Classical Physics
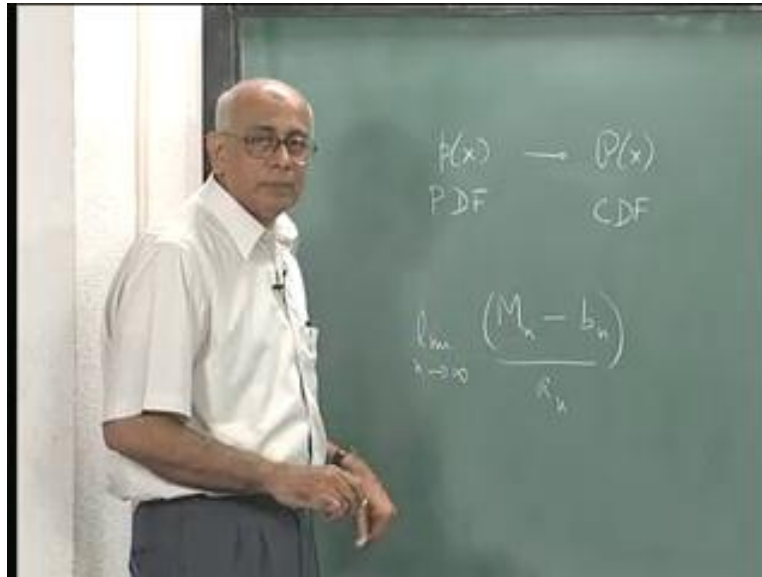**Prof. V. Balakrishnan**
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Lecture No. # 27

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As the question was if you give me a probability distribution p(x), this is the probability density function. And then from here you have the cumulative distribution function CDF p(x). This question was suppose if you take this random variable and convoluted with itself many times. So, the distribution will be convoluted many times and as the limit n goes to infinity will this tend to the Gaussian or not. The answer is know, in general we do not do that, but this idea of convoluting the distribution itself in a certain sense makes it has the meaning, which has the following. Consider a time series or a set of independent random variables whatever.

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So, there is x 1, x 2, x n. These are random variables like measurement. For example successively I get these values. Then I could ask what is the probability that the largest of these is less than or equal to some number, that I could certainly ask. So, I could ask let M sub n be the maximum of x 1, x 2, x n largest numbers. So, I take huge time series and just take n of these guys and ask look at the largest one among them.

Then I could ask what the probability that M sub n is is less than equal to some x, some particular value of x in the range of variation of these variables. Of course this also this immediately implies that it is the probability that x 1 is less than x, x 2 is less than equal to x, etc. So, it is automatically equal to probability that x 1 is less than x, x n less than x, but if these are independent identically distributed random variables. This is nothing but p(x) raise to the power m, each of them is independently distributed and it is just thing raised to the power n. And as you can see as n becomes larger and larger, it is clear that this probability will shift such that the shift to the right.

The probability mass will shift to the upper extreme, because sooner or later something is going to go larger and larger in it is range and eventually the whole thing will be concentrated at the upper, but you can ask the following question. Suppose I take this quantity M n and renormalize it rescale it, by perhaps subtracting some coefficients some constants, which depends on n and

rescale the whole thing with change the scale like we did for certain limit theorem we divided by n root sigma. So, this is a linear rescaling, there is a shift and there is a overall scale change. And then ask what about the limit as n tends to infinity of this rescaled variable?

Whatever this rescaled variable is and asks does that go to a limiting distribution? This limit does not have a definite limit as n goes to infinity, rescaled variable and these distributions are called max table distributions. And there are only three of them. In classical statistics there are only three of them and there are distributions, which if the variable runs from minus infinity to infinity. Then the limit of this kind of the limit goes as n goes to infinity of these distributions, the max stable distributions.

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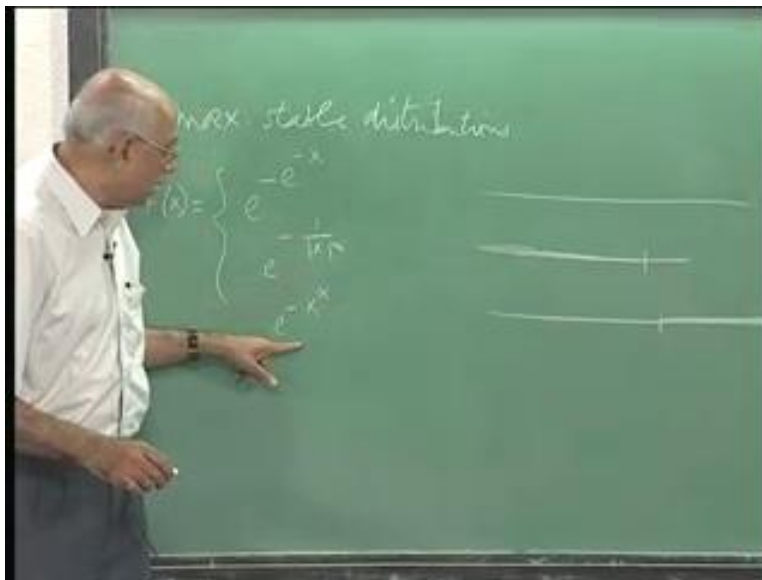
There are only three functional forms available for these max table distributions one of them is of the form e to the minus e to minus x. Let me call this max stable distribution f(x) something like this, e to the minus x and the other one there are two more one of them corresponds to the variables corresponds to running from minus infinity to infinity the other one corresponds to the variable having an upper limit. So, this is the range and then there is a upper limit and the third one corresponds to the variables having lower limit, some finite limit up to plus infinity this is plus infinity to a finite term. The two are the forms and they are called the Gumbel Weibull and Frechet distributions respectively, these are the three forms.

They can all be combined well the other one goes like e to the minus one over mod x some power alpha and then e to the minus x to the power alpha, where x is positive and x is negative here. So, this corresponds to this limit theorem this guy corresponds to this and these distributions are associated with the names Gumbel Weibull Frechet and they are the only three possible distributions. And there are conditions under, which arbitrary probability distributions script p of x would tend to one of these three limits. If at all they tend to a limit they would tend to one of these three limits and these are called the extreme valued distributions.

So, these are the distributions of the extreme values, if you look at rare events very rare events. We have got some spikes in random variable and I am going to look at all events above a certain threshold few standard deviations away from the average. When those extremes are distributed according to these one of these three distributions and they are very, very important in this study of rare events earthquakes on a certain latitude avalanche and so on and so forth; so in the study of rare or critical events or extreme value statistics very well known part of statistics.

