Nonequilibrium Statistical Mechanics
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Lecture no 29
Module no 01
Critical phenomena (Part 1)

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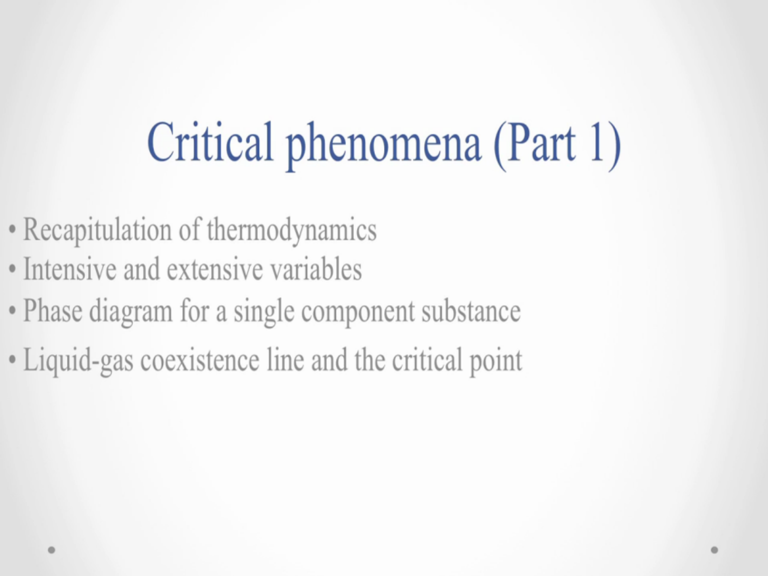

Critical phenomena (Part 1)

- Recapitulation of thermodynamics
- Intensive and extensive variables
- Phase diagram for a single component substance
- Liquid-gas coexistence line and the critical point

We will then start now to look at a completely different problem, the problem of what is called critical phenomena. Namely substances, microscopic objects collects large collections of atoms which undergo transitions from 1 phase to another like liquid to solid or solid to gas and so on and so forth okay. Now this subject, we are going to deal largely with equilibrium phase transition critical phenomena because non-equilibrium critical phenomena is an open subject at the moment, there is lot of work going on and there is no universal agreement on what comes under the umbrella of non-equilibrium phase transition and what does not, we know it when we see one in that sense.

For equilibrium phase transition for critical phenomena that is now a well established theory established over last 50 years or so and it has several features which are of interest to us. In particular, there is going to be a connection with the Langevin approach the Langevin equation and similar notions when we talk about the order parameter and the way the order parameter evolves near critical region and so on.

So let us start now with the most elementary of notions, (())(1:46) I am going to zip through the elementary parts of this because it is familiar to all of you but just for the sake of completeness and to refresh your memories as to what we are talking about, we will start with the simplest of notions okay. First let us look at what is already taught you in high school, namely the fact that you have 3 states of matters as they call them, 3 states of matter. This is not a very happy terminology to start with, but they know what they mean, they know liquid, solid and gas.

So the assumption is you have one molecular species, just one kind of molecule with some interaction between the molecules and then depending on the temperature these substances efficiently large collection of these molecules will either be a solid, crystalline solid when I say solid or a liquid or a gas. And we know there are well-defined ways of establishing what is the liquid, what is the gas, what is the solid, we will mention some of these things. And then one draws what is called phase diagonal.

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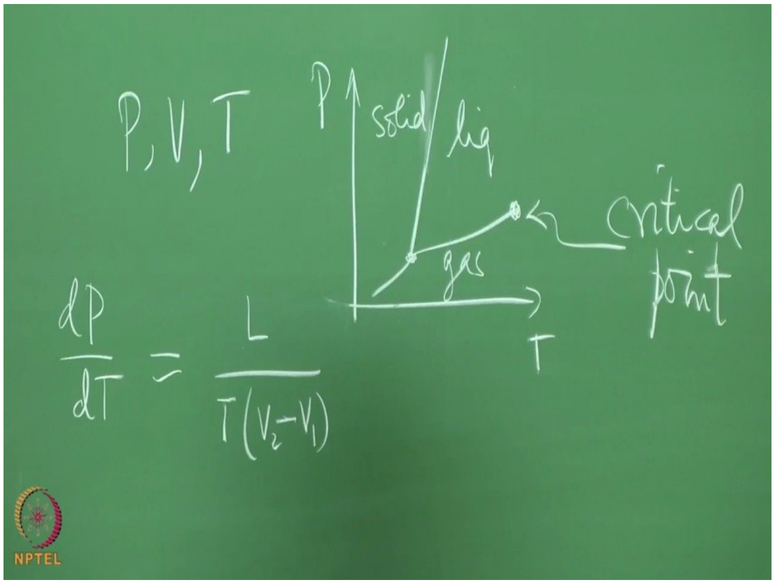

So in such a substance for a given amount of material, the thermodynamic variables P, V and T okay, as you know from elementary thermodynamics when you have just one component substance and a given amount of it, the number does not change the number of particles then we can forget about the chemical potential, we can forget about concentration of the different species and so on and the simplest thermodynamic variables are P, V and T and they are connected by an equation of state.

But this equation of state which tells you the value the value of any one of these variables in terms of the other 2, this equation of state will depend on what the temperature is and what the pressure is, etc, it depends on where you are in the space of these 3 variables. So one draws typically a P versus T diagram, of course we will also draw V versus T and T versus V versus P and so on, we will do that by and by, but one draws first a P-T diagram and then it turns out that at sufficiently high peak temperatures, this system is in general in the gas phase, at sufficiently very low temperatures it is in the solid phase and it is liquid somewhere in between okay.

So any point on this plane is a state of thermodynamic equilibrium for it okay. And then one has typically a figure like this, very schematically you have a line, it goes off like that, not necessarily a straight line and the system is in solid phase here, liquid phase here and in gas phase here and there is very often a triple point at this place. I am not drawing this to scale at all, I am not telling you what the temperatures are, what are the actual values of these quantities, no such things, just schematically it looks like this. Now the slope of this graph may be 1000 times the slope of this graph so we are not worried about that.

The question is what happens on this line? It is called a coexistent curve or coexistent line, the curve which tells you for a given value of the pressure what is the boiling point, so that if you increase the temperature you get into the gas phase. Or for a fixed temperature if you increase the pressure, you cross into a liquid phase, it condenses the gas condenses, similarly between the solid and liquid and the solid and the gas here. So what happens here as you go across is boiling or condensation from down, either freezing or melting as you come down and sublimation across this. So this is called a sublimation curve, this is called the boiling curve and that is called the melting curve.

More significantly this thing also tells you for a given pressure what the boiling point is. And as you know if you increase the pressure on gas the boiling point goes up, if you decrease it the boiling point comes down. But very notably this curve just ends in mid air so to speak, just ends at a particular finite point and this is called the critical point and it is a very special point of great interest and took a long time to unravel its mysteries because in the nutshell, thermodynamic fails at that point. So you have to go beyond thermodynamics, you have to go to statistical mechanics but even more than that you have to go, some really sophisticated techniques in statistical mechanics to understand what is happening at this point.

This curve here keeps going for ever or else it branches off to other phase transitions because there could be many many phases in this solving, not just one kind of crystalline form but many kinds of crystalline forms, it could go from BCC to FCC and so on and so forth, but we are assuming those complications do not exists and keeps going in this fashion. I have drawn a graph where if you increase the pressure, the melting point also increases but that is not necessarily true for water, it goes the other way so the slope of this curve is actually negative in the case of water which is very anomalous substance and for most materials it is actually positive but with a very high slope, numerical value in the slope.

This graph on the other hand always has a positive slope because in all cases if you increase the boiling point of a liquid, will increase if you increase the pressure so it always goes in this fashion. And we always know that there is an equation, which tells you that the slope of any of these coexistence curves in the P-T plane is given by an equation called the (())(8:32) equation on this side, which tells you how the boiling point or freezing point or whatever it is changes as a function of pressure okay.

This quantity on the right-hand side involves a latent heat divided by the temperature, times, whatever, so you are used to in writing it in elementary thermodynamic as L over T times V 2 – V 1 or something like this right, where L is latent heat, T is the boiling point in this case as per this graph and V 2 – V 1 it is the difference in volumes specific volumes in the 2 phases. Now that is not very nice way to do this because what V 2 is and what V 1 is, is completely arbitrary. What I call phase 2 and what I call phase 1 is arbitrary but that is assumed in this L.

To go from a liquid to a gas you have to supply the latent heat of boiling and combat the other way you got to supply. First case latent heat of evaporation and the other case you have to extract that heat in order to become a liquid here. But this is avoided by writing a proper equation which is the following, it is just one of the Maxwell relation in thermodynamics okay. You are familiar with what the derivative of pressure with respect to temperature is for a given volume at a constant volume what is this equal to? Are you familiar with the Maxwell relation in thermodynamics? Because what you do... You have to now respond and tell me yes or no.

Student: Yes.

Yes, so what is the relation in this case? There seem to be some doubts here.

