Basic Statistical Mechanics
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Lecture - 35
Phase Transition and Landau Theory (Part 2)

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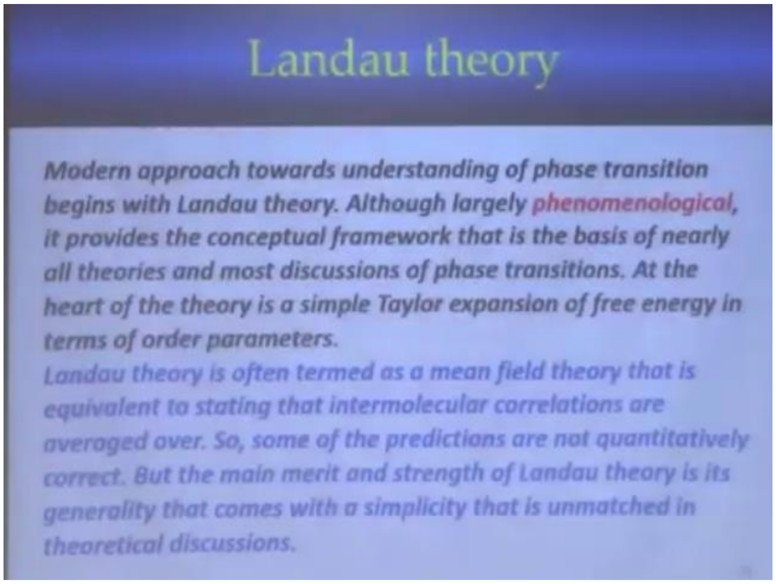

Landau theory

Modern approach towards understanding of phase transition begins with Landau theory. Although largely phenomenological, it provides the conceptual framework that is the basis of nearly all theories and most discussions of phase transitions. At the heart of the theory is a simple Taylor expansion of free energy in terms of order parameters.

Landau theory is often termed as a mean field theory that is equivalent to stating that intermolecular correlations are averaged over. So, some of the predictions are not quantitatively correct. But the main merit and strength of Landau theory is its generality that comes with a simplicity that is unmatched in theoretical discussions.

So now we go to the Landau theory, which I will spend about I think is some 15-20 minutes on that. So Landau theory is this saying that although is largely phenomenological, but it is the beginning of the conceptual framework of understanding crystallization. So read this, but also in the mean term also let me briefly tell you. So in 1937 when Landau did the theory of phase transition, it is a general theory of phase transition.

And it paves the way for everything that followed, a very simple theory, incredibly simple theory and but however, this generality that it allowed and the new concepts that brought in, which was not there before and one of the new concept that Landau brings in, he just did. He asked the questions that I was asking here.

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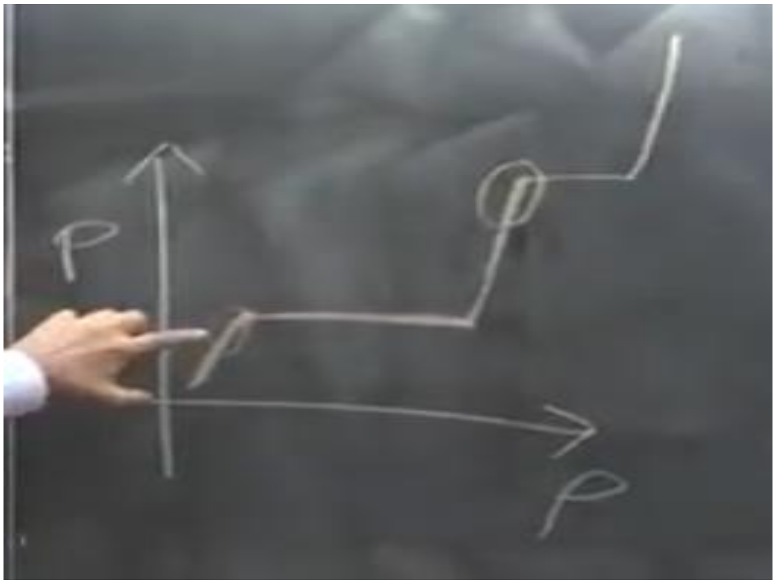

How do I take the characteristics here in the old phase which I know contain the key for the phase transition? So how do I do that? What are the way I go about incorporating this. So he now guessed that you go way to do that that I need to have, so I had the minima. I have the minima in the liquid and I have all the correlations here. So now if I can expand the free energy of this phase in terms of free energy of all the characteristics of this phase, then I can look for a certain discontinuity.

So that is of course ambitious and it is the reason, it does not fully work, but that is the one it is called. So this is again my favorite line. Some of the predictions are not quantitatively correct, but the main merit and the strength of Landau theory is its tremendous generality that comes with a simplicity that is unmatched in theoretical discussions and you will see that, but the reason I am preparing you for that, though it is a very simple theory, it opened the door for many theories and it is the generality that is absolutely mind-boggling.