Now, you could ask what goes to what and it turns out the Gaussian goes to this. So, the extreme events in a Gaussian distribution distributed random variable would eventually after rescaling go to this Gumbel distribution. So, there is a well developed theory of Maxwell's distributions this thing. Now you could ask what happens if it is a real time series and they are correlated with each other these events then we have to be very careful, but it turns out. Even, if there are correlations among these lines they are still is valid classical statistics is still valid except, when the correlations become very very strong.

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But the point is if x one take the k eth member here, x k and take after x j and this 1, 2, 3 represent time for instance

Then you have to ask what is the correlation between the k th and j th event and if this dies down like one over log modulus k minus j or faster than this theorem is still valid. So, even if they are quite strongly correlated as long as the correlation is not going to be infinite in extent in the sense that it is lower than one over log mod i minus j k minus j. You still have the whole thing changes if, you have deterministic dynamics if you have chaotic time series. Then it completely changes Gumbel Weibull Frechet distributions can be applied. I work from this problem with collaborators with extreme value statistics in chaotic dynamics. It is very different from what you get? So, this universality is completely lost, but otherwise most cases.

So, that is yet another way of deciding whether deterministic dynamics, noisy dynamics. There are lots of such tests to decide between two chaoticity and stochasticity about noise practical cases. It is very... So, I do not go further in details, any other questions?

Now, I will give a set of problems couple of problems after today on probability distribution and other aspects. But we need to move on to another aspect to statistical mechanics, which is

perhaps most important one as far as it is power is concerned. You see throughout I have been saying that thermodynamics is a kind of limiting case for statistical mechanics.

Fluctuations are neglected and that fluctuations can be taken into account to statistical mechanics and it provides corrections with thermodynamics. Many cases it goes beyond thermodynamics calculate quantities like specific heat which have input parameters in thermodynamics. Now, you could ask is there a place, where thermodynamics actually fails completely no longer valid the answer is yes. This was the hard problem of phase transitions and this took long time to resolve and it was suspected from the early days of statistical mechanics. The beginning of the twentieth century that in principle statistical mechanics equally statistical mechanics should tell everything about wisdoms in thermodynamics including what happens at phase transitions.

Great deal of progress is made, but this technique does not work all the time in non equilibrium situations. But in the case of equilibrium problems it works it is very interesting, it is very deep and it has connections to quantum physics, which is where the name renormalization is borrowed. What we will do now? What I will do is to force the problem is to tell you, what a critical point is show you why thermodynamics fails at this point and we will not go too much into critical phenomenon itself. Except a little bit of the phenomenon of the subject is essential to understand and this will also take us into the subject of real gases.

What we are going to use as a model? We are going to use the Vander walls gas as a model to describe fluid. So, let me set the state by taking a very simplistic attitude and ask what the phase diagrams of a simple single component substance, look like a typical phase diagram.
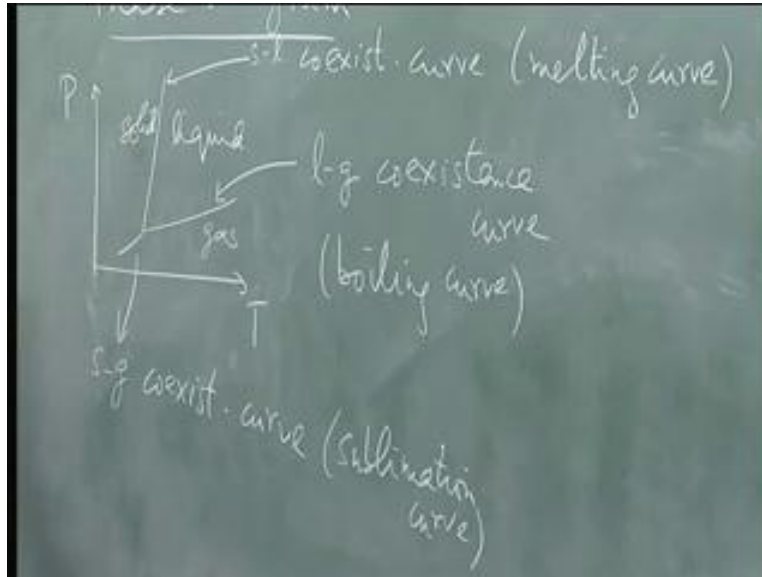
So, we can go to concept of a phase diagram. We consider ordinary substance water is not a ordinary substance. I am going to assume that this substance can stay can exist in the liquid gas and solid phases and plot the phase diagram. Now, the assumption is that the thermodynamic variables that I need to describe the system are two.

In number two in dependent variables could be the pressure and volume should be the pressure and temperature or the volume and temperature. It does not matter and these three are connected by an equation of state. Of course the equation of state in the gas phase would be different from the equation of state in the liquid phase or in the solid phase. But we are going to cut through all configurations and plot what happens in the threshold versus voltage diagram every point in this quadrant.

Pressure and volume are non negative quantities, every point in this quadrant is assumed to be a thermodynamically stable state equilibrium state of the system. But the question is in what phases in and typically this is what happens as all of you are familiar from high school chemistry. You have a line that separates the solid phase from the liquid phase. So, let me just call it solid phase and liquid phase this line is not to scale diagram is not to scale and basically it says that on this side at this pressure and volume. You have for a given temperature, because the temperature is found from the equation of state. You have a solid and a liquid by solid I mean a

crystalline solid not a glass or a amorphous solid typically something that conducts some crystalline substances.

This thing does not go down for ever what happens is at a certain state it typically joins another line and this line separates the liquid phase from the so, called gas or vapor phase. And this line also goes along and the remarkable thing the notable thing is that the slope here is much smaller than the slope here. And we will see the reason why? But these two points mostly as they are varying typically generically there is a third line here, which separates the solid phase from the gas phase. Now, you used to this and we will see what happens as we go down lower and lower this curve at some stage it would become a solid. So, cut the physical boundary of these two axis at some point, but for the moment. Just look at this and brief refresh of memories as to what we learnt in school? This curve is called the liquid gas co existence curve.

Because on that every point on that curve the liquid and gas the liquid and saturated vapor above the liquid co exist with each other. We are going to assume that matter existence only in these three places. There are many other exotic places that it could exist in depending upon what we are talking about there are many kinds of solid phase, because the first question that should arise is, what kind of crystal. We know there are many crystal systems. So, in fact there are further complications here there are phase transitions typically from the hex. You know hexagonal closed pack phase to the body centered cubic and so on and so forth.

