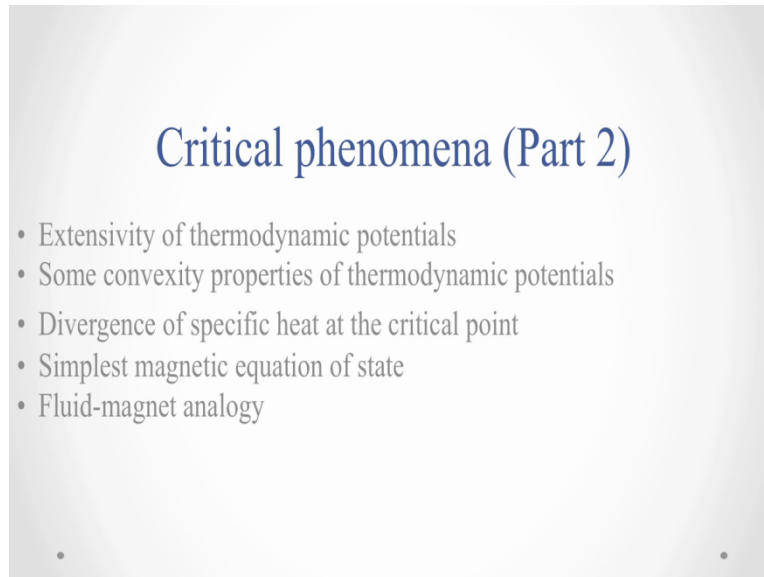


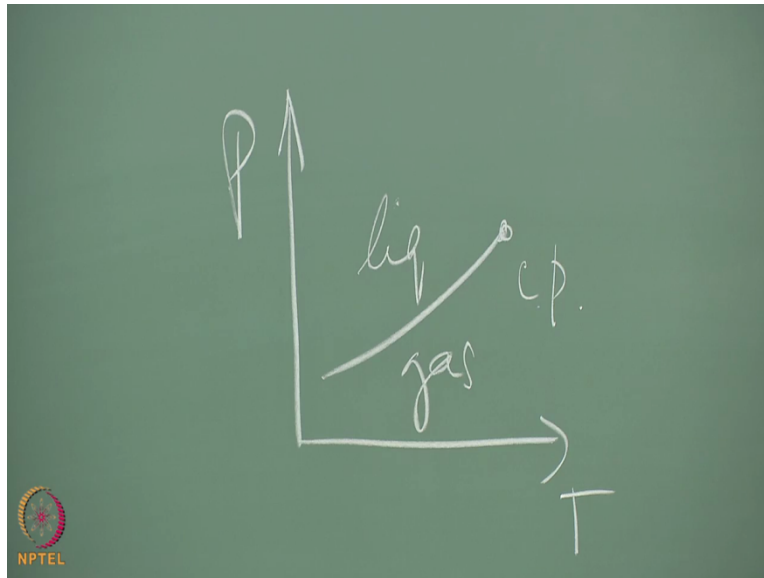
Nonequilibrium Statistical Mechanics
Professor V. Balakrishna
Department of Physics
Indian Institute of Technology Madras
Lecture no 30
Module no 01
Critical phenomena (Part 2)

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Right so we had started thinking about simple component substances for which I draw the phase diagram and then I started mentioning something about magnetic model correspond with it. Now just to recall to you what the problem is, uhh and this is the primary problem we want to focus on. If you look at the phase diagram in the P-T plain for a simple substance and you look in particular at the liquid-gas coexistence curve, it ends in a critical point here.

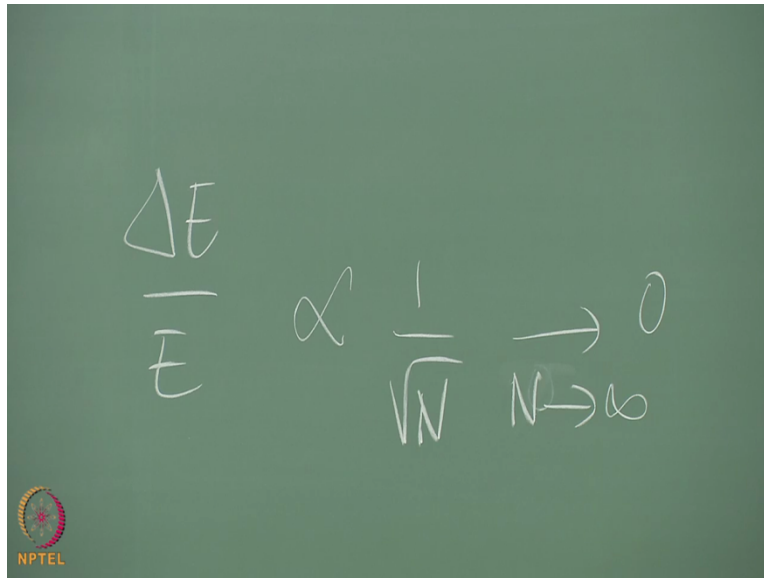
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Now across this line you have a phase transition which is said to be discontinuous in the sense that the quantity that characterises the difference between the liquid and gas would be put a homogeneous media, both are isotropic so what characterises is the huge difference in the density. So if you take that to be the case, this difference slowly vanishes till you get to the critical point but across this gap here the difference is discontinuous, there is a discontinuous change finite but discontinuous change in this so-called order parameter okay, or whatever quantity characterises the phase.

Now, the reason you have problems with this point here is the point of singularity that is something I would like to explain little bit that is the place where thermodynamics fails. And it fails for several very interesting reasons, very deep reasons, took a long time person to appreciate this and then once as I said earlier, the problem was really solved in 1970s starting with the advent of what is called the renormalisation groove okay pioneered by Wilson about all. Now what is the difficulty? The difficulty itself was recognised by long before this before 1970 and the difficulty is as follows. This is a point where fluctuation becomes significant so much so that thermodynamic itself fails.

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$$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}} \rightarrow 0 \text{ as } N \rightarrow \infty$$

As you know thermodynamic is something which deals with average quantities assuming that the fluctuations about this average are very very small, typically as we saw in very trivial model last time 1 over the square root of the number of particles, that fails once you get to the critical point because if that were so that for instance in the internal energy for instance, if it was so that ΔE over E which is normally proportional to 1 over the square root of N tends to 0 as N as N tends to infinity, this tends to 0 and you are alright as far as thermodynamics is concerned but we will see now how this breaks down at the critical point.

Another way of looking at it is the way Ehrenfest looked at it 1^{st} so-called Ehrenfest classification and this argument was as follows. This argument was to start with thermodynamic quantities of 2 kinds, there are so-called state variables and the so-called field variables, so there are intensive variables the field variables like temperature, pressure, chemical potential and there are the state variables which are the response variables such as volume, number of particles, the entropy of the system at, et cetera. So once you start with that description of thermodynamics then the derivatives of the thermodynamic potentials with respect to thermodynamic variables or other thermodynamic variables.

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Handwritten equations on a chalkboard:

$$dE = TdS - PdV + \mu dN \Rightarrow T = \left(\frac{\partial E}{\partial S} \right)_{V,N}, \text{ etc.}$$

$$dF = -SdT - PdV + \mu dN \Rightarrow S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}$$

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

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N}$$

The equations show the relationship between internal energy (E), Helmholtz free energy (F), and their derivatives with respect to entropy (S), volume (V), and temperature (T) at constant volume (V) and number of particles (N). The NPTEL logo is visible in the bottom left corner of the chalkboard image.

Just to give you an example I called E the internal energy dE, this quantity is $T dS - P dB + \mu dN$ so if you for instance took the derivative of this with respect to S keeping the N constant, you get the temperature. So did imply function that T equal to Delta E over Delta S keeping V and N, et cetera okay. Or take another example if you took the Helmholtz free energy dF, this is $- S dT - P dB + \mu dN$ and this will imply for instance that S equal to $- \Delta F / \Delta T$ at constant V and N. And similarly P is equal to $- \Delta F / \Delta V$ at constant T and N, etc, in this fashion.

