Advanced Thermodynamics and Molecular Simulations

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Lecture 09

Extensive and Intensive Variables; Gibbs Duhem Relation; Euler Theorem; Maxwell Relations

Hello all of you so in the last lecture we have been discussing the idea of thermodynamic functions why this should be minimized at equilibrium. We discussed the case of multi component systems and discuss the idea of chemical potential. So in this lecture we will discuss an important relation called the Gibbs Duhem relation and then discuss about extensive and intensive variables and finally we conclude with something called Maxwell relations.

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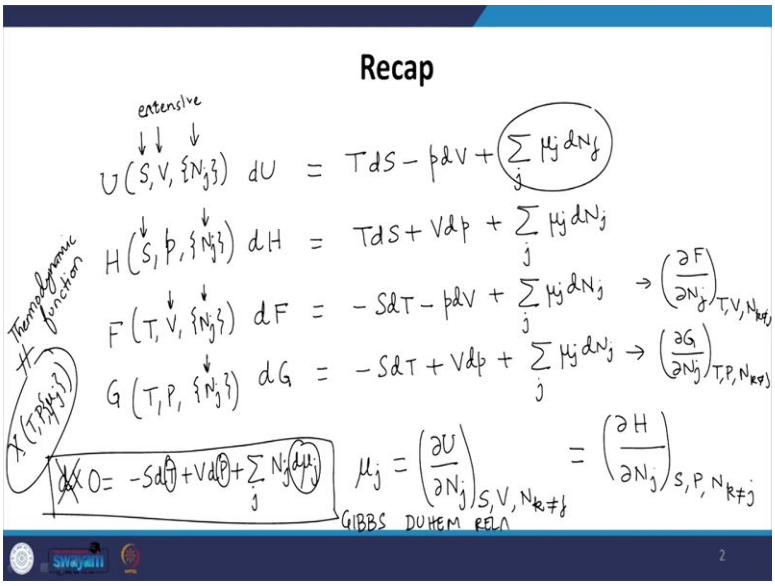

Recap

extensive

$U(S, V, \{N_j\})$ $\quad dU = TdS - pdV + \sum_j \mu_j dN_j$

$H(S, p, \{N_j\})$ $\quad dH = TdS + Vdp + \sum_j \mu_j dN_j$

$F(T, V, \{N_j\})$ $\quad dF = -SdT - pdV + \sum_j \mu_j dN_j \rightarrow \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N_{k\neq j}}$

$G(T, P, \{N_j\})$ $\quad dG = -SdT + Vdp + \sum_j \mu_j dN_j \rightarrow \left(\frac{\partial G}{\partial N_j}\right)_{T,P,N_{k\neq j}}$

Thermodynamic function

$\neq X(T, P, \{\mu_j\})$

$\boxed{\cancel{dX}\ 0 = -Sd\boxed{T} + Vd\boxed{P} + \sum_j N_j d\mu_j}$

GIBBS DUHEM RELN

$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{k\neq j}} = \left(\frac{\partial H}{\partial N_j}\right)_{S,P,N_{k\neq j}}$

So essentially what we have done so far is we have defined four thermodynamic functions the internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy and then we have written the differential form of these in terms of different choice of control variables for example-

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

$$dH = TdS + Vdp + \sum_j \mu_j dN_j$$

$$dF = -SdT - pdV + \sum_j \mu_j dN_j$$

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j$$

So obviously what is different in this thermodynamic functions are the control variables. For example-

$$U(S, V, \{N_j\})$$

We use a curly bracket because we have different number of molecules of different components. Similarly-

$$H(S, p, \{N_j\})$$

$$F(T, V, \{N_j\})$$

$$G(T, p, \{N_j\})$$

And the way to get these functions if you recall was from the Legendre transformation we converted U to H by replacing V as a control variable to p and similarly we have done for other free energies and so on. However you must have noticed one thing in its all these functions I have still kept the last term as the same so chemical potential we have defined as the change in energy per unit mole or the change in energy by adding a molecule in the system so we can define on a molecular basis or we can define per mole but the key point is that this chemical potential always is the partial derivative of whatever energy that we have defined.