Student: If we go back to P in terms of (())(10:22)

Okay, let us go let us take a breather and go back because I think that you should at all stages you should be able to go back to 1st principles and do everything from the beginning. So digression from the digression let us go back to thermodynamics, what is meant by thermodynamics? The whole point about thermodynamics is that you have a set of variables which you call thermodynamic variables and then you write in expression for what is called the internal energy.

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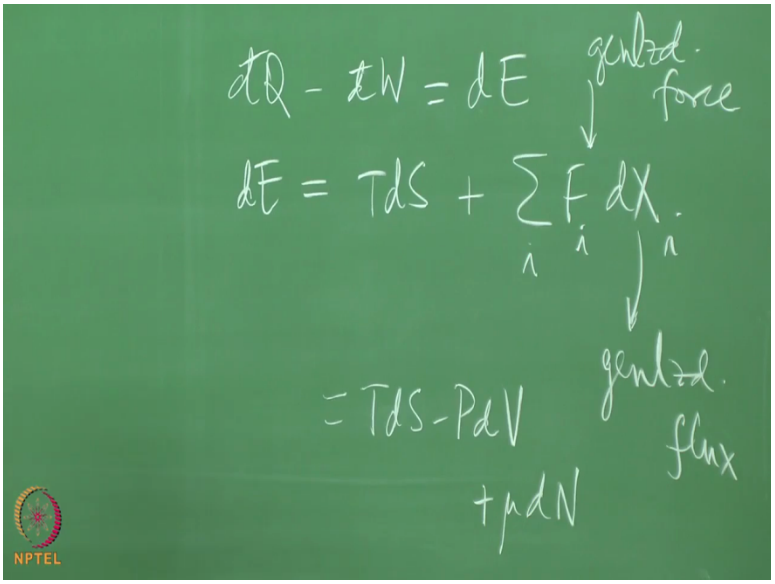

$$dQ - \bar{d}W = dE$$

genlzd. force

$$dE = TdS + \sum_i F_i \, dX_i$$

genlzd. flux

$$= TdS - PdV + \mu dN$$

This internal energy you do not in thermodynamics write an equation for it directly, what you say is that if you supply a certain amount of heat dQ to a system and it is an imperfect differential, so it is dQ denoted this way, and you extract from the system certain amount of dW then the difference dQ – dW, this is equal to the change in the internal energy of the system, I have called the internal energy E, generally one uses this U for this symbol but I prefer to call it E okay that is it. This is the law of thermodynamics, the conservation of energy, the 1st law of thermodynamics.

But you go further and you say no no no, this thing is part of a bigger system or bigger formalism which says that dE is actually equal to for a reversible thermodynamic process, this dQ can be written as with an integrating factor as T dS, so it is equal to T dS + on this side a whole set of generalised forces and corresponding conjugate variables called Fluxes. So this can be written as submission over i F i dX i where this is a generalised force, I will give you an example right away and this is called the generalised flux.

Student: We use this terminology in linear response theory also.

Yeah, we use exactly this terminology in linear response theory in fact, formulas that you are going to get I am going to write a couple of them down are linear response theory formulas for the susceptibilities, literally the susceptibility okay. So it says, once you take these integrating factors if you like and multiply the dX i, you end up with the perfect differential dE for the system. Now a classic example of this for a single component system is going to be T dS – P dV + if the number also changes Mu dN, that is the chemical potential and it is the change in the number of particles in the system.

So now you have a set of thermodynamic variables and these variables can be grouped into this portion, this portion and this portion. This is a generalised force so is P so is Mu and this is the generalised flux S, V and N, this is the entropy here. But now you immediately see that there is 2 categories of micro variables microscopic variables, there are the so-called intensive variables which the generalised forces are, they do not depend on how big system is, what the size is and so on and then the extensive variables which depends proportional to the system size. So I know that at a given pressure and temperature if I double the volume of a gas and double the number of particles, the pressure and depression do not change, nothing changes.

So these fluxes are all extensive variables and the forces are intensive variables and you notice that you always multiply this by the differential of that on that side here. From this of course it immediately follows if there is a perfect differential that T = delta E over Delta S keeping V and N, etc, all these relations follow okay. But now you can write this not in terms of just dE, you could write an equation for sum thermodynamic potential, you can choose those as independent variables after all I have S and T sitting here and then I have P and V sitting here and then I have Mu and N sitting here and in this system I have, you can draw a diagram like this and I can choose any of these 8 variables, 6 variables, any 3 of them I can choose to express thermodynamic system.

So for instance suppose I choose S, V, N, then as you can see since dE is expressible in terms of dS dV and dN as a linear combination, it implies E is function of S, V and N so you have E of S, V and N internal energy. And then you say that in thermodynamic equilibrium this is a minimum internal energy is at a minimum that is the state of thermodynamic equilibrium. Then you have to ask if it is a stable equilibrium, unstable, et cetera and there are convexity conditions which you get as a consequence. But there is no reason why I could not have chosen S, V and Mu so I could have chosen S, V and Mu and then I could have chosen S, P and Mu, so let us write this schematically so that we have.

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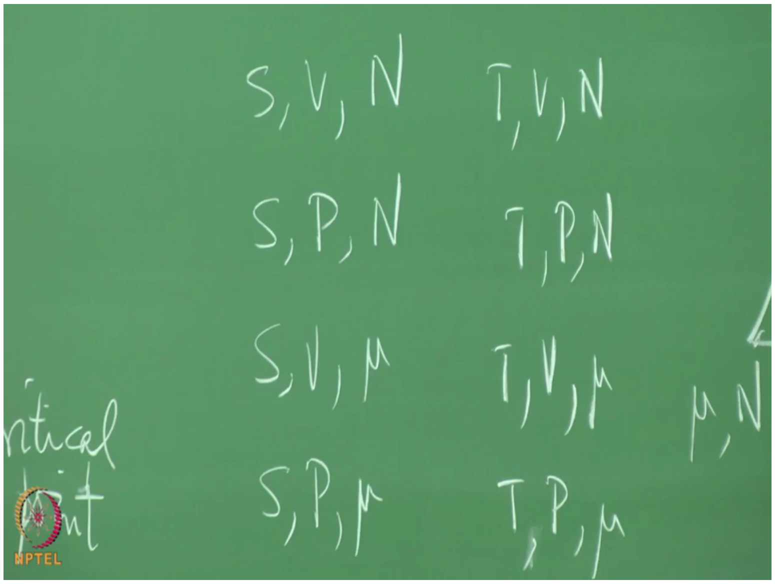

S, V and N that is one possibility, S, P and N that is another possibility, then S, V and Mu that is a possibility, S, P and Mu is a possibility, and then I have T, Mu, N then T, P and N, T, V and Mu and T, P and Mu that is it, so 2 cube = 8 these are the 8 possible variables, sets of variables that I can choose to describe the system right. Then since I have already got the laws of thermodynamics putting in this form, it is clear that thermodynamic potential that is minimum in thermal equilibrium is the internal energy E. I do a Legendre transform on it to go from S to T that is the conjugate variable here might subtracting T S from this potential and again the Helmholtz potential.

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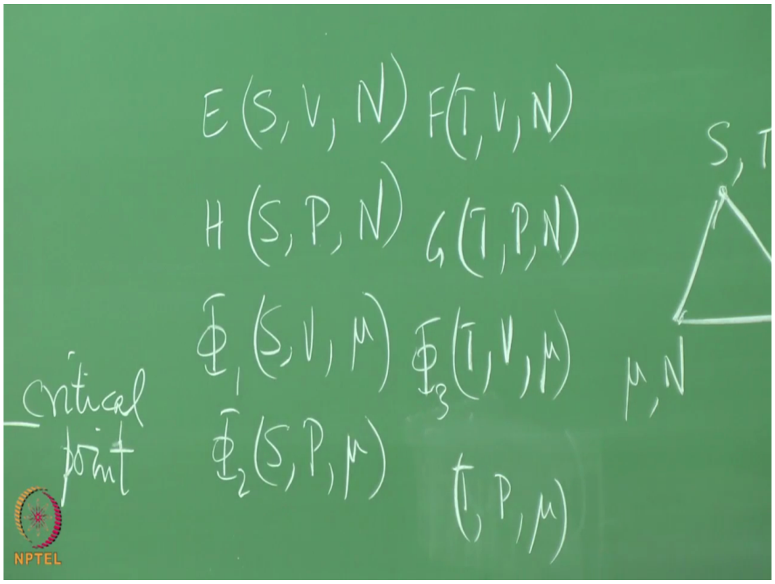

So this is F of T, V and N and then we know that at constant temperature, volume and fixed number of particles in thermal equilibrium it is Helmholtz free energy that is at minimum okay. Similarly I did not like V, I go to P and I choose S, P and N then I can do that by subtracting, by adding P, V because this has got a – P dV out here so I can add E + P V and I get the (())(18:22) H of S, P and N, which is at a minimum for a process in which you can control the temperature, the pressure, the entropy and the number of particles.

