Statistical Mechanics

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Lecture - 28
Microcanonical Excluded Volume

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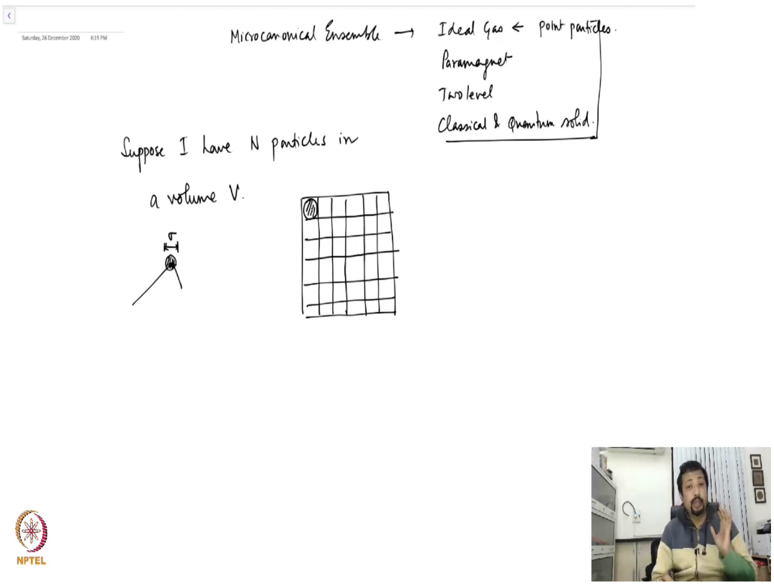

Now, in the Microcanonical example, we have so far seen examples in this ensemble, we have seen the examples of ideal gas that of a paramagnet, a two-level system as well as a classical and quantum solid which is essentially harmonic oscillators. In this lecture, we are going to take up a different example which is slightly different from all these examples that we have taken. Although it is a model for a gas and it is a very interesting and acute model.

The idea is that suppose I have N particles in a volume V. Now, typically in the ideal gas case, when we looked at it, these were like we treated them like point particles right. But now

I want to make a distinction, I want to make a slight difference in this problem. What I want to do is I want to say that look each of these particles have a certain size which is sigma.

So, essentially, if these particles have a size sigma, if one of the particle is occupying this particular position that you see over here. A second particle cannot come and sit over here and I want to treat this problem and this is essentially what is called a lattice gas model. So, I have a volume V, this is a schematic only in 2D, then what I do is I break up this volume in cells of size sigma so that I have only one particle which can occupy these cells. Either the cells are empty or I have a single particle which is occupying this.

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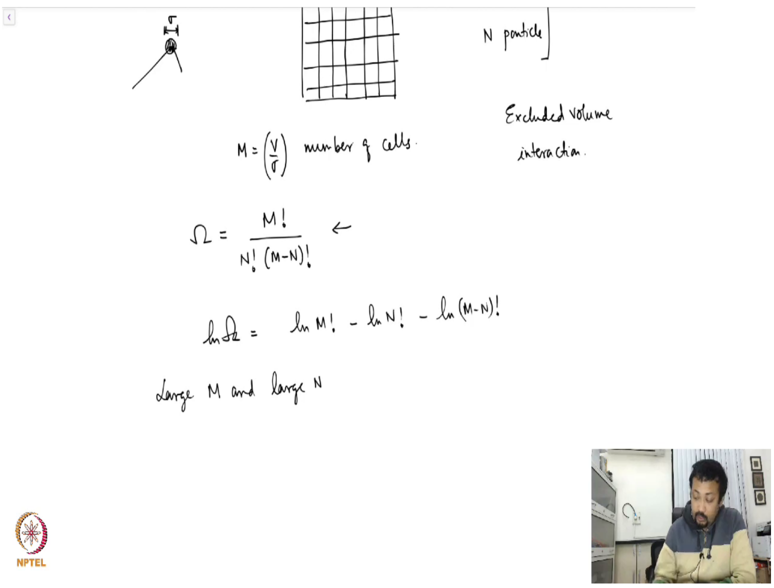

So, how many cells do I have? I have M is equal to V over sigma number of cells. The question now is what is the total number of microstates? So, there are M boxes and there are N particles and I have to put this number of particles in this boxes. And this is simply a combinatorics problems problem which most of you have done, the total number of microstates is then given by M factorial divided by N factorial M minus N factorial as simple as that.