So in the case of U it is-

$$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{(S,V,N_{k\neq j})}$$

and of course the partial derivative is for constant S constant V and constant number of all the species except j. I can write the same thing as in terms of the enthalpy-

$$\mu_j = \left(\frac{\partial H}{\partial N_j}\right)_{S,p,N_{k\neq j}}$$

but now we have constant as constant p constant k not equal to j and I can write as in the same form in term of F as-

$$\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N_{k\neq j}}$$

Similarly-

$$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,P,N_{k\neq j}}$$

You may imagine that why are we not doing a transformation of variable in the last term, why we cannot have a function which is basically something like this-

$$dX = -SdT + Vdp + \sum_j N_j d\mu_j$$

and for that function let us give it some name let me call that function some d of (x) cannot we define a function like this for which the controlling variable are T p and μj and the answer is we cannot; and that is where the idea of extensive and intensive variable comes into picture.

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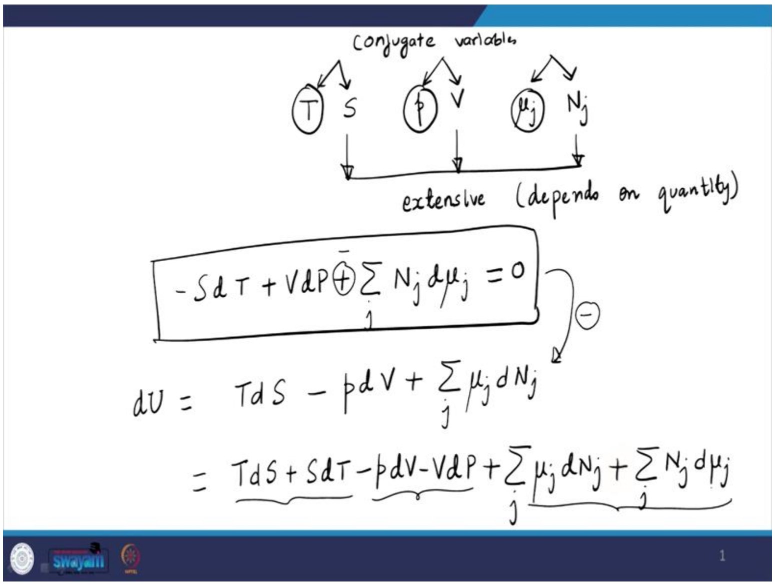

Conjugate variables

$\boxed{T}$ S $\boxed{p}$ V $\boxed{\mu_j}$ N_j

extensive (depends on quantity)

$$\boxed{-SdT + VdP \overset{-}{\oplus} \sum_j N_j d\mu_j = 0} \quad \ominus$$

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

$$= \underbrace{TdS + SdT}\underbrace{-pdV - VdP} + \underbrace{\sum_j \mu_j dN_j + \sum_j N_j d\mu_j}$$

So what you may have noticed here is that we had formed three pairs of variables which we call conjugate variables. So, T, S is a conjugate variable p, V is a conjugate variable and the $\mu_{j's}$ and the $N_{j's}$ are the conjugate variable.

However there is something interesting about this particular pairs that we have in all these pairs one of the variables is not changed if I change the amount of the substance or if I change the size of the system and the other variable does change. Let’s say for example temperature if for example I have a glass of water at 30 degree Celsius if I look at half of the glass the temperature remains the same. The same is not true for entropy we have already discussed that entropy increases as the number of molecules increases. So entropy depends on the number of molecules or the size of system under consideration but temperature does not.

Similarly pressure when we have a system at one bar pressure it does not matter whether we have one litre of that or 10 litres of that the pressure is independent of the quantity. Similarly the chemical potential it is a change in energy by adding one molecule. So even if we have

10000 molecules since we have defined chemical potential as per molecule it is going to be independent of the system size of course chemical potential may depend on composition but it will not depend on the system size itself for same composition for a larger system versus a smaller system we will have the k same chemical potential however number of molecules clearly will change when we change the system size. The volume will clearly change when we change the system size or the number of molecules the entropy as I said will clearly change if I change the number of molecules or the system size. So all these three variables are therefore called extensive variables and when I call something extensive it means that it depends on the quantity of the substance.

So now if I go back to our previous slide what you notice is that in all these cases of thermodynamic functions we have always kept at least one extensive variable as the control variable. In the first case when we had U all these three entropy, volume and the number of molecules all of them are extensive, when we did the transformation H, p is no longer extensive but S and Nj are still extensive. When we did transformation F temperature is not extensive anymore but the volume and the number of molecules still is and when we did for G number of molecules are the only extensive variable actually number of molecule for every species so we have almost N1, N2 to the number of components we have all of these are extensive variables.

So what happens if I choose only the T, p and μj for this function-

$$dX = -sdT + Vdp + \sum_j N_j d\mu_j$$

for this case all the control variables become intensive variables. So this means this x is going to be a function of temperature pressure and the chemical potentials and of course we have so many chemical potentials for every component.

