Classical Physics

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Lecture No. # 23

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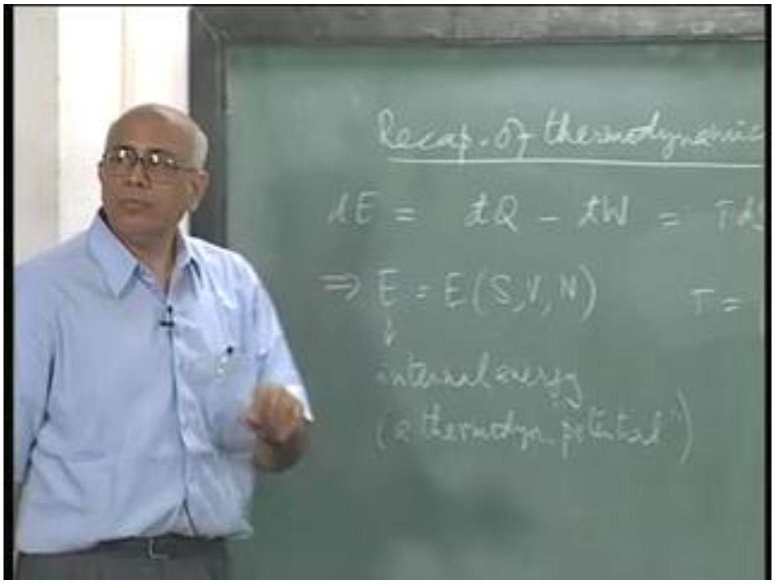

The E is some kind of thermodynamic potential, which is a function of independent variables S, V and N this was the energy representation. Now, I have written down the first 2 laws of thermodynamics here. And of course, the moment you say that E is a state function, which depends on values of these variables S, V and N. Then this at once implies for instance, that T is equal to delta E over delta S keeping V and N constant, the pressure P this coefficient is minus delta E over delta V keeping S and N constant and similarly, mu is delta E over delta N keeping S and V constant.

So, these are standard thermodynamic relations, it tells us that these coefficients the integrating factors really are these partial derivatives of E with respect to S, V and N. So, this much is obvious from elementary calculus. Now, the physical input comes in when you start asking what is the significance of various partial derivatives and derivatives of those and so on and it depends on what you would like to call control variables? It is not very convenient to call S a control variables, it is not very convenient to call S a control variable it is not easy to control the S in a system, it is easier to control E for instance.

So, 1 starts doing a set of Legendre transformations. Now, this quantity here is like a is the internal energy of the system and an example, of a thermodynamic “potential” the reason the word potential is used is because, if I take its derivatives with respect to variables S, V and N the independent variables then I get the other physical quantities here so, in that sense anything you differentiate you get other quantities from mechanical analysis where you differentiate the potential with respect to cords to get the force in the same sense if you take derivatives here of these thermodynamics of this thermodynamic potential, you end up with various physical quantities.

So, this much is elementary thermodynamics here. But you need further input to make progress and 1 of them is the following, you also must assume that you are in the so called thermodynamic limit of statistical mechanics. In other words, the limit in which the volume tends to infinity, the number of particles tends to infinity and then the ratio of volume to the number of particles to the volume, is some density its fixed that is an intensive quantity.

So, 1 would like to proceed to this thermodynamic limit and in that limit the assumption is in thermodynamics that these extensive quantities these quantities which increase with the system size, they lead to this E here and you make a further assumption that the this E is a homogenous function of these variables.

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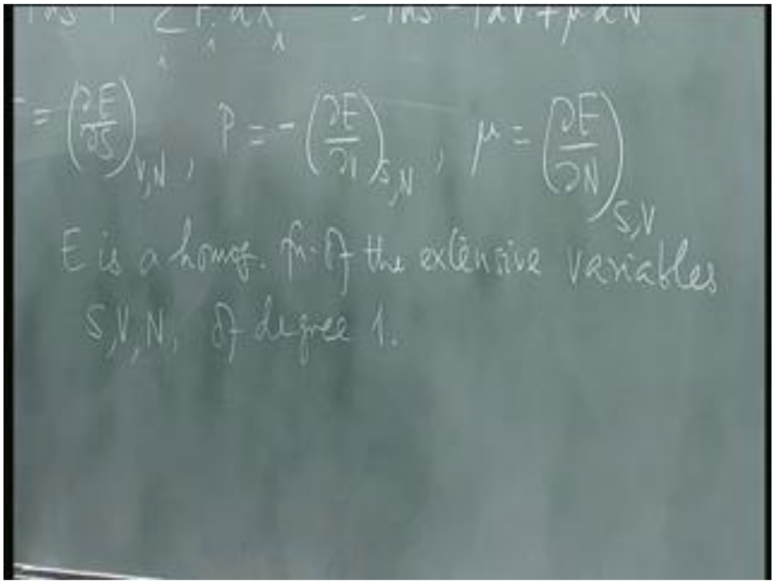

$$= \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

E is a homog. fn. of the extensive variables S, V, N, of degree 1.

So, the assumption is that E is a homogenous function of the extensive variables S, V and N. So, you increase those variables in some proportion then E increases. And further, of degree 1 this is based on our experience, that the total energy increases with number of particles linearly and not like this square or the cube or something like that.

The moment this assumption is made that it is the homogenous function of these guys, then of course elementary calculus gives you Eulers theorem tells you, remember Eulers theorem it says you have a function f of x, y, z etcetera which is a homogenous function of some degree r then it says that x delta f over delta x plus y delta f over delta y plus etcetera is equal to r times f if it is a homogeneous function of degree r. Or another way of saying it, is that is this is a homogenous function of degree r, if f of lambda x lambda y lambda z dot dot dot, where lambda is some constant change all these variables you scale them up by some lambda and this is equal to lambda to the power r f of x, y, z etcetera.

This is what is meant by homogenous function, for example x square plus x y plus y square is a homogeneous function of degree 2, because you scale up x you scale up y you get a lambda square coming out constantly there is a generalization of that concept which we will talk about you could scale up x in one way like lambda to the power alpha 1, you could scale up y by lambda to the alpha 2 and so on you could scale each 1 of them by a different scale variable.

And then of course, there is a generalized homogenous relation the analog of Eulers relation which I will talk about later on when we need it.

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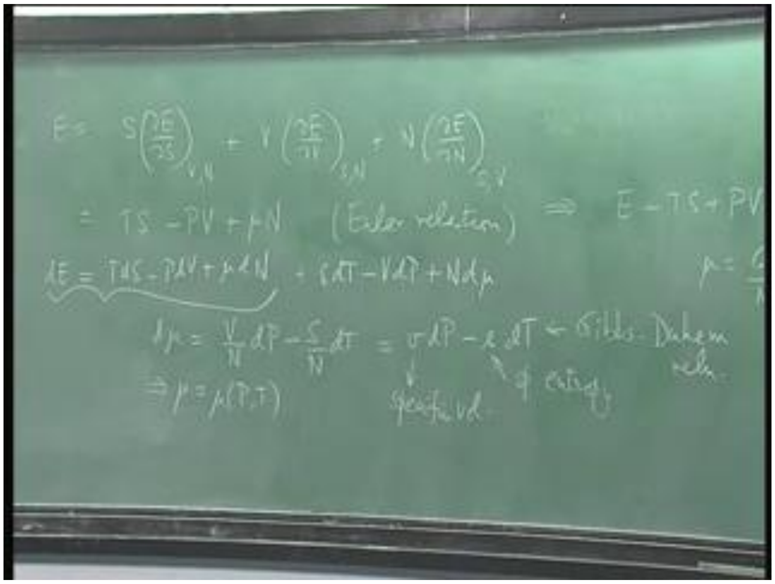


$$E = S\left(\frac{\partial E}{\partial S}\right)_{V,N} + V\left(\frac{\partial E}{\partial V}\right)_{S,N} + N\left(\frac{\partial E}{\partial N}\right)_{S,V}$$