But, now, the fact that I have put a restriction by saying that I have a certain size of part these particles will have amazing consequences on the equation of state and that is the whole purpose. You will see that even though I start off with particles which are essentially there is no interaction between them.

The Hamiltonian is does not have an interaction term, the restriction that I have put in by saying that I have a certain size of this particles make them interacting. And why would, how would how do I see that they are interacting? That is going to appear in the equation of state itself and we will elaborate this when we do interacting systems, we treat interacting systems.

In soft condensed matter or in statistical physics, this is the simplest of this interaction and is called excluded volume interaction. As the name itself suggests that I am excluding the volume because of the certain volume is being excluded because of the size of this particles.

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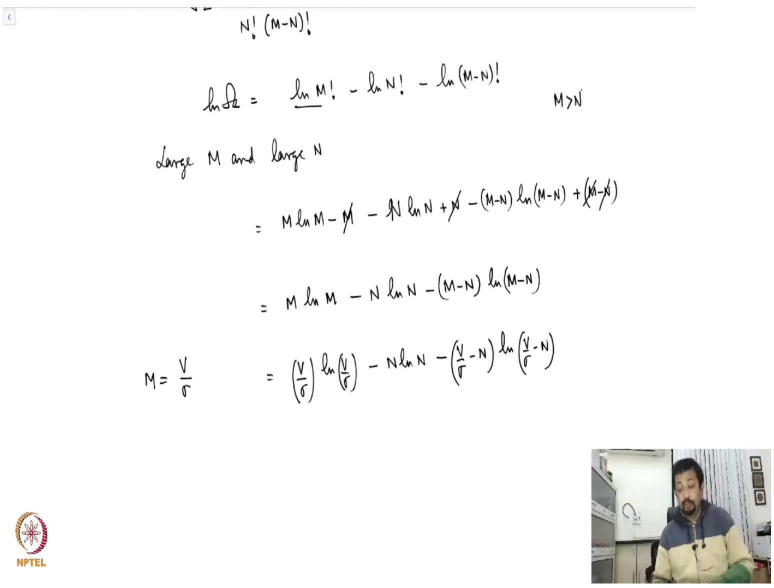

So, then let us move forward that means, ln omega, the log of this quantity is going to be ln M factorial minus ln N factorial minus ln of M minus N factorial. In the limit of large N; large M and large N what I have is the Sterling's approximation for log N factorial M factorial and M minus N factorial. So that I have M ln M minus M minus N ln N plus N minus I have M minus N ln of M minus N plus M minus N.

Now, you clearly see that from this expression, this plus N and this minus N cancels out and this plus M and this minus M cancels out so that you have M ln of M minus N ln of N minus M minus N ln of M minus N. Now, I know that M is V over sigma so that this I have V over sigma ln of V over sigma minus N ln N minus V over sigma minus N ln of V over sigma minus N. It is understood that M is greater than N and both M and N l are large.

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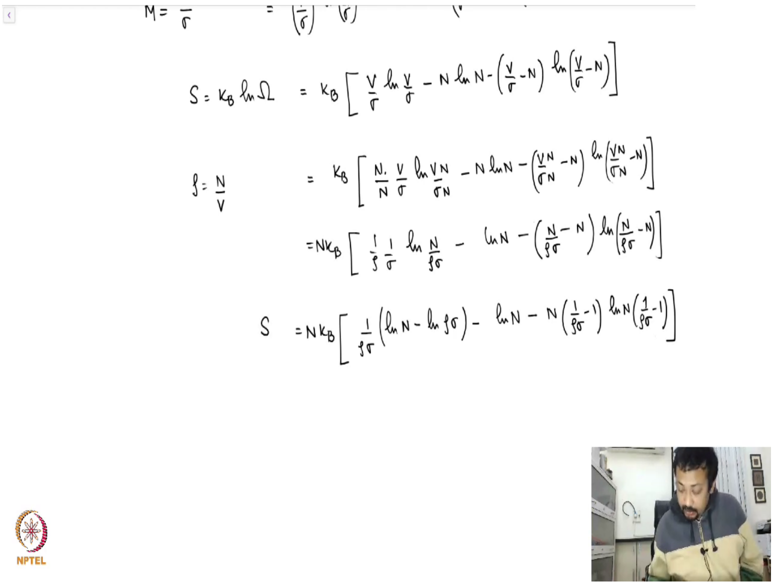

So, the entropy then is K B ln omega, this is for the microcanonical ensemble and we have seen this earlier. We have derived this earlier, and we have used this earlier also. So, this becomes K B v over sigma ln V over sigma minus N ln N minus V over sigma N ln of V over sigma minus N.