Now if I do that so now I was telling you that control variables are the one we are controlling. So in some sense we are representing the system in terms of those control variables. So if for example I do not include any extensive variable as a control variable what this means is that we have nothing that characterizes the system size as the control variable. So our system description is in some sense incomplete because if I specify the temperature pressure and the chemical potential we are not specifying the system size. If we are we specified temperature pressure and the number of molecules, the number of molecules contained the description of the system size but now when we are doing temperature pressure and chemical potential that description has been lost.

So therefore the argument we are trying to make is there must be at least one variable in the control variable that should be extensive and if it is not happening we will not have a thermodynamic function. So therefore x is not a thermodynamic function and in fact the particular relation that we have just written that must be equal to 0 and this relation is known as the Gibbs Duhem relation.

There are several ways to derive this it will suffice to say that once we have all the extensive variables, all the intensive variables as the control variables that thermodynamic functions is not defined and for that case a differential form we get should be equal to 0 and that is the Gibbs Duhem relation right that is one way to look at this there are other ways to also prove the same argument.

So now using the Gibbs Duhem relation we can now get something else and that is the following. So now since we know that-

$$-SdT + Vdp + \sum_j N_j d\mu_j = 0$$

and now if I start with the expression for dU we had-

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

I can now add this entire expression on the right hand side here because that is anyway equal to zero. So this I can write as you something like this-

$$dU = TdS + SdT - pdV - Vdp + \sum_j \mu_j dN_j + \sum_j N_j d\mu_j$$

So this I can write as you something like this you have to be slightly careful here actually this should have been a minus sign. So what essentially we are adding is this multiplied by a minus sign here and this should have been a minus sign that is what should have appeared in the in the Gibbs ah Duham equation. It becomes-

$$0 = -SdT + Vdp - \sum_j N_j d\mu_j$$

and you can see why this happens because when we went from dU to dF the TdS was replaced by - SdT when we went from dU to dH - pdV was replaced by + Vdp there is a sign change in the transformation. So when we go from μj dN j to Nj dμj we should have a minus sign in that particular expression. So keep in mind that in Gibbs Duham relation there is a minus sign in front of Nj dμj.

So with this kind of an idea what you can see now is that this becomes a derivative of T, S and this becomes a derivative of p, V and this becomes a derivative of μj multiplied by N j. So therefore I can write this as-

$$dU = d(TS) + d(-pV) + d(\sum_j \mu_j N_j)$$

$$dU = d(TS - pV + \sum_j \mu_j N_j$$

$$U = TS - pV + \sum_j \mu_j N_j$$

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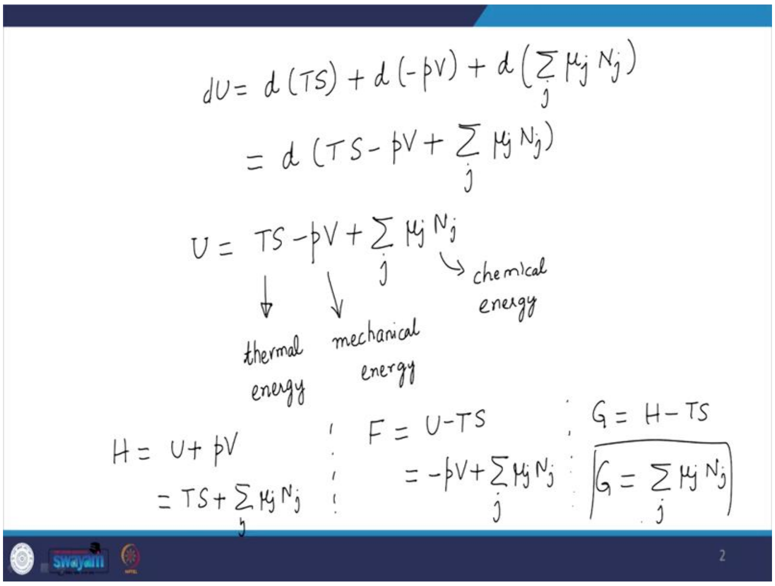

$$dU = d(TS) + d(-pV) + d(\sum_j \mu_j N_j)$$

$$= d(TS - pV + \sum_j \mu_j N_j)$$

$$U = TS - pV + \sum_j \mu_j N_j$$

thermal energy

mechanical energy

chemical energy

$$H = U + pV$$
$$= TS + \sum_j \mu_j N_j$$

$$F = U - TS$$
$$= -pV + \sum_j \mu_j N_j$$

$$G = H - TS$$
$$\boxed{G = \sum_j \mu_j N_j}$$

So if I go back to our previous expression we have not had an expression for U we had an expression for dU but using the Gibbs Duhem relation we have been able to find an expression for absolute value of U right and that expression is given by the expression right here-