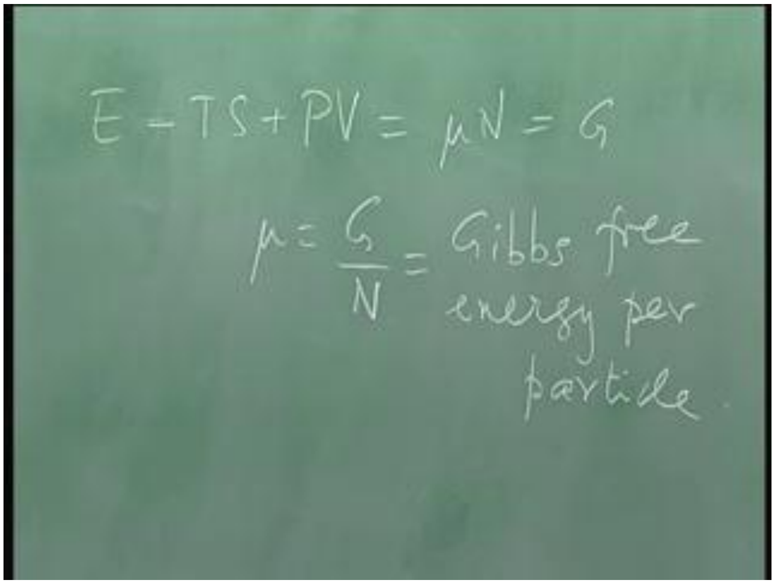
$= TS - PV + \mu N$ (Euler relation) $\Rightarrow E - TS + PV$

$\underbrace{dE = TdS - PdV + \mu dN} + SdT - VdP + Nd\mu$ $\qquad \mu =$

$d\mu = \frac{V}{N}dP - \frac{S}{N}dT = \underset{\substack{\downarrow \\ \text{specific vol.}}}{v}\,dP - s\,dT$ ← Gibbs-Duhem rel.

↖ sp. entropy

$\Rightarrow \mu = \mu(P,T)$



$E - TS + PV = \mu N = G$

$\mu = \frac{G}{N} =$ Gibbs free energy per particle.

But if you assume that E is a homogeneous function of degree 1 then it immediately follows from elementary calculus from Eulers theorem, that this assumption immediately says that E is equal to S delta E over delta S at V and N plus V delta E over delta V at S and N plus mu N sorry N delta E over delta N at S and V constant S and V of degree 1 so its E to the power 1.

But then if you substitute for what goes on here we know that, delta E over delta S is T so this is equal to T S and this is minus P V and this is plus mu N thus this quantity is mu. This relation is called Euler relation. Pease notice, that you made a further physical input here thermodynamics gives you only the loss of thermodynamics give you only increments and tells you what is dE that is it.

It does not tell you what E is at in absolute terms. But this extra assumption, this assumption of homogeneity of degree 1 that immediately tells you that E itself must be equal to this these are not increments. So, it is actually giving you an extra input you have to check against statistical mechanics whether this is really true or not, but if this is true then look at what happens it immediately incidentally this also tells you, that this implies, that E plus P V E minus T S plus P V is equal to mu N. But, what is E minus T S plus P V? It is the Gibbs free energy.

Because, if you go back here and do various Legendre transforms which I will do in a minute you can look at different independent variables here and the Gibbs free energy is in fact defined as the free energy or the potential when you have the control variables P T and N instead of S V and N. So, this is also equal to G and that gives you an interpretation of mu, the chemical potential this immediately implies, mu is equal to G over N equal to Gibbs free energy per particle. So, that is an interesting is a simple way of remembering what the physical meaning of this chemical potential is? It is in fact the Gibbs free energy per particle.

And we will see, when we talk about phase transitions, if you take a beaker and water and you boil it in this room then at the surface the pressure is 1 atmosphere and that is the same in the liquid phase or in the gas phase, exactly 1 atmosphere and its, clear that when you have a situation of boiling? When the 2 phases co-exist in thermal equilibrium, it must be energetically as easy to put it in 1 phase as in the other it must cost exactly the same energy to put it either in the liquid phase or in the vapor phase, what is the meaning of that? Means the chemical potentials are exactly the same.

That is the reason, where in the case of phase equilibrium you insist, that the chemical potentials be the same in the 2 phases. Because generally these phase transitions occur at constant pressure and a given temperature, if you change those conditions then it is of course it is some other condition. But if you took water and just boiled it freely in the atmosphere, it is the pressures that are the same and therefore the chemical potentials are the same.

So, there are other things that the I mean the chemical potential is also equal to this, it is the rate of change if internal energy with the number of particles at fixed entropy and volume but this is not a directly experimentally accessible thing unlike this which tells you immediately, what this relation is? Now, what is the consequence of this immediately? It says since, E is equal to this we could ask what is dE and that is equal to T dS minus P dV plus mu dN I differentiate all these guys here but then there extra terms plus S dT minus V dP plus N d mu so, that is the total dE.

On the other hand, the loss of thermodynamics, tell you that is equal to that. You put that N you get a relation which says that d mu is equal to V over N dP minus S over N dT, says this is zero. This set of quantities this sum here is zero which you can write as d mu is this or V over N is the volume per particle the specific volume little v so little v dP minus little s dT and this is the specific volume and that is the specific entropy. The entropy per particle and the volume per particle they are intensive quantities because, you divide it by the number of particles.

And what does that relation tells you in its turn, it says that the chemical potential of a system is a function of its of this kind of a system, is a function of its pressure and temperature alone. Because, d mu is linear combination of dP and dT so, it is says that once you know the pressure and temperature you know the chemical potential. This relation here is called the Gibbs duhem relation this thing the d mu is V dP minus S dT. What is the Gibbs duhem relation in a more general context?

Notice, that I wrote this, if I include T dS also as part of a force and a flux if I call T a generalized force and S the corresponding generalized flux.

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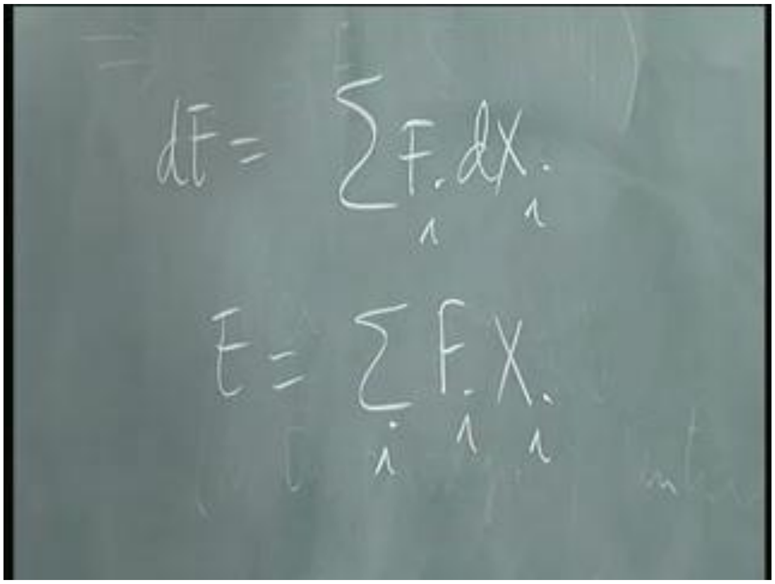
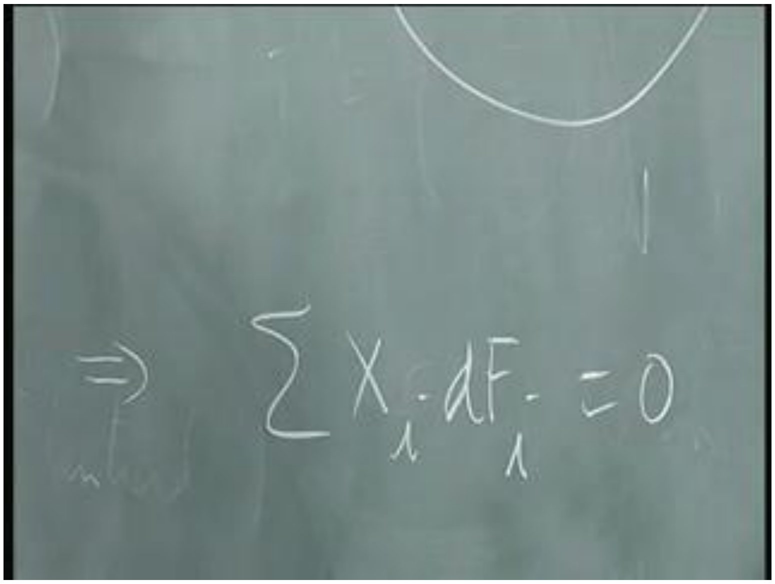


$$dE = \sum F_i dX_i$$

$$E = \sum_i F_i X_i$$



$$\Rightarrow \sum X_i dF_i = 0$$

Then you can see, that what is happening is that you end up with a relation which says loosely speaking, if dE is equal to summation Fi dXi including this also inside it, put it inside there, call that 1 more force and flux. Then that is the set of loss of thermodynamics and the homogeneity argument tells you that E equal to summation i Fi Xi and this immediately implies that summation Xi dFi must be equal to zero.