How do you define a phase?

How do I define a phase?

How much in is thermodynamic equilibrium system? Now, I have to define what is liquid? What is gas and so on? I shall do? So, but I am just taking. Now empirical phenomenon in all the gas is something, which you can put in a container adopt the shape of the container liquid as I mean flat. You can pick your hand in it and stir it around the solid has got, which you did the difference between the solid and liquid is a very tenuous one. We will talk about it is called this is the way by liquid. I mean something which does not support shear stress. So, it starts flowing if there is a shear, but a solid resistance. That is the way naively I will define this and we make it

precise. Also I know that in general the gases have much lower density than the liquid and the particles the molecules are completely random whereas, in liquid.

If you look at very carefully there is always short range order it is trying to become a solid it is trying to crystallize, but the temperature is too high. So, this order comes forms and dissolves forms and dissolves and etcetera, but certainly around the neighborhood of any given molecule. There is a little short range order what called short range order, but if you go two or three atomic distances away it disappears. On the other hand in solid there is long range order. So, we will talk about this from the point of view of symmetry and order this curve also has another name it is called the boiling curve, because it tells you as a function.

You should have stopped me right away. This is what you were sleeping is it not? What isotherms look like at all pressure versus temperature? So, this curve tells me we are going to come to the PV diagram separately this curve tells me at a given pressure. What is the boiling point and we know that as you increase the pressure the boiling point increases or as you reduce the pressure the boiling point decreases so, the slope is positive.

The same is true in general as you increase the pressure, the boiling point the freezing point increases. Is there any exception? Water is an exception. If I increase the pressure freezing point decreases so, what will happen to that line in the case of water. The slope would go to the other way still it will be quite steep, but it goes the other way. So, right away it is anomalous, but this is certainly true in the case of generic substances most substances except a few remarkable substances like water this is certainly true. So, this is also called the boiling curve. This thing here is the solid liquid co existence curve, it is also called the melting or freezing curve, which is equal to which is the solid gas co existence curve.

It is possible? Of course that this thing goes from the solid phase to the gas phase directly without going through the liquid phase. If the conditions or temperatures lower enough and the pressures low enough, this is what would happen? What do you call this curve? It is the sublimation curve. You might have read in the newspapers that part of it worry about the ice melting. The globe is not that it melts, but it also sublimates quite a lot of it will be going off into vapor directly. So, just measuring how much the water level is rising by is not enough to tell you? How much of the ice is really going so, this is a serious problem sublimation curve.

All these slopes are positive. In principle this curve goes on forever, but actually it does not do so, in practice because what happens is as you increase the pressure there would be other phase transitions from say. Let us less densely packed crystal to a more densely packed crystal and ultimately at very high pressures things would become extremely densely packed like the phase centered cubic closed pair of some kind like FCC or something. But earlier there will be other phases like body centered cubic and so on so forth. So, there is lot of structural phase diagrams for this.

Occasionally what can happen is that the liquid disordered phase can actually you could have a situation where you have a super cooled liquid essentially like a liquid, but super cooled goes into a blast phase. Becomes amorphous those are meta stable states we will not talk about it for the moment, but this is what thermodynamic equilibrium states. What do you call this point here? It is the triple point where you have co existence of three phases and a very simple rule called the Gibb's phase rule. It is not very hard to derive tells you that, if you have a single component substance just one species of molecule, when such simple substances at best you could have only three co existing phases.

So, you have a triple point on the other hand, if you have more than one kind of species inside several chemical species inside molecular species.

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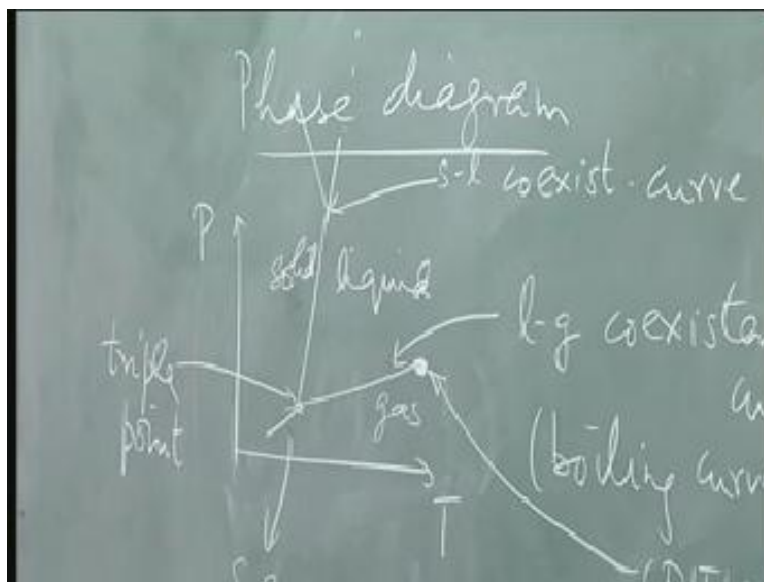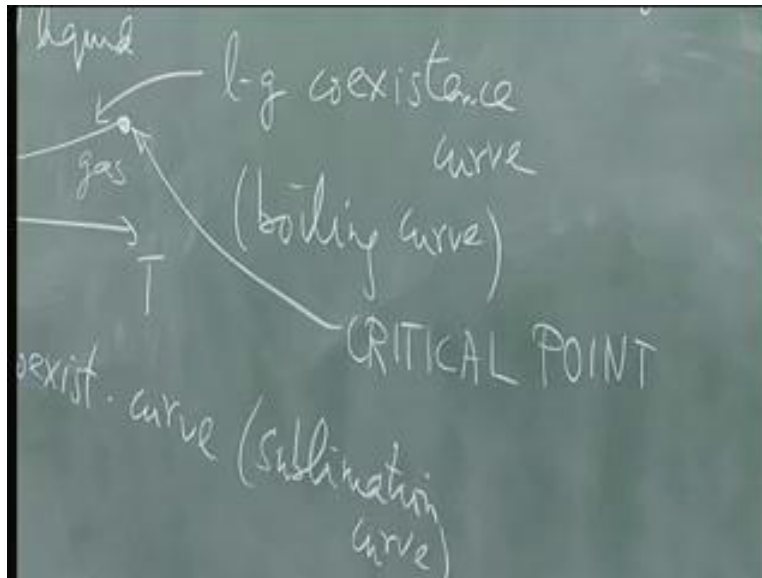
Then of course you could have points and so on and the phase rule tells you what the largest number of such points is? You have phases at one particular point? This point is not all that remarkable it turns out what is remarkable? So, let me say this curve keeps going for reasons, which will become clear. But what is remarkable is that this curve does not keep going this curve stops at certain point. It abruptly ends in the middle of know where and above that beyond that pressures and temperatures to the right of this point, which is called the critical point. You do not have a distinction between liquid and vapor liquid and gas vapor, but this point is very important.