Similarly, I can go to T, P and N and I get the Gibbs free energy here. But I can do anyone of them it does not matter, for instance I could have chosen just trying to figure out so let us call this Phi, let us call them Phi 1, Phi 2 and Phi 3 no sorry Phi 3, this is arbitrary notation okay, I do not know what is standard notation is, so what was the last one? It was T, P and Mu. I cannot do this why? It is not a good idea to choose to describe thermodynamic system using as a potential function which is a chain of T, P and Mu why is that?

Student: All 3 are intensive.

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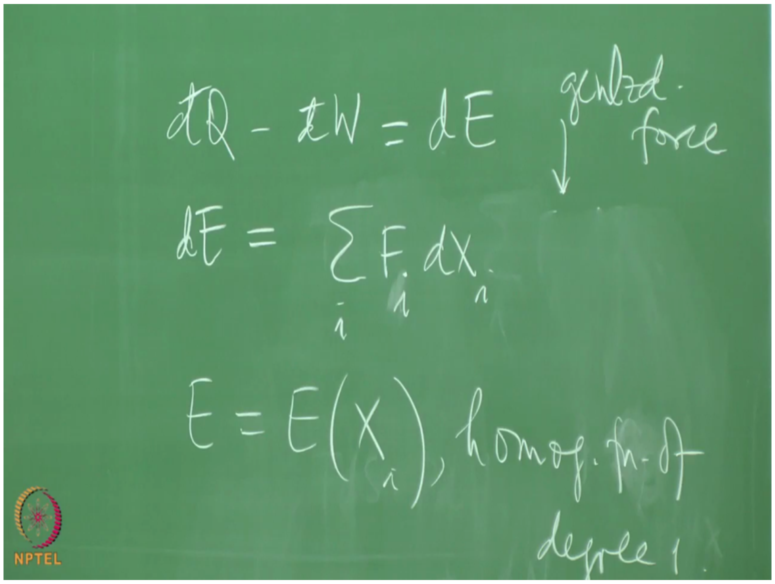

$$đQ - đW = dE$$

genlzd. force

$$dE = \sum_i F_i \, dX_i$$

$$E = E(X_i),$$ homog. fn. of degree 1.

Pardon me... All 3 are intensive, all 3 of these are intensives so there is no information about how big the system is here at all, so this is not going to work and we will see explicitly. If you do a Legendre transform on this, you will see what happens, but we need just one more step before that. You see the 1st law of the laws of thermodynamics written in this form, I could in some sense consider this also as a generalised force and this as a generalised flux, then I just put F i dX i for the whole lot, I do not have to take this separately so let me just do that. Submission over i F i dX i with the understanding that there is a generalised force called temperature and there is a corresponding flux called the entropy.

Now, extensivity implies that all these generalised flux are proportional to E right or E is proportional to this I mean differential in this form, but now we make an assumption that E is a homogeneous function of all the generalised fluxes. So we assume that E is E of X i homogeneous function of degree 1.

Student: Is not their statement of extensivity?

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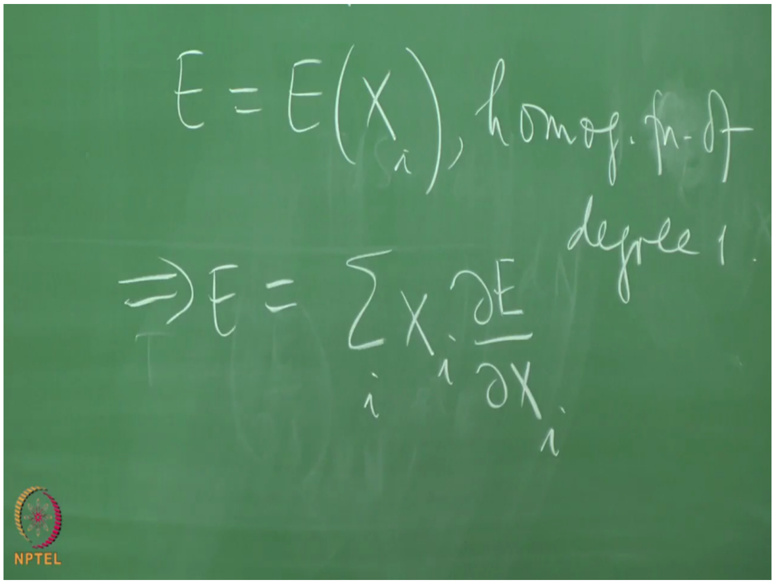

$E = E(X_i)$, homog. fn. of degree 1.

$$\Rightarrow E = \sum_i X_i \frac{\partial E}{\partial X_i}$$

Precisely, that is the statement of extensivity okay, it may not always be valid okay. For instance if you took cloud in interstellar space which is you know held together by mutual gravitational attraction of the particles, it is not clear that the total energy is proportional to the number of particles because there is a strong attraction and then various other things can happen in between. So there are cases where you have to be careful, this will not work but under normal circumstances this is a homogeneous function of degree 1.

What does that actually imply? This immediately implies by Euler's theorem that E must be of the form submission over i X i delta E over Delta X i by Euler's theorem with a power 1 here. Had this been of degree r, this would have an r that is the 1st that is the theorem you learned in calculus for homogeneous function of several variables right. But you also know from the laws of thermodynamics out here that dE Delta E over Delta X i = F i, so together these 2 imply that E = submission over i X i F i.

So you see although thermodynamics the laws of thermodynamics give you statements only about differential of E of the potential, not absolute values, the assumption of extensivity which is an extra assumption that has come in has actually given you an explicit formula here right. Now what happens in the case of single component substance that we talked about in this instant here?

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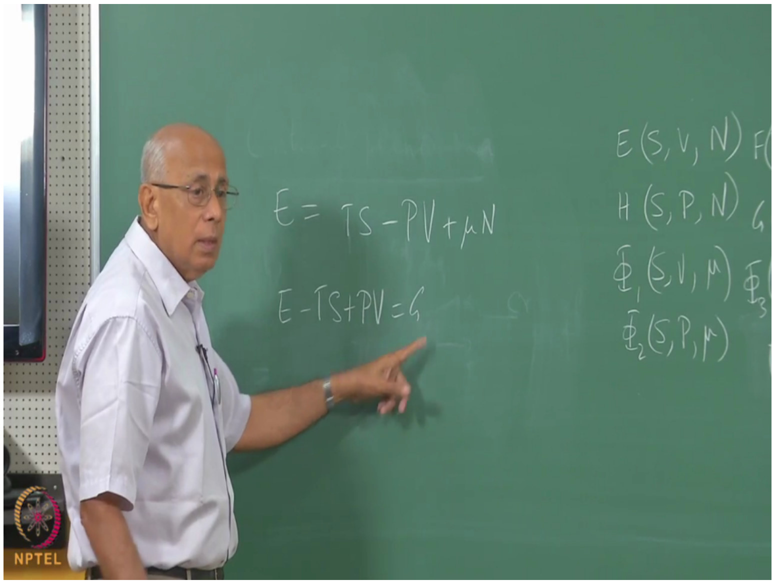

We have already seen that F 1 is T, F 2 was – P and F 3 was Mu and all we got to do is to put these fellow s in and you get an equation which says E = T S – P V + Mu N that is the Euler's relation in thermodynamics for this single component substance right. But we also know that E – T S + P V must be equal to G because that is what you get by doing a Legendre transform on this to get to this point to get to the function of T, P and N. So we have got one relation here and E – this thing = G here, so this of course immediately implies that G equal to Mu n or Mu = G over N, so the Gibbs free energy has a physical meaning of being at the Gibbs free energy particle is the chemical potential, so that is the physical meaning of the chemical potential okay.

We will come in a minute to why in phase equilibrium under normal circumstances you say that chemical potentials have to be equal along the side, this is how you find phase equilibrium, you try to find out condition for phase equilibrium if you boil water for instance in a beaker here then the pressure, temperature and chemical potential in the 2 phases are equal to each other, we will see in a minute why. Essentially what it says, this Gibbs free energy per particle being chemical potential, it tells you it costs just as much at the boiling point at the instant time of boiling condition of boiling it causes just as much energy to put a molecule additional molecule in the gas phase as in the liquid phase that is why we have an equilibrium okay.