Now, let us introduce the density. The density rho is N over V so that, I can write down this as N times we will say this to be V over sigma N ln V over sigma N and N minus N ln N minus V over sigma N N minus N ln V over sigma N N minus N.

And this becomes K B I can take out one N outside that big makes it N K B 1 over rho 1 by sigma ln of I have N divided by rho sigma minus N ln N. And here, I have minus of N minus N and this is being divided by rho sigma, I have ln of N by rho sigma minus N.

So, that this is going to be N K B 1 over rho sigma ln N minus ln of rho sigma minus N ln N sorry N has this N factor is not going to be there. Because I have taken N outside, I have ln N and then, I have N 1 over rho sigma minus 1 ln N 1 over rho sigma minus 1. So, this is going to be my entropy.

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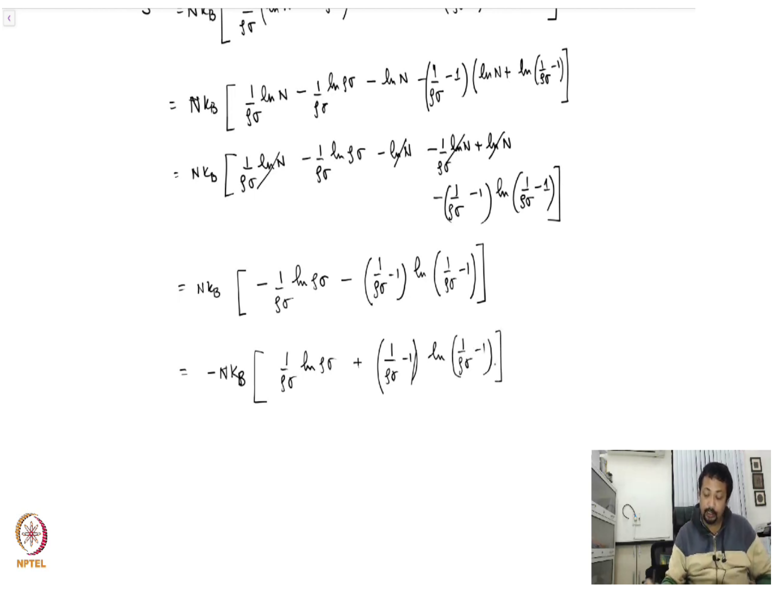

Can I simplify this further? Possibly yes, I can and again I have made an error over here, this N is not going to be there. Because I have taken one N outside, this becomes 1 over rho sigma minus 1.

So, this is N oops N K B 1 over rho sigma ln N minus 1 over rho sigma ln of rho sigma minus ln of N, I have minus 1 over rho sigma, let us open the bracket over here ok. Let us just do it step by step so that we do not make any mistake times ln N minus plus ln of 1 over rho sigma minus 1.

So, this is N K B 1 over rho sigma ln N minus 1 over rho sigma ln rho sigma minus ln N minus 1 over rho sigma times ln N. And then, I have plus ln of N and I have minus 1 over rho sigma minus 1 ln of 1 over rho sigma minus 1. Let us check whether we have done this correctly. Now, this and this cancels out, this and this so, this is minus N K B 1 over rho sigma ln of rho sigma plus 1 over rho sigma minus 1 and I have ln of 1 over rho sigma minus 1.

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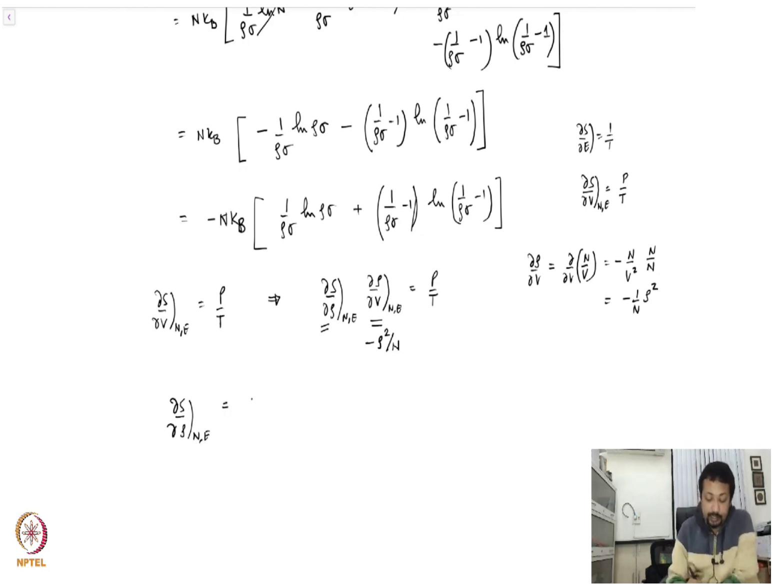