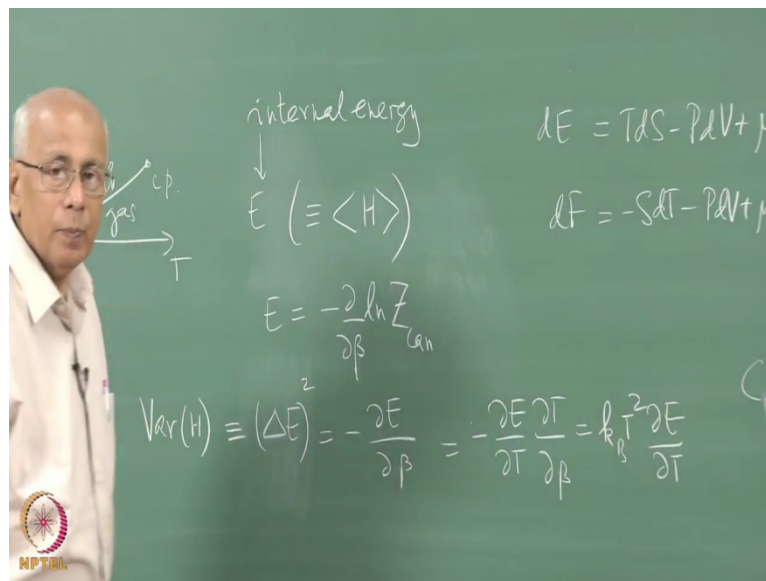
So in this case what is happening is that you are getting some thermodynamic variables from derivative, every thermodynamic variable from the derivative of the suitable thermodynamic potential with respect to the conjugate to the variable you want okay. What happens to 2nd derivatives of these quantities? For instance, if you took this equation here and I differentiate it a 2nd time so this says Delta S over Delta T keeping V, N constant is $- d^2 F / d T^2$ keeping V and N constant. And similarly Delta P over Delta V equal to $- d^2 F / d V^2$ keeping T, N constant.

But what is the Delta S over Delta T? If I multiply this by T on both sides, so this is equal to $- T$ on this side, this is T dS differentiated with respect to T keeping V and N constant and what is that equal to? T dS as you know is dQ this is the specific at constant volume so this is equal to C_v right, it is therefore a response function and that is typically the 2nd derivative of a free energy

of this kind. Similarly I could differentiate this, you will get this quantity here Delta P over Delta V and that is related of course to the bulk modulus of the system right.

So the bulk modulus of the system if I write it up here this implies that n the isothermal bulk modulus, it is equal to $-V \Delta P / \Delta V$ at T, N that is equal to $V \Delta^2 F / \Delta V^2$ that is the volume at T and N. So we see that the response susceptibilities are related, these are sort these are response susceptibilities they measure, they are related to the 2nd derivatives of thermodynamic potential okay, 1st derivative give other thermodynamic variables and this is typical absolutely typical the structure of thermodynamics here.

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But we also saw something else, let us be careful my notation, so we saw that the internal energy E internal energy, which is by the way by definition equal to the expectation value of the Hamiltonian in the canonical ensemble for instance right. This quantity E was equal to $-\Delta / \Delta \beta \log$ the canonical partition function and $\Delta E / \Delta \beta$ was equal to the variance of H is by definition is denoted as ΔE^2 , this is equal to $-\Delta E / \Delta \beta$ where this is the average energy right. Now if I want to write this in terms of temperature, I could write this as equal to $-\Delta E / \Delta T \Delta T / \Delta \beta$ equal to $k_B T^2 \Delta E / \Delta T$.

But what is $\Delta E / \Delta T$? You kept all other thermodynamic variables fixed in this, so this fellow was a function of S, D and N you kept everything fixed including V and then you

differentiate it right. So this is the specific heat at constant volume, the derivative of the internal energy with respect to temperature by definition is the specific heat at constant volume. So this is equal to $k_B T^2 C_v$, variance cannot be negative it is got to be positive right, so it immediately says this is greater than 0. We therefore have the rigorous inequality which says that specific heat cannot be negative at constant volume cannot be negative right. It follows the fact that the variance of a random variable cannot be negative.

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But this poses a convexity condition on the corresponding free energy because this says now that this quantity which was C_v must be greater than 0 which implies $\frac{\partial^2 F}{\partial T^2}$ is less than 0. So it puts a condition on the kind of curvature that this function F can have, it has got to be a convex function in the sense that it has got to be concave on, looking from above it is going to be concave right, the curvature has got to be positive. This is of course a function of many variables V , T and N but as further its dependence on T is concerned, there is a strict inequality which is dictated ultimately by thermodynamic stability which tells you that this this quantity is now this thing here the variance being positive is in fact an expression of thermodynamic stability as you can see.

In exactly the same with the compressive the bulk modulus cannot be negative so this quantity has to be positive this 2nd derivative. So it tells you that when you fix one variable and differentiate with respect to the other, what is the curvature going to look like of the surface

representing the free energy or some suitable thermodynamic potential? Our immediate interest was in this statement here because now we know we know that E is proportional to the number of particles N okay by extensivity we know this thing here, therefore right we argued this is an extensive quantity that is how we got the extensivity relation.

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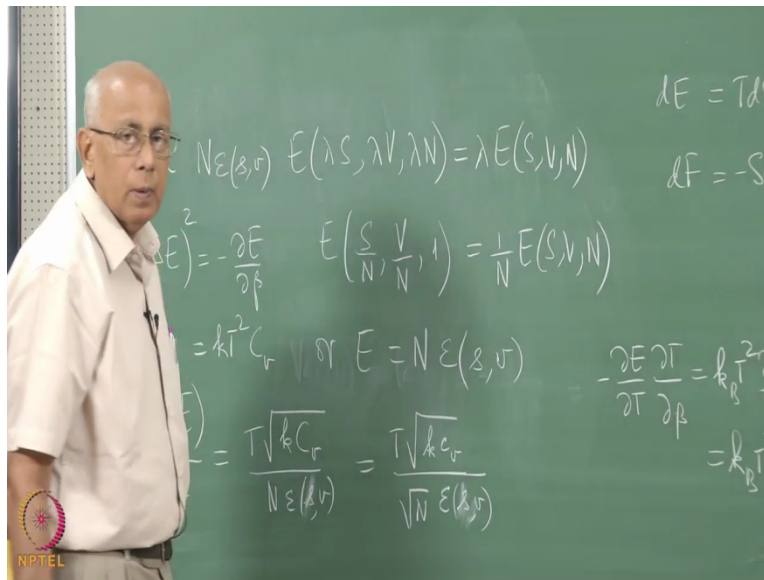
$$E \propto N \epsilon(S, V) \quad E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

$$E\left(\frac{S}{N}, \frac{V}{N}, 1\right) = \frac{1}{N} E(S, V, N)$$

$$\text{or } E = N \epsilon(S, V)$$

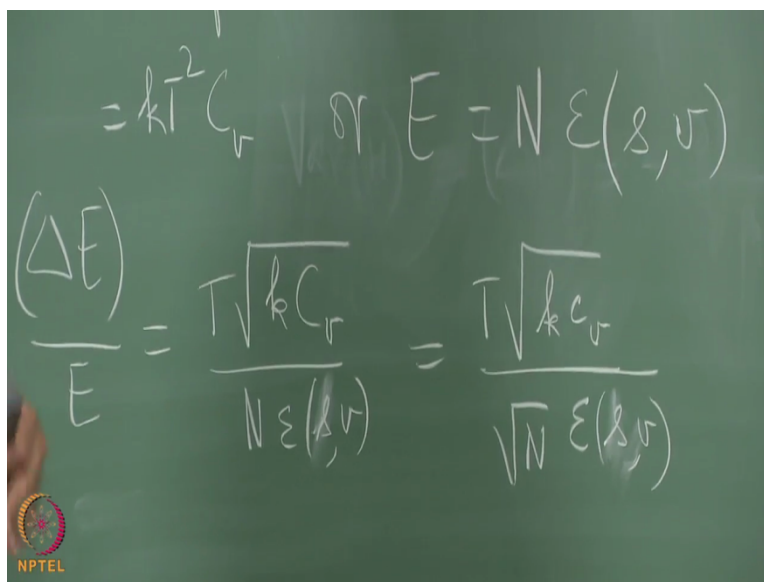
And we said that E is a function of S , V and N homogeneous function of degree 1, which immediately implies that this thing is equal to which immediately implies that E of λS , λV , λN equal to λ times E of S , V and N homogeneous function of degree 1 which implies this. Well, choose λ to be $1/N$, λ is completely arbitrary any real positive constant will do, choose it to be $1/N$. So this says E of S/N , V/N , 1 equal to $1/N$ E of S , V and N . Or you can rewrite this as E equal to N times this quantity here. Something being a function of 1 is irrelevant, you can get rid of it right, this is equal to ϵ of S/N entropy per particle that is the specific entropy right, let us use small s for it.