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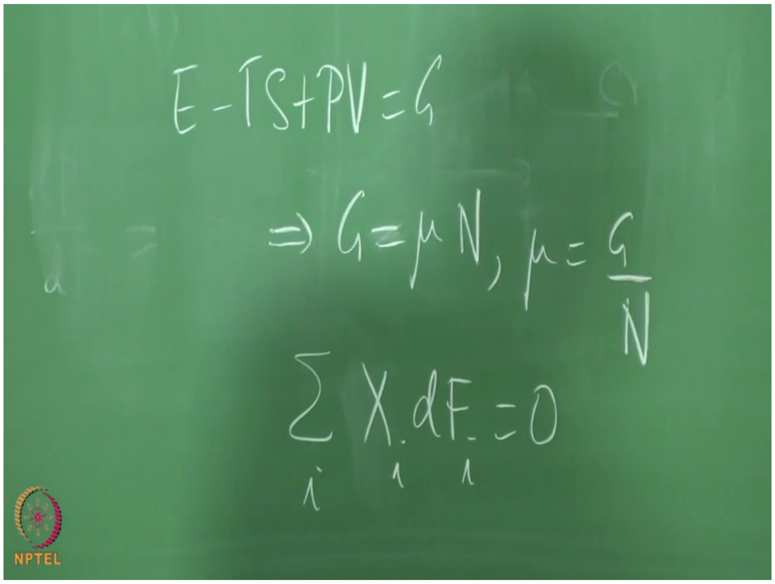

$$E - TS + PV = G$$

$$\Rightarrow G = \mu N, \quad \mu = \frac{G}{N}$$

$$\sum_i X_i \, dF_i = 0$$

So coming back to this because you have this, if I differentiate this guy dE, you see immediately this will also imply that dE = submission over i F i dX i + submission over i X i dF i because E is X i dF F i. But the loss of thermodynamics tells you that dE is F I dX i already, so this implies that submission over i X i dF i = 0, whatever I have done is that correct? Yah that is correct. So while E is X i F i summed over i, DE by the loss of thermodynamics is F i dX i therefore, X i dF i must be equal to 0 out here.

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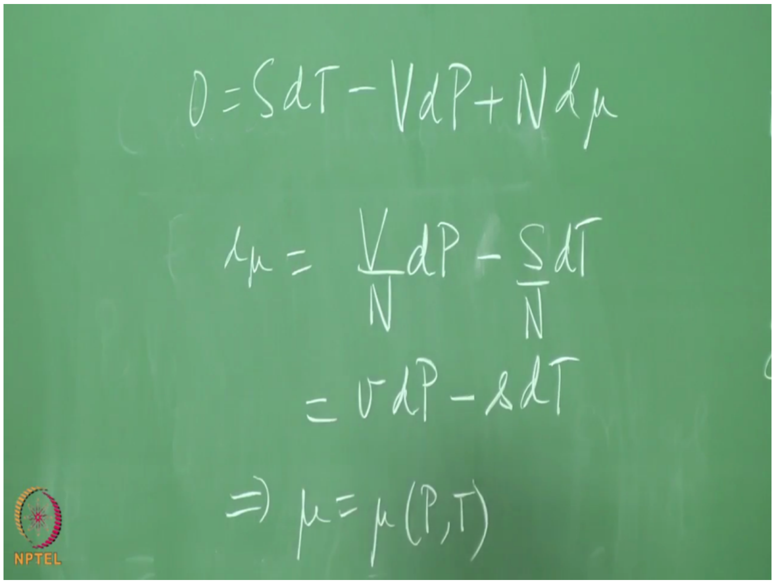

$$0 = S\,dT - V\,dP + N\,d\mu$$

$$d\mu = \frac{V}{N} dP - \frac{S}{N} dT$$

$$= v\,dP - s\,dT$$

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

What does it mean in this language? It says 0 = S dT – V dP + N d Mu alright. Or at this instance it also means that d Mu = V over N dP – S over N dT which is equal to little v dP – little s dP where this is the specific volume, specific entropy namely entropy per particle that is the specific volume, volume per particle, all intensive quantities because you divided by N. So this implies immediately that Mu is a function of P and T and this relation is called the Gibbs Duhem relation okay. Now what is going to happen if you try to find a potential here, this side is not going to work?

Student: Identically 0.

It will turn out to be identically 0 because you will end up by subtracting from this – S T + P V – Mu N and that by this relationship is identically 0 okay by the relation here the Euler relation for E, you subtract everything out you get 0 okay. That is indication that is already telling you that that is not a good thermodynamic potential because it is entirely in terms of intensive quantities and won't serve okay, alright. Now the Maxwell relations tell you the following and this let me let us take the example here and do this, let us go back to, let us look at F for instance.

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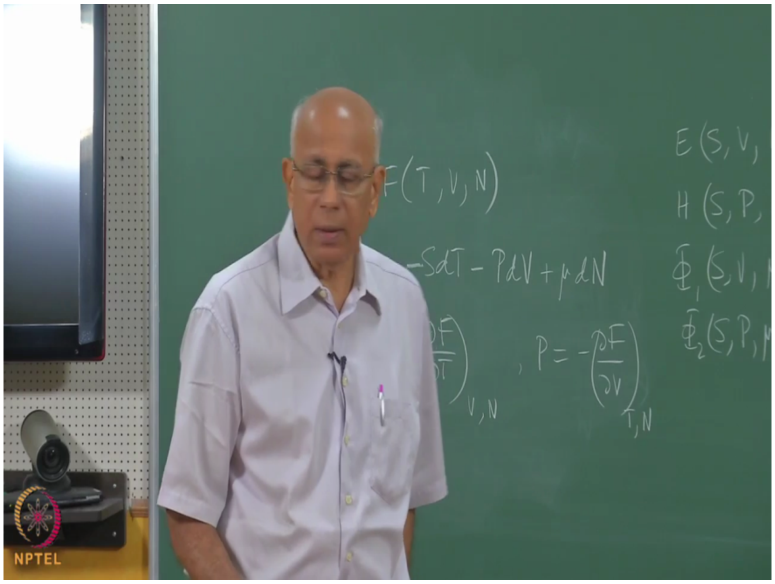

So F = a function of T, V and N and what is DF, this is found by going from S to T, so we have T dS interregional dE and we are now finding E – T S, which is what this F is so this is going to be – S dT + P dV because V does not change and then + T dS again, I want to be careful about the sign no no – P dV + Mu dN. So this will imply that S = Delta F by Delta T at constant let us see, T is T dS – P dV + Mu dN yeah it is okay at V and N, and similarly P = – Delta F by Delta V at T and N constant T and N. So this sort of thing is telling you that because of this relationship, the fact that this is an exact differential, it is telling you that the derivatives of this of thermodynamic potential with respect to these variables the X i are other thermodynamic variables, they are the conjugate forces of the generalised fluxes okay.

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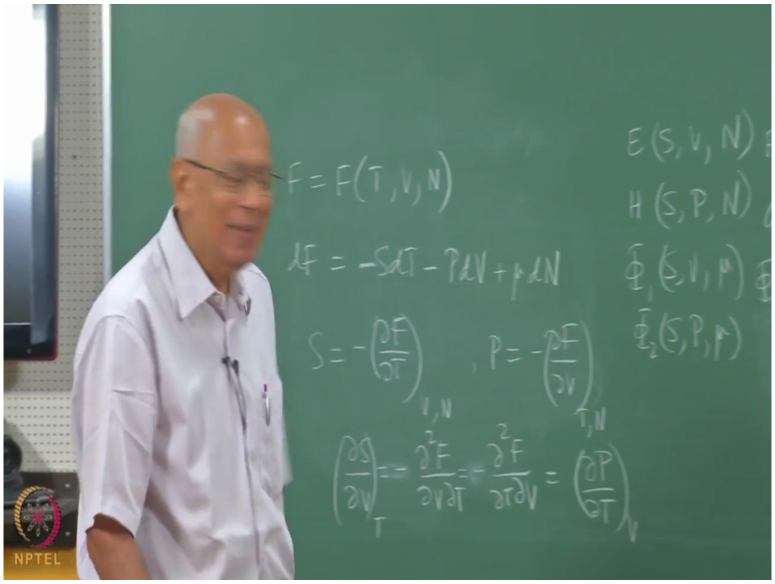

On the other hand, there is nothing to stop you from differentiating 2nd time in 2 different orders and we know this is going to be equal to each other. So if I now differentiate this 2nd time with respect to V then I get Delta S over Delta V = d 2 F over Delta V Delta T but that must be equal to d 2 F over Delta T Delta V, which must be equal to...

Student: S = – d F.

Alright, so Delta S over Delta V = – this guy, that is equal to – this guy yeah, which is same as Delta P over Delta T, and this is at constant T and that is at constant V okay. It is called the Maxwell relation, I will let you have fun by finding all the other Maxwell relations, so for our purpose because that it is I mean for (())(32:32) I did not plan in this way, I just took a random one but that is precisely the one we need because we are trying to find dP over dT so it turns out, I should remember this, so it is the one with F and does this okay, so we have a 1st Maxwell relation and we can go back now.

