Statistical Mechanics
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Lecture – 15
Consequence of Stability of Thermodynamic Potentials

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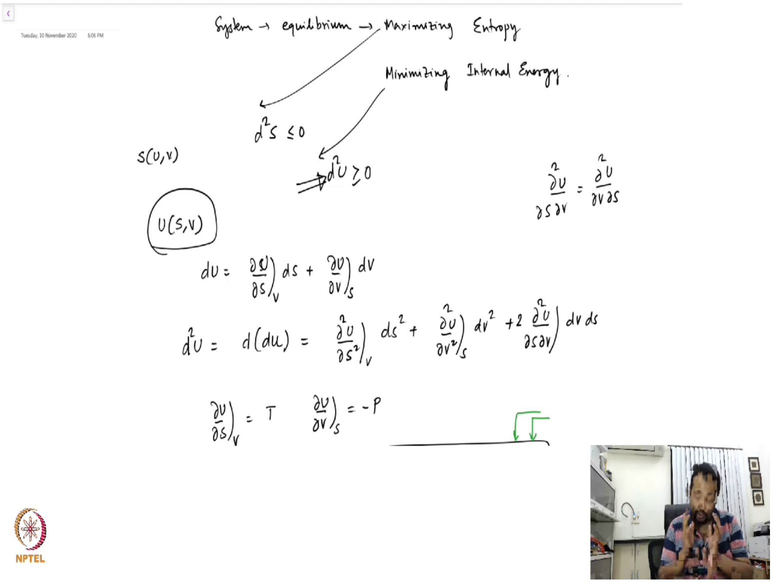

Tuesday, 10 November 2020 6:06 PM

System → equilibrium → Maximizing Entropy

Minimizing Internal Energy.

$d^2S \leq 0$

$S(U,V)$

$\Rightarrow d^2U \geq 0$

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

$U(S,V)$

$$dU = \left.\frac{\partial U}{\partial S}\right)_V dS + \left.\frac{\partial U}{\partial V}\right)_S dV$$

$$d^2U = d(dU) = \left.\frac{\partial^2 U}{\partial S^2}\right)_V dS^2 + \left.\frac{\partial^2 U}{\partial V^2}\right)_S dV^2 + 2\left.\frac{\partial^2 U}{\partial S \partial V}\right) dV\,dS$$

$$\left.\frac{\partial U}{\partial S}\right)_V = T \qquad \left.\frac{\partial U}{\partial V}\right)_S = -P$$

Welcome back. So, we looked at the stability criteria for a thermodynamic system and we essentially said that a system goes into an equilibrium by maximizing entropy or alternatively minimizing internal energy.

Now, this we had seen in a earlier lecture that this would mean that d 2 S must be less than equal to 0 and this means that d 2 U is greater than equal to 0. But, the idea now is what does it really mean for the system this is all very good I mean I have written down an expression, a differential form of my stability criteria, but what it mean real life how does the stability criteria translate to the system.

So, for that we want to consider U as a function of S and V. So, essentially I am going to focus on the minimization of the internal energy, one can also do the maximization of the entropy and one should expect to get this one should get the same result.

Now, clearly here if I write down the change in the internal energy this would be del U del S volume constant time dS plus del U del V entropy constant time dV. I now want to calculate the second d 2 U and for that I can just write down this way treat du as a function. And, once one does this algebra, this calculus one will come up with the expression dS square plus del 2 u del V 2 S dV square plus del 2 U del S del V.

There is going to be two factor dU d sorry, this is dV dS. The two factor comes in because essentially we have said that the mixed derivatives are equal which means that del 2 U del S del V is equal to del 2 U del V del S and that essentially follows because U is a state function.