Now, here, from this, I cannot calculate del S del E because that is equal to 1 by T, I cannot calculate that because S is not a function of E here. I can only calculate the equation of state which is del S del V N held constant and E held constant was P by T.

So, del S del V N, E held constant is P by T and this implies del S del rho N and E held constant times del rho del V N and E held constant is going to be P over T which essentially means that del rho del V. I can use as del del V of N over V which is minus N over V square, I multiply with N divided by N, this gives me minus 1 over N rho square. So that I have this derivative as minus rho square over N. It is this derivative which I have to calculate.

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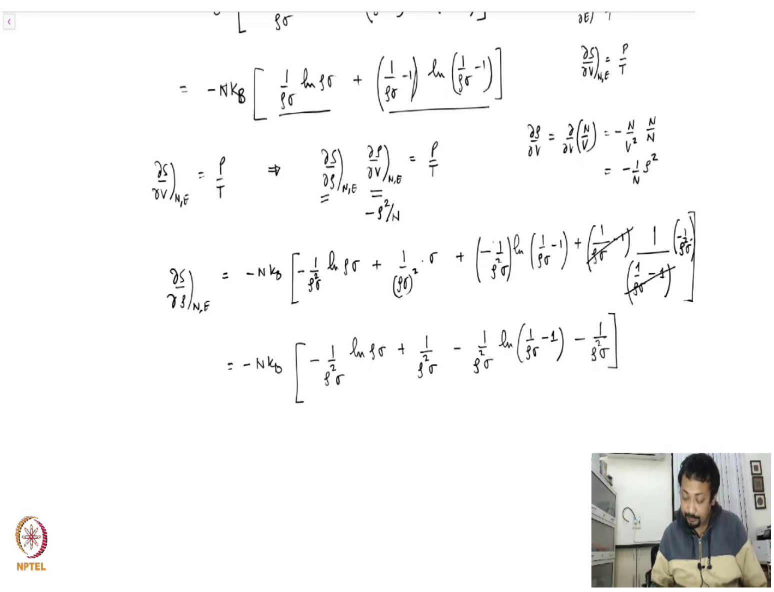

So, del S del rho N and E held constant is minus of N K B the first term, the derivative of this first term I can do it as rho square sigma minus ln of rho sigma right plus 1 over rho square sigma sorry 1 over rho square rho sigma whole square 1 over rho sigma whole square times sigma plus the (Refer Time: 13:46), if I look at the derivative of this term, this is going to be minus 1 over rho square sigma ln of 1 over rho sigma minus 1.

And then, of course, comes the second derivative, the derivative of the second term which is going to be 1 over rho sigma minus 1 and then, I have 1 over rho sigma minus 1 and I have minus 1 over rho times rho square times sigma.

So, that I have minus of N k B this is minus rho square of times sigma ln rho overs times sigma plus 1 over rho square sigma minus 1 over rho square sigma ln of 1 by rho sigma minus 1. And then, I will have plus again a minus sign here, because this is going to cancel with this, I am going to have minus 1 over rho square sigma.