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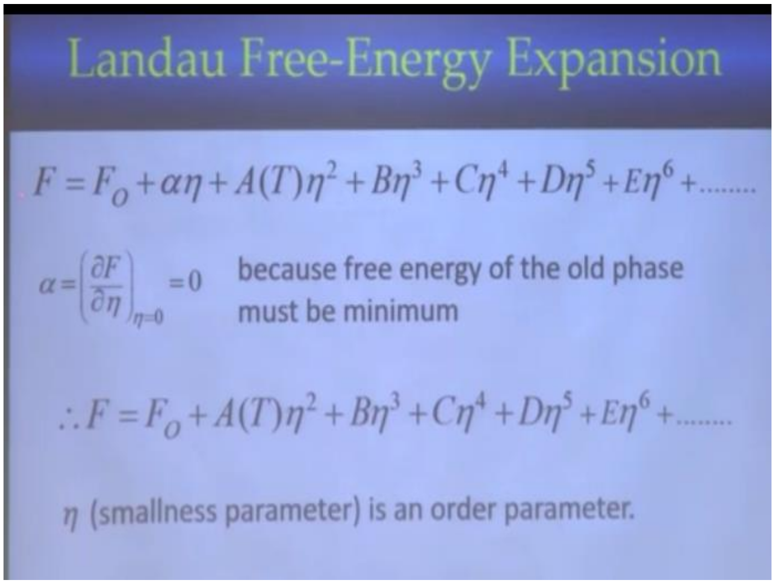

Landau Free-Energy Expansion

$$F = F_O + \alpha\eta + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + ...$$

$\alpha = \left(\frac{\partial F}{\partial \eta}\right)_{\eta=0} = 0$ because free energy of the old phase must be minimum

$$\therefore F = F_O + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + ...$$

η (smallness parameter) is an order parameter.

So what did he do? After saying all these things, what Landau did okay, let me write down the free energy of the new phase, where F is the new free energy of the new phase in terms of simply called Landau expansion. Expansion of the Taylor series, see people are all very perplexed for many years, decades. Nobody wrote down such a simple expansion, but Landau wrote down. That is what actually probably the simplicity or whatever, he is a genius.

So he expands. So when you expand like that, then η is the order parameter. So I am expanding free energy in the order parameter. In the old phase order parameter is 0, so $F = F_0$. Now my aim is to find a solution of the free energy in terms when the eta is non-zero okay. So this is the search of a solution. What are the conditions? Then where did the answer lies? The answer lies, as I said, answer lies in this branch.

And why are this branch are going to all these quantities, α, A, B, C, all of them are temperature dependent. This is explicitly put out for reasons I will describe a little later. All of them are temperature dependent. Now what are these quantities? How do I get α, A, B, C? Exactly, you take the derivatives, so that is the characteristic I was saying. We need the derivatives and once you try to find the derivatives, you go a little deeper.

You find the derivatives are in fact not only just specific heat or compressibility, but they are also giving a little higher level theory intermolecular correlations in the old phase, which we are not going to go. So this is the famous Landau expansion. There are many other terms there. When you put the gradients here, delta, eta from that becomes against what Landau and that is one of theory of superconductivity people use or superfluidity.

Ginzburg got the Nobel prize later for this and many other things. So now, we start playing some game. So these are first important things that are determined by the derivatives of the free energy in the old phase. So these are determined by the old phase and we are trying to by Taylor expansion just like we do, how do we do a Taylor expansion? We always do Taylor expansion by going from known to unknown; that is the Taylor expansion, right interpolation, extrapolation.

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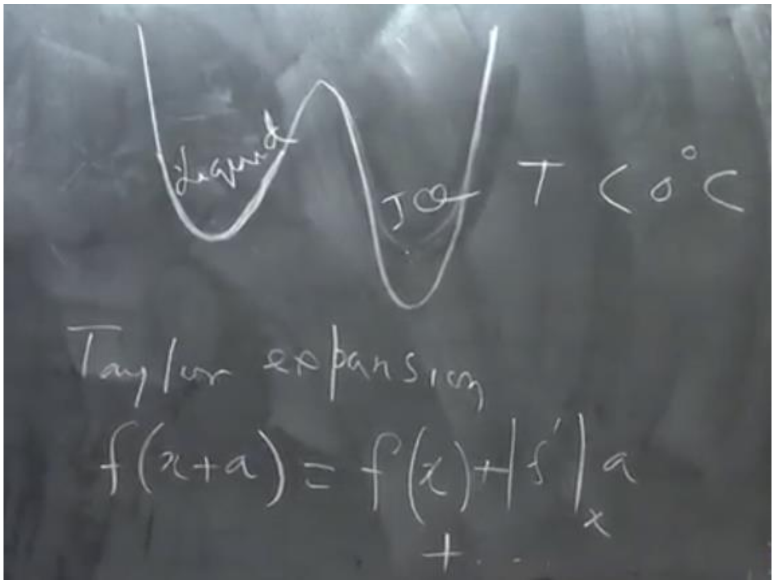

So we use Taylor expansion always like we do f(x+a). We do a Taylor expansion f(x) plus then first derivative, but evaluated at x = a. So whole idea is that of going from known to unknown and known, we know. We are entitled to know everything about the old phase and then you are trying to do new. Now first thing is that, because this is a free energy minima, because this is a minima here in the liquid phase, this is 0. So now it becomes simpler that the free energy is one term less. Next, very importantly one quantity is done.