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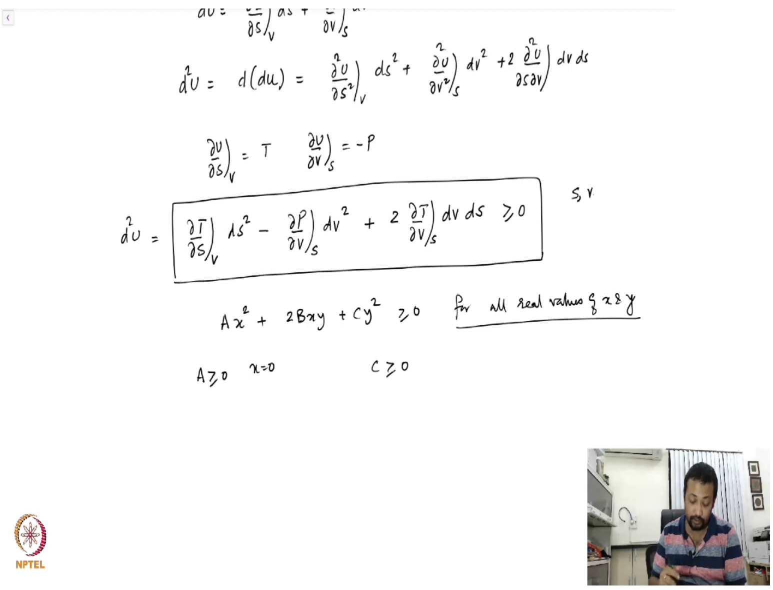

$$dU = \left.\frac{}{\partial S}\right)_V dS + \left.\frac{}{\partial V}\right)_S$$

$$d^2U = d(dU) = \left.\frac{\partial^2 U}{\partial S^2}\right)_V dS^2 + \left.\frac{\partial^2 U}{\partial V^2}\right)_S dV^2 + 2\left.\frac{\partial^2 U}{\partial S \partial V}\right) dV\,dS$$

$$\left.\frac{\partial U}{\partial S}\right)_V = T \qquad \left.\frac{\partial U}{\partial V}\right)_S = -P$$

$$d^2U = \boxed{\left.\frac{\partial T}{\partial S}\right)_V dS^2 - \left.\frac{\partial P}{\partial V}\right)_S dV^2 + 2\left.\frac{\partial T}{\partial V}\right)_S dV\,dS \geq 0} \qquad S, V$$

$$Ax^2 + 2Bxy + Cy^2 \geq 0 \quad \underline{\text{for all real values of } x \,\&\, y}$$

$$A \geq 0 \quad x=0 \qquad\qquad C \geq 0$$

Now, I can write down this in terms of the derivative. So, if you recall then I know that del U del S volume constant is temperature and del U del V entropy constant is minus pressure.

So, if I use this then it follows that d 2 U is equal to del T del S volume constant d S square plus. So, it is minus because this is del P del V entropy constant dV square plus twice del T del V entropy constant dV dS and our minimization principle means that this must be greater than equal to 0.

So, question is how to what restrictions? So, this must be true for any arbitrary variation in S, V, but what does it really mean? Now, for that let us for a second step back and look at the following inequality Ax square plus twice Bxy plus Cy square is greater than 0 for all real values of x and y.

Now, clearly the obvious thing that you should say or that will come to the mind that if this is inequality is true for any real value of x and y this would mean that a must be greater than equal to 0 and C must be greater than equal to 0.

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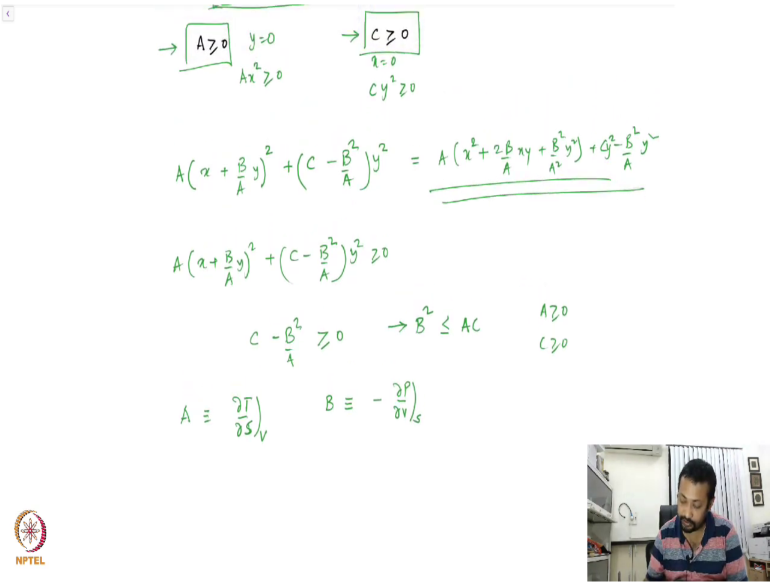