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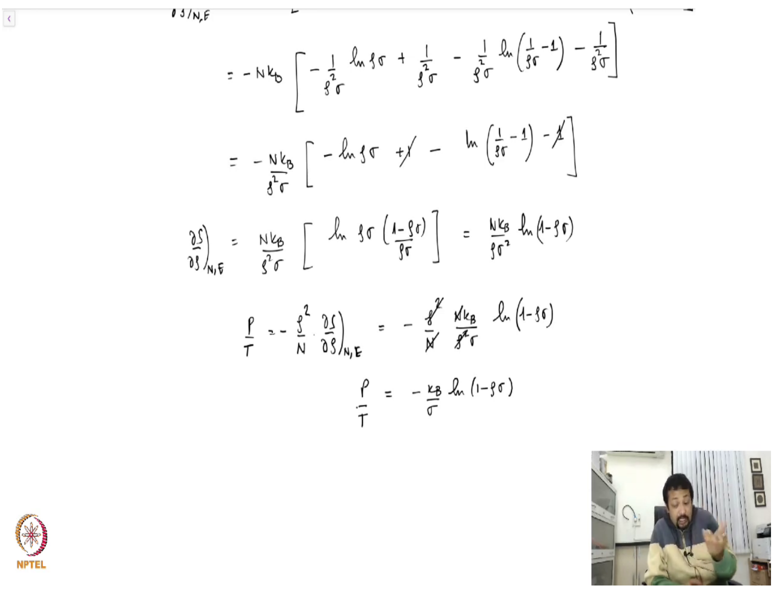

So, that I have minus N K B I can take out rho square sigma outside so, if I take out rho square sigma, I have minus ln of rho sigma plus 1 minus ln of 1 rho sigma minus 1 minus 1. This, this cancels out and I have N K B divided by rho square sigma times ln of rho sigma 1 minus rho sigma divided by rho sigma which is going to be N K B over rho sigma square ln of 1 minus rho sigma. And this is your equation of state well, sorry now, this is not the equation of state, this one has del S del rho N and E held constant.

So, the equation of state P by T which was minus N rho square or rather rho square divided by N times del S del rho N and E held constant becomes minus rho square over N N K B rho square sigma ln of 1 minus rho sigma. Things simplify out rho square rho square cancels out, N and N cancels out and I have minus K B divided by sigma ln 1 minus sigma P over T.

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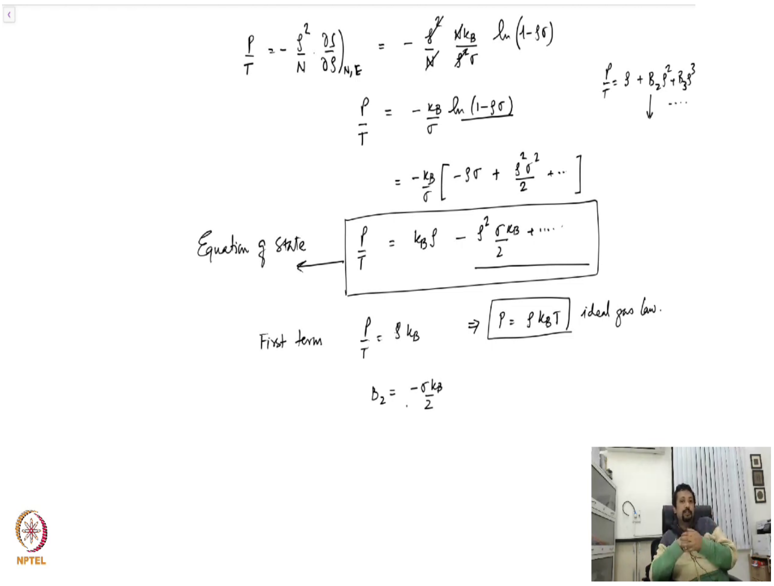

Remarkably, even though you started off with a non-interacting system of particles, you have an equation of state which does not follow the ideal gas law. Therefore, you clearly see that this system behaves in a different way as if it is interacting.

To look at this for weaken of density, I can expand the law and the first term is going to be minus divide times minus of rho sigma plus rho square sigma square divided by 2 and higher order terms. So that the first term I have is K B times rho and then, I have minus rho sigma K B divided by 2 plus higher order terms P by T.

This equation of state has a form of a virial expansion and you learn about this virial expansion, when you do a interacting system. Essentially, you write down the equation of as rho plus a 1 or rather there has to be square over here. B 2 rho square plus B 3 rho cube so on and so forth and this is essentially are the virial coefficients.

So, looking at this, the first term which is P by T is rho times K B implies the pressure is rho K B T is the ideal gas law. The rest of this are corrections to this ideal gas law and one immediately sees that B 2, the first coefficient, the coefficient of rho square is minus sigma over K B over 2.

So, the system behaves as if there is a some kind of an interaction inbuilt and that has essentially come from the fact that you have used the excluded volume by saying that look two particles cannot sit on top of each other because one particle has certain amount of size. You will later on learn about this virial expansion more when we do interacting systems.