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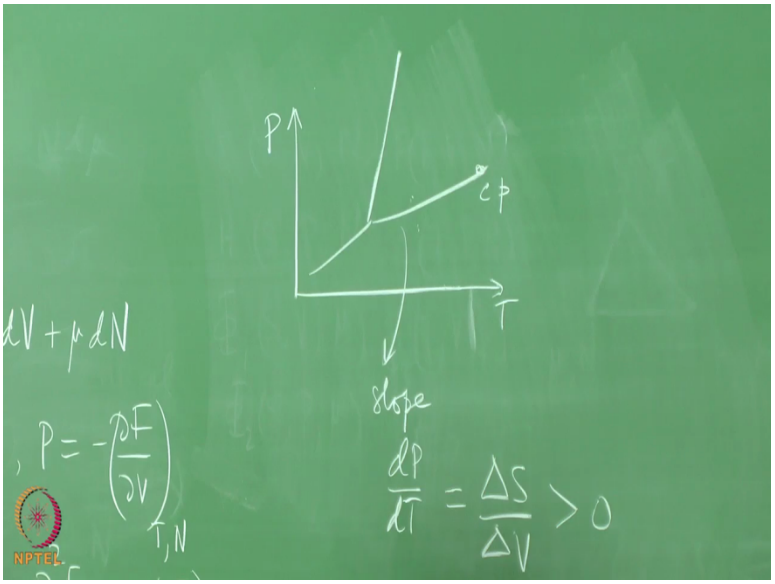

So, on the boiling curve now with the critical point which will come to slowly here is T, here is P, on this boiling curve the slope of this curve slope dP over dT okay is given by Delta S by Delta V. So across this curve there is a discontinuity in entropy because as you can see the volume for given amount of material the entropy of the gas is much higher than the entropy of the liquid, much greater disorder many more accessible micro-states. Similarly, as far as the volume is concerned the specific volume of gas is far higher than the specific volume of liquid, so this thing should really be written as Delta S over Delta V. And I do not then care which is called phase 1 and which is phase 2, whatever convention you use, I find Delta S and Delta V with the same convention.

So this could be for instance S gas – S liquid, V gas – V liquid. Now clearly this is positive because the entropy of the gas is definitely higher than that of a liquid, the volume of the gas is definitely higher than that of liquid in all cases so this is certainly greater than 0 and it is a large denominator, so the slope is generally very very small, which explains why this fellow has this behaviour. On the other hand if you look at this and apply the same equation between say liquid and solid then S liquid is definitely greater than that of solid but V liquid need not be greater than V the volume of solid, in fact in case of water it is about 8 percent less, ice floats on water so therefore you have a negative slope.

Student: Delta S will be?

Delta S for liquid is always going to be greater I mean the S for a liquid is always going to be greater than that of solid unless we are talking about super fluid, then of course you have a small entropy system in (())(35:32) state in the system right, okay so this slope could be this way or that. And we also see that the liquid is practically incompressible so Delta V in that case is going to be V liquid – V solid for a given amount of material is small but the entropy changes large. So you got a small denominator, large numerator and therefore the slope is large in magnitude in that case, otherwise it is small in this case here, similar argument for the sublimation curve as well.

Now the reason that this does not end at a critical point is because you have to ask now what the hell is meant by this critical point. What is meant by this is that as you go and let us look at the example of liquid gas specificity, you need a latent heat to be supplied to the gas in order to make it the liquid to make it gas, to cause it to evaporate. As you go up here down this curve, it turns out that this latent heat starts decreasing and finally vanishes at that point okay.

Student: (())(36:45)

So you do not need yeah you do not need any heat in order to go from one phase to another at this stage, but we will see that the distinction between 2 phases disappears. What is the other thing that keeps distinguishes a liquid from a gas, there is after all a surface and there is a surface tension that surface tension starts decreasing and at this point the surface tension also vanishes here. So after this you get a homogeneous mesh of some kind, it is a fluid I just call it a fluid phase, neither liquid nor gas, there is no way of distinguishing so it is beyond this point it is a fluid.

Student: But there could be like higher order discontinuity.

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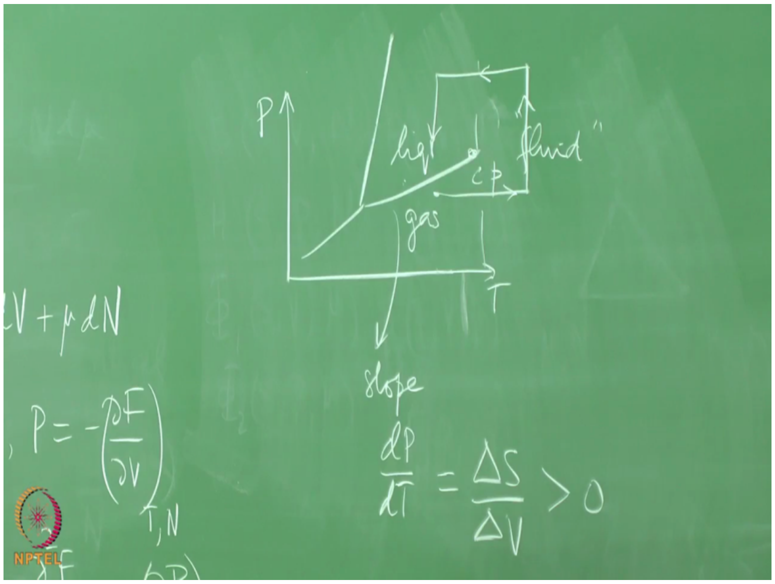

There could there could at this moment, we will we will see we will see what happens at this critical point. When I do the magnet analogy then it will become much clearer as to what this fellow is, what this critical point is. Now you cannot have that the critical point on this graph because you have a critical point on this graph it means that I pointed out that every point on this graph on this plane is a state of thermal equilibrium. So in principle I could start at this point, I am at sufficiently low pressure and a high-temperature I mean the gas phase and I go through this process. I take the temperature up at constant pressure and then I take this up here, at constant temperature I increase the pressure, go down in pressure and come down here.

At every stage I am in thermal equilibrium, I am not cross any coexistence curve, I have continuously moved from the gas phase to the liquid phase without encountering any discontinuity whatsoever. Whereas if I try to do it directly and encounter a discontinuity in the volume as well as the entropy but it is not happening here so the point about having a critical point, the point where the phase transition line coexistent line ends at some finite point is simply that you can continuously go from one phase to the other and you will not know it but you moved into the other phase alright.

Something does happen when you cross this point here or this point but we will not get into that here, but it is a continuous path there is no other distinguishing feature on this phase plane on this plane. But you cannot do that here because if you did, then it would imply you can go from a state of isotropic state, the liquid is all directions are exactly the same, it is homogeneous, it is isotropic and so on to a crystalline phase where the symmetry is broken, the rotational symmetry and translation symmetry of a liquid is broken because the Crystal has only a smaller group of symmetries, it does not look the same if you rotate it by an arbitrary angle, you got to rotate it by 1 an angle which belongs to the space group so to say and also translation only by lattice factors will give you the same system again.

So the symmetry is lower here in an ordered phase, it is much higher here in the disorder phase and you cannot continuously go from one to the other. So graph like this must either end in other phase other coexistent line or they must end in some physical boundaries like if it is on this side it can hit this point here or it can hit absolute 0 about here, there is no critical point on the liquid gas crystalline crystalline solid-liquid phase coexistence curve okay. Now what happens here at this point?

This is very very hard problem because what essentially happens is that normal thermodynamics fails and fluctuations on all scales all length scales start playing a role and this took a long time to realise how to handle this, how to find the physical relevant physical quantity in such a situation, in particular how to explain this apparently universal behaviour of systems at these critical points. And this entire problem is an outstanding problem in physics and finally in the 1970s it got resolved with Wilson and Fishers uhh Wilson's introduction of the renormalisation groove okay.

So to understand it properly to calculate critical exponents, we need some heavy machinery here, but the physics of it can be explained in much simpler terms and we will do that and we will adopt this so-called (())(41:39) approach which is phenomenological approach, which does pretty much the same thing provided that we know what we do not and it is a very very physical kind of argument, so let us do that in several slow steps.

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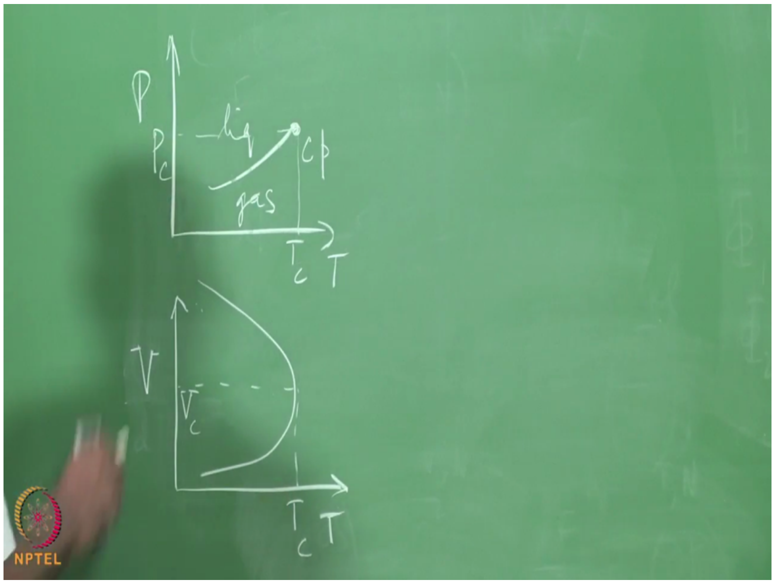

First thing I have to do is to ask what happens if I try to draw this graph in the other 2 planes here. And just to be specific so we do not get confused, I am going to focus only on this line liquid and gas just 2 phases, we are not going to worry about the solid phase and sublimation curve and so on okay. So now let us draw this, T and P and you have a graph like this with a critical point here. This was liquid, this was gas, what happens if I draw t here and volume here, conventionally one does not draw the volume, one draws the density which is like the reciprocal of the volume for a fixed number of particles but let us do the volume you can see physically what is happening more clearly.