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V over N, the volume per particle specific volume, so let us use small v, these are densities, these are concentrations if you like so they are all intensive quantities, the extensive part as sitting right here so that is why I said E is proportional to N times some Epsilon so let us put Epsilon s, v okay. Then he lets use the other result that we had, Delta E whole square is equal to – Delta E over Delta beta, this is equal to K T square C v which is showed there.

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Therefore, Delta E divided by E the standard deviation divided by the average energy is equal to T times square root of K C v divided by N times Epsilon of S, V but this is the specific heat or

heat capacity of N particles which is N times the capacity per particle so this is equal to T square root of $K c_v$ divided by square root of N times $\epsilon_{s,v}$. And indeed this goes to 0 as we have been saying all along as capital N goes to infinity because all these are finite quantities they have nothing to do with N except for one possibility uhh when is it that is relative fluctuation will not go to 0 when N becomes large at a critical point.

We have already seen that at a critical point I said the Central limit Theorem fails that thermodynamic fails because it is predicated on the assumption of extensivity which in turn requires that the fluctuation will be neglected but that is failing here and when is that going what is that going to show up to here, what is the only possibility? C_v must diverge, must become infinite, if this quantity diverges at some point in the phase plane then there is a singularity in C_v and then you can have the possibility that this quantity does not go to 0 as N tends to infinity okay. So now we see the failure of Ehrenfest classification Theorem.

His classification said that you have an n th order phase transition when some n th derivative of some thermodynamic potential becomes discontinuous okay. The previous $N - 1$ derivatives starting with the potential itself will be continuous but the n th derivative becomes discontinuous yeah.

Student: It also says like C_v should diverge at least as fast as \sqrt{N} or as fast as N , but here C_v ...

Yeah yeah, we are going to see we are going to see what happens. No no no no no it is not that no no no it is not that at all, it is saying that you may have hit when you compute C_v whether quantity somehow for some special value of control parameter whatever they are, in this case they are the function of S whatever this is the function of temperature and something else in particular the temperature, there is a singularity, at that point thermodynamic fails.

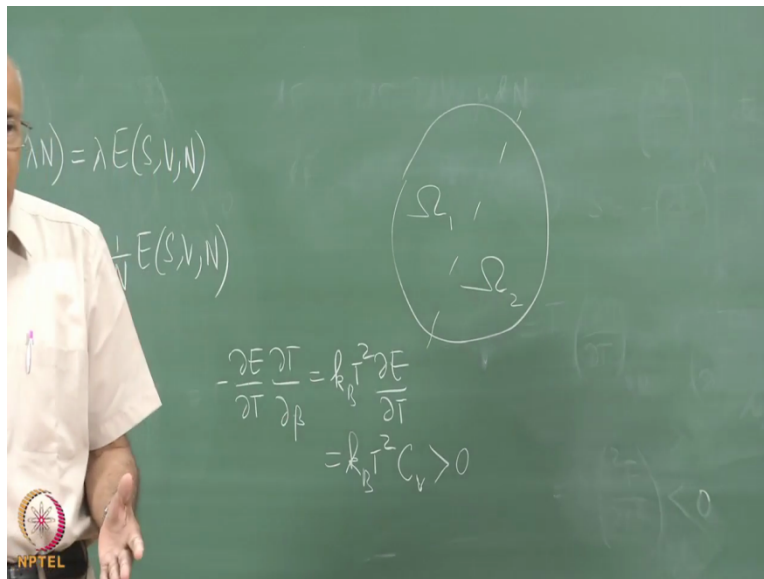
Student: In fact this whole calculation...

This whole calculation fails right, and all these things become extensivity is gone completely, so something very serious has happened, the whole formalism breaks down. If you do not have extensivity when even the equivalence between different ensembles in equilibrium statistical

mechanics fails, it is completely predicated on I mean how did how did we start let me let me go back. Just go back a few steps and look at the equilibrium statistical mechanics.

What did we start with? We started by saying here is a huge system in equilibrium isolated system in thermal equilibrium, by that we mean that if you take longtime averages of physical or microscopic quantities they will all be time independent completely and then you made a postulate which said that every accessible micro-states of this system is equally probable that was it, that was the fundamental postulate. From that you drive all the consequences including from fact that you can define the temperature as $\Delta \log \Omega$ over ΔE and so on and so forth.

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And then you said let us consider a small subsystem here which is so small that the fluctuation driven into it by the bar are very significant but it does not react very much on the bar and assumptions made were very obvious. When you construct a micro-canonical ensemble to show that field variables were all equal on this side, the temperature have to be equal if I do an imaginary partition, the temperature here have to be that here, the pressure here have to be the pressure here, the chemical potentials have to be equal and so on.

What was the essential assumption, that the number of micro-states of the full system is a product of the micro-states here and here, which means the number of degrees of freedom on the boundary is negligible compared to both these guys and the energy is in some sense additive, the

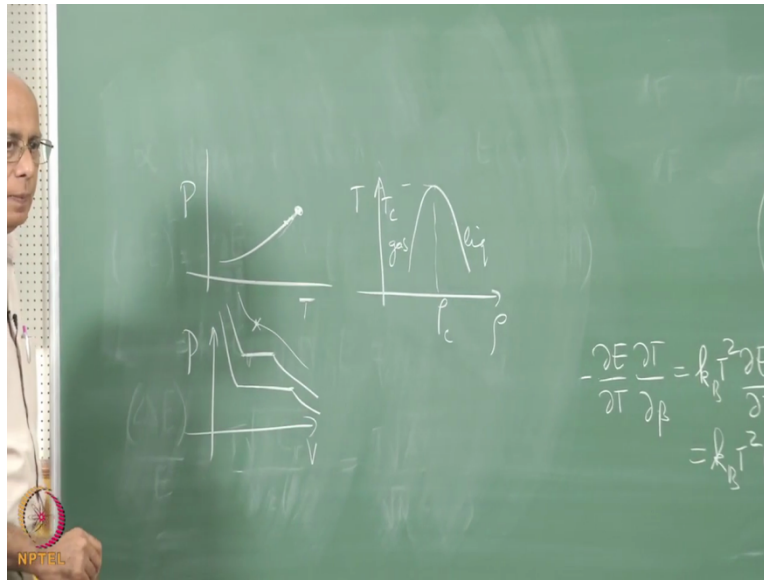
entropy additive right, because we definitely said that the total number of micro-states of this full system is a product of Ω_1 and Ω_2 here therefore, $\log \Omega_1 + \log \Omega_2 = \log(\Omega_1 \Omega_2)$, in other words the entropy was additive and then everything else followed that was the extensivity led to additivity of these entropies, volume, et cetera, et cetera.

That is breaking down, it completely breaking down here, so somewhere there is a similarity and we need to know where. Now this is the reason why the Ehrenfest Theorem classification also breaks down because it only says nothing is singular some some derivative certain order derivative of some free energy or some thermodynamic potential becomes discontinuous at some point, very very roughly the picture was as follows. If you have 2 phases, again some configuration variables here you computed some free energy as a function of some thermodynamic variables right.