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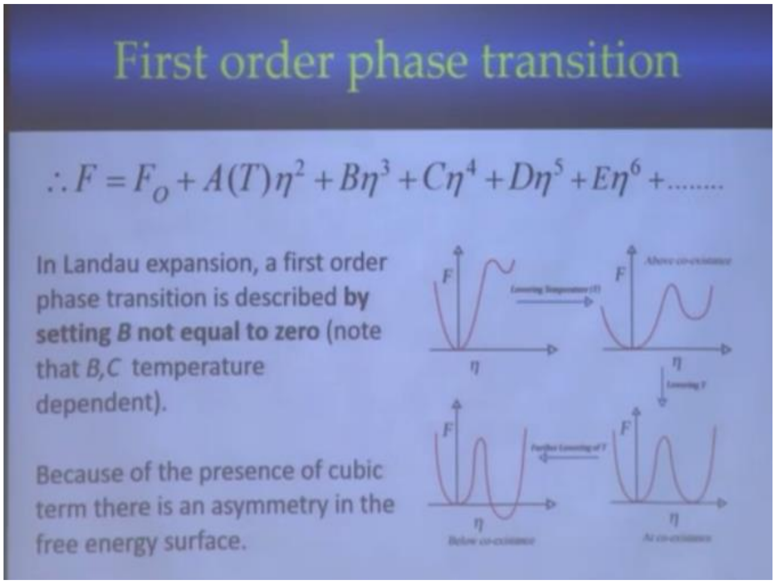

First order phase transition

$$\therefore F = F_O + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + \ldots\ldots$$

In Landau expansion, a first order phase transition is described **by setting *B* not equal to zero** (note that *B,C* temperature dependent).

Because of the presence of cubic term there is an asymmetry in the free energy surface.

Now I make a distinction between first and second order phase transition and this is very important. So I will now describe something else that is coming here, but coming at a later stage, so I better do it here. This is extremely important thing and essence important part of the Landau theory okay.

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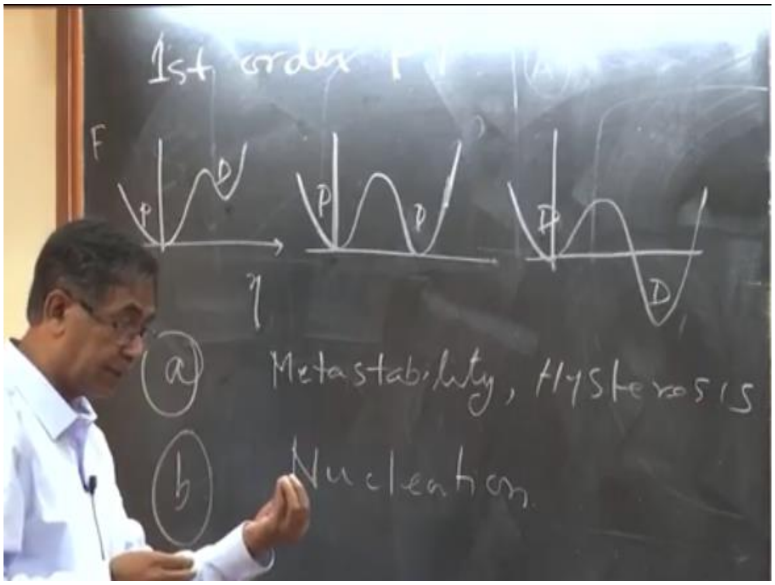

So in a first order phase transition, free energy surface behaves like that against order parameter, free energy and I am lowering temperature towards the transition. So this is the old, my parent phase. This is the daughter phase, parent-daughter. Now parent and daughter become stable. Now what is in my pressure-density? What is this point? Exactly, this is the coexistence point. So this is the metastable characteristics of first order phase transition.

There is always a metastable phase. One of the major characteristics and what is the manifestation of the metastability? We see it all the time. What is the most important manifestation or a signature of metastability? Hysteresis, you see in the presence of magnetic field, huge hysteresis that is because system remains trapped. Even when this is stable, system is trapped here. That is one of the reasons.

Another reason, even at coexistence there is a large barrier in first order phase transition. What is the consequence of this large barrier in a first order phase transition, gas to liquid, liquid to solid, or nanomaterials forever, nucleation. You cannot spontaneously go over from one phase to other phase, because it is macroscopic barrier which is proportional to number of particles in the system. So it must be new phase, it must be nucleated okay.