$\rightarrow \boxed{A \geq 0}$ $y = 0$ $Ax^2 \geq 0$ $\rightarrow \boxed{C \geq 0}$ $x = 0$ $Cy^2 \geq 0$

$$A\left(x + \frac{B}{A}y\right)^2 + \left(C - \frac{B^2}{A}\right)y^2 = \underline{\underline{A\left(x^2 + \frac{2B}{A}xy + \frac{B^2}{A^2}y^2\right) + Cy^2 - \frac{B^2}{A}y^2}}$$

$$A\left(x + \frac{B}{A}y\right)^2 + \left(C - \frac{B^2}{A}\right)y^2 \geq 0$$

$$C - \frac{B^2}{A} \geq 0 \quad \rightarrow B^2 \leq AC \qquad A \geq 0 \quad C \geq 0$$

$$A \equiv \left.\frac{\partial T}{\partial S}\right)_V \qquad B \equiv -\left.\frac{\partial P}{\partial V}\right)_S$$

Why? Because I can choose x equal to 0. Sorry, in this case I will choose y is equal to 0 and that means, inequality now will take the form Ax square is greater than 0 since x is being square it is always positive. Therefore, it also means that A has to be positive. And, here also it means here of course, we will take x equal to 0 and the inequality takes the form Cy square is equal to 0. Once again y is being squared here therefore, y is a positive quantity therefore, C has to be a positive quantity.

So, these are the two obvious restrictions on the coefficients that I have, correct? Now, can I do more? As it turns out I can do more I can recast this equation in terms of perfect squares, how? Well, that is little bit of an algebra that you have to do. So, I can write down this as B over A y whole square plus C minus B square over A y square.

If you expand the right left hand side and if you just expand this expression you will see that this is going to be x square twice B over A xy plus B square over A square y square plus C minus B square over A y square Cy square. And, if you just do the simple algebra then you will see that the this expression on the right hand side is exactly the expression that we have written down over here.

So, therefore, this inequality I can recast in the form that A of x plus B over A y whole square plus C minus B square over A y square must be greater than equal to 0. Once again this would mean that C minus B square over a must be greater than equal to 0 which means that B square must be less than a times C

Note that together with the previous constraint these this one a superfluous because I already know that A is positive, C is positive. For example, if B square is less than AC and A is greater than equal to 0, then C is also greater than equal to 0 anyway. So, we will consider the all the three conditions together. So, we have a positive C positive and B square positive this, right.

Once I have this now let us identify what A, B and C is corresponding to this inequality that we have written down for the minimization of the energy. So, it means that A is identical to del T del S volume constant, B is identical to minus del P del V entropy constant and C is identical to del T del V entropy constant.

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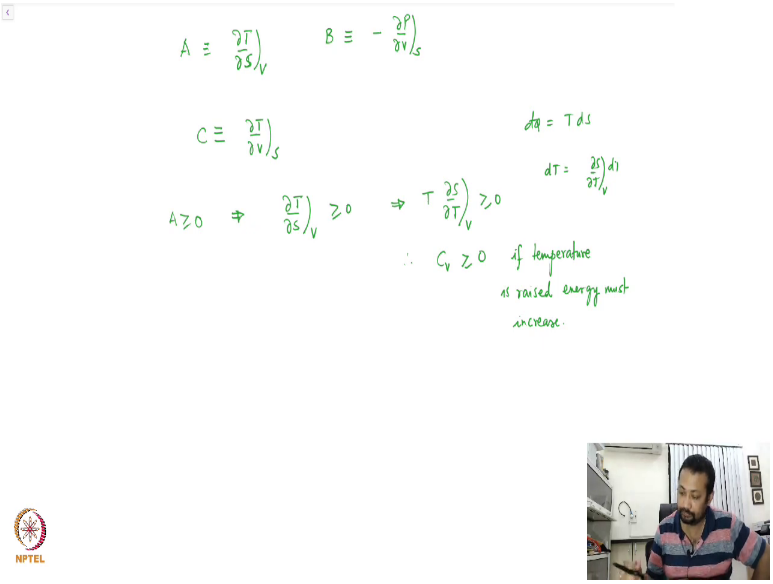

$$A \equiv \left.\frac{\partial T}{\partial S}\right)_V \qquad B \equiv -\left.\frac{\partial P}{\partial V}\right)_S$$

$$C \equiv \left.\frac{\partial T}{\partial V}\right)_S$$

$$đq = T\,dS$$

$$dT = \left.\frac{\partial S}{\partial T}\right)_V dT$$

$$A \geq 0 \Rightarrow \left.\frac{\partial T}{\partial S}\right)_V \geq 0 \Rightarrow T\left.\frac{\partial S}{\partial T}\right)_V \geq 0$$

$\therefore\ C_V \geq 0$ if temperature is raised energy must increase.