And let us say in one phase it was like this and in the other phase it was like this, right. When since the potential has to be at a minimum thermal equilibrium, this phase thermodynamic potential is larger than this so the system moves along here but then when it crosses this point, it jumps to this phase and therefore at this point the slope of this free energy is discontinuous and you have what is called first order phase transition okay. But the same thing could happen not to the free energy itself but derivative of the free energy then you got the second-order phase transition and so on, this was his original classification.

But we see that at a critical point that is not what is happening, is something far more serious is happening, the whole mechanism the whole formalism is completely wrong it is breaking down okay. The fluctuations have become so large that you cannot ignore it, this classification is useless in some sense. So today we do not use this as a classification, we what we say is that there are 2 kinds of phase transition, there are continuous and discontinuous phase transitions, then there is a concept of an order parameter introduced and it says when it changes discontinuously, you have a discontinuous phase transition also called first order and when it changes continuously you have continuous phase transition which is called the second-order phase transition but it is loose terminology, we should really say discontinuous and continuous right.

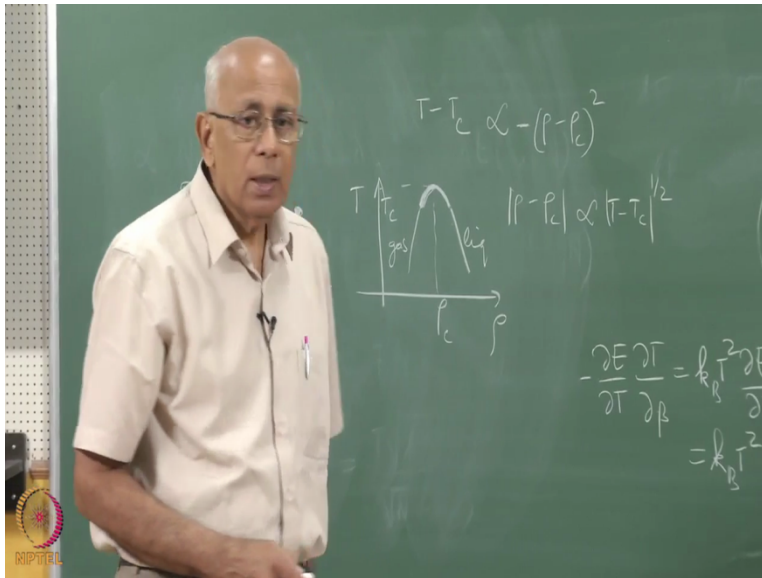
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And what is happening with going back to our original example going back to our liquid gas example, which was this in the P-T plane ending in a critical point here. Definitely as you cross this line along anywhere along the body of the line except here, does it change in the density discontinuously? And yesterday I drew the diagram when I was getting confused between the velocity the volume and the density, let us draw it in the way which is transparent. The way to draw this would be to put temperature here and the density here, let us put the density alright.

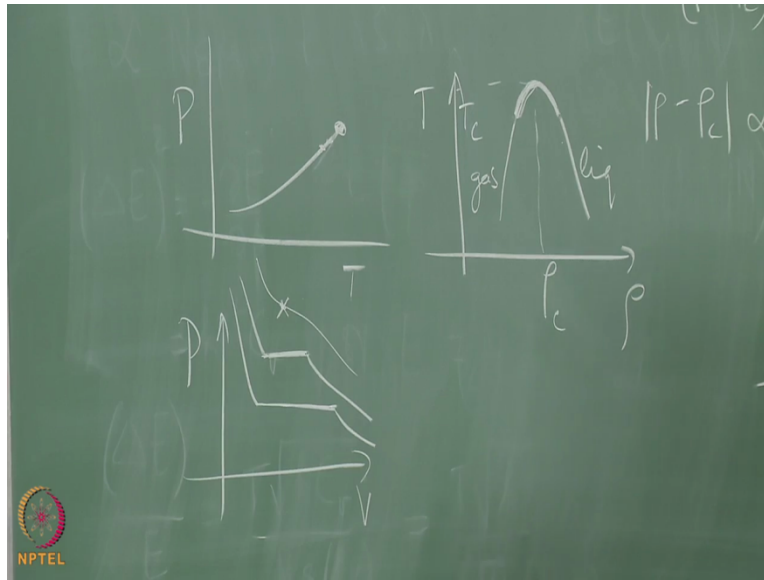
Then in the vicinity of this point close to this, as you know every point on this line coexistent line corresponds in the Rho T plane to a region because that is the full coexistent region corresponding to every point here okay. Just to recall to you what is going on, if you plot the isotherm is V versus P, these isotherms were like this okay. So point here would correspond with this region here, point here would correspond to this region here, this point would correspond to the place where you actually have just a single point an inflection point where the slope is flat. This is liquid, this is Gas and this is the coexistence region with the sty line construction put in to this.

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What is it look like in this figure? Well, as you can see this is going to look something like this, this Rho_c , this is T_c , the higher density region, which one is liquid, which one is gas? What does it look like? T versus plot T versus Rho that is the whole point of it yeah, it is easier to see in this picture. So Rho_c , T_c here, the higher density is liquid, this is the gas, this width here is reflected here in this picture. And at T_c , the density between the liquid and the gas vanishes okay and close to it here one would guess one would guess that in normal circumstances given no other information, the naive guess would be that it looks like a parabola out there, you can always fit a simple minimum to the parabola if you (())(27:45).

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And since you have shifted T by T_c so this is really saying that $T - T_c$ is the vertical coordinate measured with respect to this origin is going like since it is an inverted parabola, it is going to go like $\rho - \rho_c$ the whole square with a $-$ sign. Instead of this it is more convenient to take, instead of $\rho - \rho_c$ it is more convenient to take this $-$ that it would not make a difference to us, but let us retain this. Incidentally this is also telling us now that modulus $\rho - \rho_c$ modulus is proportional to $T - T_c$ to the power half that is the square root square behavior near a parabola, this is what we would expect like, no we just said it in words, we have not proved it in any sense okay.

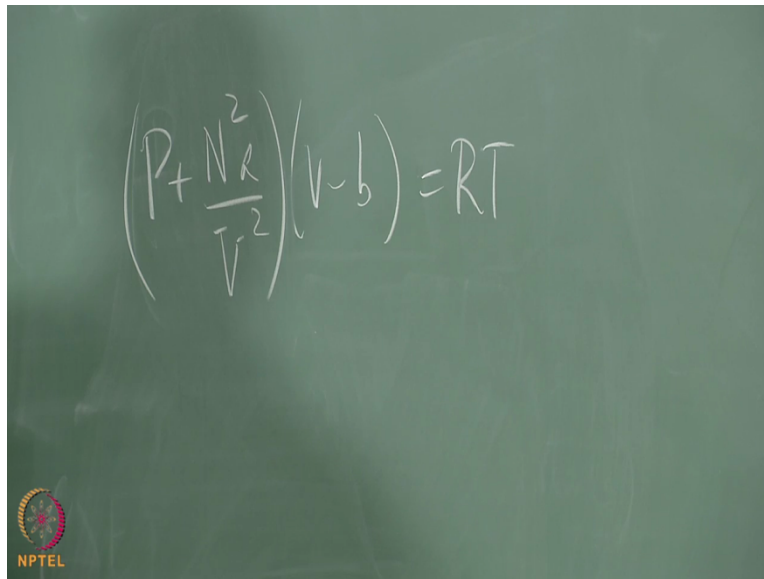
So the fact that you have a singularity here is a serious matter as I said and we have to take a lot of this, we have to redo the whole calculation. Now turns out that doing this there is a hard it is not so trivial at all, the whole subject of critical phenomena depends on this but we need to keep I need to introduce a little more standard material before you can get to this in a sensible form okay, let me do that.