I pointed out that beyond this curve there is no difference at all and across this curve there is a discontinuity, so it is clear that across this curve the discontinuity means this on this curve the 2 phases coexist, but if they coexist the volumes are very different, the volume of specific volume of a gas and that of a liquid are very different. So this means that if you solve for V as a function of T it must be double value clearly at a given temperature, at any fix temperature there must be 2 volumes if you are on this curve. So this curve will open would open into a region and it will look like this, very crudely to look like this fashion.

So let us say that this P is at what I call vertical temperature T c and this is at P c so this is at T c and this is at V c. All the while there is an equation of state of the system, which will tell you what one of the variables is given the other 2, so if you give me P c and T c I should be able to tell you V c, et cetera, so that is why I am not writing the 3rd variable down. In this graph the assumption is when you are here and you tell me P and T, you have also told me V except the 2 possibilities for this V, but at this point there is just one because at this point the distinction between liquid and gas vanishes and I will call those variables V c, P c and T c that is a standard notation.

So it is very easy to see which of these is going to correspond to the gas and which is to the liquid okay.

Student: (())(44:47)

Well it is not drawn too well, one should really draw one should really draw the density, should not it be the density that one pardon me?

Student: (())(45:06) because when the temperature is increasing for the gas.

Because when the temperature is increasing, the specific volume also increases there is thermal expansion right. So it is opposite, so this is not a happy picture.

Student: Make it Rho.

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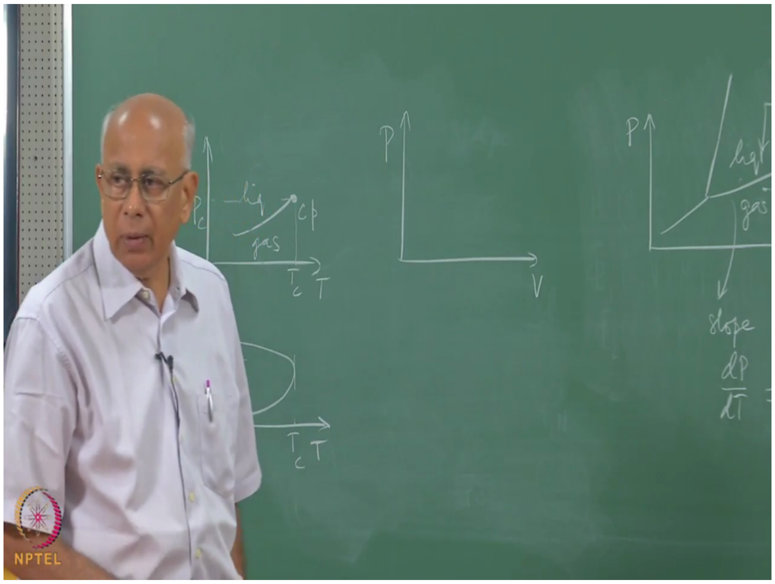

Make it Rho okay. One of these high-density phase in this picture it will look like this. Well, actually it is not Rho, it is difference between the 2 it is being drawn Rho liquid – Rho gas – Rho liquid or the other way about, Rho liquid – Rho gas whatever, it will become clear as we go along. The liquid has got higher density; it does not change as much so it is more likely to be like this okay. But what about the isotherm? For a fix temperature what does P versus V look like and that you are all familiar with P versus V. If it were an ideal gas, it will be just hyperbolas P-V is a constant time times temperature and it fix temperature it is just a constant, which is a rectangular hyperbola that happens at sufficiently high temperatures.

But as you come down at lower temperatures, you have a real gas like a Vander Wal's gas for instance for which the isotherm typically looks like this, it actually not drawn to scale but better if figure would be this, a high slope here and very small slope here okay. This is a typical Vander Wal's kind of isotherm for a real gas and it says that for a given pressure temperature is constant on this isotherm, for a given pressure there are 3 possible values of the volume okay, it is clearly not true. It also says that one of them has a high slope with respect to V at a constant temperature and the other has very very small slope.

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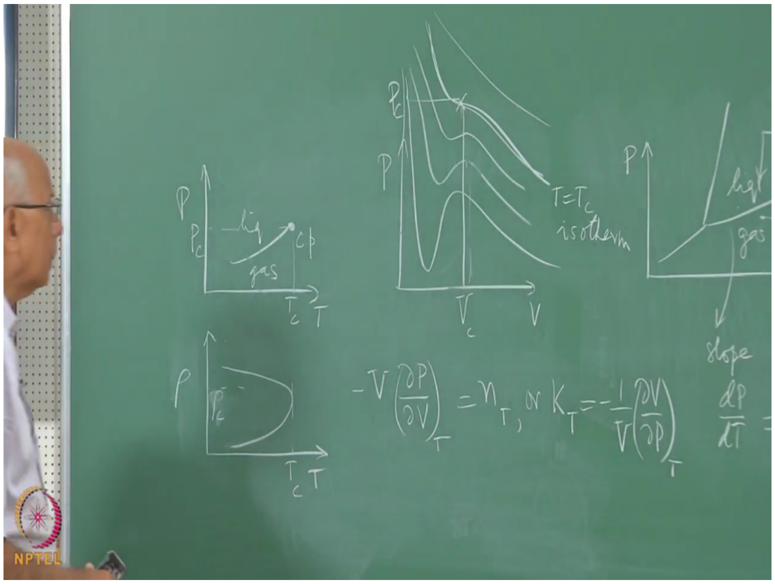

So what is the slow? Remember that Delta P over Delta V at constant T 1 over V times this what is equal to?

Student: (())(47:52)

Delta V over V sorry, V times this, what is this guy equal to?

Student: (())(48:04)

This is equal to the bulk the modulus right, it is equal to the isothermal bulk modulus and since when you increase pressure the volume decreases – this or the isothermal compressibility K of T = – 1 over V Delta V over Delta P at constant temperature. So let us stare at this guy here, you can see that this is a very incompressible part of the isotherm and this is very compressible here. It has also got other problems, now how is this graph go in to at sufficiently high temperatures into that mesh about the critical point. The only way it can do it if it does so continuously is that this graph at some point develops an inflection point and after that that inflection point splits into a maximum and a minimum and as you get lower and lower it gets more pronounced that is the only way can do it.

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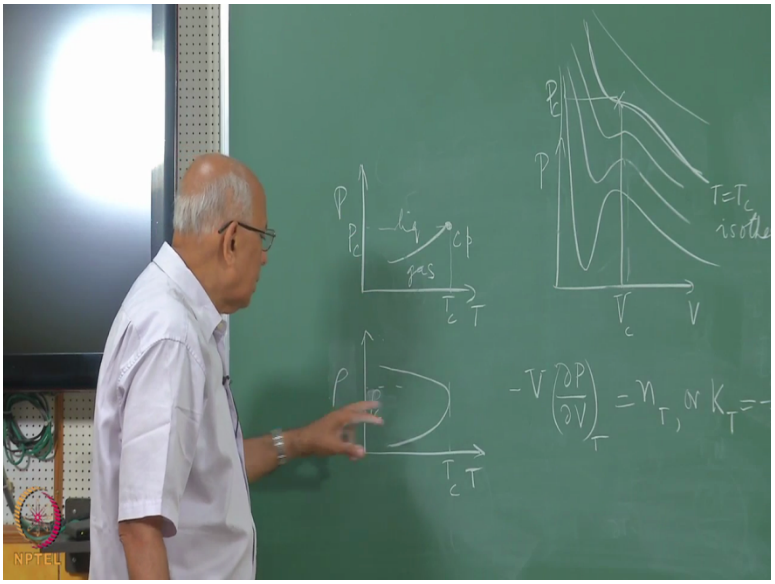

Now, one can got is in a very fancy language but this is the only way this can happen. So there exists an isotherm a critical isotherm which has an inflection point this point here and that is P c, this is V c and the corresponding temperature and the corresponding temperature is given by the equation of state, so this is T = T c isotherm. So we have all 3 diagrams now, there is a P-T diagram, there is a V-T diagram essentially and the P-V diagram out here. What is got to be recognized is that this coexistent line is the coexistence region here whole region. But this cannot be a correct picture because it says that if I start T is fixed, remember this is an isotherm, I take at this point I start at this time at low pressure and I increase the pressure on the system keeping the temperature constant.

Then the system is compelled to move along this graph up to here and then jump to this point and similarly it has to be moved down along this graph and jump to this point if I reduce the pressure from the liquid phase. This means there is hysteresis, your refrigerator will not work if there we know that there is no hysteresis in the condensation phenomena right. So this part of the graph is not correct, there is another problem with this part of the graph and that has to do with the fact that out here the slope dP over dV is positive, this fellow is positive that will make the bulk modulus negative which is not possible, it violate thermodynamic stability, you put pressure on the system, the volume cannot increase right.