It is called the critical point that is the point at which conventional thermodynamics fails and we will see why this happens? But above this you could ask what is to the right of this, but you have a homogenous fluid well. You cannot tell the difference between a liquid and a gas. You cannot tell whether it is a liquid or a gas. Now, what is it that distinguishes between a liquid and a gas? What do you need to go from here to here? Suppose I start at this pressure and I cross this line at constant temperature and I go in this path. So, here I have liquid here. I have gas what have I done? I have put beaker on and taken beaker of liquid and heated with supplied heat to it kept the pressure constant.

Let it go in the gas what do I need to supply to the liquid to do this? I need to supply late entry. So, in the process a certain amount of heat is necessary to take you infinite decimally close to this point here to that point across this phase. This line here separates two phases this continues the transition is discontinuous in a certain sense, because the density of the system changes, this

continuous jumps from the liquid phase to the solid gas phase. I need the latent heat as I go up this curve the amount of latent heat needed to do this becomes less and less.

Till the latent heat vanishes at that point and belong that there is no distance what else distinguishes a liquid from a gas. So, certainly there is the surface tension so, that too vanishes at that point critical point. So, the surface tension decreases as you increase along this curve as we move up till at the critical point the surface tension vanishes. So, the meniscus disappears and then you have a much. So, the phase above that is relatively simple it is just a homogeneous fluid case, but below that there is a distinction. So, that is the way nature is right many other things happen at that point. So, this critical point all distinction between a liquid and a gas disappears. That is what is observed? Yes, of course all these properties are correlated definitely.

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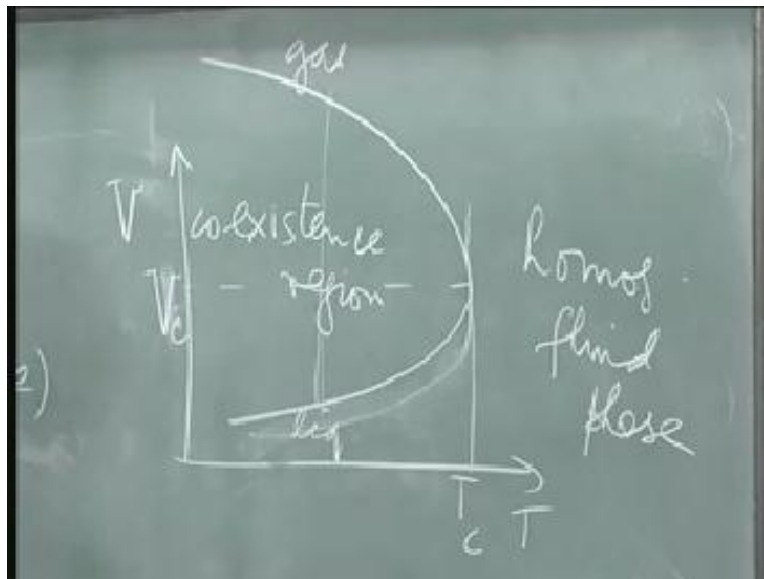
So, everything that distinguishes a gas from a liquid disappear even the density starts matching, because you see I could also draw this in the so, called T versus V plane and ask what does this curve look like well? Actually what happens is it is clear that the volume of the gas is much greater than the volume of the liquid? So, if you are at the liquid phase you are on this side little bit on this side and you go on changing the temperature the curve by which this volume change will look like this from the gas side. However volumes are much larger this is not round to scale.

So, we end up with a curve like that certainly not to scale, because change in liquid volume is not all that high and this corresponds to liquid that corresponds to gas and this is the critical point.

Let me denote start by saying T sub c critical point so, here from this curve to T c and this is the critical pressure P c the V c the critical volume is known in terms of P c and T c. Because there is a equation of state and presumably the equation of state for liquid and the equation of state for the gas would give you identical results at that particular point. We are going to write down both these equations. So, this is the question is what is happening inside? So, you see this diagram, if you are on the curve here. You are actually in the whole region here from this place.

So, it could be anywhere in this line on this region so, this looks like a line in the V T diagram has become a region. In the V T diagram that portion is gas this portion is liquid and what is the region in between that is the region of co existence of the liquid. Now, you should ask next question what a physical system will do. What will it really do well? The answer is if you bring the system to that point as we will see it will split into portion to portion will become a liquid. A portion will become vapor above and there is a definite rule, which tells you how much of this and how much of that?

But the important thing is the difference between the gas volume and the liquid volume vanishes at this point both this branch has come together and after that there is no distinction. So, this is a homogenous fluid phase, this is the liquid phase, gas phase, liquid phase and this is the co existence region. Again you see something strange is happening at the critical point distinction is disappearing the curve has got a tangent layer. Now, of course what one should do to understand this more thoroughly is to draw the third diagram and what does it look like in the P V plane, when you draw isotherms in the P V plane.

I will come to that in a second, but let me say the following. Let me say that they are not going to consider this transition except to make noise about it all this transition later. After you do phase transitions little bit we will look at other substances like some exotic substances like liquid helium or helium. For example, which has all kinds of phases at very low temperatures; it becomes super fluid and so on. We will come to that separately, but the point I want to make here is the difference between the liquid and the gas. Here is manifested in the difference in the

density, I could also plot the density because that is the reciprocal for the volume for a given number of molecules. It will just be converted to this direction.

That difference in density goes on vanishing till this critical point and then the difference disappears. Therefore, what one says is this is a discontinuous phase, because it jumps this density jumps on the other hand at the critical point. The discontinuous phase transition becomes continuous phase transition, because this density no longer jumps, but still the limiting point of phase transitions and this is the modern definition of a difference between phase transitions. Earlier, there was a classification given based on what happens to free energy and so on, where people used to call first order phase transition, second order phase transitions, higher order phase transitions so on. I will explain what those things mean they refer to the fact.

That a first order phase transition refers to the fact that the first derivative of some free energy is discontinuous jumps that would typically be volume in this case, because if you differentiate the Gibb's free energy with respect to the pressure. You get the volume on the other hand the first derivative is continuous, but the second derivative is discontinuous and the curvature is discontinuous. We call the second order phase transition. Now, I have already mentioned that second derivatives are things like specific heats compressibility's susceptibilities and so on. If that changes discontinuously you call it a second order and similarly for the third higher and so on.