So, A is greater than equal to 0, implies that del T del S at volume constant is greater than 0 which in turn implies that del S del T times T volume constant must be greater than equal to 0. And, therefore, you immediately conclude that the specific heat at constant volume must be positive which essentially means that if temperature is raised energy must increase or in other words if you give heat to the system it is temperature must increase.

Because T dS remember is equal to d cut q over t. So, if you are giving if T dS is positive delta T must be also positive because this derivative T dS del S del T volume constant is positive. So, if you do not if you have trouble recalling things, then you can immediately see that your dT must be del S del T volume constant right.

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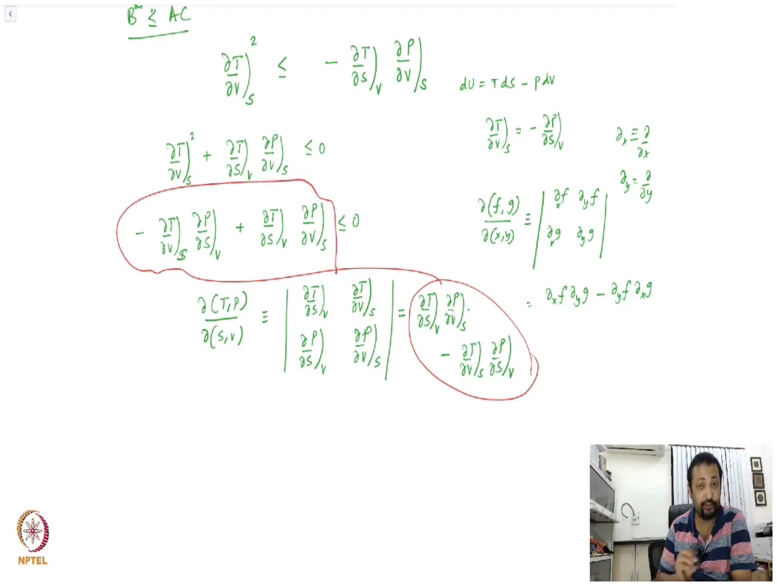

$B^2 \leq AC$

$$\left.\frac{\partial T}{\partial V}\right)_S^2 \leq -\left.\frac{\partial T}{\partial S}\right)_V \left.\frac{\partial P}{\partial V}\right)_S$$

$dU = TdS - PdV$

$$\left.\frac{\partial T}{\partial V}\right)_S = -\left.\frac{\partial P}{\partial S}\right)_V$$

$\partial_x \equiv \frac{\partial}{\partial x}$

$\partial_y = \frac{\partial}{\partial y}$

$$\left.\frac{\partial T}{\partial V}\right)_S^2 + \left.\frac{\partial T}{\partial S}\right)_V \left.\frac{\partial P}{\partial V}\right)_S \leq 0$$

$$\frac{\partial(f,g)}{\partial(x,y)} \equiv \begin{vmatrix} \partial_x f & \partial_y f \\ \partial_x g & \partial_y g \end{vmatrix} = \partial_x f \partial_y g - \partial_y f \partial_x g$$

$$-\left.\frac{\partial T}{\partial V}\right)_S \left.\frac{\partial P}{\partial S}\right)_V + \left.\frac{\partial T}{\partial S}\right)_V \left.\frac{\partial P}{\partial V}\right)_S \leq 0$$

$$\frac{\partial(T,P)}{\partial(S,V)} \equiv \begin{vmatrix} \left.\frac{\partial T}{\partial S}\right)_V & \left.\frac{\partial T}{\partial V}\right)_S \\ \left.\frac{\partial P}{\partial S}\right)_V & \left.\frac{\partial P}{\partial V}\right)_S \end{vmatrix} = \left.\frac{\partial T}{\partial S}\right)_V \left.\frac{\partial P}{\partial V}\right)_S - \left.\frac{\partial T}{\partial V}\right)_S \left.\frac{\partial P}{\partial S}\right)_V$$

Now, B greater than 0, implies that minus del P del V is good entropy constant is greater than 0. So, this essentially means that del V del P 1 by V minus is also a positive quantity and this effectively means that kappa T must be sorry, kappa S because your entropy has being held over constant over here must be positive quantity.