So two important characteristics of first order phase transition is a metastability, hysteresis, b it must have nucleation, because there is a macroscopic barrier. So the system must be, it is like winning a war. You must get into the fort okay. This is the first order phase transition. What happens is, so this is the Landau free energy surface for first order phase transition. What happened to Landau free energy surface for second order phase transition like the order-disorder transition, like superfluidity.

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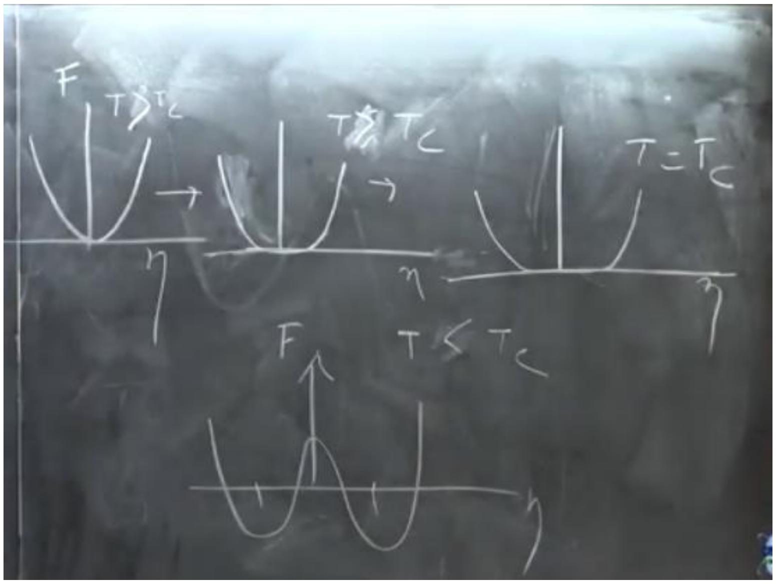

Now, this is very nice and this is what is the Landau theory gives you, a nice physical picture. This is low temperature. Now I am increasing temperature or you can say decrease temperature or whatever. We will see so uniquely different. I wish this time I really miss a big board. This T = Tc, this T is less than Tc, T near Tc and then T greater than Tc. Let me T greater than Tc, T greater than = Tc and T less than Tc. So they are the four diagrams.

So there is no metastability in a second order phase transition. There is no nucleation. So as I go to the transition point the systems, remember I told in the response function, second derivative are the springs that hold the system together. Here this spring is compressibility or susceptibility or the specific heat and that spring slowly goes away. That is why you have infinitely compressible at critical point and the free energy surface becomes really broad and shallow in the minima.

And this is where things are diverging and just little below that you get this spontaneous symmetry breaking of the system. So this is Landau, he provides this free energy landscape. The free energy provided this beautiful picture, how a first order phase transition happens and then second order phase transition happens. This is how first order what is shown here is first order. What I have drawn there is first order and there is a huge change in going from melting is a case where there is no second order phase transition and there is a beautiful logic again.

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Landau logic that in a gas-liquid; however, there is a second order phase transition. This becomes narrow. You remember the isotherm, then this is the critical point, inflection point, this is Tc and so as you approach that then free energy surface, even in the minima start become flatter and then the whole second minima completely disappears and you get this. So this is the one that is shown there is the first order phase transition with metastability and then I will do the Landau theory in a minute.

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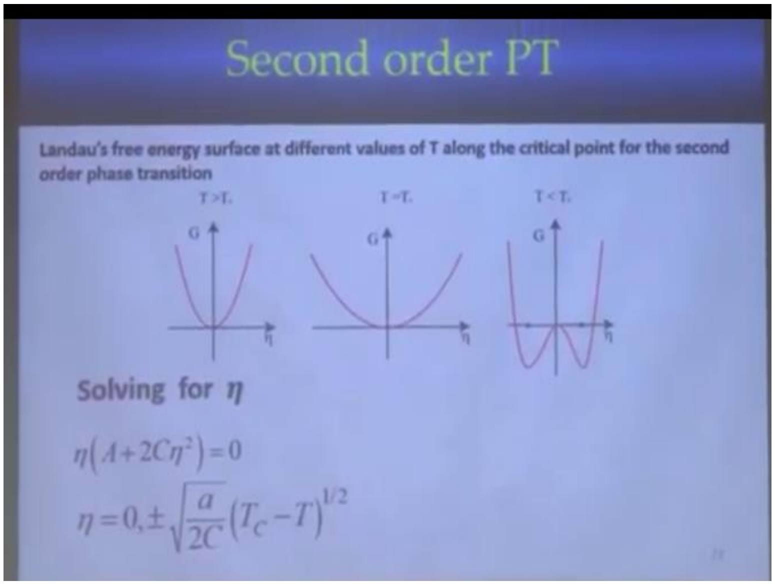

Second order PT

Landau's free energy surface at different values of T along the critical point for the second order phase transition

Solving for η

$$\eta\left(A+2C\eta^2\right)=0$$

$$\eta=0,\pm\sqrt{\frac{a}{2C}}\left(T_c-T\right)^{1/2}$$

And this is the flat and then this is the spontaneous symmetry breaking in a second order phase transition. So let us do the Landau theory quickly and so knowing that free energy surfaces are very different Landau trivially now into he said okay. First thing, I again mentioned that is an order parameter. That is why order parameters will be introduced, so that I can expend a free energy. Order parameter is the change and you know the free energy expansion is done in Taylor expansion.