$$U = TS - pV + \sum_j \mu_j N_j$$

and you can see it clearly demonstrate that my energy is composed of basically three kinds of energy and let me give them some names. The first relates to temperature so let me call this thermal energy. The second relates to the pressure volume work so let me call it the mechanical energy thinking of a piston that is trying to do a work when the volume is changed and then finally the last one relates to components being added or removed so we call this the chemical energy.

Using now the definition of U we can find the value of other thermodynamic functions for example-

$$H = U + pV$$

$$H = TS + \sum_j \mu_j N_j$$

$$F = U - TS$$

$$F = -pV + \sum_j \mu_j N_j$$

$$G = H - TS$$

$$G = \sum_j \mu_j N_j$$

So what this tells me is that indeed chemical potential and the Gibbs energy are very closely related if I multiply the chemical potential with the number of molecules and sum it over all the components we get the Gibbs free energy. So when we define the chemical potential as the partial molar Gibbs energy we are not wrong in doing that but when we look in the differential expressions then we have to keep in mind that the chemical potential is also a partial derivative of other energy functions actually whatever energy function or thermodynamic function is appropriate given the control variable should be used for the description of chemical potential.

So this should be like very clear on our minds that although the chemical potential has a close relation with the Gibbs energy that does not mean that we have to always use the Gibbs energy all it means is that we have to first look at which variable is being controlled in the particular problem.

So using these ideas we can now define I would say more rigorously why exactly we get that and to do that we first discuss the idea of homogeneous functions. The thermodynamic functions are examples of homogeneous functions and on these functions there is a theorem called the Euler theorem and if I use the Euler theorem I basically get the same result that I have got using the Gibbs Duhem relation. So the homogeneous function is defined in the following way.

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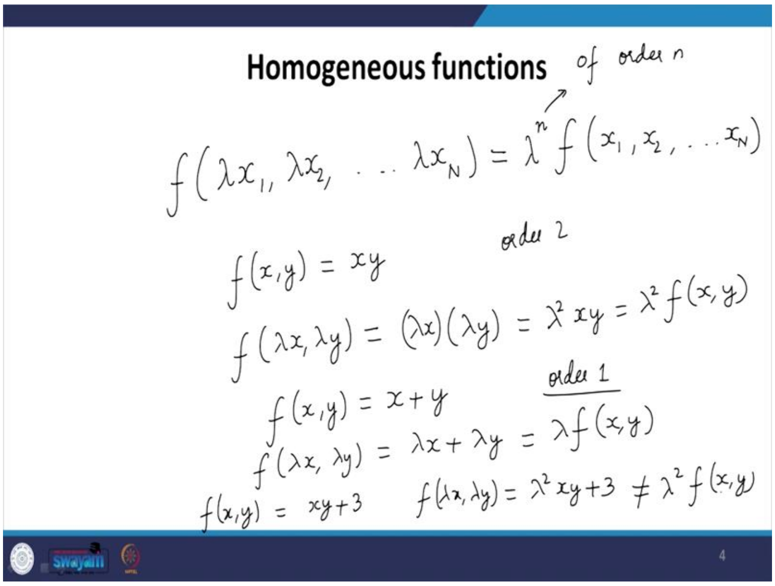

Homogeneous functions of order n

$$f(\lambda x_1, \lambda x_2, \dots \lambda x_N) = \lambda^n f(x_1, x_2, \dots x_N)$$

order 2

$$f(x,y) = xy$$

$$f(\lambda x, \lambda y) = (\lambda x)(\lambda y) = \lambda^2 xy = \lambda^2 f(x,y)$$

order 1

$$f(x,y) = x+y$$

$$f(\lambda x, \lambda y) = \lambda x + \lambda y = \lambda f(x,y)$$

$$f(x,y) = xy+3 \qquad f(\lambda x, \lambda y) = \lambda^2 xy + 3 \neq \lambda^2 f(x,y)$$

Let us say for example a function of variable x_1 x_2 to some variable x_n is such that if I multiply every variable with λ we get-

$$f(\lambda x_1, \lambda x_2 \dots \dots \dots \dots \dots \dots \dots \lambda x_N) = \lambda^n (x_1, x_2 \dots \dots \dots \dots \dots \dots \dots x_N)$$

this is what we call a homogeneous function.