But the modern definition has something quietly different it does not bother about this, because all kinds of mixtures possible in straight you talk about continuous and discontinuous first transitions. So, you have a line of discontinuous transitions or first order transitions ending in a critical point, which is a second order continuous.
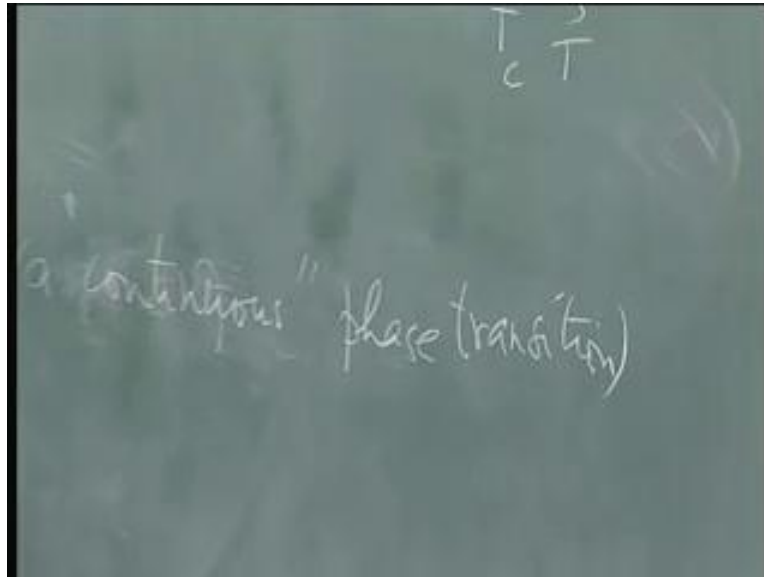
A point continuous whereas, these lines the co existence line themselves are lines of discontinuous or colloquially first order phase transitions. So, typically first order phase transition ends in a critical point, which is the second order transition in the old line. Our idea is to understand this curve and ask why this does happen in this plane. Why this happens and let us see what happens at that point and can be said something more of this?

This is our immediate goal so, far that let us go over and look at the third diagram the P V diagram the isotherms.
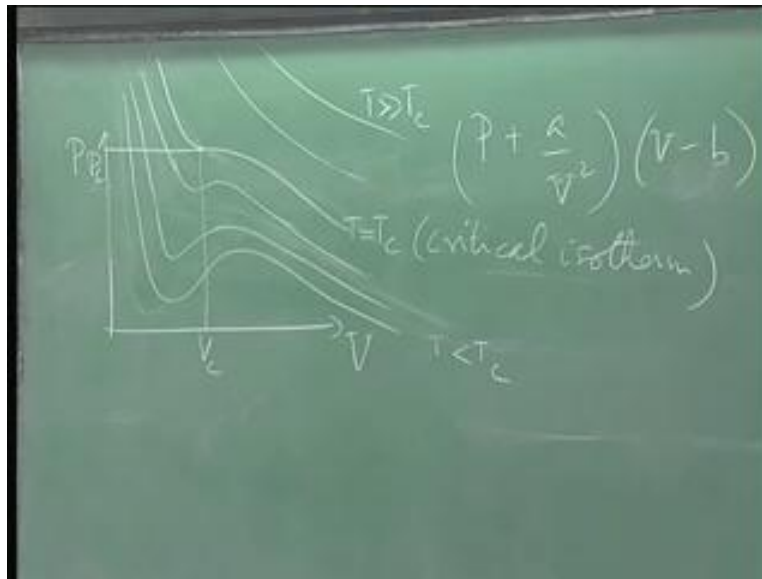
Now, I am focusing only on the liquid vapor transition only on this transition. My idea is to just look at this and so on. Now, of course if I took an ideal gas P V equal to R T then the isotherms are just hyperbolas nothing much happens and I could say well at the highest temperatures. You do have something like that at very high temperatures I compare to the critical temperature this is what happens? Now, you see immediately the existence of the critical point provides for me a temperature scale. It tells me there is a natural temperature associated with the system called the critical temperature. And when I say very high temperature I mean something very much higher

than the critical temperature and it looks roughly like these hyperbolas Boyle's law or whatever it is.

These are the isotherms, but as I come to lower temperatures I should really look at the some equation of state, which is going to give me some cognizance of the fact. That these particles attack each other these particles attach each other and typically one looks like the Vanderwaal equation of state, which has all the essential features and what does that equation look like? It is like P plus a over v square times v minus b equal to R for one mole and this is the cubic equation in V. So, if you keep T constant and plot T versus V you are going to get a cubic term of some kind, because it involves cube of it and very typically. It looks like this again this is not to scale in reality, which obeys the Vander wall's equation of state could not look like this at all at lower temperatures.

It would be an extremely steep thing very sharp rise here and a very slow fall off. In fact the slope here can be three or four orders of magnitude greater than the slope and why is that because this equation really describes two phases. It requires the liquid phase as well as the gas phase and that slope there is directly related to the compressibility, because we know that on a isotherm the isothermal compressibility is K sub t equal to minus one over V delta V over delta P. So, this slope here is extremely steep, because this guy is highly incompressible on the other hand if it is very flat, which means it is very compressible.

And then you have a gas phase it is natural to ask whether these two portions really describe the liquid and gas phases or not and turns out yes the simplest. Now, how would a curve like this go into a curve like that? So, it is clear that this is an isotherm for less than T c and these are isotherms for T greater than T c. How would this guy go into that?

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Well, it could happen by the minimum and the maximum coming together and then disappearing this would typically what would happen? So, what would you get when a minimum and a maximum come together? This guy goes down that guy goes up and at some stage you have inflection point. So, at that stage you have some curve here this curve keeps getting distorted till at some stage. You have this and there is an inflection sequences and below that below that it is

this, then it broadens out and so on. There is a critical point isotherm. So, it is natural to say this is P c this is V c and this is T equal to T c and this is called critical isotherm.

So, the Vanderwaal equation of state is a good model for liquid gas phase so, it is just a empirical form, but it has the possibility. That you can actually see where the critical point is? Now, the question is what is the coexistence region? Can I identify these guys well? The first problem that arises is the following the first problem is this equation cannot be right completely. Before I do that how do I find this thing here? That is not hard to find, because at this point you have a inflection point. So, you have delta P over delta V at constant T equal to 0 at P c at the critical point the slope is flat and the second derivative is also zero. See, I have also this and you have the equation of state.

