Statistical Mechanics
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Lecture - 09
Maxwell's Relations - Part II

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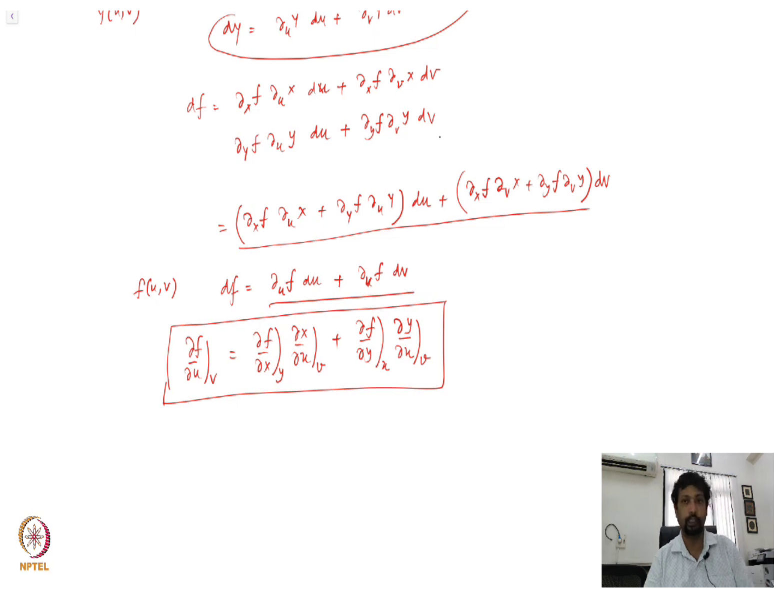

So welcome back, in the last class we were looking at partial derivatives and we had derived all of this in terms of Jacobians.

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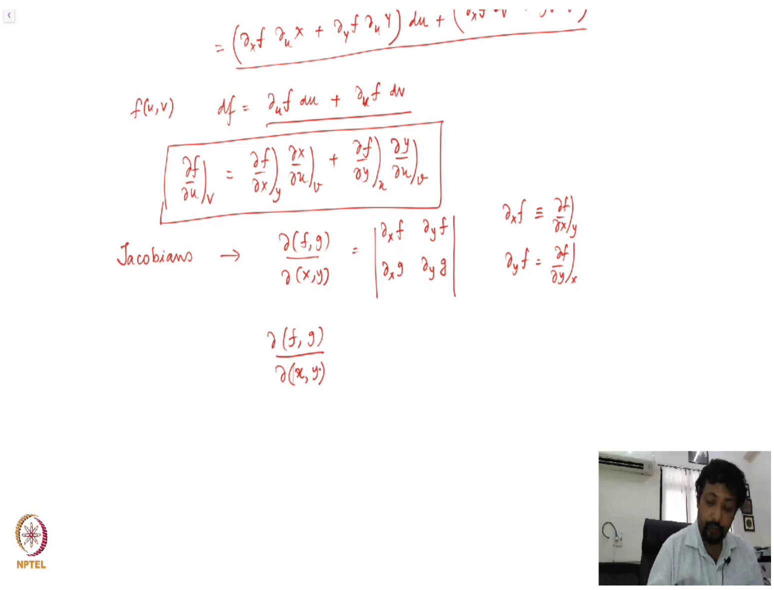

So, now very briefly Jacobians are defined in the following way, that I have two functions f of g x of y and this is the determinant del x f del y f del x g and del y g right. Where this is synonymous with del f del x y held constant and del y f is synonymous with del f del y x held constant. It should be noted here that if I have del of f comma g del of x comma y.