Let us take an example let us say we have-

$$f(x,y) = xy$$

$$f(\lambda x, \lambda y) = (\lambda x)(\lambda y) = \lambda^2 xy = \lambda^2 f(x,y)$$

So in this case n is equal to 2 and n is the order of the homogeneous function so this is a homogeneous function of order 2 if we have some other function it may have a lower order.

Let us say for example we have-

$$f(x,y) = x + y$$

$$f(\lambda x, \lambda y) = \lambda x + \lambda y = \lambda f(xy)$$

So now in this case we have an order 1 homogeneous function in the other case we had order two homogeneous function.

We can think of functions which are not homogeneous, let us say for example if we had-

$$f(x,y) = xy + 3$$

$$f(\lambda x, \lambda y) = \lambda^2 xy + 3 \neq \lambda^2 f(x, y)$$

this is not equal to λ^2 multiplied with function of x and y because if I do that the constant term will be 3 λ^2 not equal to 3.

So only some functions are homogeneous not all the functions are homogeneous. However the functions that we are interested in are all homogeneous function but will come to that in a minute. Let us first discuss the property of homogeneous functions called the Euler theorem.

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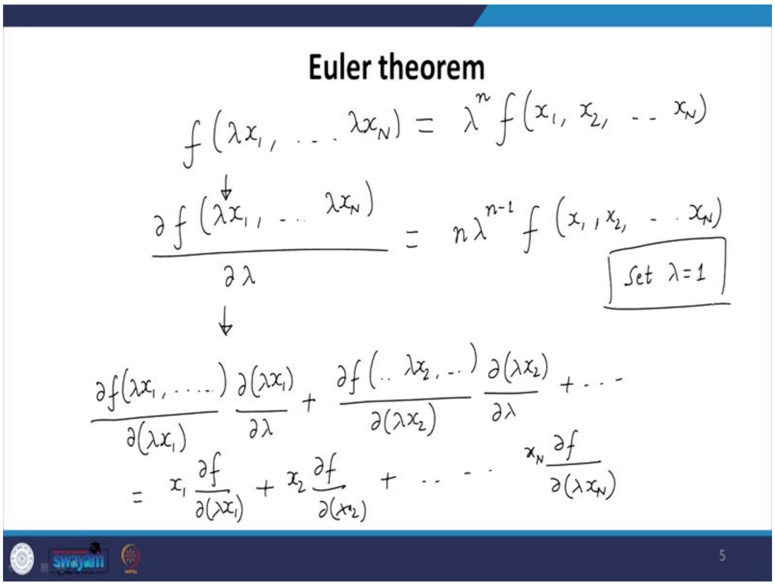

Euler theorem

$$f(\lambda x_1, \ldots \lambda x_N) = \lambda^n f(x_1, x_2, \ldots x_N)$$

$$\downarrow$$

$$\frac{\partial f(\lambda x_1, \ldots \lambda x_N)}{\partial \lambda} = n\lambda^{n-1} f(x_1, x_2, \ldots x_N) \quad \boxed{\text{Set } \lambda = 1}$$

$$\downarrow$$

$$\frac{\partial f(\lambda x_1, \ldots)}{\partial(\lambda x_1)} \frac{\partial(\lambda x_1)}{\partial \lambda} + \frac{\partial f(\ldots \lambda x_2, \ldots)}{\partial(\lambda x_2)} \frac{\partial(\lambda x_2)}{\partial \lambda} + \ldots$$

$$= x_1 \frac{\partial f}{\partial(\lambda x_1)} + x_2 \frac{\partial f}{\partial(\lambda x_2)} + \ldots \; x_N \frac{\partial f}{\partial(\lambda x_N)}$$

So if I start with this particular relation so if I go back to the expression we had for the Euler theorem we had this-

$$f(\lambda\, x_1, \lambda x_2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \lambda x_N = \lambda^n (x_1, x_2 \ldots \ldots \ldots \ldots \ldots \ldots x_N)$$