So, if pressure is applied then volume must decrease. Come down to the third equation; the third condition where we had B square is less than equal to AC. Now, B square in our particular case B is del T del V entropy constant. Therefore, this whole square is less than equal to minus del T del S volume constant and del P del V entropy constant right.

So, now, what I can do over here is I will write down this as del T del V entropy constant square plus del T del S volume constant del P del V entropy constant must be less than equal to 0. So, now there is a very clever manipulation if you recall d U was T dS minus p dV and therefore, del T del V entropy constant is minus del P del S volume constant.

So, I am going to keep one del T del V entropy constant and you will see in a moment why I want to keep it and I am going to replace the other one thus another big since is a square del P del S volume constant minus plus del T del S volume constant del P del V entropy constant must be less than equal to 0.

Now, can you see that this is T comma P del of S comma V. Why? Because if you just remember the Jacobian del of f, g comma x comma y is equivalent to del f del y del x del y which was del x f del y g minus del y f del x g, where del x is identical to del del x and del y is identical to del del y.

Of course, when I write down del x it means the y is being held constant. So, if I look at this is identical to del T del S volume constant, del T del V entropy constant, del P del S volume constant, del P del V entropy constant which is equal to del T del S volume constant times del P del V entropy constant minus I will write down in the next line minus del T del V entropy constant del P del S volume constant.

And, this expression that you have seen over here in the right hand side is exactly the expression in the right hands in the left hand side of the inequality. So, we basically very cleverly manipulated this expression in the form of into the form of a Jacobian.

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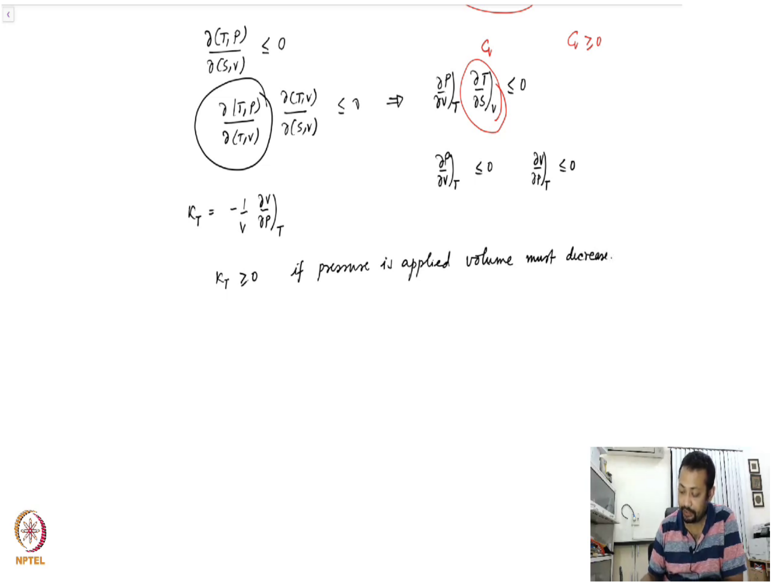

$$\frac{\partial(T,P)}{\partial(S,V)} \leq 0$$

$$\frac{\partial(T,P)}{\partial(T,V)} \frac{\partial(T,V)}{\partial(S,V)} \leq 0 \Rightarrow \left.\frac{\partial P}{\partial V}\right)_T \overset{C_v}{\left.\frac{\partial T}{\partial S}\right)_V} \leq 0 \qquad C_v \geq 0$$

$$\left.\frac{\partial P}{\partial V}\right)_T \leq 0 \qquad \left.\frac{\partial V}{\partial P}\right)_T \leq 0$$

$$K_T = -\frac{1}{V} \left.\frac{\partial V}{\partial P}\right)_T$$

$K_T \geq 0$ if pressure is applied volume must decrease.