So, the fluxes times the increments in the generalized forces that must be equal to zero, that is the generalized Gibbs duhem relation, which arose a consequence of our homogeneity assumption and that breaks down and of course, this is not true. There are systems where this is not true, where the energy may increase like not the power like N but N to a higher power than 1 and then of course, such systems you do not have this extensively property and normal conventional thermodynamics could not be valid.

You would have to make modifications, this could happen for instance, if you have gravitational force, then if you have a sufficient number of particles that could collapse. But all in the lone field attract each other and fall in and you may not have stable thermal equilibrium in such a situation. But apart from those exotic situation in most normal cases, this is what happens although I did this in a language of single component fluid here you can generalize this in this fashion whole thing is susceptible to generalization.

Now, what are their Legendre transforms? We talked about well, let us write those potentials down.

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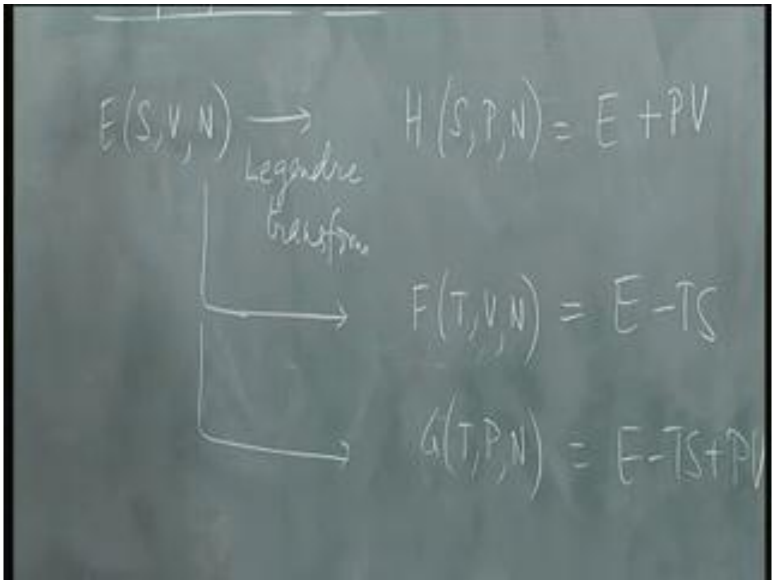
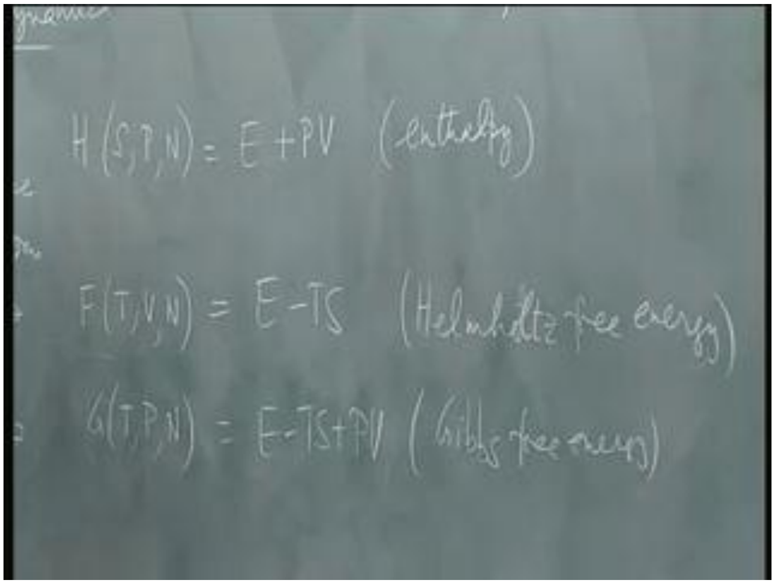


$$E(S,V,N) \xrightarrow{\text{Legendre transfm}} H(S,P,N) = E + PV$$

$$F(T,V,N) = E - TS$$

$$G(T,P,N) = E - TS + PV$$



So, we have E as a function of S, V and N and from here, I do a little legendre transform to a function H of S, P and N and what must that be this must be recall that dE equal to T dS minus P dV plus mu dN for out standard thermodynamic system. Therefore, this here is E plus P V because, if I add a plus P V to it then if I do a dH this P dV cancels and you end up with a minus V dP and therefore, what is left is a thermodynamic potential in which the control variables are S, P and N. So, what do you call this quantity, it is called the enthalpy it is the enthalpy chemical engineers are very fond of enthalpy because, it is easier for them to control P from the theory of heat engines you constantly talk about enthalpy but it is just a legendre transform from the internal energy.

You could also go from here to a function f of T, V and N and that must be formed by taking E and subtracting the portion here so E minus T S and what you call this quantity? The helmholtz free energy. While you could make another legendre transform and go to T G of T, P and N which would be equal to E minus T S plus P V and this of course, is the Gibbs free energy. These are the 4 standard thermodynamic potential the internal energy the enthalpy the helmholtz free energy and Gibbs free energy.

But you could make other transformations for instance you could go from this thing you could make a transformation and let us say we have E instead of that, I would like to have S V and mu instead of N and since you had a mu N here this must be equal to E minus mu N expansion and that is the thermodynamic potential so let me call it some phi 1.

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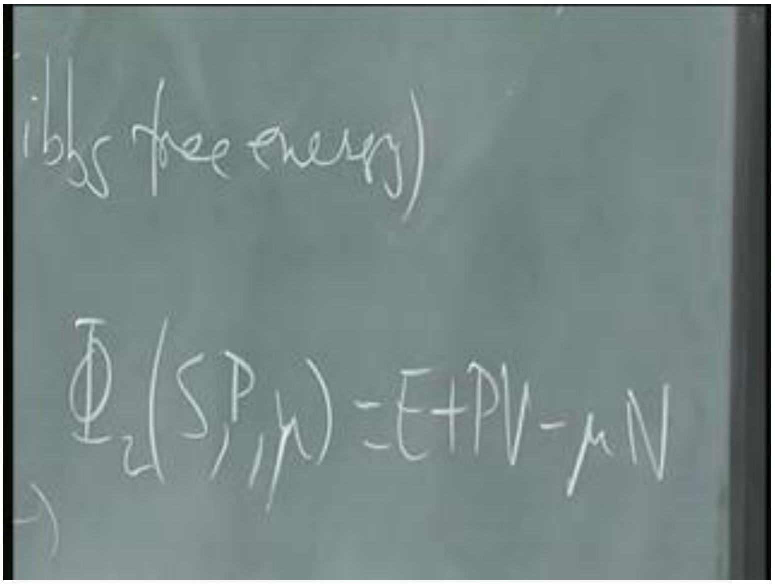

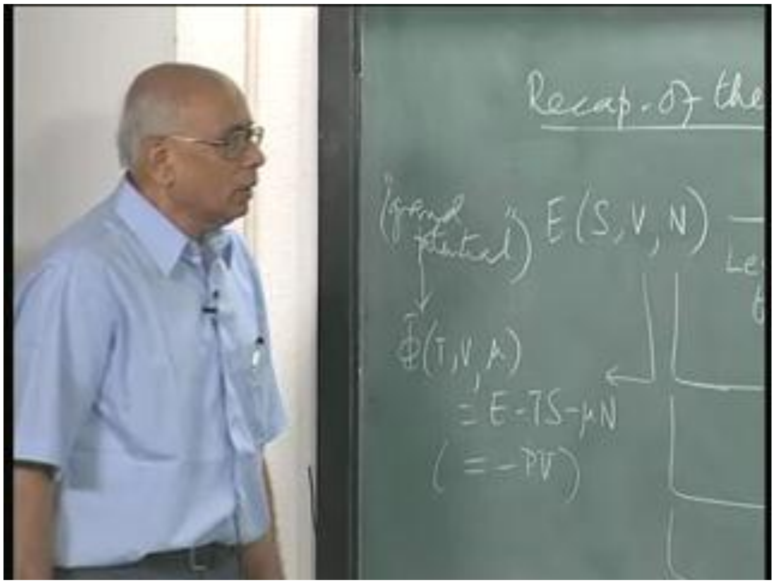

You could make another transform go also to a phi 2 instead of S, V and mu. I could have S, P and mu so, it is this equal to E plus P, V minus mu N and so on. And you could have yet 1 more, which would be let us see T, V and mu so, you could have T, V and mu so, you could make another transform which goes to a function phi of T V and mu and that is equal to E minus T S plus mu minus mu N.

