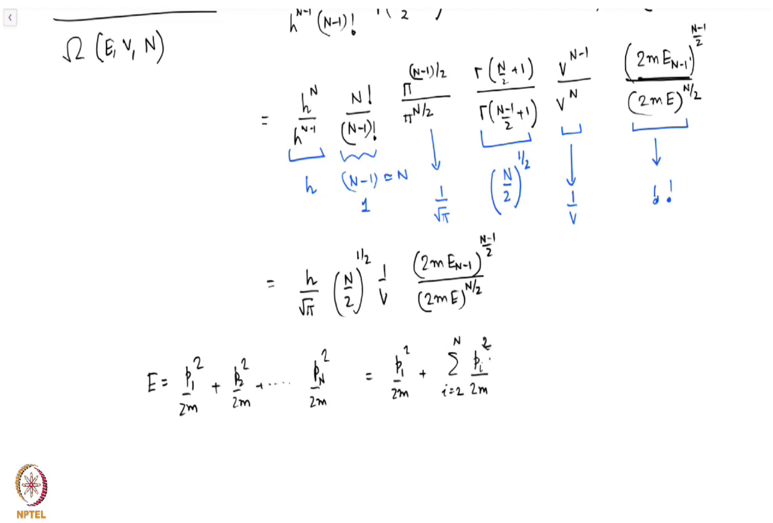

Let us collect these terms together that I have h to the power N h to the power N minus 1 N factorial N minus 1 factorial the 2 2 gets cancelled out. So, that I have pi to the power N minus 1 by 2 divided by pi to the power N by 2, I am going to have gamma of N by 2 plus 1 gamma of N minus 1 by 2 plus 1 and then I am going to have V to the power N minus 1 V to the power N twice m E N minus 1 raised to the power N minus 1 by 2 divided by twice m E raised to the power N by 2.

This part gives me an h and this part assuming that N is in the thermodynamic limit N minus 1 is equal to N gives me a unity fact this one gives me 1 over square root pi. Using the same limit of this N minus 1 is approximately going to be N using Sterling's formula for large enough N this is going to be N by 2 raised to the power half and this gives me a factor 1 by V, this is what I have to determine.

So, let us just collect all these terms together this gives me h and this is over square root pi and then I have N by 2 raised to the power half 1 over V twice m E N minus 1 raised to power N minus 1 by 2 and twice m E raised to the power N by 2.

Now, the conservation of energy tells me that E is going to be p 1 square over twice m plus p 2 square over twice m all the way up to p N square over twice m. So, this is essentially p 1 square over twice m plus some over i is equal to 2 to N p i square over twice m.

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$$E = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots \frac{p_N^2}{2m} = \frac{p_1^2}{2m} + \boxed{\sum_{i=2}^{N} \frac{p_i^2}{2m}} \rightarrow \text{Energy of the rest } N-1 \text{ particles.}$$

$$\equiv E_{N-1}$$

$$E_{N-1} = E - \frac{p_1^2}{2m}$$

$$\frac{\Omega(E_{N-1}, V_{N-1}, N-1)}{\Omega(E, V, N)} = \frac{h}{\sqrt{\pi}} \left(\frac{N}{2}\right)^{1/2} \frac{1}{V} \frac{\left[2m\left(E - p_1^2/2m\right)\right]^{\frac{N-1}{2}}}{(2mE)^{N/2}}$$

$$= \frac{h}{\sqrt{\pi}} \left(\frac{N}{2}\right)^{1/2} \frac{1}{V} \boxed{\frac{(2mE - p_1^2)^{\frac{N-1}{2}}}{(2mE)^{N/2}}}$$

$$N-1 \simeq N$$

$$= \frac{h}{\sqrt{\pi}} \left(\frac{N}{2}\right)^{1/2} \frac{1}{V} \frac{1}{(2mE)^{1/2}} \left(\frac{2mE - p_1^2}{2mE}\right)^{\frac{N-1}{2}}$$

You immediately realize that this is the term the first term is the energy of the first particle whereas, this is the energy of the rest N minus 1 particles. So, essentially this is equal to E of N minus 1. So, hence we write E of N minus 1 as E minus p 1 square over twice m, I am sorry this pen is behaving little erratic. So, that the ratio of the two face base volumes E N minus 1 V N minus 1 N minus 1 divided by omega of E V and N is going to be h over square root pi N by 2 raised to the power half 1 over V.