So let us make this let us let us make it fluid magnet analogy, what this says is that you have a complete analogue of this phase transition, this continuous phase transition at this point with 90 system, and for everything that you say here you can make a corresponding statement there. The system is characterized by pressure, volume and temperature, the magnetic system is similarly characterized by not a pressure, but magnetic field which I called H , should be a vector but let us

avoid in essential complications here. The response if you increase the pressure the volume changes similarly, if you apply a magnetic field you have a magnetization and T, so this is the one-to-one correspondence between these variables.

Now here you can have a P versus V diagram, you have an equation of state connecting these 3 variables; you can have a P versus V diagram which is an isotherm, a line which is an isotherm. Similarly, you would have there an H versus M figure then you have a V versus T diagram as in this case or a density versus T, you can have M versus T diagram here and finally you have a P versus T which is H with T this place, let us see now let us draw all these 6 pictures and see what would happen. But I need a model of a magnet to write the equation of state, I need a model for the liquid gas system for which I can write an equation of state right the either case, let us do this since we are more familiar with this, let us do this first.

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

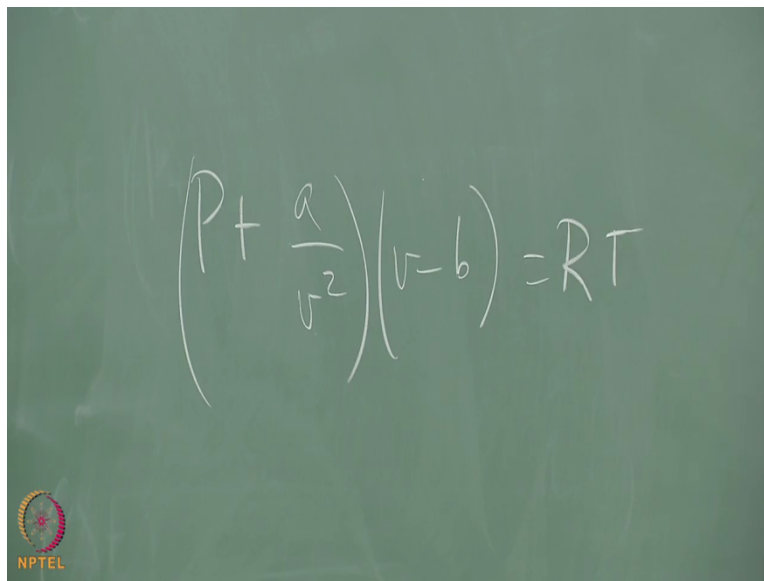
The model as we can see is the so-called Van Der Waal's equation of state uhh. And we are not going to write down the algebra idea but basically it is something like $P + A$ over V square times $V - b$ equal to RT this is the Van Der Waal's equation of state. You are familiar from elementary physics that this b measures the so-called excluded volume, this A measure the force of attraction.

Student: Specific volume (v)(32:26) intensive variable.

I need an intensive variable here because there is a V square here so... okay okay... I am not too happy with this notation but okay, it has got a point it says after all this is an intensive variable and that should be $1/2$ you cannot add arbitrary and similarly for b , but let us do the following, I am going to assume A in the suitable dimension suitable figure, I mean I am interested right now in the in the dependence on V .

Student: I think you still need to write little v instead of V , there was an N, R, T , it is not... The equation of state you write was for specific volume okay.

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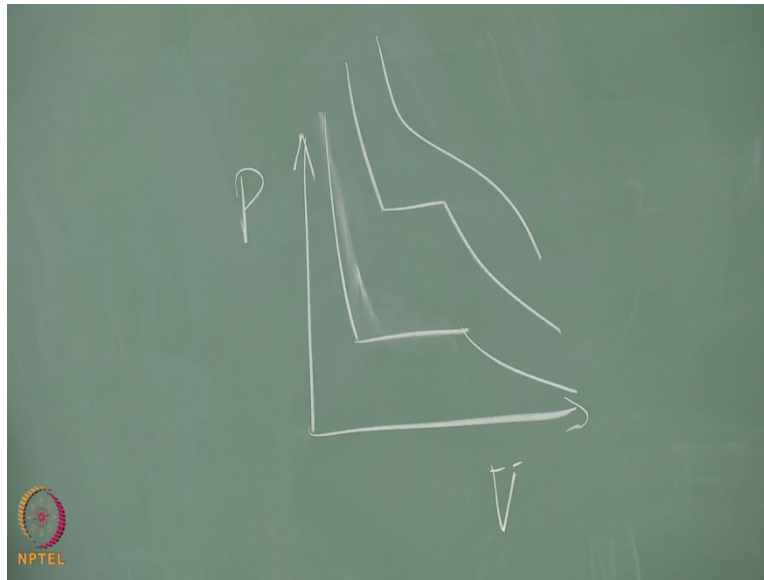

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT$$

Yeah okay he is right $P + a$ over v square yeah I think that is the least harmful.

Student: (())(33:44)

Yeah I know it is a big mess okay, yeah in fact it is convenient to do it this way okay. This is the volume yeah this is very convenient because this is really telling you in the naive picture it is telling you this b is the excluded volume due to the finite size of each molecule right, and little v the volume per molecule so it is only reasonable that this b has this interpretation, otherwise I got a full round of number of particles everywhere good. Now this is a cubic equation for V that is the reason you get those 3 roots and so on and let us see what is the interesting part of it is.

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So if I plot P versus V P - V diagram, we have already seen that you get below a certain critical temperature you end up with 3 roots of which there is an unstable root in the middle there are 2 stable roots on either sides corresponding to liquid and gas respectively and you should draw byline, et cetera so let us go through this thing again, something like this, et cetera very schematically. Now in (())(35:04) how the hell you get this equation of state? Now throughout 19 centuries people had the feeling that there was probably some universal equation of state for gases for real gases okay and they were trying to find it very hard.

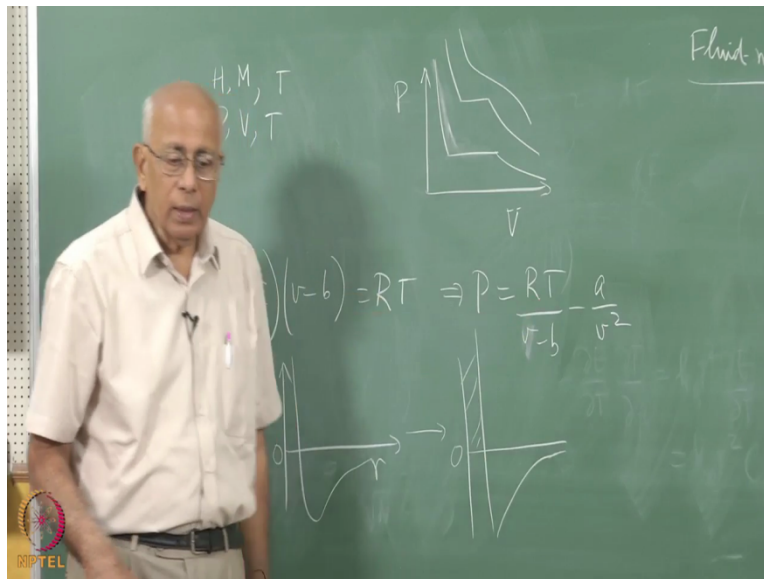
And one idea was maybe there is some scaling here and then uhh with respect to some standard, depending on each gas there is a characteristic pressure, characteristic volume, characteristic temperature such that if you scale with respect to those variables you get an equation of state which was universal okay. This program ended in failure, there is no such equation because these quantities a and b in a sense are not symmetrical hard spear kinds of quantities, they are quantum mechanical objects you have to compute what this is, it is due to the repulsive part of such intermolecular potential, this is due to the long-range attractive part and it will depend on the nature of the molecules.

The force between 2 water molecules for instance is very different from the force between 2 Argon atoms and so on, so there is really no universal equation of this kind.

Students: But this equation is that way.