Incidentally if we go back here, E minus T S minus mu N is in fact minus P V, so, just minus P V this is also equal to minus P V. And this is also sometimes used this is called the grand potential. The reason is it is connected to grand canonical ensemble in statistical mechanics, where as these guys are connected to canonical ensemble where you replaced S and use T instead. Now, you have even replaced N and used mu instead and this is called the grand potential.

So, for everything that you get in statistical mechanics is a corresponding analog and thermodynamics there has to be and this is a sort of these are all the potentials that you would use. But you notice 1 feature here notice that in our separation into forces and fluxes, we always discovered in a relation like this for example, we discover that these quantities occur in thermodynamically conjugate pairs. In some sense, 1 of them is the cause and other is the response the stimulus and the response which 1 use as the stimulus? Which you use as the response?

Is a little shaky, but the fact is not very unambiguous the fact is this and this are extensive variables and I call them field variables, state variables, on the other hand this quantity, this quantity and that quantity are intensive quantities and I call them field variables.

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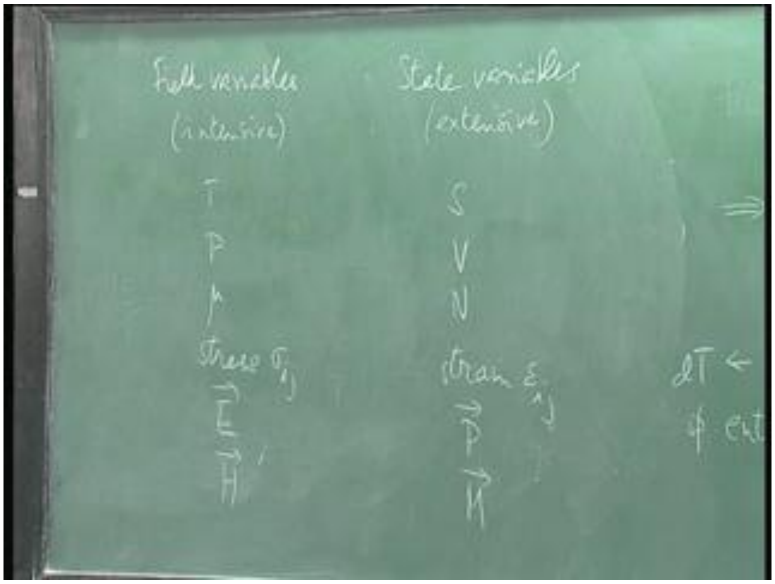

Field variables (intensive)	State variables (extensive)
T	S
P	V
μ	N
stress σ_{ij}	strain ε_{ij}
$\vec{E}$	$\vec{P}$
$\vec{H}$	$\vec{M}$

So, we can classify all thermodynamic quantities, into field variables and state variables, these guys generally are extensive and these are intensive. You can form other intensive quantities from the various state variables. But this thing here is T and that is S this is P that is V this is mu that is N and you can add to this list.

You could in general say stress and strain. And stress is a tensor so, this is some sigma i j and this is epsilon i j right expansion. Then this could be the electric field which you apply on a system and here would be polarization, the medium gets polarized or a magnetic field that you apply on the system and the response is the magnetization on the other side and so on you can make things much much more complicated.

So, you can generalize thermodynamics for very complex systems by proceeding along these lines here and using as your postulate relations Gibbs duhem type relation plus this relation that dE is equal to a generalized Fi dXi kind of product. And there is a very extensive literature on this the very thermodynamics is generalized, but in the nutshell this is what it does? But there is 1 more thing let us look at for example, let us look at what the consequences of this would be. So, F and G are the most useful in practice.

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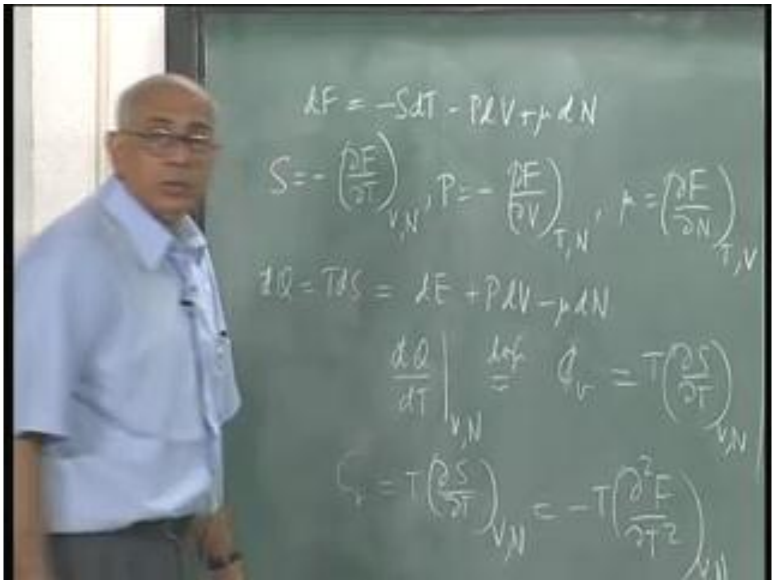

So, let us write what is dF? dF is equal to de that is T dS minus P dV plus mu dN that is dE minus T dS minus S dT left with minus S dT.

And similarly, let us also write what dG is? dG equal to so you going to have a minus S dT from here and then you added a plus V P V so, this becomes a plus V dP plus mu dN lets just look at these 2 relations. Now this immediately tells you, playing with little bit of partial derivatives this tells you that S is delta F over delta T with a minus sign S equal to minus this at constant V and N, but it is also equal to S is also equal to minus delta G over delta T at constant P and N and these must be equal to each other, identically it is a same quantity.

We further have so, let us write this out V is delta G over delta P at constant T and N very important to keep track of what is kept constant in the partial derivatives? And similarly, mu is delta G over delta N at constant P and T that is not too surprising it is not too surprising. Because, we already know that mu is G over N itself and its a function of P and T so, if you keeping P and T constant then its immediately cleared that mu is also the partial derivatives with these 2 constants so, this is in exact correspondence with what we already proved there.

Now, what are the relations here this says P is delta F over delta V at constant T and N with a minus sign, and mu can also be written as delta F over delta N at constant T and V. Now, that is a very important relation because, it says that the chemical potential is also the rate of change of the free energy with respect to the number of particles at constant T and V a little later I will assign may be this is an exercise you can also show that if I define this little F as the F over N free energy per particle and instead of N here I talk about the density the number of particles per unit volume then you can also rewrite this as the partial derivative of the free energy per particle divided by with respect to the density.

So, that is another useful relation here but now, what does this mean it says these thermodynamic potential their first derivatives with respect to the independent variables on which they depend are other thermodynamic variables. That is exactly what has happened here in fact, you recovered the field variables by differentiating the potentials with respect to various state variables and vice versa so you recover thermodynamic pairs in this fashion.

Now what happens if you differentiate a second time? What are the second derivatives of these potentials? What do they physically represent? For instance, if I differentiate it F a second time with respect to T, what would happen? Remember the law that we have, namely dQ is the T dS this is equal to dE plus P dV minus mu dN, which I rewrote in many many different ways. If you are at constant V and N, then dQ over dT at constant V and N, what you call this? What you call this?