Now if I take a derivative of this function with respect to λ what do we have is-

$$\partial f(\lambda x\_1 \ldots \ldots \ldots \ldots \lambda x\_N\,)/\partial\lambda = n\lambda\text{^}(n-1)\;\; f(x\_1, x\_2 \ldots \ldots \ldots \ldots \ldots x\_N)$$

because f of (x1 to xn) is not a function of λ so if I now want to take a derivative with respect to λ on the left hand side what you notice is that I want to first take a derivative with respect to the first argument. So the way to do that is we do something like this-

$$\frac{\partial f(\lambda x_1 \ldots \ldots \ldots ..)}{\partial(\lambda x_1)} \frac{\partial(\lambda x_1)}{\partial\lambda} + \frac{\partial f(x_2 \ldots \ldots \ldots)}{\partial(\lambda x_2)} \frac{\partial(\lambda x_2)}{\partial\lambda} + \cdots \ldots \ldots \ldots \ldots ..$$

So what do we get from here is we get-

$$x_1 \frac{\partial f}{\partial(\lambda x_1)} + x_1 \frac{\partial f}{\partial(\lambda x_2)} + \cdots \ldots \ldots \ldots \ldots \ldots \ldots x_N x_1 \frac{\partial f}{\partial(\lambda x_N)}$$

So now if I set the value of λ is equal to 1, what we get is the statement of the Euler theorem that says that-

$$nf(x_1, x_2 \ldots\ldots\ldots\ldots\ldots) = x_1\frac{\partial f}{\partial x_1} + x_2\frac{\partial f}{\partial x_2} + \cdots \ldots\ldots\ldots\ldots..$$

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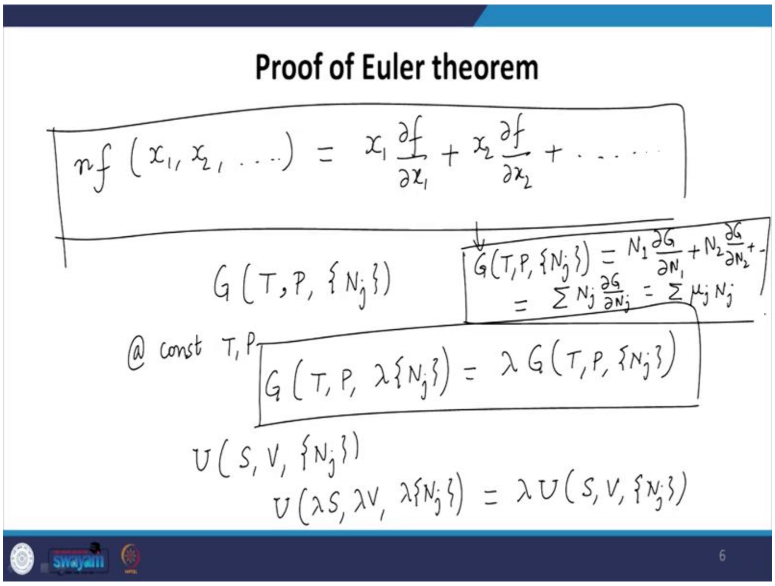

Proof of Euler theorem

$$\boxed{nf(x_1, x_2, \ldots) = x_1\frac{\partial f}{\partial x_1} + x_2\frac{\partial f}{\partial x_2} + \ldots\ldots}$$

$$G(T, P, \{N_j\})$$

$$\boxed{\begin{aligned} G(T,P,\{N_j\}) &= N_1\frac{\partial G}{\partial N_1} + N_2\frac{\partial G}{\partial N_2} + \ldots \\ &= \sum N_j \frac{\partial G}{\partial N_j} = \sum \mu_j N_j \end{aligned}}$$

@ const T, P

$$\boxed{G(T, P, \lambda\{N_j\}) = \lambda G(T, P, \{N_j\})}$$

$$U(S, V, \{N_j\})$$

$$U(\lambda S, \lambda V, \lambda\{N_j\}) = \lambda U(S, V, \{N_j\})$$

So this is what establishes the Euler theorem, we start with the description of the homogeneous function and then take a derivative with respect to λ on both sides and then finally set λ equal to 1 and we get the relation for the Euler theorem.

So now let us see how it is applied in practice let us say for example if I am interested in my Gibbs free energy. So my Gibbs free energy is in terms of temperature pressure and number of molecules. Now clearly temperature and pressure are intensive variable but the number of molecules is not. So in this case I cannot simply multiply temperature with λ or pressure with λ it does not have any meaning but we can multiply N_j with λ and if I do that my system becomes λ times. So my system becomes λ times my energy should also become λ times. So let us say for example if I am working at a constant temperature and pressure because clearly multiplying temperature and pressure by λ time does not make any sense what we have is that-

$$G(T, P, \lambda\{N_j\}) = \lambda G(T, P, \{N_j\})$$

So therefore the Gibbs free energy is a homogeneous function of order 1. Now even if I am doing some other thermodynamic function that still is homogeneous function of order one and why that is- Let us say for example if I look at my internal energy. So now we have S, V and N_j now if I multiply all of them with λ what do we have we have energy of a system of entropy λS of volume λV and of number of molecules λN_j. So clearly if I make my number of molecules λ times entropy automatically becomes λ time volume automatically become λ time and the energy should also become λ times it should not be λ^2 times. So when we increase the system size energy increases in proportion to the system size. So this is also λ (U, S, V, N_j).