But this equation is that in some very very profound sense and it is as follows. How do you get such an equation, while getting it from an actual intermolecular potential is a very nontrivial, it requires many body theory and getting an equation in close form is next to impossible okay. Instead what it does is the following, we know that physically if I plot r versus the potential between 2 atoms the distance are apart, then due to Van Der Waal's interaction even if they are spherical and symmetric molecules, is a long-range attraction which goes whose potential goes like 1 over r to the 6 and whose force therefore goes like 1 over r to the 7 this is the long-range attraction.

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At very short ranges the problem becomes much harder because quantum mechanics really kicks in here and finally it is the Pauli exclusion principle which make sure that the 2 electron clouds do not sit in the same state at any instant of time so there is a short range repulsion here hard-core repulsion, effectively the potential of like this. Now doing any serious calculation of the things like this especially because you do not know what is the exact power here if at all it is a power is very very nontrivial but you can make an approximation to this a very crude approximation.

And that is to say that this is approximated by something which is essentially infinite below a certain distance and b plays a role of that distance and beyond it there is a 1 over r to 6 attraction

like this long-range attraction so you approximate this potential by that. And then you make a whole lot of other approximations and then finally you end up with an equation like this okay.

Now the fact that this is $1/V^2$ is not very hard to understand because it is really saying that each molecule is saying, you are asking what is the decrease in the pressure due to the fact or the force that the molecules exert on the walls due to the fact that they attract each other, that is why this goes to the right-hand side and it gives you a diminution of the pressure right because you can write this as $P = RT/V - b - a/v^2$. This part comes from the short-range repulsion of the potential, this part comes from the internal energy of this gas because these particles are not like an ideal gas they are attracting each other and therefore there is a decrease in the force exerted per unit time per unit area on the walls of the container due to this attraction which is this.

Now why $1/v^2$? That is not very hard to understand because this is like the concentration, you put N in here, there is an N^2/V^2 that is how you get the v^2 here right. So each particle if you assume is interacting with all the particles around it then the total interaction strength is proportional to the concentration in, but in unit volume there are n such particles little n such particles therefore the total interaction energy is proportional to $1/n^2$, which is the same and $1/v^2$ okay so this is called a Mean field theory where you say that and we will see a better example of it or more transparent example of it in a few minutes okay.

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P, V, T

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT \Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2}, \left(\frac{\partial P}{\partial v}\right)_T = 0, \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

Whatever it is, this part takes care of long-range attraction, this part takes care of short-range repulsion, so it looks like a very typical equation of state. I am sure enough it produces for you an inflection point here because these points whose coordinates are P_c , V_c and T_c are determined completely as you know very well from elementary physics by 1 equation of state + 2 more conditions, one of them says that the slope here is flat so at that point you have this and then you have ΔP over ΔV equal to 0 on the isotherm and it is an inflection point. And as you know it is a very simple exercise in high school physics to compute what this P_c , V_c and T_c are in terms of these 3 equations. From these 3 questions all 3 are known, you can solve uniquely for it when you get this.

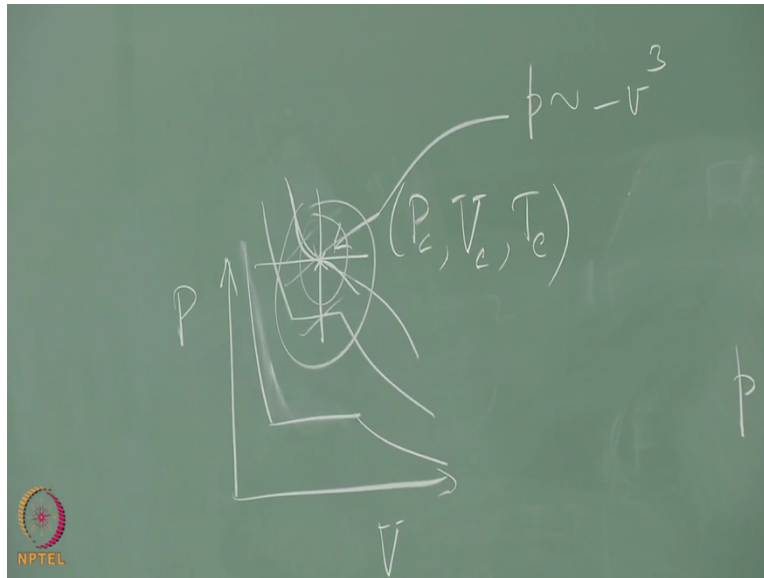
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$$p = \frac{P - P_c}{P_c}, \quad v = \frac{V - V_c}{V_c}, \quad t = \frac{T - T_c}{T_c}$$
$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Now we are interested in a critical region so we are really interested in what is going on here in this region, we are not interested elsewhere this whole thing. So it is very convenient to shift variables to this point and to define little p equal to $P - P_c$ and you make it dimensionless by dividing by P_c , similarly v equal to I am sorry for the bad rotation it is $V - V_c$ over V_c , I use this for specific volume but now I am using it for reduce dimensionless reduce volume okay. One of the characteristics of theoretical physics says that they assume their notations are usually terrible because they, the philosophy is those who understood it understand it, those who do not, do not worry about it by context you know what I mean.

And you use I am sorry again t which now will be used for time, this is used for $T - T_c$ over T_c the reduced temperature okay. I leave it to you as a simple exercise, you could have done in school to rewrite the Vander Waal's equation of state in terms of these variables. So 1st you have to solve these 3 equations, find out what P_c , V_c , T_c are by the way V_c is trivial maybe trivial and then you have to work a little harder to find other 2, T_c is also fairly simple but P_c you have to do little bit of algebra okay.

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And then you write you find that if this neighborhood in here you find not unsurprisingly, the curve goes like this, it is an inflection point it is not linear it is an odd function so the next one is a cubic dependence. You discover that in this region P goes like $-v$ cube okay so it is the power 3 that emerges and I want you to show this okay, this is crucial it is called the critical exponent. Well, you can also do many other things you can ask what happens if I take the same equation and draw P versus V but I do the other variables right, the P versus V has these little horizontal pieces out here, the P versus T we already know is a curve in the P - T plane which ends in the critical point and then finally there is a T versus V the density thing, again I leave you to work that out because you get that parabolic curve okay.

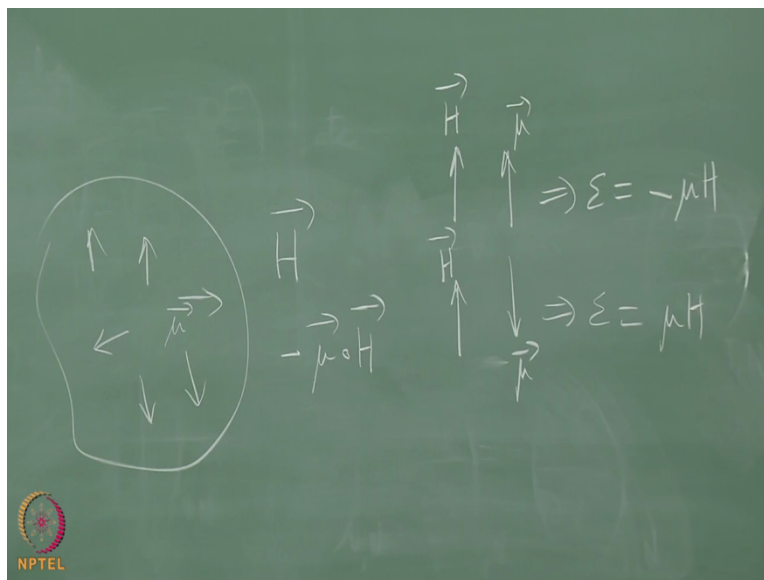
Now let us go to our magnet analogy, I am in a hurry to do that uhh. What is going to be the simplest magnetic equation of state? Well, we want to look at the substance which undergoes a phase transition from a non-magnetized or paramagnetic state to a magnetized or ferromagnetic state. Lots and lots of models of magnetism and it is intrinsically a quantum mechanical phenomena. 2 ways in which you can get a phase transition nontrivial behaviour, one of them is to say that there is an interaction between the different constituents which leads to the leads to phase transition.