It is a specific heat it is the rate at which the heat is absorbed I mean how much heat you must supply to change the temperature by a given amount at constant V and N. By definition, this is equal to C V by definition so, this by definition is equal to T delta S over delta T at constant V and N. By definition, of course C V is also equal to dE over dT because V and N are constant so, these 2 go away in this case. So, this is your definition of specific heat, if I put that in here this relation it says, that C V equal to T delta S over delta T at constant V and N.

But S itself is this quantity here at constant V and N so, this is equal to minus T delta 2F over delta T2 at V and N. In other words, response functions are second derivatives of thermodynamic potential, first derivatives are other thermodynamic variables but the second derivatives are quantities like response function C V this tells you what is the efficiency with which the system can absorb energy and change its temperature. It also tells you something very crucial, C V cannot be negative.

That is thermodynamic stability implies that, in a state of thermal equilibrium at constant T V and N this quantity is at an absolute minimum which means its second derivatives must have specific signs and 1 of those conditions stability condition leads to the fact that C V this quantity here must be positive. That means this quantity must be negative d2F over dT2 must be negative and that says, specific convexity properties of F as function of T. So, this is called stability thermodynamic stability it is also called chateliers principle. That is nothing but a word for thermodynamic stability. And it essentially says that these potentials are at minima correspond to the equilibrium states.

So, this is an example of such a relation with a second derivative it is a response function here. You derive exactly the same thing here, what is C P?

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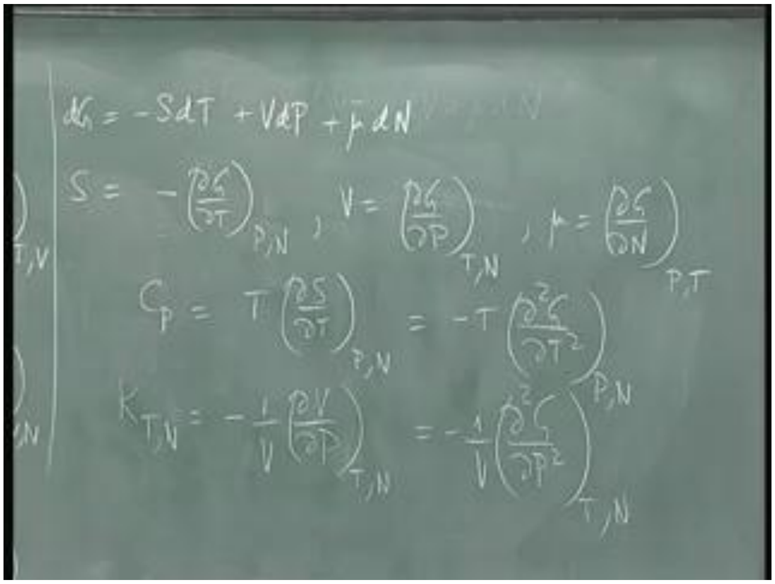

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}$$

$$K_{T,N} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N}$$

C P is equal to T delta S over delta T at constant pressure and N but at constant pressure and N you have delta G here sitting for you so this is equal to minus T delta 2G over delta T2 at P and N

And of course, you can show that C P must be greater than C V. I am going to give all these thermodynamics identities as exercises it is not very hard to show, that this quantities in fact bigger than, this quantity and this quantity is bigger than zero for thermodynamic stability. But again second derivative implies certain convexity properties in it. What is the isothermal compressibility? How did you find the isothermal compressibility? For gas KT equal to at constant temperature and fixed number of particles so, let us call it KT comma N this is equal to the volumetric strain over the change in pressure right.

So, this is equal to minus 1 over V delta V over delta P at constant T and N. That is the isothermal compressibility, we could have an adiabatic compressibility where you have S constant instead of N. But let us look at the isothermal compressibility, it is this quantity and I need the minus sign because, as you know in the generalized force law F dX its minus P dV that appears because, if I increase P the volume shrinks. So, I take that into account the minus sign there and then this is so, it tells you correctly what the work done is and then this is the definition of the isothermal compressibility.

Now can we write this in terms of these relations here yes indeed, because delta V over delta P would be the second derivative here. So, you could also write this as equal to minus 1 over V delta 2G over delta P2 at constant T N, again the positivity of this quantity here if you increase the volume, if you increase the pressure, the volume must decrease rather than increase and so on. In some directions the things could expand actually if it has negative Poisson ratio.

But, if you use hydrostatic pressure things must decrease that stability. Are you familiar with the Poisson ratio? Yes are there any limits on the Poisson ratio? It cannot exceed a half and what about can it be negative? Is it positive? You do not know, you see what is Poisson ratio for those who forgotten that is being charitable, if I take piece of material like this and I pull it in this direction, then it could contract in the transverse directions right.

Overall there will extension in this direction, there would be possibly contraction in the other direction the ratio of that contraction strain, to the extension strain is called Poisson ratio. On the other hand, if the Poisson ratio is negative it means that, if I pull in this direction it also expands in this direction as well what we do know for stability is not very hard to prove, you look at the total change in volume it is easy to see that this ratio new, Poisson ratio must be less than half. In absolute terms cannot be bigger than half otherwise thermodynamics stability is violated.

But the question is, can it be negative? If I pull it in this direction will it also blow up in this direction. Is it is positive? Is it possible it is theoretically possible. Is it possible, in practice there are materials tell me 1, here is a loose analogy who can spare a sheet of paper? who can spare a sheet of paper? Do not tare notebooks feel bad about this he has a sheet of paper i hope it is a notice from administration. So, we can see that it is a I compel it up in this fashion imagine this is a sort of composite material like a network material or some kind.

You have to use your imagination, but look at what happens to its size? So you see it expands at the other direction too. And it is happening because, it is a sort of network kind of object its very very crude model of it so it is possible to have Poisson ratio that is negative. But it cannot be more negative, than minus 1 so, it runs from minus 1 to plus half and what it is it for most materials most metals normal stuff over 0.25, 0.23 and something like that right so, that is the order of magnitude of this quantity.

Now, the compressibility on the other hand the isothermal compressibility must always be positive and its relation of this kind, good we could write down this is incidentally, how is this related to the bulk modulus? It is the inverse of the bulk modulus, it is the reciprocal of the bulk modulus. Give me an experiment where people measure this compressibility. Pardon me how many of you have cycles? Everybody has a cycle, how does the guy who fills tyre the drill boy the person, how does he test whether you have enough pressure or not know he kicks the tyre right or he presses it, what is he actually doing?

How he is getting the information about pressure by kicking it he finds out how rigid it is. So, he is really measuring the compressibility of this object but, how come he is finding the pressure by doing that? Practical thermodynamics come on you are all engineers, who are going to send a machine to a moon. How does he do that let go and lets work this out you need to work out all these things? What does that poor kid outside the central school do when he kicks your tyre.

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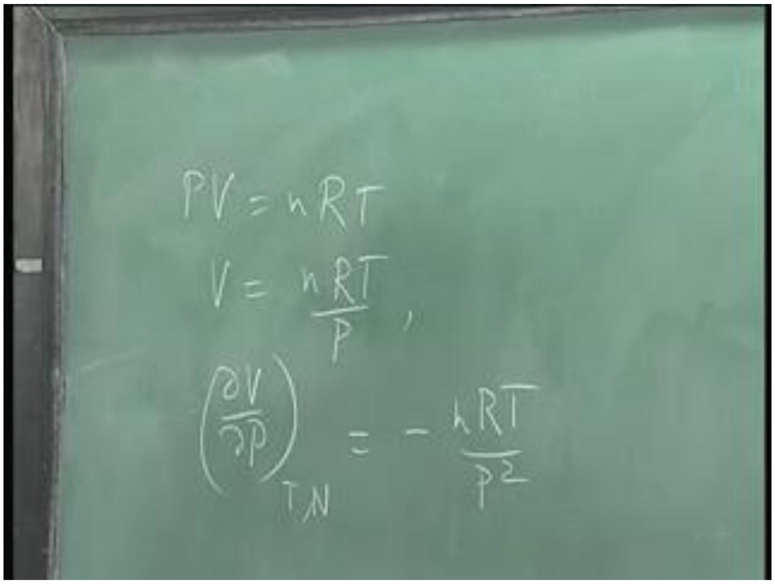