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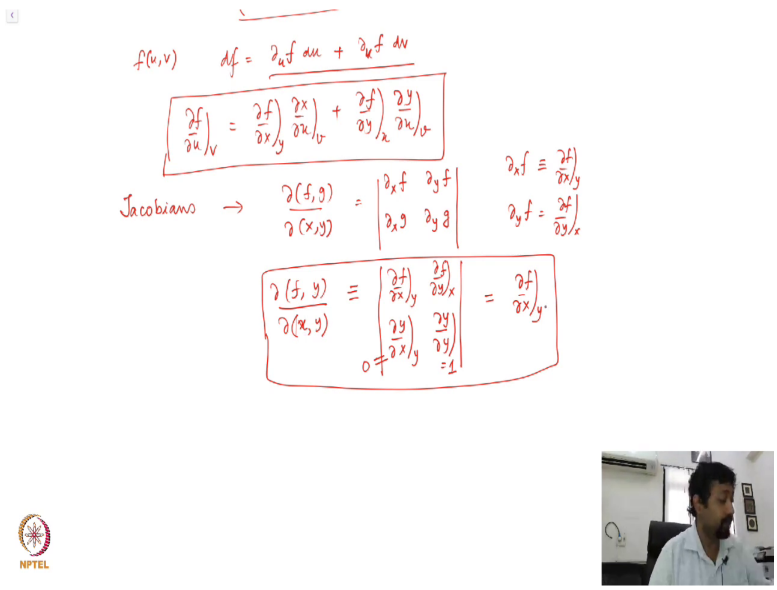

Now if I replace g by y which I can do. Then this is equivalent to del f del x y held constant, del y del y x held constant, del x del y I am sorry this has to be del y del x y held constant and this is going to be again del y del y and this one has to be del f del y.

So, that I am replacing g by y and this determinant is this is equal to 1, this is del f del y excelled constant and this is equal to 0 is just del f del x y constant. So, we are going to repeatedly use this relation that del of f comma y and del x comma y is equal to del f del x y held constant.

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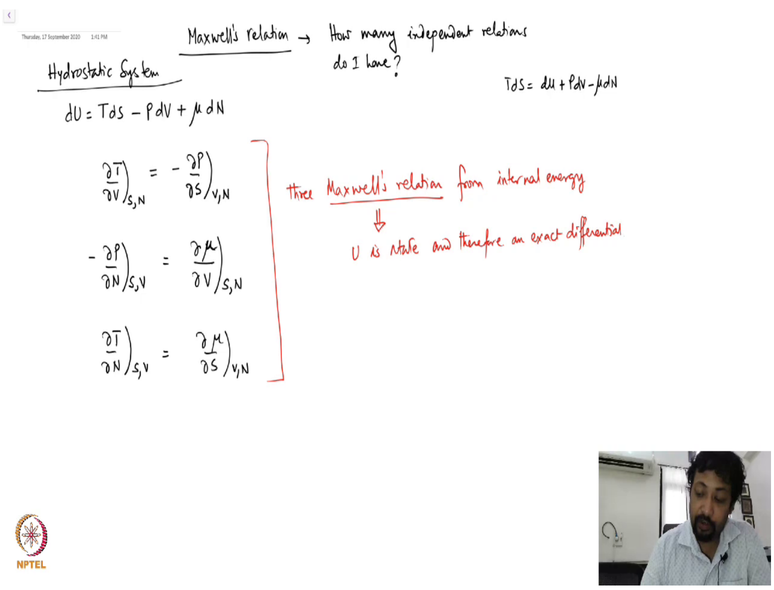

So, now we were looking at Maxwell's relation and our original question was how many of them how many independent relations do I have? So, let us start again. So, d U this is for a hydrostatic system we are looking at, so let us just write on top Hydrostatic System.

For a hydrostatic system I have d S well T d S is d U plus P d V therefore, d U is T d S minus P d V plus mu d N. Always remember the first law which is T d S is d u for a hydrostatic system it is d u plus P d V minus mu d N then you can manipulate this. And my Maxwell's relation read the following that del T del V S and N held constant.

This is because u is a state function and therefore is an exact differential is minus del P del S V and N held constant, then we had minus del P del N del P del N S and V held constant was del mu del mu del V S and N held constant. Finally, we had del T del N del T del N S and V are held constant is equal to del mu del S del mu del S V and N are held constant.

So, these are the 3 Maxwell's relations that we get from the internal energy. Once again very briefly this is a consequence of the fact that U is a state function and therefore an exact differential right.