It is statement of thermodynamic stability it says the thermodynamic potential corresponding potential is at minimum, not at a maximum or saddle point so this will have to be positive, it can only happen if this is a negative slope. So this portion of the graph has to be excised anyway, it says it is an un-physical model but it is even verse because even if you remove this, this is not what happens in a real system, the actual system comes here and at a fixed value of the pressure it changes to, it condenses to a liquid and the way back it does so without hysteresis here, this is called Maxwell sty line construction to do Vander Wal isotherm and insures that there is a unique at which condensation or evaporation happens at a given temperature okay, there is no hysteresis.

So the actual isotherm looks like this, there is a flat portion and then comes out and you have a family of such isotherms going all the way up to the critical point.

Student: Like you can get superheated phases.

We will not we are not going to get into that right, there are metastable phases actually yes okay, since he is mentioning this let us take this little more seriously and see what happens. You see if I excise these portions all the way through then they form a curve going through the minima and the maxima which looks like this, but I am excising a little more beyond that. And the way the sty line construction is done I do not think you can see anything from this figure now is that this area should be equal to that area, it is called the equal area rule and there are ways of justifying it heuristically, deriving its rigorously is quite hard quite hard to do.

Student: Has it been derived? I do not think it is heuristic.

It is heuristic, I can give a sort of very crude argument because you can see you know by telling which is not a correct argument in terms of the chemical potential but not relevant here. So what I want to say is you removing this portion, inside here is an unstable region but you are actually exercising a bigger region for which looks like this, let us draw this figure again.

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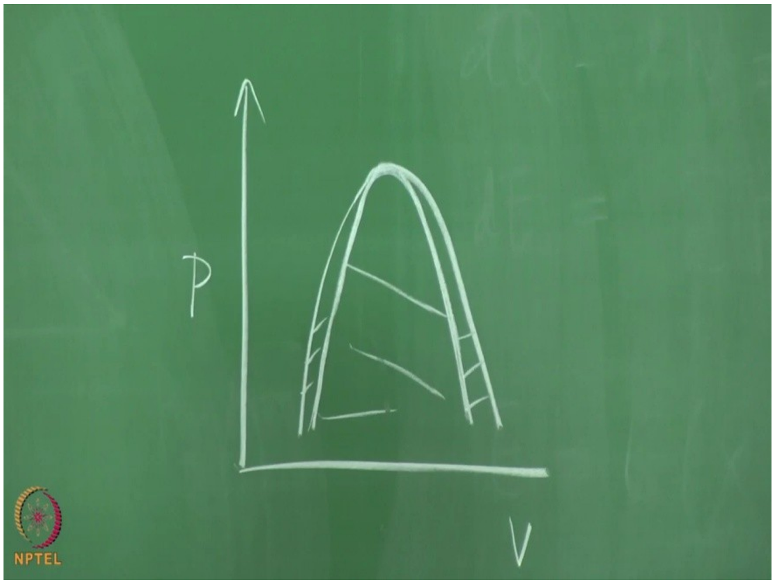

In this figure getting rid of everything else there is a curve like this and there is a curve out like that slightly bigger than that and this is V and P. This is the locus of the minima and then the maxima of these cubic curves in the Vander Wal case where as, the sty line construction which tells you where the phase transition occurs on either side is a slightly bigger curve in that and the system is unstable here and metastable here okay. So if you rapidly quench it in into this state from above then it will phase separate into a portion that is gas and the portion that is liquid. And there is a simple lever rule which will tell you how much of it is gas or saturated vapour and how much of it is liquid.

Now technically this portion of it, it will get through extremely fast because it is thermodynamically unstable and because this portion is metastable this is called the spinodal curve this is going to be much slower. In the case of liquid gas it happens pretty fast in any case, but in the case of binary metallic alloys for example, this might take a long time, it can happen very slowly and then there is theory whole theory for the spinodal decomposition, the curve and so on right, it is a separate subject altogether right. On the other hand, we are not concerned with that, the point that I want to make is that if I now draw what the actual isotherms are, they look like this and this is the point I wanted to make.

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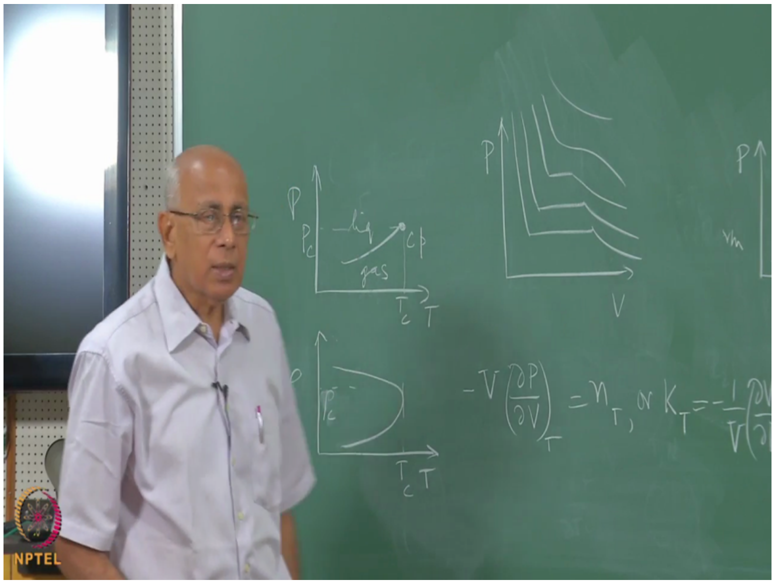

So here is V, here is P, these fellows come down like this till there is an inflection point and there is nothing beyond that, so gas-liquid gas-liquid, above the critical point there is nothing neither gas nor liquid but homogeneous fluid okay. So that is the P-V diagram, V-T diagram and the P-T diagram.

Now let us look at a magnet okay, and we look at the simplest example of magnet, something which is got magnetic moments, you apply a field and they align in the direction of the field and switch it off the field, the magnetisation goes to 0 okay. On the other hand, the substances which are ferromagnetic where even if you switch of the field you still have a Remanent magnetisation. So the paramagnet below a certain temperature makes the transition to a ferromagnetic and this is the one that has a direct analogy with the liquid gas phase transition that is what we are going to look at. So let us look at that little more detail, we need a simple model of magnetism.

Fortunately for us we have much simpler models of magnetism than we have of fluids because the interaction here is very complicated whereas, in magnetism the interaction looks relatively simple, and general it is something called the Heisenberg exchange interaction and many many applications have been done to it, we are going to take the simplest of these things which already captures the essential features of what I want to see okay. The 1st point I want to tell you and this is something which we will not need I mean what we want to study later on is that under normal circumstances when the system is in thermal equilibrium microscopic system, there are always fluctuations about this equilibrium state, but the question is how big are the fluctuations?

What is the relative magnitude of these fluctuations relative to say the average value of some variable? If that were not small then thermodynamics would be useless because thermodynamics is the science of averages, you generally expect it to be extremely small in measurably small, 1 part in 10 to the 12 or something like that right. On the other hand, at a phase transition these fluctuations will become fairly large because as we will see the very shape of the graph will change, the Centre limit theorem will change completely. But 1st I want to show you since I want to make the self-contained that thermodynamic fluctuations in normal state of equilibrium are really very small for microscopic objects provided the number of degrees of freedom is sufficiently large, so let us take the 3rd best of thing which you can imagine.

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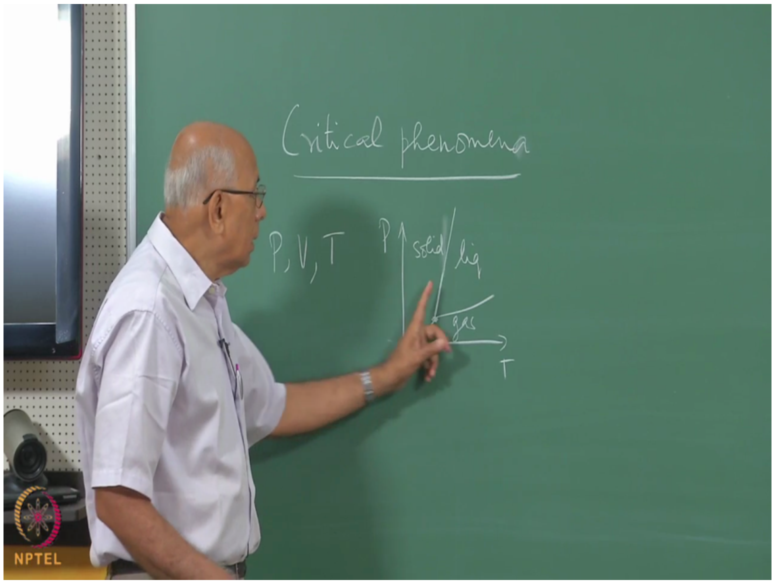

A caricature of a caricature, let us take a whole lots of atoms N of them and let us assume that each of them has only 2 energy states possible as simple as that. So let us assume that the 2 states, there is an energy 0 and there is an energy Epsilon nothing more than that. And you have N of these particles not interacting with each other, so they will not undergo phase transition and all these particles each of them has energy either 0 or Epsilon and it is put in contact with the heat path at temperature inverse temperature Beta, then the question is what is the average energy what is the variance of the energy here, the trivial calculation.