Therefore, now our inequality is del T comma p del S comma V must be less than equal to 0 what can we do now again now I know. So, I know how to manipulate Jacobians. So, I am going to write down this as T comma P divided by del of T comma V del of T comma V del of S comma V must be less than equal to 0.

This from the definition of Jacobian this implies this first part of it is del P del V temperature constant and the second part of it is del T del S and volume constant must be less than equal to 0. But, this derivative del T del S is nothing, but specific heat C V.

Now, C V is positive. Since C V is positive it follows that del P del V temperature constant is less than equal to 0, which means of course, del V del P temperature constant is less than equal to 0. The isothermal compressibility just as we had defined the adiabatic compressibility or isentropic compressibility is defined as minus 1 by V del V del P temperature constant.

And, since del V del P temperature constant is less than 0, this would mean that the at isothermal compressibility is also a positive quantity which means if pressure is applied volume must decrease. So, therefore, the whole point of this discussion that we have been having for so long is that the stability criteria essentially puts a severe restriction on the response function.

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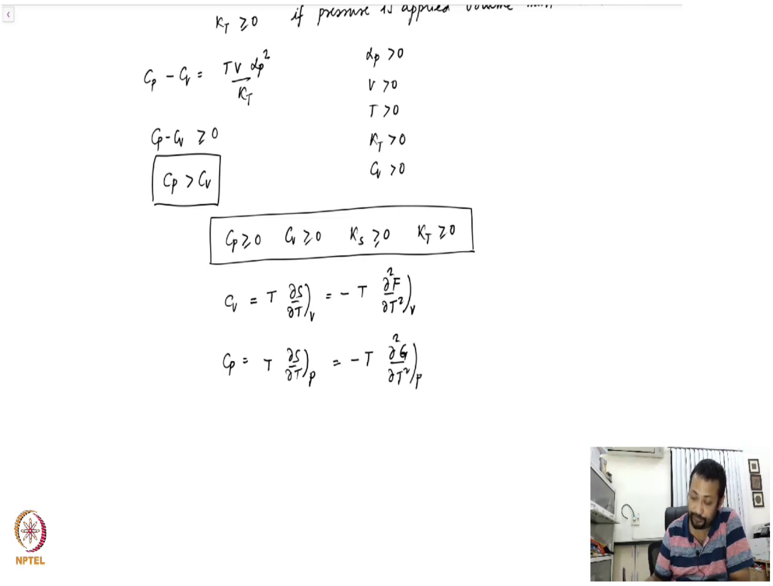

$\kappa_T \geq 0$ if pressure is applied volume

$$C_p - C_v = \frac{T V \alpha_p^2}{\kappa_T}$$

$\alpha_p > 0$

$V > 0$

$T > 0$

$\kappa_T > 0$

$C_v > 0$

$C_p - C_v \geq 0$

$$\boxed{C_p > C_v}$$

$$\boxed{C_p \geq 0 \quad C_v \geq 0 \quad \kappa_s \geq 0 \quad \kappa_T \geq 0}$$

$$C_v = T \left.\frac{\partial S}{\partial T}\right)_V = -T \left.\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$C_p = T \left.\frac{\partial S}{\partial T}\right)_P = -T \left.\frac{\partial^2 G}{\partial T^2}\right)_P$$

The specific heats C P minus C V which is T V alpha P square over kappa T alpha P is positive volume is positive temperature is positive kappa T is positive and further C V is also positive this means that C P minus C V is greater than equal to 0 and therefore, it follows that C P is greater than C V.

So, the whole this stability criteria that we have minimized the energy you will get the same identical results if you had used the entropy maximization principle this means C V greater than 0 kappa S greater than 0 kappa T greater than equal to 0. So, this is the restrictions on my response function.

Now, thermodynamics puts this restrictions from a different perspective namely that my equilibrium is a stable equilibrium. If the equilibrium is an unstable equilibrium, then I violate the minimization of the energy principle inequality corresponding to that and therefore, all these inequalities, all these restrictions of the positivity of the response function does not hold.

Statistical mechanics once we when we do it we will also see that status in statistical mechanics essentially you also have the same positivity of the response function they emerge from a different idea. In state may it is a fluctuations which are more important and you will see that the distribution of this fluctuations of any physical quantity are very important.