If you start with an in this case if you start with an ideal gas, $P V$ equal to $R T$ and there is no phase transition at all, you need the short-range repulsion and the long-range attraction to

produce a liquefaction (46:11) and that attraction definitely to produce liquefaction, so some interaction has been taken into account. In exactly the same way if I just start with a lot of independent atomic magnetic moments, I do not get any phase transitions at all it remains a paramagnet which is magnetized when you apply a field and demagnetized when you remove the field.

To get the phase transition to a state of permanent magnetisation I must include an interaction between the different atomic moments, which turns out to be fairly complicated because you need something called the exchange interaction. There is another way to do this which is to say that which is to do what you did here, this term we did not write any explicit inter-atomic potential, we just said logically the effect of this attraction is mimic by this reduction in the pressure out here and you give a hand waving argument for why it should be $1/v^2$ and not $1/v^3$ or $1/v^4$ or anything like that right.

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In the same spirit one can introduce an external field an effective field an internal field in the system, which says the effect of the interaction between spins is mimic by an effective magnetic field in the medium itself and that plays the role of interaction, this gives you what is called the wise molecular field theory okay, let us see how this works. Now we know that if you have a substance with a lot of independent atomic magnetic moments pointing every which way, et cetera, we ignore everything except the magnetic property, we do not worry about the Kinetic

energy we do not worry about any other degree of freedom, we are looking only at the magnetic properties.

Then I apply a magnetic field to this, if each magnetic moment is μ in the presence of an external field H magnetic field in some direction say fixed direction, the potential energy for each magnetic moment is $\mu \cdot H$ in the presence of a field with a $-$ sign okay. Now I make a further simplification, this of course says that depending on the direction of the field and the direction of the dipole you get any energy you like from a maximum which is equal to μH to a minimum which is $-\mu H$. Now I make a glorious simplification and say look I allow only 2 possibilities; either the 2 are parallel to each other or anti parallel to each other.

When they are parallel to each other $\cos \theta$ is 1 and the energy is $-\mu H$ so this configuration is the direction of H and this is the direction of μ implies the energy is in $-\mu H$, and this other possibility this is H , this is $-\mu$ this is μ implies ϵ equal to μH okay. They are actually substances which should behave in exactly this fashion and that is now due to the quantum mechanical nature of this magnetic moment which comes in turn from the spin of the particle and the spin sometimes it can be half in certain cases such as the electron and then it can have only 2 possible projections along any direction okay.

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The image shows a chalkboard with the following handwritten derivation:

$$M = N \langle \mu \rangle = N \frac{\mu e^{\beta \mu H} - \mu e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}}$$

$$= N \mu \tanh \left(\frac{\mu H}{k_B T} \right)$$

In the bottom left corner of the chalkboard, there is a small circular logo with the text "NPTEL" below it.

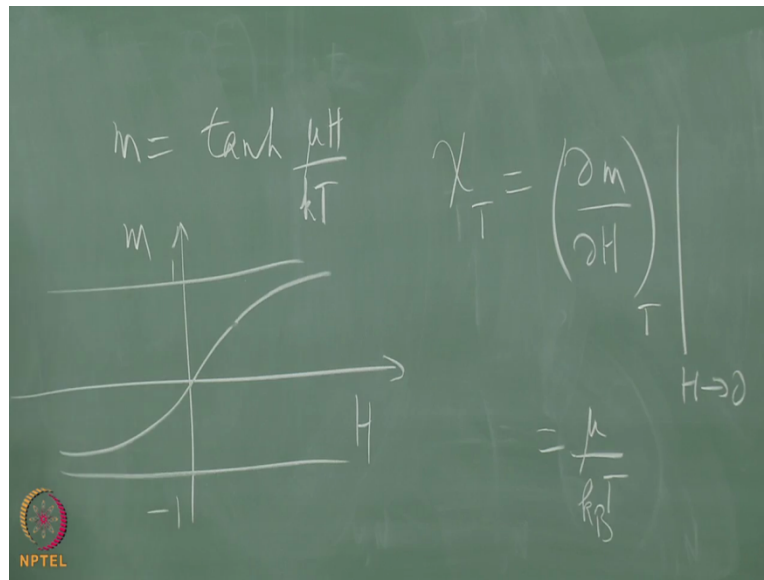
Whatever, these are the 2 possible energy states of any of these elementary magnetic moments right. What is the magnetisation then if this is the case and they are not interacting with each

other? So what is the magnetisation, you can write this down trivially, the magnetisation is, since they are all independent of each other and I have N of them it is M and we want the thermal average. If you did not have the temperature, the whole thing was absolute 0 then the whole system would go into its ground state, state of least energy which means that that all of them will point along the field and the total energy is $-N$ times μH that is it.

But now thermal agitation is causing them to flip back and forth and at any given temperature you can ask what is going to be the magnetisation right, you want to know the average magnetisation, so this is equal to N times the average value of μ with respect to e to the $-\beta \mu H$ et cetera. But this is now trivial because this is equal to N times there are only 2 possibilities for each one of them; if it is up then the magnetic moment is $+\mu$ and the probability is e to the power $-\beta \mu H$ which is $\beta \mu H$ relative probability $+$ the magnetic moment is $-\mu$ so we put a $-\mu e$ to the $-\beta \mu H$ divided by the partition function which in this case is $\beta \mu H$ because this factor divided by this is a relative is the absolute probability that the moment is $+\mu$, this is the absolute probability that is $-\mu$.

So this is equal to $N \mu \tanh(\beta \mu H)$ let us write it as μH over $k_B T$, this is my magnetic equation of state if you like for this trivial problem. It expresses the volume analogue terms of the system size the number of particles with temperature and the pressure analogue so it is the equivalent of $P + N \frac{A}{v^2}$ times whatever it is $V - M V$ equal to $N R T$ okay. But this is very trivial, we can now plot what this is, we want things in terms of intensive quantities specific quantities so let us define m equal to M divided by $N \mu$.

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It has dual advantage it is magnetisation per particle and it also dimensional less because you divided by magnetic dipole model. So we have m equal to \tanh hyperbolic μH over $k T$ and they are all set now, the equivalent of the P-V diagram the isotherm is you fix the temperature and you plot H versus M or versus H , the reason we chose P in the vertical axis, V on the horizontal axis is because you have in mind the historical reason, historical idea that you had a cylinder with a piston, you change the volume and the pressure got adjusted okay whereas, here you normally apply the field and you measure the magnetisation so you just plot M here and H here okay and isotherms are very trivial to write down in this case.

Just these lines that is the \tanh hyperbolic function and \tanh hyperbolic can never exceed -1 or $+1$ on this side or that side okay. Notice, it saturates when all of them have moved in the direction of the field that is it, there is no nothing more possible as far as M is concerned and M cannot be less than $-N \mu$, in this case there is an extra symmetry present in the problem which is not present in the P-V as you can see it is not overtly. And that is if you change the direction of H , M changes so there is a symmetry present here and it is going to have implications. Now what is the slope at the origin?

Well the isothermal susceptibility the magnetic susceptibility is defined as a rate of change of the magnetisation with respect to the field at a given temperature, so it is equal to Δm over ΔH at constant temperature so this formula χ is m over H is not correct because there is a non-

linear relation between m and H , it is only true near the origin where you have a linear region. So you have to take that into account by writing here H tends to 0, so the suitability is defined as a slope at the linear region of this isotherm okay that is trivial to find because what does \tan hyperbolic x do as x goes to 0? It goes like x , so this immediately says this quantity is equal to μ over k Boltzmann T .

This theory is the law of paramagnetism, which says that the paramagnetic susceptibility is proportional to 1 over the temperature right. Nothing much is there in this model because there is no interaction, so there is nothing interested to do okay. Now the question is we know that in real substances this is not what happens that the phase transition actually happens and if I plot it for instance as a function of temperature T if I plot it M , in the absence of a field... Let us let us go on this a little bit...