So since each can be either 0 or Epsilon, the probability is proportional to the Boltzmann factor e to the – Beta Epsilon then you have to normalise it. So the so-called partition function is submission over e to the – Beta e Epsilon and since Epsilon is 0, you get a 1 and the other one is Epsilon so you get 1 + e to the – Beta Epsilon and the partition function for the full system is just the product of partition function for all these guys because the number of states is just a product and that is it that is the partition function. What is the average value of the energy? I call it E but let me call it this to make sure let me understand this, it is a thermal average the internal energy is the average value of the energy Hamiltonian.

What is this equal to? There is a simple formula for this, this is equal to – Delta Log Z over Delta Beta here, this is = differentiate you get N you get 1 + e to the – Beta Epsilon out here and then N Epsilon e to the – Beta Epsilon times this, which is equal to N Epsilon over E to the Beta Epsilon + 1 that is it okay.

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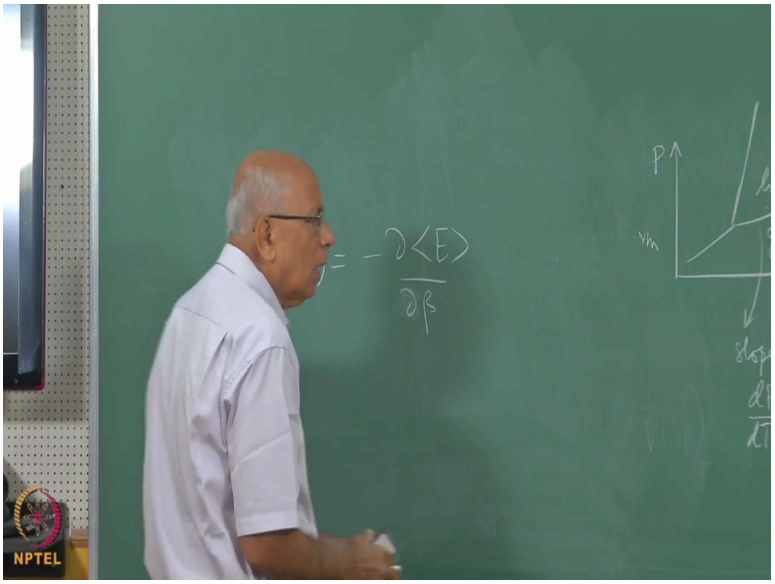

And what is the variance of this energy? Luckily there is a simple formula for it, you can painfully sit down and do the 2nd derivative and things like that but it is actually the derivative of the average energy the internal energy with respect to Beta okay. So that gives us this is equal to N Epsilon over e to the Beta Epsilon + 1 the whole square, the – sign cancels out and then Epsilon square e to the Beta Epsilon, so the standard deviation is square root of N and this goes away. So the standard deviation of E divided by the average value of E is, this guy goes away, the Epsilon goes away, 1 over root N okay.

Now that is typical, it says the fluctuation relative fluctuation in any microscopic variable will be typically in a state of thermal equilibrium 1 over the square root of number of degrees of freedom. And if this is of the order of Avogadro's number or 10 to the 24 or something, this is one part in 10 to the 12, so it is the reason you forget about fluctuations in general okay. But you see if you are in a paramagnet, where you say that the magnetisation is 0 when the field is 0 and you are in the state of permanent magnetisation then what happens is if I plot the magnetisation for which let us call it M and the probability that the magnetisation is some value M in this fashion then in a Paramagnetic phase in the absence of any external field, the magnetisation is 0 on the average, but on average the fluctuations about the average.

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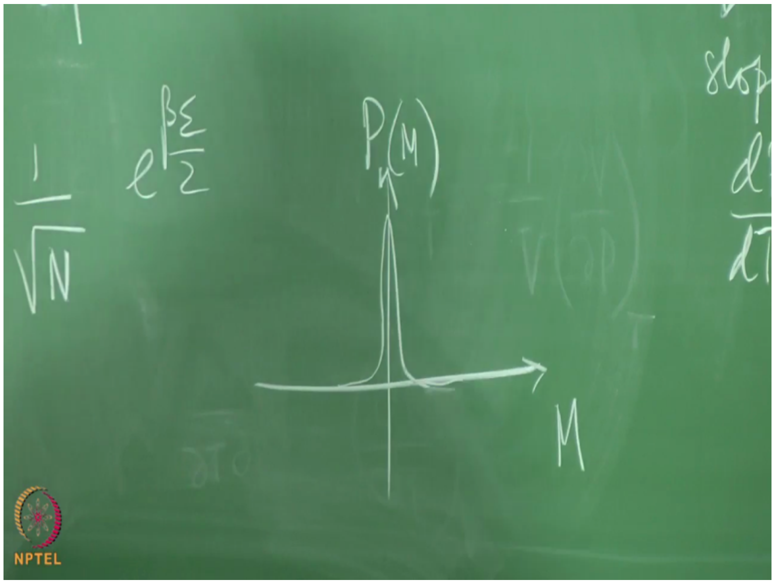

So what you really have is a curve which is extremely sharply peaked about this point, an extremely narrow peak which goes to 0 in the limit when the number of particles becomes infinite, so every time you measure this object you are going to get on the average you are going to get 0 okay. On the other hand, if it has a permanent magnetisation, it could have either be a magnet point of down if you just take the simplest case of just 2 possibilities, then you get either a peak here or you get a peek here depending on what your initial condition was. Now how is the distribution like this is going to go to a distribution like that as you cross the curie point curie temperature that makes you go from paramagnet to a ferromagnetic.

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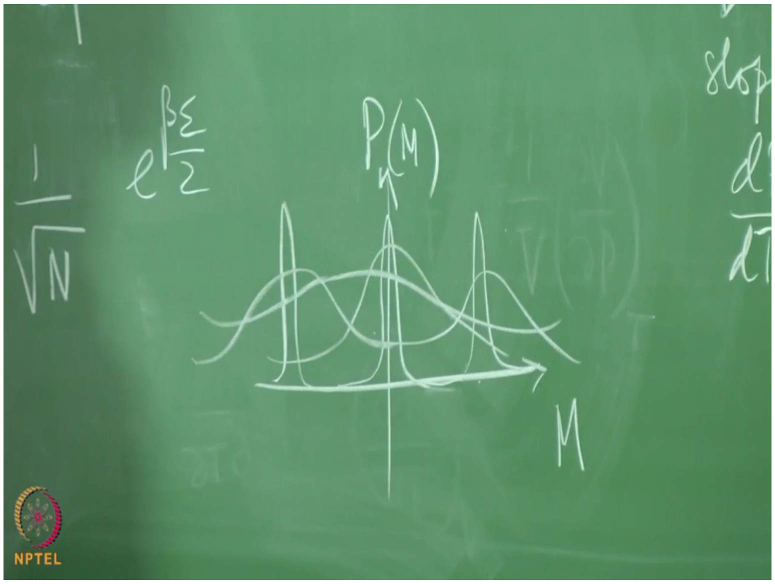

The only way it can do it is as you approach this curie temperature from above and go beyond left, this distribution must start getting widened out, so it must eventually do this and then it does this and then it fixes at this point, not as a function of time as a function of temperature as I lower the temperature across the critical point. Infinite above the critical point is this, infinite as below is this, which means at the critical point the distribution is extremely broad and this statement fails, the fluctuation becomes as big as mean the standard deviation becomes as big as the mean itself okay.

So if you like, you can say that phase transition with a critical point at the critical point you have the failure of the Central limit Theorem, you have failure of this sharp Gaussian and so on, so that is the probabilistic way of looking at this failure. It already tells you therefore that thermodynamics is going to fail because the fluctuations have become too large and therefore you expect thermodynamics which deals only with averages to fail okay. Now the question is how are we going to deal with this situation and that is the task of understanding the critical phenomena? Okay.

Now having come to this point, we will stop here today but next time we will take a simple magnet model and brought the analogue of these 3 figures for the fluid, develop the magnitude fluid analogy and then see what the so-called critical exponents, we define them see what they are and then try to see whether we can find a theory which will encompass, which will tell us what critical points behaviour should be like the time-dependent way there is few more steps to be done before that eventually but that is our goal okay.

Student: We will do time-dependent?

Yeah because whole point here is non-equilibrium, what happens (())(66:28) words here, what happens is that since fluctuations on all length scale will become important, the timescale also will become slower and slower if you look at large fluctuation, they will take longer and longer to heal so something called critical slowing down appears at the critical point, which makes the very interesting dynamics