So if I use that argument for the first function that we started with and I use Euler theorem what do we notice is that my 'n' that refers to the order that is equal to one. So we have G for temperature, pressure and N_j should be equal to-

$$G(T,P,\{N_j\}) = N_1\frac{\partial G}{\partial N_1} + N_2\frac{\partial G}{\partial N_2}\ldots\ldots\ldots\ldots\ldots. = \sum N_j\frac{\partial G}{\partial N_j} = \sum \mu_j N_j$$

and that is equal to chemical potential.

So what we establish is that the Gibbs free energy is equal to chemical potential multiplied by the number of molecule summed over all the species in the in the system, which is the same result that I have obtained when using the Gibbs Duhem relation.

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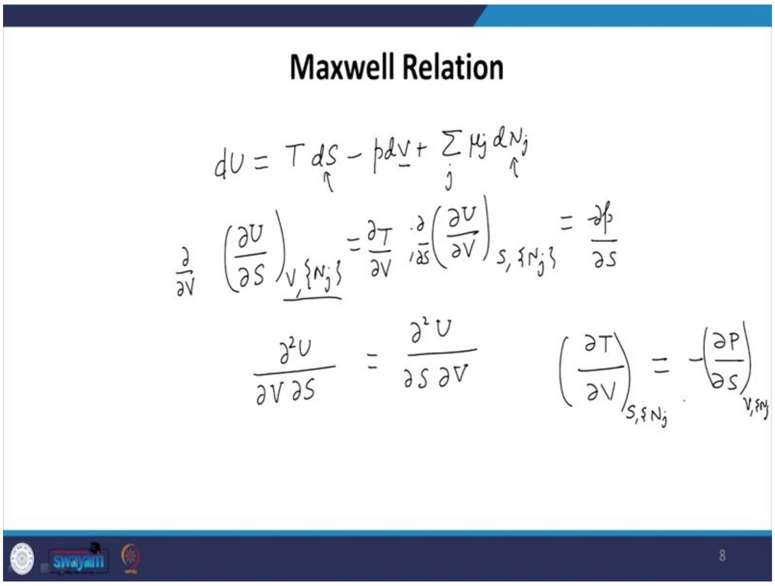

Maxwell Relation

$$dU = T\,\underset{\uparrow}{dS} - p\,d\underline{V} + \sum_j \mu_j\,\underset{\uparrow}{dN_j}$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{\underline{V,\{N_j\}}} = \frac{\partial T}{\partial V} \qquad \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_{S,\{N_j\}} = -\frac{\partial p}{\partial S}$$

$$\frac{\partial^2 U}{\partial V\,\partial S} = \frac{\partial^2 U}{\partial S\,\partial V} \qquad \left(\frac{\partial T}{\partial V}\right)_{S,\{N_j\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{N_j\}}$$

So finally before I conclude I briefly discussed the idea of Maxwell relations although this has been elaborated in the previous thermodynamics class that you may have had it can be easily derived from whatever we have discussed. So the Maxwell relations are based on the idea that if for example if I start with any of the differential forms that I wrote and I compute the first partial derivative what we have is-

$$dU = TdS - pdV + \sum_{j} \mu_j dN_j$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,\{N_j\}} = T$$

$$\left(\frac{\partial U}{\partial S}\right)_{S,\{N_j\}} = -p$$

And now once I have found the first derivative I can take a second derivative with respect to the other variable, and when I take a second derivative there are two possibilities we can take-

$$\frac{\partial}{\partial V} = \frac{\partial^2 U}{\partial V \partial S} \; or \; \frac{\partial}{\partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

So you have a second derivative of U either in the order that we first take derivative with respect to S then with V or we do opposite of that and the argument over which the Maxwell relation builds is both of these has to be the same there is some math that goes behind it but we are not getting in there.

The key point is if I take the derivative in any order for the second derivative we will get the same result. So what we get from here is if I take a derivative with so V we have ∂T by ∂V and we have ∂p by ∂S here. So therefore what we find is ∂T by ∂V is equal to - ∂p by ∂S here we have to be slightly careful about what is being held fixed there. So we already have held the volume fixed in the first derivative with S but when we take derivative with respect to volume we should take the other guys fixed.