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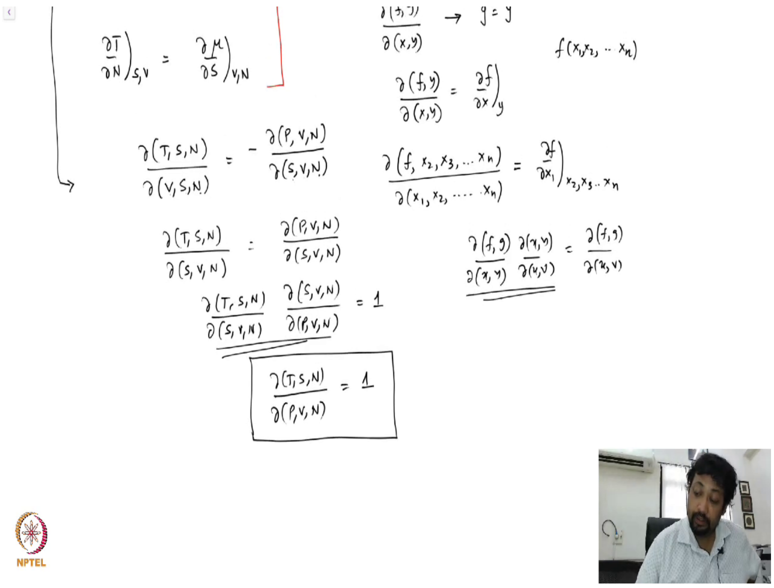

Now, I want to use my knowledge of Jacobians correct. So, when we did Jacobians we understood that del f comma g del x comma y we had this and this relation in this relation if I substitute g is equal to y, then it follows that del f y del x comma y is equal to del f del x y held constant.

But here I have treated the function as a function of two variable in principle it can be a function of N variables, which one the generalization of this would be if f is a function of x 1 x 2 all the way up to x n then del f del comma x 2 x 3 x n del of x 1 x 2 all the way up to x n is equivalently del f del x 1 x 2 x 3 and x n being held fixed.

So, if you have learnt partial derivatives by now then you should be familiar with all of this terminology good, I want to apply this over here. So, then let us look at the first equation, the first equation is this and I want to write down the first equation in the following range.

So, del of T comma S comma N del of V comma S comma N is equal to minus del of P comma V comma N as del of and del of S comma V comma N. So, I see that the denominator here is V, S, N on the other hand it is S, V, N. But I can alter these two and if I alter these two then I should have del of T comma S comma N del of S comma V comma N is equal to del of P, V, N del of S, V, N.

Which means we had learned this when we in the earlier class, I can bring it on the left hand side to write it down as is equal to 1. Now remember del of f g del of x y del of x y del of f g is equal to sorry not this one, the result I want to use is del of x g del of x y del of x y del of u v is equal to del of f g del of u v.

But this equation is particularly cast in this way if you look at the left hand side and compare this path you will see that it is exactly done in that way. And therefore I can write it down del of T of S comma N del of P, V, N is equal to 1 right. So, this is my first Maxwell’s relation.

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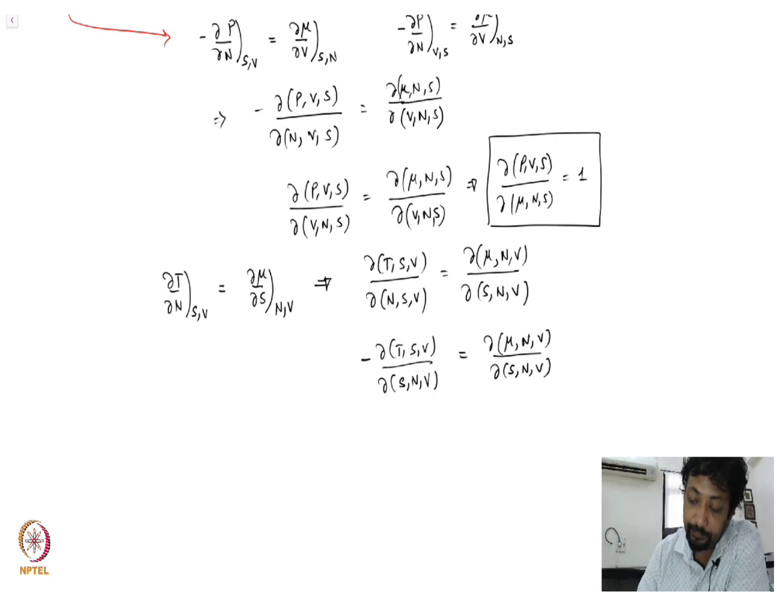