I have to change. So in f(x+a) our Taylor expansion, a is the order parameter. You are expanding around that and so order parameter is the smallness parameter. That is number one. Second one, now we going to do the second order phase, if we do first order phase transition, then these quantity B is non-zero and if B is non-zero I can make B negative and by making B negative, I described these transition and that is exactly the way Landau Dijan theory of liquid crystal was done.

de Gennes was given well place for 2 work. One is liquid-crystal, another is polymer, three a semiconductor also. In these two, liquid-crystal and that; he did the landau theory. So is it beautifully one can describe and it turns out I can do the calculations of B and in first order phase transition, they are negative.

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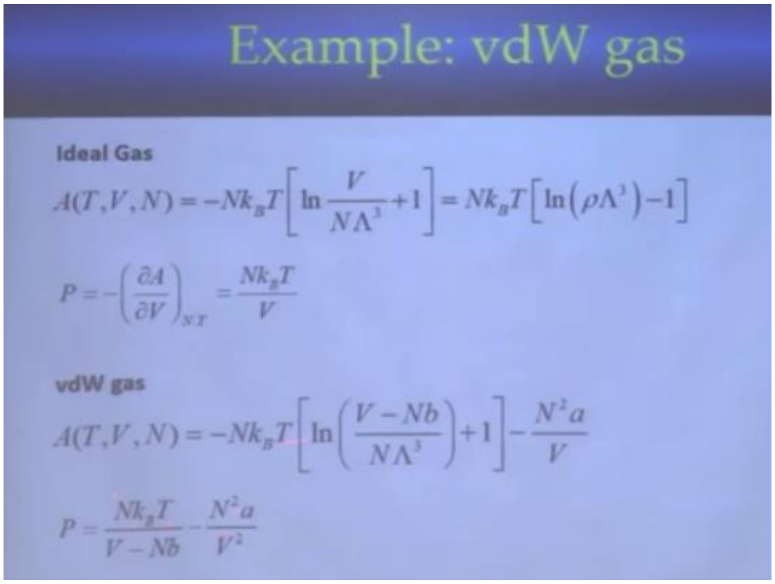

Example: vdW gas

Ideal Gas

$$A(T,V,N) = -Nk_BT\left[\ln\frac{V}{N\Lambda^3}+1\right] = Nk_BT\left[\ln\left(\rho\Lambda^3\right)-1\right]$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{NT} = \frac{Nk_BT}{V}$$

vdW gas

$$A(T,V,N) = -Nk_BT\left[\ln\left(\frac{V-Nb}{N\Lambda^3}\right)+1\right]-\frac{N^2a}{V}$$

$$P = \frac{Nk_BT}{V-Nb}-\frac{N^2a}{V^2}$$

What is an example? Let us do van Der Waals gas and we take again and again. So this is the van Der Waals gas, our famous van Der Waals and then this is free energy. From integrating this one, you get the free energy and I can plot the free energy landscape from Van Der Waals.

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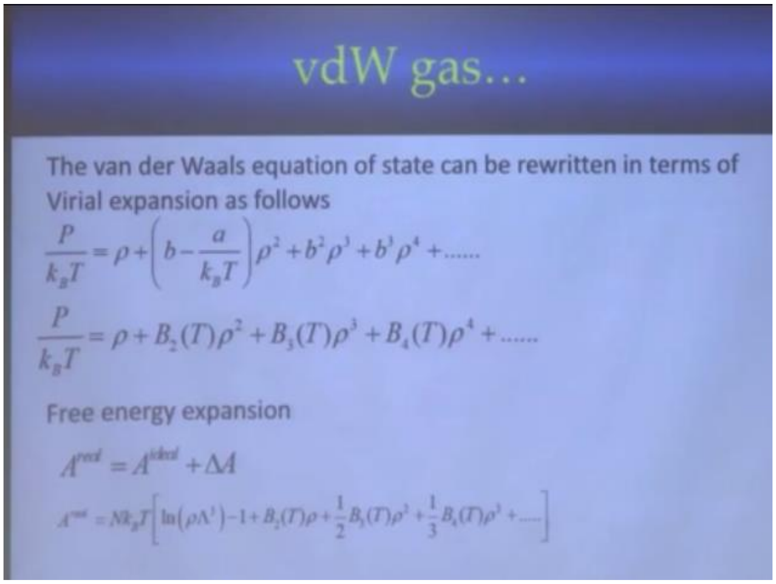