And then I have twice m of E minus p 1 square over twice m raised to the power N minus 1 over 2 divided by twice m E raised to the power N by 2. Let us take the twice m inside the bracket so that, this gives me h over square root pi N by 2 raised to the power half 1 by V twice m E minus p 1 square raised to the power N minus 1 by 2 divided by twice m E raised to the power N by 2.

What I am going to do is I am going to take out a factor of twice m E in the denominator raised to the power half and rewrite them as twice m E twice m E minus p 1 square raised to the power N minus 1 over 2. Now here is a word of caution that in this case in this step here itself I could have said that look N minus 1 is approximate N correct.

But that would have given you a wrong result you will I mean you can go ahead with this approximation here itself in this step and you will see that you will arrive at a wrong expression for this rho single particle probability density. So, one has to be very very careful where you are taking the limit how you are taking the limit.

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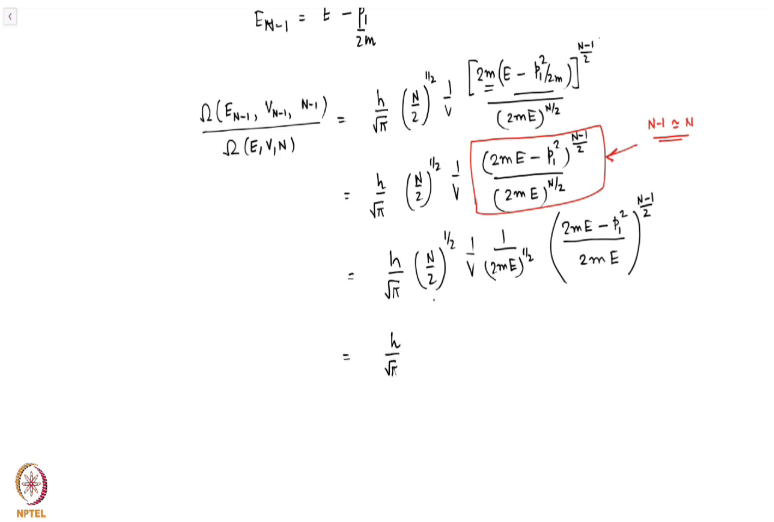

Coming back to this I have h over square root pi.

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$$= \frac{h}{\sqrt{\pi}} \left(\frac{N}{2}\right)^{1/2} \frac{1}{V} \frac{1}{(2mE)^{1/2}} \left(\frac{2mE - p_1}{2mE}\right)$$

$$= \frac{h}{V} \left(\frac{N}{4\pi m E}\right)^{1/2} \underbrace{\left(1 - \frac{p_1^2}{2mE}\right)^{\frac{N}{2}}}_{e^{-p_1^2/2mE}} \qquad \frac{N-1}{2} \simeq \frac{N}{2} \qquad E \sim N \qquad (2mE)^{-1}$$

$$= \frac{h}{V} \left(\frac{N}{4\pi m E}\right)^{1/2} \left(e^{-p_1^2/2mE}\right)^{N/2}$$

$$\frac{\Omega(E_{N-1}, V_{N-1}, (N-1))}{\Omega(E, V, N)} = \frac{h}{V} \left(\frac{N}{4\pi m E}\right)^{1/2} e^{-\frac{N p_1^2}{2mE}}$$

Let us take all the quantities within the square root together. So, I have h divided by V and then I have N this 2 and this 2 gives me a 4 there is a pi over here. So, this is 4 pi m times E raised to the power half and then I have 1 minus p 1 square divided by twice m E, this is raised to the power N minus 1 by 2 and here I make the approximation N minus 1 by 2 is approximately N by 2. So, that I have this result.

Now, clearly from this expression if we want to move ahead we have to see that I know that the energy is an extensive quantity therefore, E would scale with N. So, the denominator is a very large number because I am looking in large system. So, therefore, this inverse of this twice m E inverse is a very small number.

Consequently what I can take this expression 1 minus this and I can replace it by the exponential p 1 square over twice m E because this first root this expression that we have over here is essentially it looks like the Taylor expansion the first two terms of the Taylor expansion of this exponential.

So, that this becomes h over N, N divided by 4 pi m times E raised to the power half e to the power minus p 1 square over twice m E raised to the power N by 2 and this I can nicely write down as by sorry this has to be h over V h over V N divided by 4 pi m E raised to the power half e to the power minus N p 1 square over twice m E and this is the ratio of E N minus 1 V N minus 1 N minus 1 divided by omega of E, V, N.