So, in fact you can find the critical point if it exists uniquely, because you have 1, 2, 3 equations connecting three variables and you can solve problems. I leave it as an exercise to you to find out what is T c, P c, V c for that particular equation also. And as you are aware it would take these typical values and you divide by them you get reduced pressure reduced temperature reduced volume it is a dimensionless quantity. We express this equation of state and one of the big holy grails of the nineteenth century was to find out. Whether, there is a universal equation single equation for all substances the answer is known there is because as I explained the reason why things are condensed?

Someone has to do with interactions and these interactions cannot be modeled very easily, because there is no universal way of doing this. And we know typically there is short range repulsion and long range attraction and these are modeled. So, while there is no equation of state universal equation of state some things do become universal independent of the subscripts of this point.

We will see what it is, but this as I said this equation cannot be fully correct. The reason is that, if I plot, if I connect all the minima together and all the maxima together. Then in between the minimum and maximum not all are too well. This curve goes up in this fashion and it says, if you increase the volume the pressure increases or it increase the pressure the volume increases at constant temperature.

That is absurd, because it violates the fact that the compressibility cannot be neglected. So, it is not stable this is against thermodynamics stability so, this part of the curve cannot be right. This portion has to be wrong the portion where delta P over delta V is positive making the compressibility negative. That is not possible it is unfeasible and it is unphysical because this is after all a model and it has it is imperfections and one of them very serious. One is that this curve cannot be correct between the minimum and the maximum. So, we delete we say this is unstable this portion is unstable something else happens all together.

So, what can happen follow what happens as I increase and decrease the pressure or increase the pressure on an isotherm? So, I start here and it is in the gas phase this is the liquid phase on this side, I increase the pressure on the system. So, the volume decreases normally it would have started going down, again in this fashion, but that is not possible. So, it jumps to this point and after that as I increase the pressure, it is now become a liquid.

So, what has happened? Now is that I took a gas, I increase the pressure on it and the volume shrank till at some stage just liquid condensed and after that it was not. So, compressible after that and I had to increase the pressure hell of a lot in order to make small changes in the volume. Fine, but if I reverse the procedure and start in the liquid phase and slowly decrease the pressure on it keeping the temperature constant it starts slowly expanding till it comes here to this point. So, this still continuous on the liquid branch and then jumps to this place, because it has know where else to go and then becomes a gas.

So, in the forward cycle and the reverse cycle in this expansion and contraction the phase transition is occurring at different values of pressure. What do you call this phenomenon?

It is called hysteresis.

Yes hysteresis, because that is exactly what happens in the case of the magnet as we know when we start with the Ferro magnet and you cut off and there is going to be a deep analogy. And you decrease you have a Ferro magnetic that is got a eminent magnetization in the positive direction and you decrease the field to zero it still has a permanent moment. Then you have to give a negative field before you make it zero, and on the reverse cycle. You have to do it at different point change it at different, you have to give a positive field in order to make magnetization field. This is hysteresis which happens in magnets, but now you see this is going to happen according to this even in a liquid gas system, but phenomenon logically experimentally. We know it never happens it does not have so, that too is wrong in this model.

Therefore, just deleting this region is not enough. No, hysteresis happens in this phase transition. If it did your refrigerators will not work, this is what happens in a refrigerator. There is a condensation and evaporation cycle there is no hysteresis. What happens instead is the following what happens is you come along and at some point in between. So, let us call it on this curve to come along instead of going all the way up there at some point here. It decides to condense in between the minimum and the maximum at some particular point very specific point and then on the way back. When you come down exactly at the same point it comes and pass this.

So, that is what is observed and at the higher temperature it is again observed a similar thing is observed. So, what is happening is that the Vander wall's gas the equation of state is not

accurate. You must remove not only the unstable region, but you have to move slightly bigger region also and if I plot that correctly the envelope of that goes like this.

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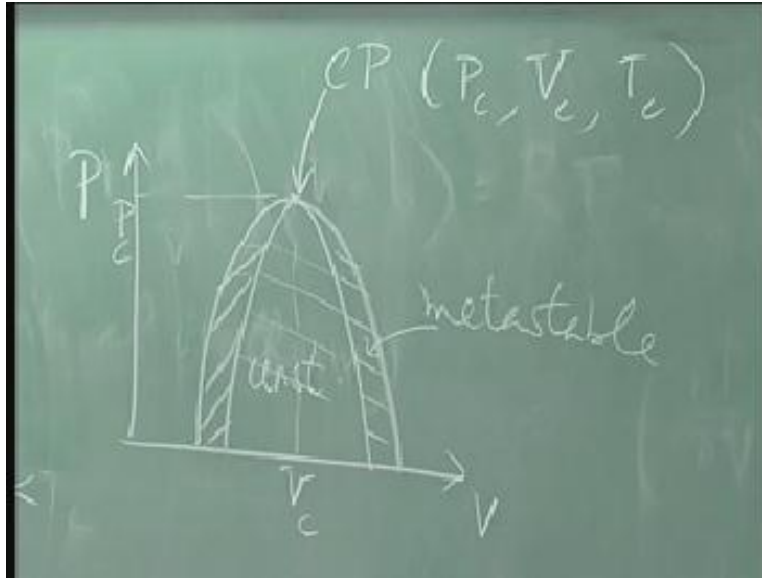
If, I just draw that portion this clarity, you have a situation like this and in between there is like this. This is V, this is P, this is V c, this is P c and at this point this is the critical point where your P c V c T c typical isotherms.

This region is unstable this is the region between the minimum and the maximum in the Vander wall's isotherm, but this region is the real region. Where it changes from liquid to gas, a gas to liquid and liquid to a gas and this curve this portion is called meta stable and in practice. What happens is it switches from one to the other? So, now you could ask what happens. If I took the system at this pressure and volume and simply drop the temperature instantaneously I quenched it. So, that it fell into this point quench it down and then I make the pressure and volume this. That is what is going to happen well. What happens? Now, is that instantaneously phase separation occurs.

A portion of it becomes liquid a portion of it becomes the vapor above so, quench into this region will immediately cause. A phase separation with a definite amount becoming liquid and definite amount becoming gas and they are in thermal equilibrium to each other. How much is

liquid? How much is gas? Can be computed with this model it is very easy to compute. There is a general rule for this called the weaver rule, which I talked about. But this is what happens? Therefore you can see that is the region I called the co existence region, because this is where the liquid and gas co exist, so you quench the system in here portion of it goes there and a portion of it goes here.