$$PV = nRT$$

$$V = \frac{nRT}{P},$$

$$\left(\frac{\partial V}{\partial P}\right)_{T,N} = -\frac{nRT}{P^2}$$

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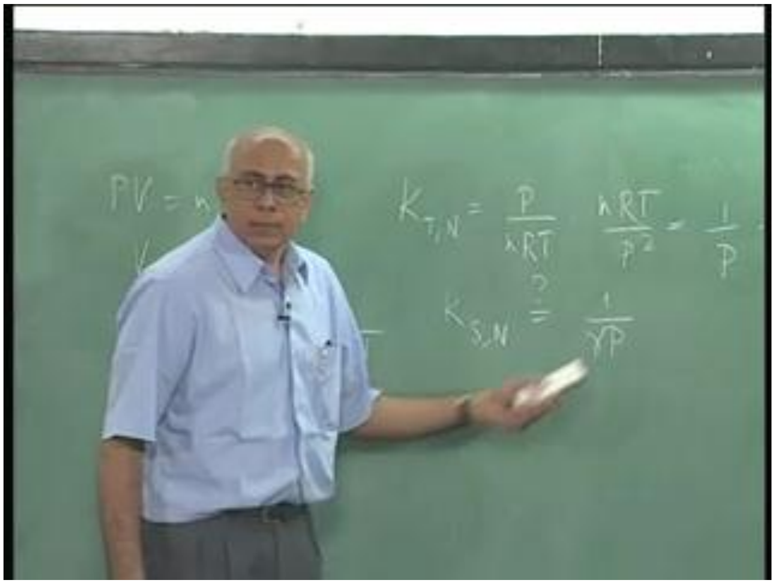

So, we would like to calculate this quantity minus 1 over V delta V over delta P so, let us do that for an ideal gas you have P V equal to n RT it is an ideal gas. So, V equal to n RT over P and now, let us compute for a fixed number of particles lets compute delta V over delta P at constant T and n this is equal to minus n RT over P square. So, K T and N equal to minus 1 over V minus sign is cancelled so, its 1 over V and 1 over V is P over n RT multiplied by n RT over P squared which is equal to 1 over P so you see the bulk modulus is the pressure.

Now, the compressibility is indeed the pressure if it is very compressible the pressure is low, but if it is not compressible the compressibility is low it is a very rigid object the pressure is high. So, that poor guy actually knows this and that is the reason why he kicks the tyre in order to find out what is the pressure is although he is measuring the compressibility. Its directly related to this I leave it as an exercise to you to find out, what will happen if the process is adiabatic? You might actually say this guy is pumping there pipe fast.

So, you cannot say that temperature is constant because it does get heated up. But the process is sufficiently first adiabatic, then what happens, constant entropy process rather than constant temperature not isothermal, what would happen? What would this be? You already know the answer, it is just that you are not relating this. In this ideal gas, what do you think it will be gamma very good. You know Newtons formula for this velocity of sound in a gas, its square root of T over rho but then Newton pointed out that this is really an adiabatic process because, this stress waves propagate quite the rarefaction and so on is not an isothermal process.

And therefore, much better approximation is an adiabatic process and then the formula is square root of gamma P over rho. So, all that happened is that P is replaced by gamma P this thing here. I leave you to find out what it is for a van Dover gas, where you have actually included the attraction between particles at long distances? What is the van Dover equation of state?

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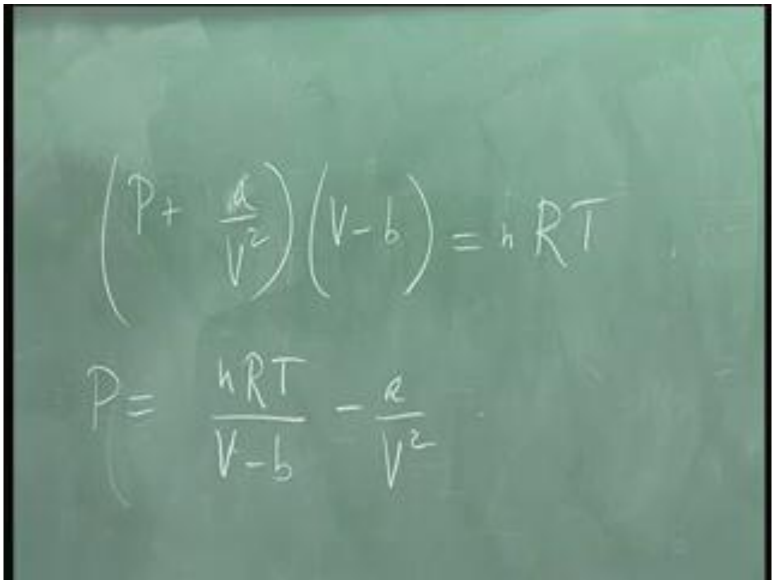

$$\left(P+\frac{a}{V^2}\right)(V-b)=nRT$$

$$P=\frac{nRT}{V-b}-\frac{a}{V^2}$$

This is important it is not P plus A over V square V minus b equal to n RT so it is a crude approximation to what is happens to gases. You say that the volume V is replaced by an effective volume V minus B because, these particles occupies some space how to speak actually that is not really true we will see what is that in a minute. And then you have a term which says that the pressure is actually reduced a little bit ought the original pressure so, you should really rewrite this equation as P equal to n RT over V minus b minus a over V square that is the way to write it you write the pressure as the function of the temperature and the volume that is called the equation of state of the system.

Now compared to the ideal gas, you did not have this term and you have a V instead of V minus b so, what is happened is that the volume has effectively reduced by a certain amount and this is because, these particles are supposed to have finite volume that is not strictly true we will see what it really means and the other term minus a over V square say that the pressure is less than what it would normally be, what is the physical reason A for that? Attraction between particles.

So, there is not as much force on the walls, you put in an external wall or something and ask, what is the force per unit area? There is some attraction between the particles and that is 1 over V square.

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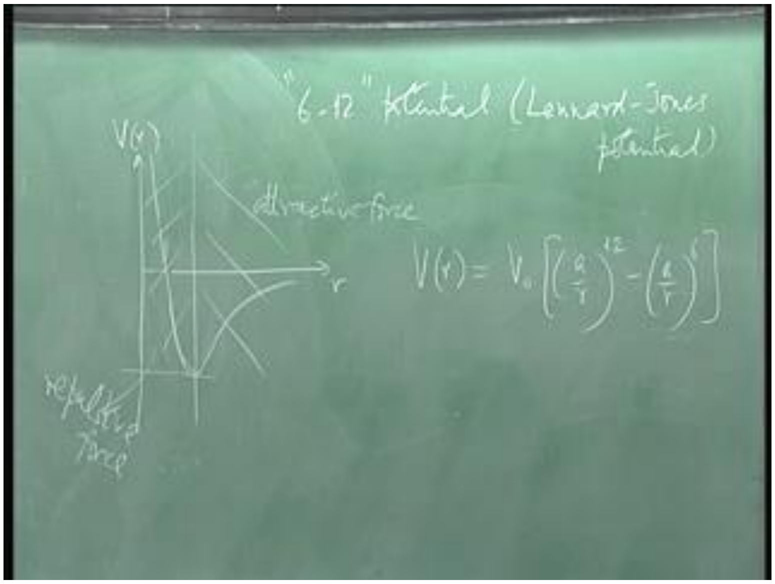

Now, what really happens is that if you plot the potential seen by a particle, due to another particle at a distance R from it this intermolecular potential has a very, very generic shape independent of various other factors and it is something like this.

So, this portion of it this portion and then here is a minimum so, till the minimum dV over dR here is negative so, minus dV over dR is positive, in other words particles pushed away. So, it is hard core repulsion some kind at short distances and at long distances there is an attraction. So, that is the origin of this intermolecular potential it is very crude origin. This portion of it this region here corresponds to repulsive force and this portion correspond to attractive force at long distances. What is the repulsive force due to in real life due to actual molecules these are not spheres or anything they are not billiard balls and so on.