What about the second one? The second Maxwell's relation is minus del P del N S comma V is equal to del mu del V S comma N right. For the ease of it I will simply write down this as minus del P del N, since S is constant on both sides I will simply write it down as del mu del V N comma S.

And using this relation again if I borrow it then this implies that minus del of P, V, S del of N, V, S is equal to del mu of V comma N comma S and del of V comma N comma S. Again you see that there is a change in if I interchange N and V I will absorb the minus sign here and I can write down this as P V S del of V N S is equal to del of mu N S del of V N S.

This implies I will use the same argument that I have used before del of mu N S must be equal to 1 this is my second Maxwell's relation. What about the third, the third is del T del N

S comma V this is the relation between T d S term and mu d N term right you have del mu del S N comma V.

So, that you have del of T, S, V del of N, S,V is equal to del mu N, V del of S, N and V. So, one possibility is that there is something yeah this is fine ok. So now N S if I interchange this becomes S, N, V. But I bring a minus sign in front of it is equal to del mu N, V del of S, N, V.

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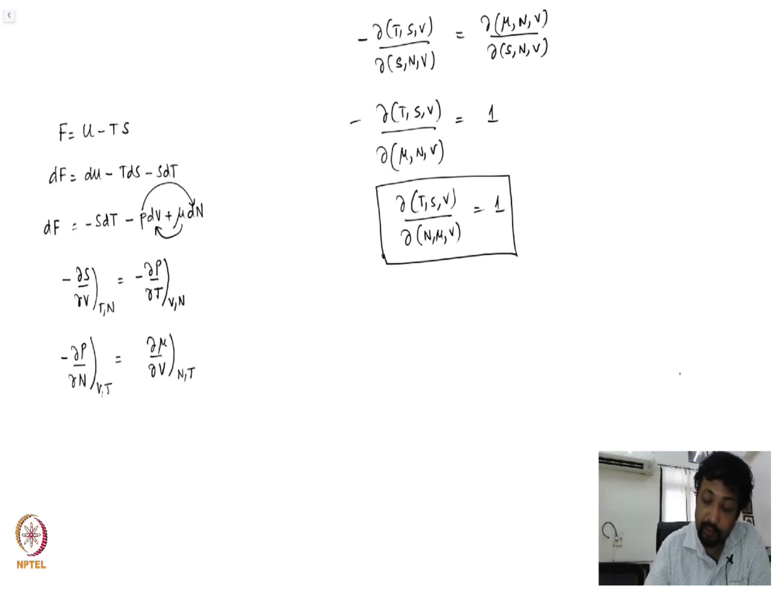

And therefore, I have minus del T, S, V del of mu, N, V is equal to 1, I can interchange mu and N here again. So, that this becomes T S V del of N, mu, V is equal to 1. So, this one is your third Maxwell's relation.

Now, with all of this did I make my life more complicated let us try to see. So now, as I as we said we derived this Maxwell's relation stating U as an exact differential, because U is a state function and therefore we could arrive at all the these two Maxwell's relation. The same argument is also valid for all the other free energies that we had defined.

So, remember we had defined Helmholtz free energy F was u minus T S and your differential d f was d u minus T d S minus S d T. And if you now follow the first law which we had written down on top somewhere yeah exactly d U minus T d S is minus p d V plus mu d N. So, this becomes minus S d T minus p d V plus mu d N, this was the differential in the Helmholtz free energy.

So, let us apply f is also an exact differential it is a free energy it is derived from u by simply replacing the entropy with this conjugate variable T. Now so the first Maxwell relation would be minus del S del V T and N held constant is minus del P del T del P del T V and N held constant.