Now, the reason this is called unstable. That is called meta stable is because in other phase transitions. The mechanisms are such that the unstable portion would immediately very fast mechanism would operate by which it moves to the boundary and then the meta stable region can be slowed down. In the case of liquid gas this is equally fast it is practically equally fast. This curve is called the spinodal curve and now you have to go beyond normal linear thermodynamics to understand this. And there is a whole history whole subject of these spinodal curves, spinodal decomposition and so on.

But this is a technical importance because, when you look at binary alloys when you look at alloys, liquid alloys. For example, this or even solid phase transitions of this kind then the metastable portion can be made extremely slow. You can take hours, you can take days, and you can take years to happen. And that is why it is very important to know what you do here and there are definite mechanisms for how nucleation and growth occurs across this phase separation that is a subject by itself. That is what we are getting to it, but right now I just want to say that this portion here has to be put in from outside on the Vanderwaal's isotherms.
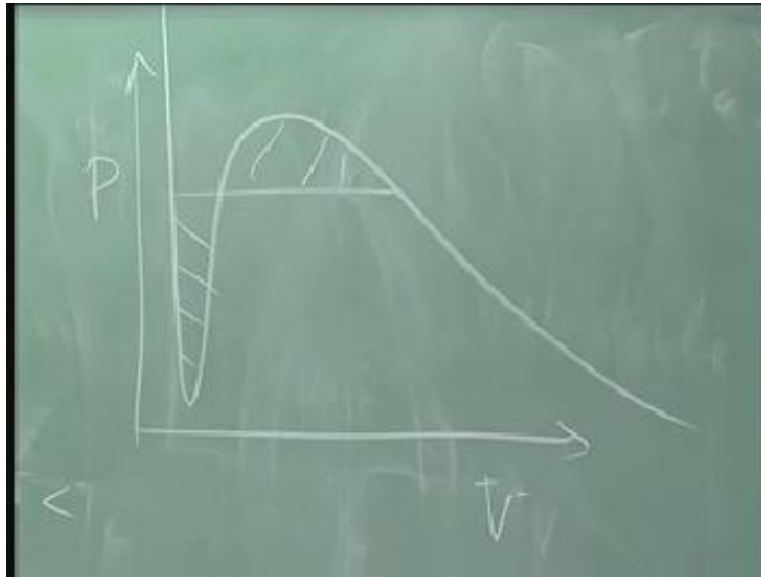
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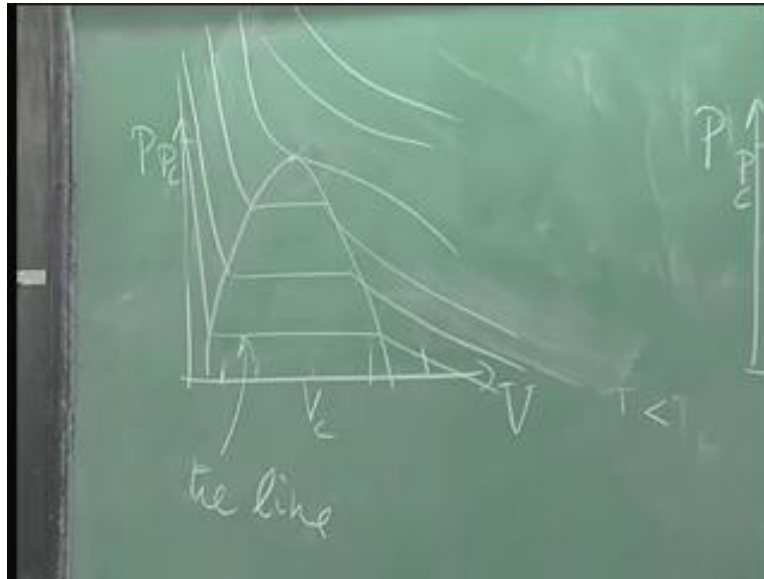
These co existence curves then what does the system look like after that the P V diagram with that correction looks like this.

So, you have these isotherms then you have this line here and then you have this etcetera. This is the curve this is the co existence region, which includes the metastable and the unstable regions, and this is the critical point and above that you have this homogeneous space. So, again now our phase diagram is complete this is what it looks like in the P T plane, this is what it looks like in the V T plane and these horizontal lines let me call tie line. They would correspond to tie lines here in this fashion. So, this is what this phenomenon is our idea. Now is to try where does this come from what do we do? How do we explain? This I have to mention that there is a definite way of finding out where this tie line should go and that goes all the way beck to Maxwell.

The rigorous derivation of this is a different story altogether it is not universal it depends upon system etcetera. But there is a crude hand waving argument, which Maxwell gave an argument, which is not quite correct technically, which tells you where that tie line should be placed. It is not placed at the half way point between maxima and minima.

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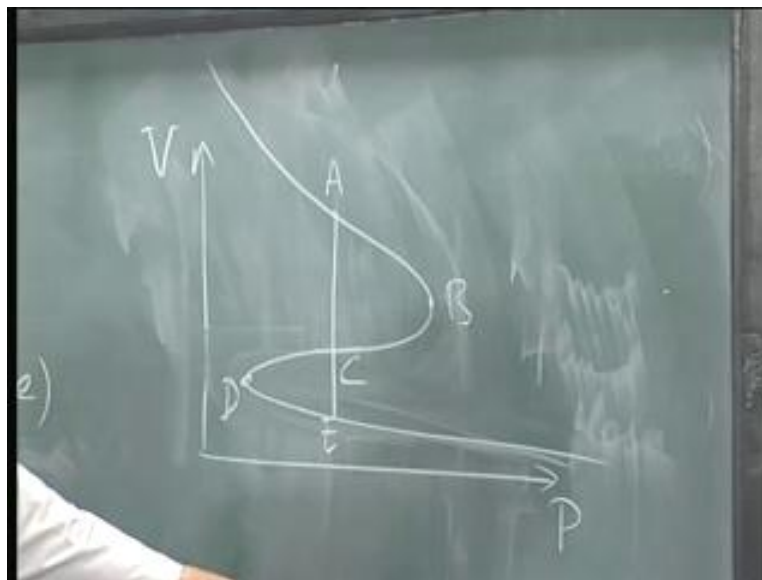
$$G = U - TS + PV$$
$$dG = T\,dS - P\,dV - T\,dS - S\,dT$$
$$\qquad\qquad + P\,dV + V\,dP$$
$$\quad = -S\,dT + V\,dP$$

In fact the curve I have exaggerated the curve actually looks like this the more realistic curve looks like this. This is what it looks like and then the tie line is placed at some point like this in between such that the area. Here is equal to the area there and it is called Maxwell's equal area rule.