What do you think is the repulsive force due to essentially? Pardon me, a nucleus is very unlikely because it is very, very unlikely because a nucleus is 10 to the minus 15 meters and the atom or molecule are of the sizes of order of 10 to the minus 10 meters or some multiple of 10 to minus 10 meters so, 5 orders of magnitude the chances that 2 nuclei will actually hit each other. In a gas is very small the Pauli Exclusion principle, not even the electron repulsion.

The Pauli exclusion principle the fact that you cannot put 2 electrons in the same state at the same time no 2 electrons in the universe can be same state at same time causes this repulsion so large contribution to that is this shape of potential here is due to the Pauli exclusion principle so it is very quantum mechanical in origin and that is the reason why it is very difficult to model and its very molecule dependent in the standard molecular physics the approximation for close shell for inert gases for example would be something called a 612 potential.

So, the first portion goes like a1 over r to the power 12 it is a very high power as r goes to zero and the long range attraction potential attraction potential goes like 1 over r to the power 6 with a minus sign. What is the origin of this attractive force? Where does this come from? So, this 612 potential which also is called the Lennard Jones potential is of the form, V of r is equal to some constant V not times some a over r to the power 12 minus a over r to the power 6 and this minimum here is at some multiple of a2 to the 16 times a or something like that. So, there is a scale factor a and then there is a minimum here this is proportional to V not minus 4V not or something like that.

So, this thing here is general Lennard Jones form, this portion is their repulsive part leads to the repulsive force and that leads to the long range attractive force. This is strictly, an empirical model here it could be 18 it could be E to the power whatever minus 1 over r and so on. But the fact is that this is the completely quantum effect at this stage, of the model in the exact terms the other term the attractive portion is more empirically model more easily, where does it come from? Where does this r to the 6 come from? It is a very simple physical explanation for the 6.

Its dipole interaction, because after all if you took 2 neutral atoms and they are completely spherically symmetrical, there should be no force at all, no electrostatic force at all.

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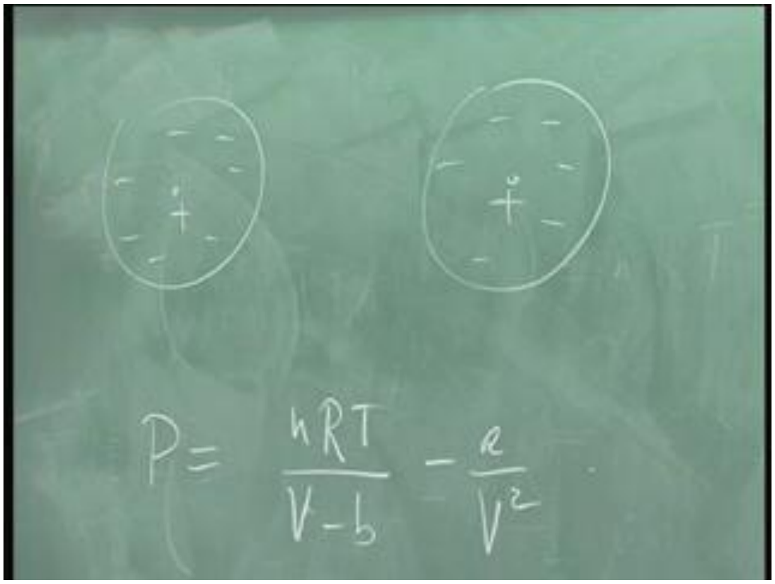
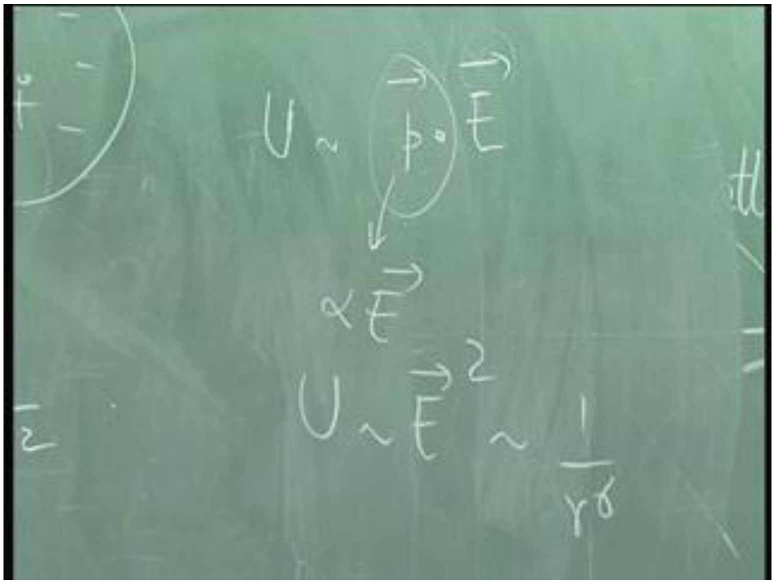


$$P = \frac{nRT}{V-b} - \frac{a}{V^2}$$



$$U \sim \vec{p} \cdot \vec{E}$$

$$\alpha \vec{E}$$

$$U \sim \vec{E}^2 \sim \frac{1}{r^6}$$

So, if I took 2 neutral atoms. I have an atom and an atom there and this is the plus charge and this is a minus cloud around it, this is plus this is all minus around it, each of them is spherically symmetrical, then there is no force outside no field outside completely for these neutral atoms, if the charge distribution is spherically symmetrical.

But the fact is that these are actually dynamic entities they are changing all the time and there are fluctuations, so instantaneous fluctuations can cause a dipole moment here it momentarily shifts from the centre of attractions here, there could be a dipole moment here and if there is a similar dipole moment there then there, is a dipole dipole interaction. Now what happens is that dipole moment here?

If there is a dipole moment P1 electric dipole moment, it causes an electric field at the other end there. And what does the energy go like? The energy the potential energy U goes like P dot E, is what the energy is going to E if you put a dipole of moment P in an electric field E goes like P dot E. But, this polarization of this molecule, this E is due to the dipole moment here. And what does that E go like?

It goes like 1 over r cube because a monopole field will go like 1 over r square the potential goes like 1 over r the field goes like 1 over r square a dipole field the potential goes like 1 over r square the field goes like 1 over r cube But the greater the field here the greater the separation here so, this P itself is some alpha times E where alpha is the polarizability so, the whole potential energy U goes like E square and that goes like 1 over r to the power 6 1 over r cube square.

So this is the simple explanation of where this things come from its called the van Dover force. The more complicated explanation is for detailed explanation of theory is possible but this is the origin of it this is where it comes from Now what is the assumption I made here? I made the assumption that these do not have permanent dipoles, these guys actually are spherically symmetric charge distributions and so, only they induce dipole effect that I have looked at.

If these molecules had permanent dipole moments, then this is not the answer. Water molecules would not attract each other with this kind of force. What has got a permanent electric dipole moment? Then what do you think the answer is, 1 by r cube its P1 dot P2 over r cube and P1 and P2 are the permanent dipole moments divided by r cube. So, the force will go like a 1 over r to the 4 in that case. Lots of the normalized properties are water arrest actually traceable to the fact that it is got a permanent electric dipole moment. Many, many are not anomalous properties in fact, water is the most anomalous substance known almost every property of it is anomalous, it is not a simple thing to explain it has a very complex behavior.

And even the number of phases of water is not fully understood here so, it has all kinds of crazy things and all these things go out of the window, but this is the origin of van Dovers. Now coming back here, how does this mimic the 1 over r6, where does that come from? Why should it be 1 over V squared and not anything else and the idea has to go I am going to discuss, this when we do phase transitions it has to do with what is called mean field theory.