vdW gas…

The van der Waals equation of state can be rewritten in terms of Virial expansion as follows

$$\frac{P}{k_BT} = \rho+\left(b-\frac{a}{k_BT}\right)\rho^2+b^2\rho^3+b^3\rho^4+......$$

$$\frac{P}{k_BT} = \rho+B_2(T)\rho^2+B_3(T)\rho^3+B_4(T)\rho^4+......$$

Free energy expansion

$$A^{real} = A^{ideal}+\Delta A$$

$$A^{real} = Nk_BT\left[\ln\left(\rho\Lambda^3\right)-1+B_2(T)\rho+\frac{1}{2}B_3(T)\rho^2+\frac{1}{3}B_4(T)\rho^3+.....\right]$$

I can also do expand free energy in a Taylor expansion. van Der Waals gives you exactly these, what we discussed the other day virials. These are virial series. Beauty is that the second coefficient is this thing. Now free energy is derivative of, go over you get a key term, cubic term, you integrate that, get the free energy. These term becomes negative at a low temperature simulating the phase transition first order restoration.

And the cubic term goes to even small near the gas liquid critical point that does not fully describe this theory, but Landau theory is essentially Van Der Waals theory. These are called mean field theory in the sense that I am neglecting fluctuations. I am using a simply Taylor expansion to describe. If I integrate that rho square, rho cube that comes in. So van Der Waals free energy is exactly Landau free energy, except I now have some little bit of ideas where B2 B3 are there. It already has that. Now the strength of Landau theory is in providing a description of the second order in a trivial way.

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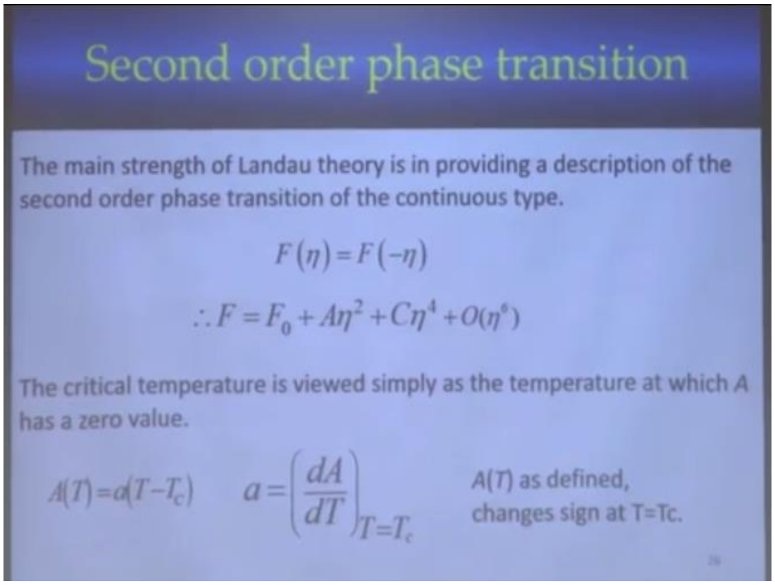

Second order phase transition

The main strength of Landau theory is in providing a description of the second order phase transition of the continuous type.

$$F(\eta) = F(-\eta)$$

$$\therefore F = F_0 + A\eta^2 + C\eta^4 + O(\eta^6)$$

The critical temperature is viewed simply as the temperature at which A has a zero value.

$$A(T) = a(T - T_c) \qquad a = \left(\frac{dA}{dT}\right)_{T=T_c}$$

$A(T)$ as defined, changes sign at T=Tc.

Now second order phase transition here there is a symmetry. The symmetry is that free energy is invariant. If it is 0, this is plus, this is minus. This is same. This is called the degeneracy. So if it is so, again this free energy, the condition often called the parity a symmetric condition and then this becomes simple like that, this is very famous. Particle physics theories many, many theories you know, Wilson himself did it.

It has a huge impact on the enormous field of field theory in this landau thing, that the 0 and in so many differentiation all polymer is. I told you liquid-crystal everything is done in this language. This is more I like to tell that this actually gives you the language of the phase transition. That teaches you how to think about this phase transition. How to think of free energy change and order parameter? So this is now simplifies and now Landau made this brilliant thing.

He said okay A is strongly temperature-dependent. I assume A(T). This is the not free energy series constant A and this is a universal language of Landau theory. This kind of expansion is the absolutely standard. Now you get, so I make this. Why do I do that? I did it because when T goes to Tc, so this is this term then, this term is the one that is the spring. That is the frequency right and told you that is response function, this we know will be specific heat.