Then of course, it follows minus del P del N p with N and mu with V is equal to del mu del V. Here of course, when you do del P del N V and T are held constant when you do del mu del V N and T are held constant. And finally you have the last relation where you use S with N, so S with N and mu with T.

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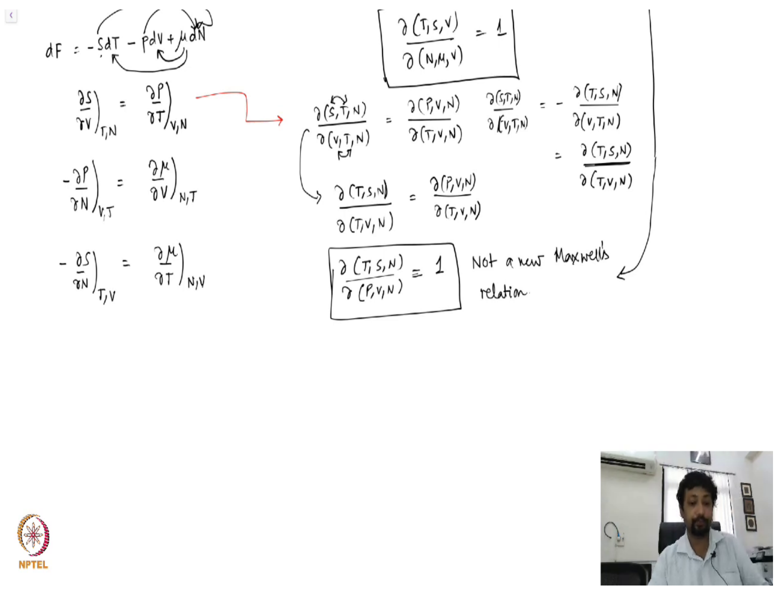

So, minus del S del N is equal to del mu del T when you do del mu del T your N and V are held constant. In this case when you do del S del N your T and V are held constant. So, clearly now I can simplify my life a little bit I remove the minus sign from the first.

So, if I now look at the first equation what is the corresponding way of writing it down in that in terms of the Jacobian. Let us see so this gives me del S T N and I have del V T and N is equal to del P, V, N del T, V, N. Let us interchange V and T in the denominator over here and T and S in the denominator then in the numerator.

So, this means if I have del T, S, N I will bring a minus sign which I will use to do it like this is del P, V, N del T, V, N. So, effectively in coming from here to here what you have done here is del T, S, N. So, del of S, T, N del of V, T and N is equal to minus del of T, S, N. And I have del of T, V and N which is equal to del of T comma S comma N and I will interchange V and T in the denominator to write it as sorry this was V, T, N.

This itself was V, T, N so I will write V, T and N and I will write this as T, V and N; the minus sign is now absorbed in the in redefining the denominator. So therefore, I have del of T, S and N and del of P, V and N is equal to 1. Let us see oops look at this equation is del of T, S, N del of P, V, N equal to 1.

So del of T, S, N del of P, V, N so this is not a new Maxwell's relation, we have already got this Maxwell's relation from the internal energy. So, if you compare this and go all the way down then we will see that we have the same equation that we had derived earlier, both of them are consistent.

Now, what we want to do. So, let me just see if I can zoom out. So, that you can now see that this equation and this equation are the same thing. Now let us zoom in so that we can have this yeah ok. Now let us look at the second Maxwell's relation which is over here we want to look at this one now.

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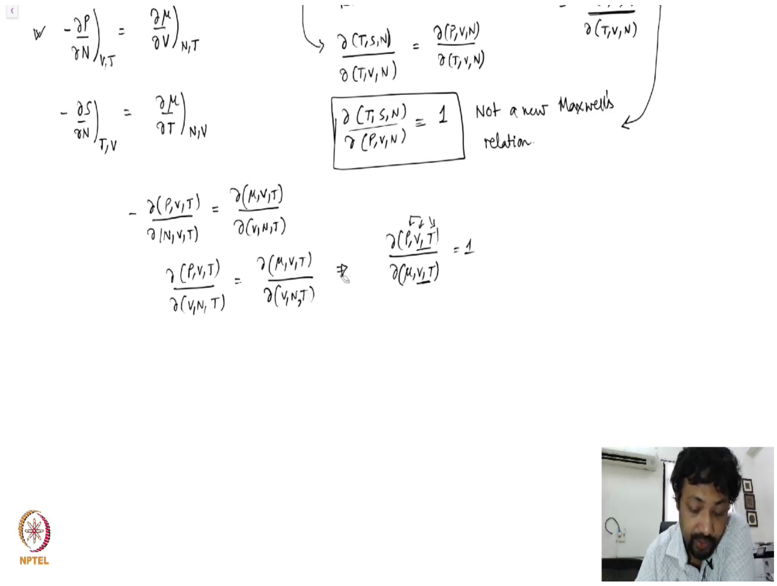