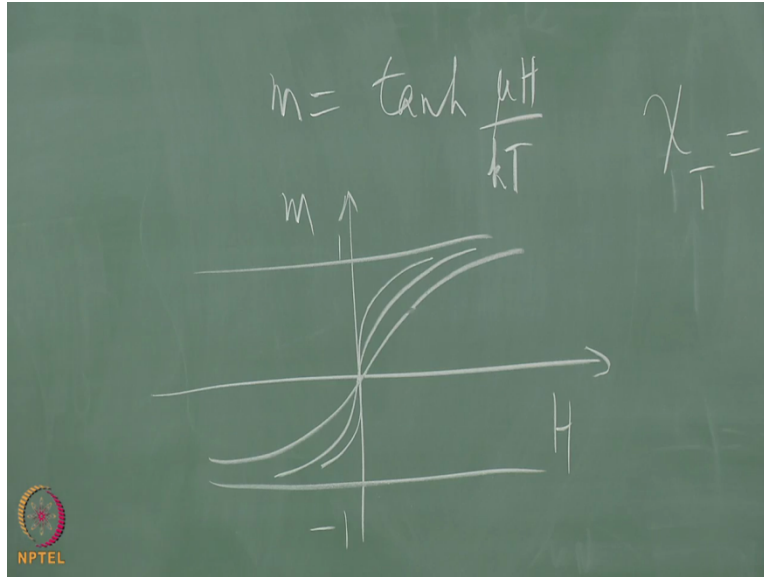
What happens in a real substance as I lower the temperature? As I lower the temperature the slope becomes higher and higher right, it cannot go beyond saturation so it does this. Now ideally this is all this (57:52) then it will go on like this and the slope would become infinite only at absolute 0 of temperature, but there is always an interaction between these magnetic moments. And if you are at sufficiently low temperatures then the thermal agitation cannot override those and therefore there will be some kind of magnetic ordering and sufficiently low temperatures no matter how weak the interaction.

In the case of iron it already happens when you hit of the order of 10 to the 3 Kelvin because that is the (58:28) temperature anything below that you will have permanent magnetisation. But this is entirely a (58:33) system you are looking at to see if you get magnetic ordering or not uhh. So what looks like high-temperature or low temperature depends on the characteristic interaction energy in the problem between any 2 magnetic moments as compared to kT which is the thermal interaction energy right?

If you look at substance like helium, solid helium 3 for instance, that becomes an anti-ferromagnetic, a nuclear anti-ferromagnetic at some crazy temperature which is of the order millikelvins so for that material looks completely non-magnetic it is an inert gas, for that material 1 degree Kelvin is already very high temperature. If you look at very very high purity copper which is a non-magnetic material at 50 Nano Kelvin it becomes a nuclear anti-Ferromagnetic so

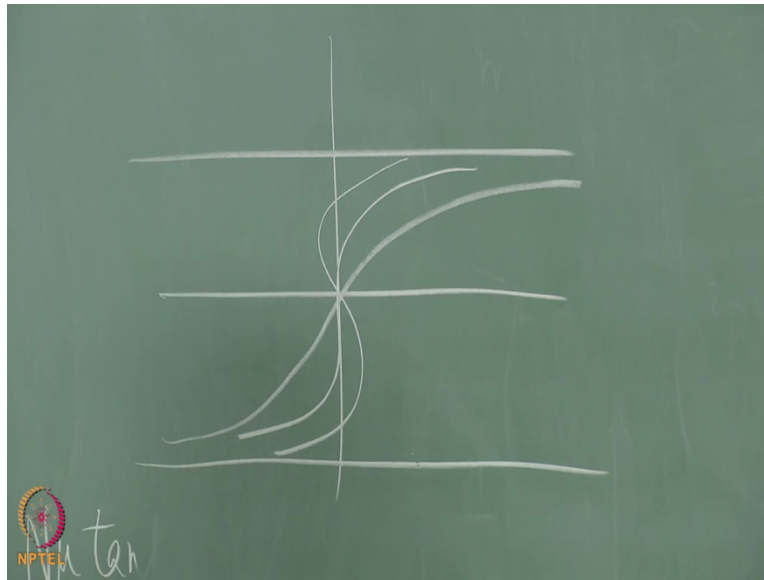
for that material microkelvin is a very high-temperature as far as magnetic properties are concern. So this as Physics says we have to understand when you say low and high it is the question of what scale you are talking.

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Now for most of substances what happens is that as you lower the temperature, there comes a finite temperature at which the slope becomes infinite I mean the flat this becomes a curve, very reminiscent of the critical isotherm except that it is tilted by 90 degree because I did not plot P in the vertical axis, I did not plot H in the vertical axis okay. What happens if you lower it even further? Well, in principle it would do this if you just believe in the continuity of all these curves, you will believe that once it finish that then it is going to do this right, it just keeps bending backwards so let us draw that and see what it does.

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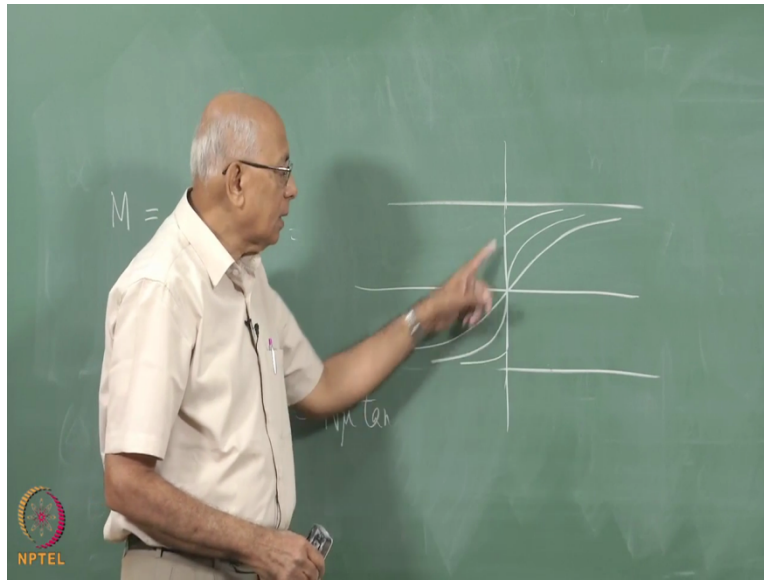


So it should really do this right? I just draw 3 curves, one is and does that with a finite slope, the 2nd is when the slope has become infinite and the 3rd is when it does this. This reminds also that Van Der Waal's equation when you went down and up again and we said ha that is not true because it is violating stability somewhere. Indeed that is true because in this region from here to here dM over dH is negative except that is not a diamagnetic substance so this certainly cannot be true at all, it violates again the convexity property of one of the free energy. Just as in the other case the compressibility turned out to be negative and that violated the convexity property which in turn came from extensivity that is similar sort of thing happens here.

So if you excise this portion then what the system does is come here, go down jump to this and go off and on the other way back it comes all the way up to here jumps here and goes back. What does that curve look like?

Student: Hysteresis.

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It looks like a hysteresis loop and indeed that happens except in the refrigerator it did not happen but in the magnetic system hysteresis does happen all the time. However, if you have hysteresis happen for other technical reasons, it happens because all the domains in the medium do not reorient at the same time at the same field and that happens sequentially. But if you look at the single domain ideal substance there will be no hysteresis and the curve becomes discontinuous. At high-temperature it does this, at some crazy critical temperature it does this and below that it does this, as you lower the temperature it keeps doing this cutting it higher and higher. Does not this remind you of what happened in the sty line construction?

The only difference is, there for different isotherms you ended up with different sty lines but here there is only one, all of them have become degenerative here.

Student: (())(62:58)

That is because of the symmetry which is not overly present in the fluid case, there is symmetry but it is not immediately obvious. So we can see that we are leading up to this thing here, the next thing to do is to do a trick which is to put an effective field there and show you that you get a cubic curve here the 3 the exponent is going to show up then the half exponent which we got for the density difference is going to show off in the magnetisation, so we will take it from there and then go beyond that next time.