So when we are doing the second derivative what is being held fixed is the entropy and the number of moles. In the second case we are taking a derivative with respect to S the second derivative the first derivative does not matter here. The second derivative is with respect to S and therefore we should keep the volume and number of moles constant N-

$$\left(\frac{\partial T}{\partial V}\right)_{S,\{N_j\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{N_j\}}$$

Just like what we have done here for U we can get the same result for other thermodynamic functions.

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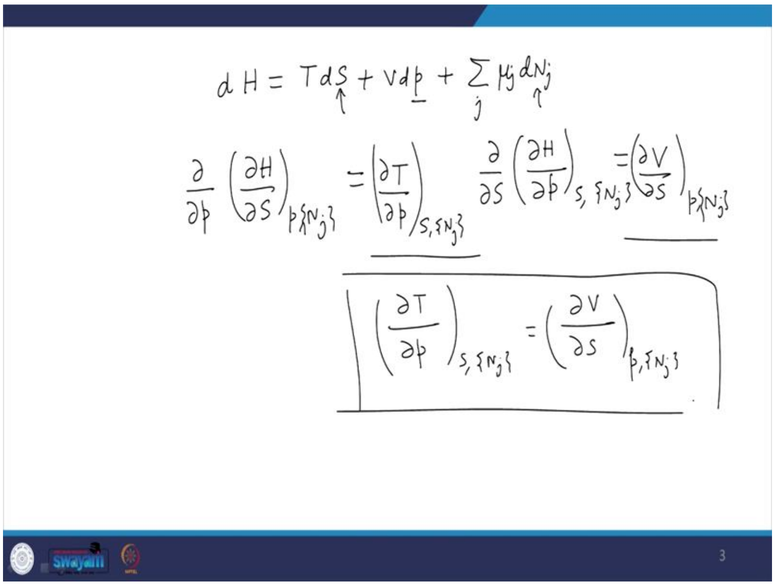

$$dH = Td\underset{\uparrow}{S} + Vd\underline{p} + \sum_j \mu_j d\underset{\uparrow}{N_j}$$

$$\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right)_{p\{N_j\}} = \underline{\left(\frac{\partial T}{\partial p}\right)_{S,\{N_j\}}} \qquad \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)_{S,\{N_j\}} = \underline{\left(\frac{\partial V}{\partial S}\right)_{p\{N_j\}}}$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_{S,\{N_j\}} = \left(\frac{\partial V}{\partial S}\right)_{p,\{N_j\}}}$$

Let us say for example we have-

$$dH = TdS + Vdp + \sum_j \mu_j dN_j$$

$$\left(\frac{\partial H}{\partial S}\right)_{p,\{N_j\}} = T$$

$$\left(\frac{\partial H}{\partial P}\right)_{p,\{N_j\}} = V$$

Now if I take a second derivative the first time I will take with pressure that is the second variable here so what we have is dou T by dou p and now since we are doing with respect to p the variable that is constant is S and Nj and in this case we do with respect to my S so what we have is-

$$\frac{\partial}{\partial S}\left(\left(\frac{\partial H}{\partial P}\right)\right)_{S,N_j} = \left(\left(\frac{\partial V}{\partial S}\right)\right)_{p,N_j}$$

and the variable that is constant is p and N j and therefore these two should be the same so we should have-

$$\left(\frac{\partial T}{\partial P}\right)_{S,\{N_j\}} = \left(\frac{\partial V}{\partial S}\right)_{p,\{N_j\}}$$

And we can do it for all combinations of variables for all thermodynamic functions so in total we will have so many Maxwell relations. Now the key advantage of Maxwell relations is the following if for example I know the pressure volume temperature relation for any system and this i can get from experiments let us say for the case of an ideal gas we know PV = NRT. If it is some other system we may have to do experiments and find that. Now once we have found that then using that p, V, T relation or the equation of state that is what it is called we can find the thermodynamic functions by the use of the Maxwell relations.

So in this lecture I have basically demonstrated few concepts the first was the idea of Gibbs Duham relation that is we cannot have only the intensive variable as controlling variables. Then we discussed the idea of homogeneous functions we established the well the relations for absolute values of thermodynamic functions and finally we discussed the idea of Maxwell relations and I touched it very briefly because this is something that you must have done in your undergrad thermodynamics.

So with that I conclude here, thank you.

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