So, this gives me minus del of P, V, T and del of N, V, T is equal to del of mu, V, T and del of V, N, T. So, this is easy to do I will just do one permutation in the denominator here to give you V, N, T is equal to del of mu, V, T and del of V, N, T. And this implies the Maxwell's relation in terms of the Jacobian is del of P, V, T del of mu, V, T is equal to 1. Let us go up and see whether we have any of this.

We have P, V S we have mu, N, S we have T, S, V we have N, mu, V but we do not have P P V, but this is something wrong here is this correct because there are 2 variables which are common. So, V and T are both common in the numerator as well as in the denominator.

So, this is equivalently saying so let us see what where do we go wrong del P del N, V and T are held constant you have del mu del V, N and T are held constant. So V, N, T so then this is del mu del V V, N, T correct.

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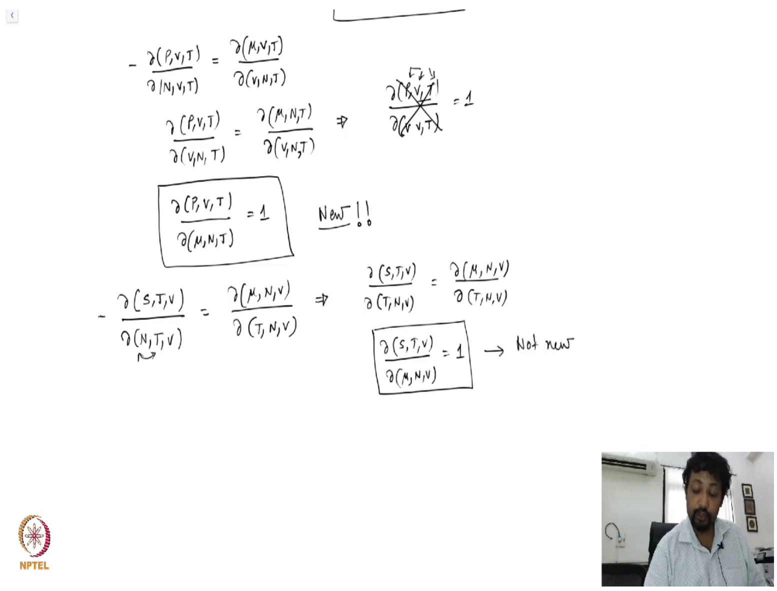

So therefore this is actually V comma N comma T. I am sorry this is the part where it went wrong. So, this is mu comma N comma T because I have mu, N, T and this is V, N, T and therefore this is not the right equation we are looking for. The right equation is del P, V and T and del of mu, N, T is equal to 1 and we go back to the other ones we do not have a combination of P, V, T; do we have a combination of P, V, T we do not have.

Therefore this is a new Maxwell's relation that we have found out, this is new. Finally, the last one is del of S, T, V del of N, T, V is equal to del of mu, N, V and del of T and V. There is a minus sign in front of it which implies this becomes del of S, T, V del of T, N, V I absorb the minus sign by switching N and T here is del of mu, N, V and del of T, N, V.

And therefore the Maxwell's relation in terms of the Jacobian is del of mu, N, V is equal to 1. We do not have the combination S, T, V we have this here. So, we already have T, S, V and N, V and it is exactly this one, so this is again something which is not new. So, from that Helmholtz free energy we only get this as my new Maxwell's relation right.