Actually 1 over specific heat, so this thing is going to be flat. So that is why he assumes that it goes to 0 as (T-Tc) and then I solve for eta with that condition, put this here. Now I go and find out these. Take a derivative, when I take the derivative I get $\eta = 0$ always driven a trivial solution because these phase always remains a trivial solution. This is minimum here, but in maximum the same condition also holds and then I solve that, I get this.

So the order parameter, this is a remarkable prediction that order parameter has this non-classical dependence, that means even when, look at this beautiful thing. If (T-Tc) is 0.1, I go below 0.1. I am in this regime. I am going below the critical temperature. What is square root of 0.1? 0.33, right. I go to 0.01. What is square root of 0.01? 0.1. What does it mean? These kind of fractional exponent means he say huge dependence and this is the real hallmark of critical phenomena.

These fractional exponents, these exponent is called alpha; this is the specific heat, no sorry this called beta, because it is in terms of order parameter and beta is the universally 0.3 or one-third close to. This is amazing, you do so many different systems, define the order parameter and consider the temperature dependent order parameter and you find the fractional exponent or almost always 0.3.

That is why it captured the absolutely a of imagination of scientists across the discipline. This universality is the characteristics of critical phenomena and these are called critical exponents. Yes, no what do you have actually you have absolute here and there are lot of this exponent beta above and lower called beta and beta prime and there have been a lot of work on that and beta and beta prime are almost always the same.

They might be slightly difficult, but very difficult do the experiments exactly very close to that, but experiments were known for a very long time. This is exactly exponent you find from van Der Waal's theory also. These are called the Landau theory, does not get correct exponent one-third, but it captures the one of the essence that the eta is the change. So eta will be if I go below this, I come from here to here, then these will be the order parameter. So what I am saying is that by giving change is small amount the eta is going to change by a big amount okay. That is a singularity that we talked about N order parameter okay.

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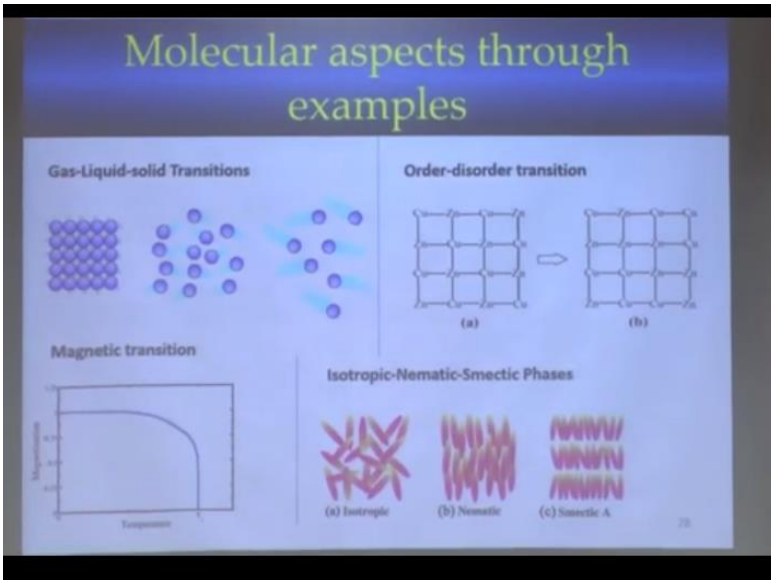

Molecular aspects through examples

Gas-Liquid-solid Transitions

Order-disorder transition

Magnetic transition

Isotropic-Nematic-Smectic Phases

So there are all these different kind of order-disorder transition, isotropic-nematic is very closely second order and then gas-liquid is the thing. So going back to first order phase transition now like liquid-crystals or Van Der Waal describes the first order fairly well, that then B is not zero anymore. It is the V that changes the sign. Now what Dijan did in liquid-crystal transition in isotropic-nematic, he noticed that isotropic-nematic is nearly second order, though first order.

So he kept Landau theory. He kept Landau this part and then he also kept the B term and it developed a theory. Again same spirit, same phonology nothing great, but he again captured described the liquid, isotropic-nematic phase transition in liquid crystals, which is given even here. I think this is what I wanted to tell, the Landau theory and the free energy landscape of Landau theory, then the critical exponents.

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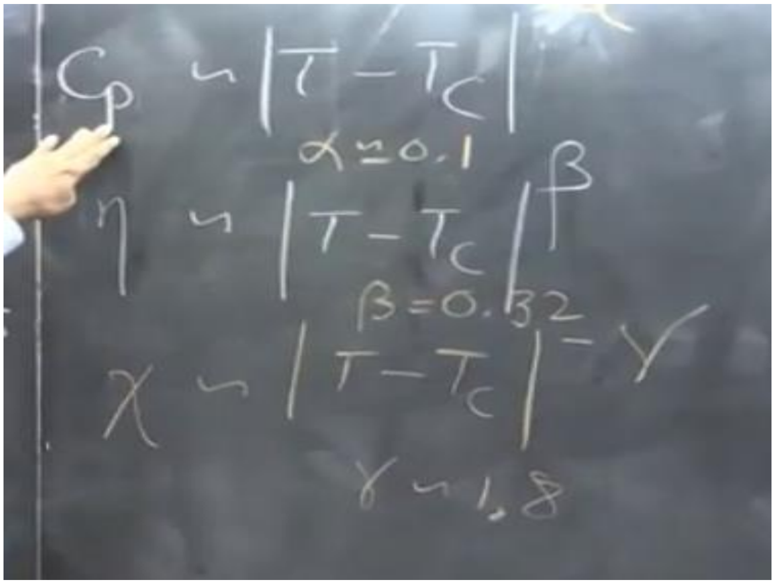