And, you will see that the distribution of this fluctuations of these physical quantities the width of this distributions are determined by the response function we shall deal with it when we come to that. Right now we want to write down is C V is T del S del T volume constant and therefore, this if I recall is del 2 F del T 2 volume constant. C p you recall is T del S del T pressure constant which is minus T del 2 G del T 2 pressure constant.

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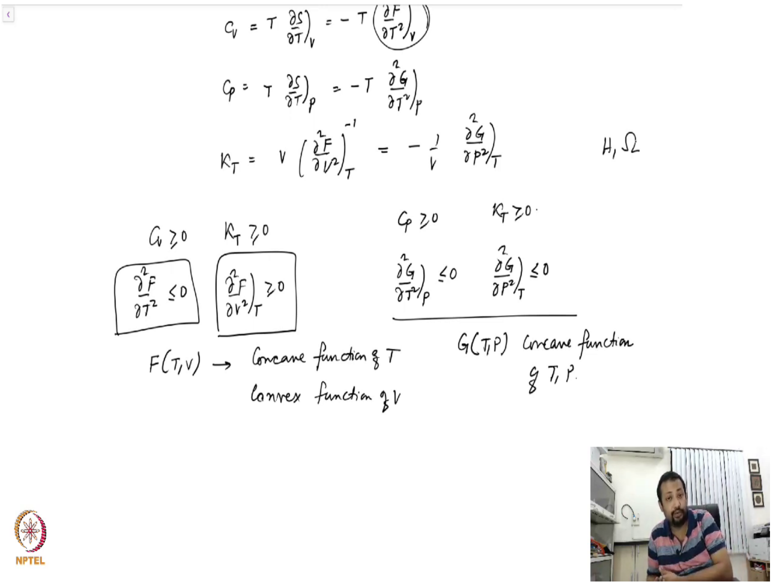

$$C_V = T \left.\frac{\partial S}{\partial T}\right)_V = -T \left(\left.\frac{\partial^2 F}{\partial T^2}\right)_V\right)$$

$$C_P = T \left.\frac{\partial S}{\partial T}\right)_P = -T \left.\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$\kappa_T = V \left(\left.\frac{\partial^2 F}{\partial V^2}\right)_T\right)^{-1} = -\frac{1}{V} \left.\frac{\partial^2 G}{\partial P^2}\right)_T \qquad H, \Omega$$

$C_V \geq 0$ $\quad$ $\kappa_T \geq 0$

$\boxed{\frac{\partial^2 F}{\partial T^2} \leq 0}$ $\quad$ $\boxed{\left.\frac{\partial^2 F}{\partial V^2}\right)_T \geq 0}$

$F(T,V) \rightarrow$ Concave function of T

Convex function of V

$C_P \geq 0$ $\quad$ $\kappa_T \geq 0$

$\left.\frac{\partial^2 G}{\partial T^2}\right)_P \leq 0$ $\quad$ $\left.\frac{\partial^2 G}{\partial P^2}\right)_T \leq 0$

$G(T,P)$ Concave function of T, P.

And kappa T the isothermal compressibility is V del 2 f del V 2 inverse temperature constant. If you write down it if you want to write down in terms of Gibbs free energy it is minus 1 by V del 2 G del P 2 temperature constant right.

So, C V is greater than equal to 0 and kappa T is greater than equal to 0 right and this essentially means that if I look at this expression over here this would mean that del 2 F del T 2 must be less than equal to 0. The kappa T is positive would mean that del 2 F del V 2 temperature constant must be positive, correct.

I also have C P greater than 0 and kappa T greater than 0 which would mean that del 2 G del T 2 P is less than equal to 0 and del 2 G del P 2 temperature constant must be less than equal to 0. Therefore, the stability criteria of the energy means that the Helmholtz free energy F which is a function of T V and n I am suppressing the n because I have considered it to be a fixed quantity is essentially a concave function of T because of this and a convex function of volume.

So, F is a concave function of T and a convex function of volume. In contrast the Gibbs free energy G which is a function of T and P is a concave function of T and P. So, we will conclude this discussion on stability criteria I invite you to look at H and omega and to figure out how this functions thermodynamic potentials are going to behave. I leave it as to you as an exercise.

I will also leave you that I will as an exercise that if you start with entropy where we had started with U as S comma V, if you start with S as function of U and V you should do the calculation and see that you will come to the same result.