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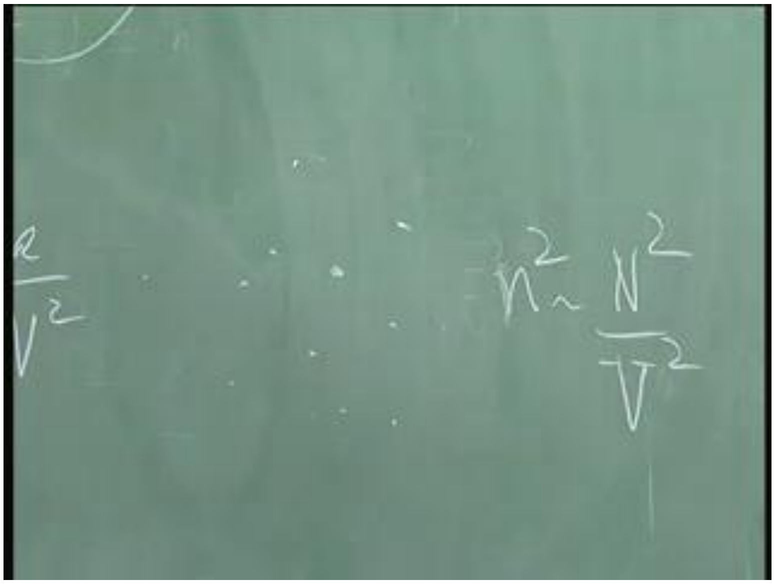

It says you have all these molecules and you are trying to find out the correction to the pressure which is the energy density, pressure has the same dimensions as the energy per unit volume.

And you are trying to find out the correction to this energy density, from the attractive force. Between, the molecules and the idea is any 1 of these guys is going to be affected by all of them around. And if you assume, in the simplest approximation that they are affected equally by all of them around everyone is affected by everybody else, in exactly the same fashion independent of the distance. Then this goes has each of them each molecule has an energy proportional to the concentration of particles n and there are n of them per unit volume so, the whole energy goes like n squared and that is like n square over V square.

And you hidden the N square in the parameter a, and taken only the V square. Now so that is how van Dover came out with this 1 over V square. And today we understand the van Dover equation of state as what is called the mean field approximation? And we are going to do that in some detail in statistical physics and when we do phase transitions, but the van Dover equation of state is an example, of a mean field theory of a fluid. In which attractive forces included, this is of course, completely empirical.

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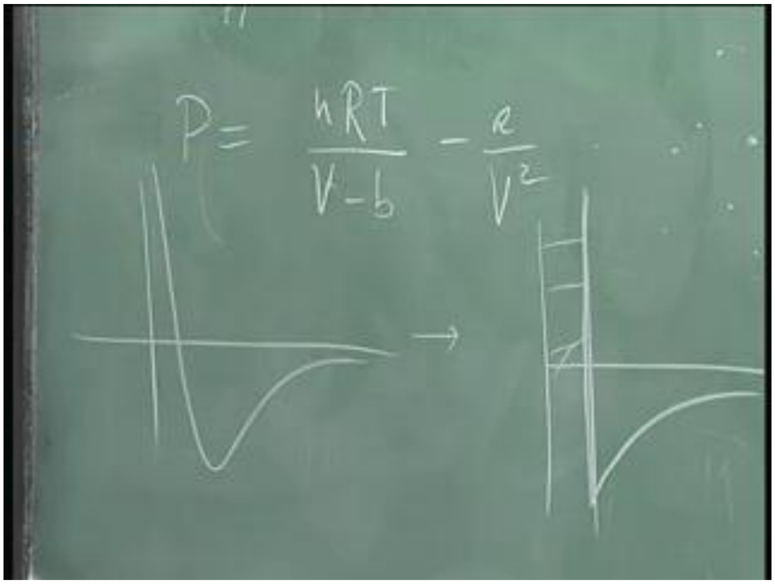

So, what this van Dover does, is to say that this complicated inter atomic intermolecular potential is approximated by saying that, there is a hardcore repulsion where the potential is infinite and then there is a 1 over r6 attraction.

So, that is an approximation to the true intermolecular force and in that approximation, you can start with statistical mechanics put in this interaction, put in this approximate potential, etcetera and then after lot of jugglery you end with a van Dover equation of state which is completely empirical. Deriving it is non-trivial there is no single regress derivation for it, there is no universal equation of state for gases this is what the people were searching for in the 19 century, before they realized that this is an intrinsically quantum mechanical effect it depends on the molecular species, it depends on what kind of system you have.

Therefore, apart from situations near phase transitions, near critical points, everywhere else systems are very specific to themselves there is no universal equation of state. But this is a holy grail in the 19 century to try to find the correct equation of state today.

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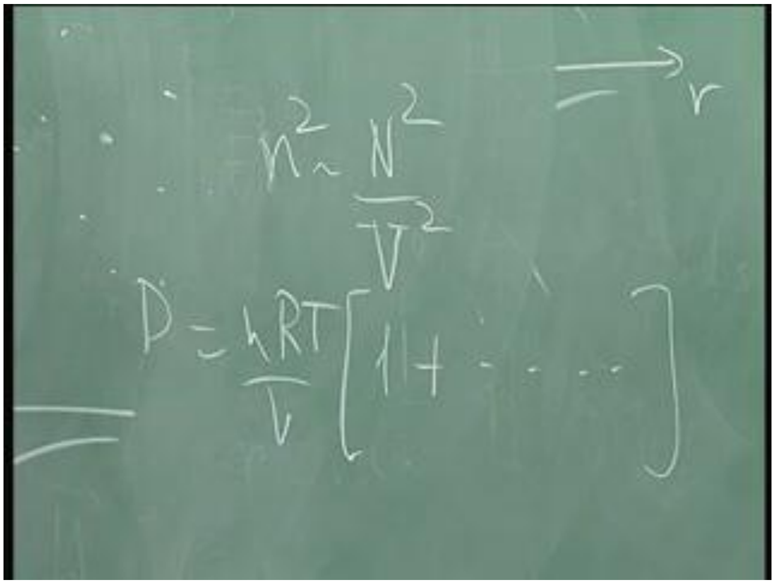

We know that what statistical mechanics will tell you, is that the pressure is equal to n RT P equal to n RT over V times a power series 1 plus higher order terms and this is called the virial expansion.

And all these terms would have coefficients that depend on temperature divided by increasing powers of V in the denominator, V square V cube V to the 4 and so on. And the van Dover is the very very special case, of it in which all the virial coefficients degenerated and put in to 1 parameter here, because there is already a 1 over V square and if I expand this binomially in inverse powers of V, then you will see that all the coefficients are just the powers of V upon r, So, it is a very degenerate case in that sense so, good to know where the phenomenology of 19 century stands when you do statistical mechanics.

It is a very great incite, it is very, very important development in the theory of condensed matter itself. Van Dover thesis was on this problem and it was so important that Maxwell learnt Dutch in order to be able to read van Dover thesis in the original. He regarded this is very important piece of work and since, he was 1 of founders of statistical mechanics he thought its sufficiently important to know this and it is a great inputs here. So, let us come back here, we were talking about second derivatives the last thing I want to ask is what happens if you took cross derivatives?

We have said second derivatives, of thermodynamic potentials lead to response functions like this specific heat etcetera what would be cross derivatives? I differentiate with respect to temperature and volume for instance etcetera, what would they correspond to? I leave it as an exercise to you to show that there are other response functions for example, what is the isothermal coefficient, what is the coefficient of linear expansion thermal expansion the coefficient of thermal expansion.

The rate at which volume changes with respect to the temperature; so compute that number and then you discover it is a mixed derivative 1 with respect to T1 with respect to V and so on. So, they too are response functions and since we know that the stability will involve when you have functions of 2 variables for example, stability will involve an absolute minimum of a function of x and y means that delta 2f over delta x2 is positive delta 2f over delta y2 is positive and the product of these 2 must be greater than delta 2f over delta x delta y the whole square.

So, there are other stability conditions that come in, from imposing the requirement of some stable thermal equilibrium so, this is roughly what we are. The only thing I did not do was Maxwell relations and I leave you to figure out I will give it as a problem itself. Each of these things, each of these relations each time you write a thermodynamic potential as a function of 3 variables you have 3 Maxwell equations because you can differentiate this with respect to T and then P or P and then T and equate the 2 and you get a Maxwell relation.

And for each of them you are going to get 3 relations. Since, there are 6 thermodynamic potentials we have looked at there are going to be 18 Maxwell relations. Can write them down normally you keep n fixed, in which cases you reduce to just 4 Maxwell relations. But otherwise, you have very large number of time so, that is thermodynamics in a nutshell and the rest will be in a problem sheet.