So, that is the rule not half way between the maxima and minima. So, where does this transition occur, it occurs such that the area here is equal to the area there. Now we can understand that why that so, by the following argument, which is not correct technically. But it looks convincing at the first sight. Let us invert that figure flip it around ninety degrees so, that we have P versus V here. Then what would that curve look like? I am not drawing this to scale, but it looks something like this. This is what it happens? When we flip that around and draw it in the P V plane and then the question is where the tie line is? I want to understand where to draw the tie line and let us give it some names. Let us call A, this point B, this point C, this point D, this point E and this is the V versus P plane.

Now, let us consider the Gibb's free energy remember that these phase transitions. You keep pressure and temperature constant at a particular phase transition. Then the Gibb's free energy particle is same on both the sides the change in the Gibb's free energy is therefore zero. So, let us use that fact and let us write G as U minus T S plus P V, since I do not remember d G. Let us work this out this d G, which is T dS minus P dV plus mu d n, which is a fixed amount. So, d n is

0 d U minus T dS minus S dT plus P dV plus V dP, where of course these things get cancelled. That is the whole idea of this and therefore this is equal to minus S dT plus V dP.

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Now, if you have a isotherm on an isotherm d G equal to V dP, because d T is zero on an isotherm. So, let us compute what dG is to go from A to E so, integral A to E dG the integral to go from A to B plus B to C plus C to D plus integral D to E V dP and this must be zero, because A and E must have exactly the same Gibb's free energy either in the liquid phase or in the gas phase.
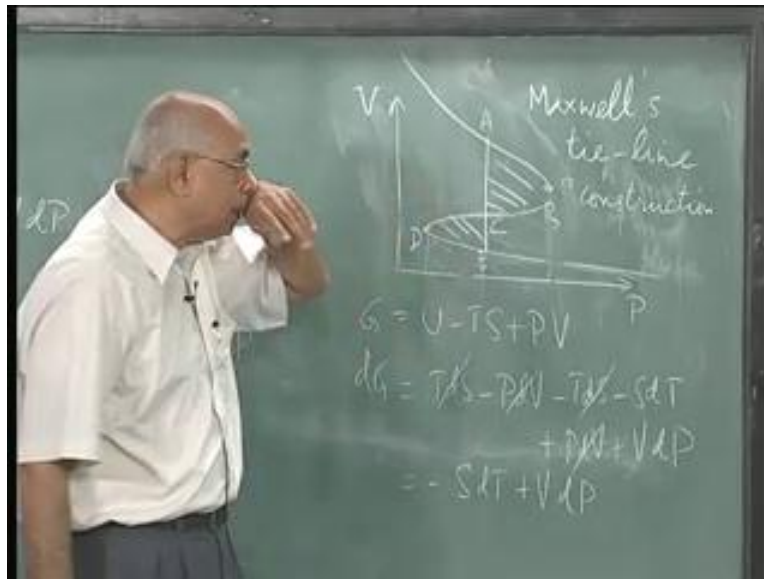
You must have the same Gibb's energy for a given number of coordinates, but what does A to B the integral A to B is this area under the curve all the way down the full area. But when you go from B to C you cancel out this area the one below it and therefore it leaves you just this portion that is the sum of the first two terms A to B and B to C plus C to D. It is minus this area and then you add D to E you add this area. So, it is equal to minus this area and it says this area minus this area equal to zero it says the two areas are equal.

So, this was Maxwell's tie construction tie line construction not quite rigorous why is it not rigorous. What is wrong with this argument? It contradicts with what I said earlier in what way pardon me. It goes through regions of unstable thermodynamically unstable regions that curve cannot be there. When it is not a zero these are not thermodynamically stable this cannot be thermodynamically stable state line. So, it is not, but it is empirically found to be true then the question is why does it happen? When there are theories, which will tell you why that tie line construction is so and it will give an analogy here at the ends. That is the simplest way to understand you see what really happening is that you have a situation when you are going from one stable state to another stable state in between. So, some kind of some configuration space some minimum here to another minimum here.

So, look at the way the following happens I start with a curve in which there is a minimum. This is just a completely general configuration and then at some state it develops if I change some parameter it develops an inflection. As I change the parameter further this inflection point does this I change it a little further. This guy comes down and at some state it becomes equal minima and then creeping the other direction and eventually it does this and finally the minimum goes to the new position. So, this is the left well and this is the right well. So, I start with the left well with the right well so, let us call this right and then this becomes the length this is right, left, right this is left, right this is left and fully left.

So, what happened is if I put a ball here and start doing this jiggling around. They will come at a stage where it will fall into the right well wrong well. So, where does it happen nothing happens, here nothing happens, here nothing happens, here nothing happens, here nothing happens, here nothing happens, here but here it becomes unstable and it falls into this? So, the transition is happening at this stage so, it falls till then it was here it is happening at that state, but if I start at this point and reverse it. So, I start here it remains, here at this point it remains, here at this point, it still remains here, it still remains here and at this stage it falls.

So, the phase transition is happening at this point this is hysteresis that is the mechanism behind hysteresis, that the change in shape of a generic double well potential it leads in a natural way to

hysteresis. And now you can have different possibilities this is what would happen in the mechanical case, but there are other situations where it would happen in the symmetric case. It could tunnel from here to there or there to here fluctuations could push it in etcetera. So, you have many possibilities of phase transitions and it depends on the system, it depends on the mechanism. The Maxwell tie line construction happens to work, when something like this is valid when there is some equilibrium in terms of energy, some free energy and then the system moves from one to another, whereas a purely mechanical system would display that kind of hysteresis.

So, there is a branch of mathematics which is related which called the capacity theory. Where people talk about changes of shapes of these generic potentials and what would have when you have different possibilities? Incidentally, since I mentioned that this thermodynamically unstable it turns out that you cannot have a free energy configuration like this. It violates convexity relations. So, you need to have what is called the convex hull of these potentials? So, you need to have what are called surgered manifolds and do surgery on it and so on and so forth.

So, it is a very extensive theory, but in very simple naive term this is basically odd the reason for this is various situations. So, this argument when it is not rigorous it still gives you the right answers and then the question is how do you justify it? But that I said this is a different question altogether. So, this is what happens in a typical system? Now our task next is to see what happens near the phase transition and also to understand why it does not why such a critical point does not exist, when it comes to the liquid gas, liquid solid transition. So, we will talk about symmetry and symmetry breaking.