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$$\frac{\Omega(E_{N-1}, V_{N-1}, (N-1))}{\Omega(E,V,N)} = \frac{h}{V}\left(\frac{\quad}{4\pi m E}\right)$$

$$\rho_1(p_1,q_1) = \frac{1}{h}\,\frac{\Omega(E_{N-1}, V_{N-1}, N-1)}{\Omega(E,V,N)} = \frac{1}{V}\left(\frac{N}{4\pi m E}\right)^{1/2} e^{-N p_1^2/2mE}$$

$$E = \frac{N}{2} k_B T$$

$$\rho_1(p_1,q_1) = \frac{1}{V}\left[\frac{\cancel{N}}{2\cancel{4}\pi m \frac{\cancel{N} k_B T}{\cancel{2}}}\right]^{1/2} e^{-\frac{\cancel{N} p_1^2}{2\cancel{4} m \frac{\cancel{N} k_B T}{2}}}$$

$$= \frac{1}{V}\,\frac{1}{\sqrt{2\pi m k_B T}}\, e^{-\frac{p_1^2}{2 m k_B T}}$$

Now, the single particle probability density rho of rho 1 of p 1 q 1 is given by 1 by h times omega of E N minus 1, V N minus 1 N minus 1 omega of E, V and N. So, this 1 by this h cancels with this h over here, and we have this nice expression which is N over 4 pi m E raised to the power half e to the power minus N p 1 square over twice m E.

Clearly, it is a nice expression, but not very familiar for that we substitute E I know that for an ideal gas in 1 dimension the energy of the gas is given by E is equal to N by 2 K B T. So, that rho 1, p 1, q 1 is 1 by V 4 pi m N by 2 N by 2 K B T times N raised to the power half. And then I have e to the power minus N p 1 square this has to be 4 because this is raised to the power N by 2 this has to be 4 here. So, this is going to be 4 m N by 2 K B T.

There are cancellations this gives me 2 this N and this N cancels out. Similarly here also, this gives me 2 and this N this N cancels out. So, that I have 1 over V 1 over square root 2 pi m K B T e to the power minus p 1 square over twice m K B T.

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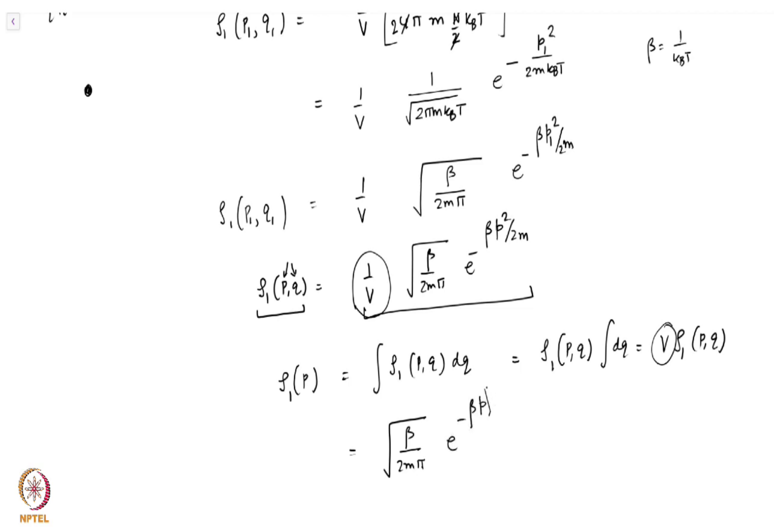

If you write down beta is equal to 1 over k B T then this quantity is 1 over V square root beta over 2 m pi e to the power minus beta p 1 square over twice m rho 1 of p 1, q 1. Now, you see that this distribution is the canonical distribution. So, starting from the microcanonical ensemble we have shown explicitly that your canonical distribution function follows if you consider one subsystem one part of the subsystem to be in the path to be immerse as if it is immersed in the path of the rest of the system.

I have determined the single particle probable density of course, one can do 2 particle 3 particular and one should get a sum over the momentum here. This number this so I have treated one single particle as a subsystem which is moving in the path of the rest of the system one can in principle take subset of this moment as part of the subsystem and you will see that you are going to get the canonical distribution.

Since p 1 and q 1 is nothing special because my I am not the particles are indistinguishable the single particle probability density rho p q is going to be 1 over beta over 2 m pi e to the power minus beta p square over twice m. If you really now say that look that I am not worried about the coordinates I can from this is also a joint probability distribution of p and q.

If I just want to know the probability distribution of the momenta rho p is integral rho 1 p q d q which is rho 1 p q this part does not depend on the coordinates and therefore, you have d q which is V times rho 1 p q and then this V factor will cancel with this V factor and you are going to come up with the Maxwell's Boltzmann distribution twice m pi e to the power minus beta p square over twice m.