So there are some other critical exponents, which are I do not like to aid at, but the other critical exponents are the following, specific heat, alpha, beta, I might keep missing something wrong. This is beta, specific heat alpha, I should have had that, then order parameter is the beta and there is gamma, delta a series of critical exponents, which is compressibility. Compressibility goes as gamma, specific heat alpha. Alpha is typically 0.1, beta is typically 0.32, gamma is typically 1.8.

Landau theory predicts this is half, Landau theory finite discontinuity here and this one landau theory predict 1. So Landau theory gives half, the value is wrong, but it does get the basic physics correct. So should I write it separately these C_P C_V or you can see these things C_P η and χ and these are the critical exponents, α, β, γ and as I said they are universal. That means they are nearly the same across all the systems.

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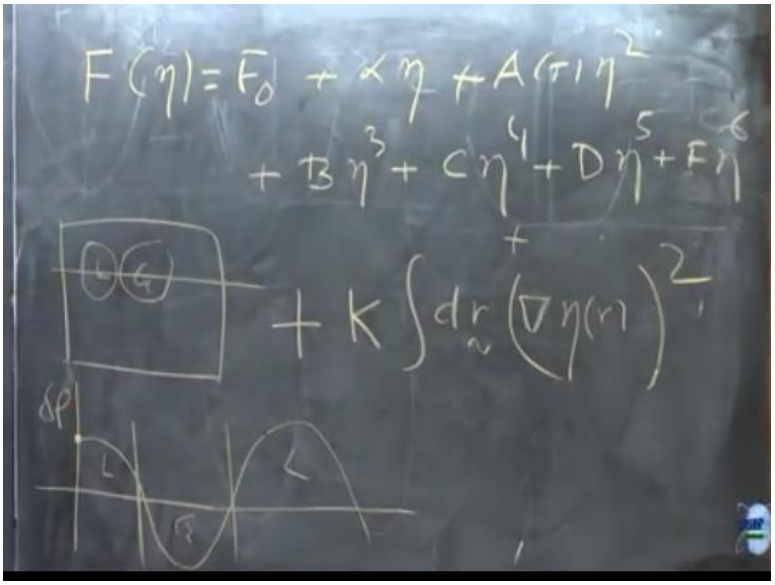

$$F(\eta) = F_0 + \alpha\eta + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + F\eta^6 + K\int d\underset{\sim}{r}\,(\nabla\eta(r))^2$$

This is a good question, van Der Waals is a mean field, Ramakrishnan Yussouff is a mean field, Landau is a mean field all are the same at the end of the day. The reason is that, when I expand that these are the ones with guys working on phase transition right the day in and day out. Now in all these things. Now let us consider gas-liquid simple thing in a gas liquid near the critical point what happens?

There are regions which are liquid like; there are regions next to it which are gas like, large-scale density fluctuations. You look at the density and now I look at the density as a fluctuations around the average density. In my critical ρ* language, critical density is again universal in near 0.3, the very interesting near 0.3. I take that out and look at fluctuations, then what do I see? I see there is a region like here where is my origin, I draw like that.

There is a large value, then after that it becomes negative, then become large, then becomes negative. I find like that. So delta rho, this is liquid, this is gas, this is liquid like that; need not be periodic. There is not periodic, but they are. So what are these now? These are interfaces. what does interphase bring in bring in surface tension? It is an extra energy. Where is that in Landau theory? It is not.

So Landau theory has to be supplemented by and lo and behold, you have one of the most powerful theory of the world, this is Ginzberg-Landau. So Landau, Van Der Waals does not have this extra term, which is we call effect of fluctuations. So mean field theory does not have the effect of fluctuations, you have to go to Ginzberg-Landau to do that. That we all do, when you do surface tension. In my book, we have dealt with it at length.

Surface phenomena, nucleation, these are one of the main topics in my book, which are not dealt either in physics or in chemistry books. No, you do not have the coexistence. You have a point. See coexistence is a line. So as I drew there that line collides, it becomes a point, point of singularity here. This is where large fluctuations are going on, gas-like and liquid-like. In a magnetic phase transitions, you have the up spin and down spin and ordered and disordered.

That means one place is ordered followed by a disordered region. So then the order goes away and it becomes fully disordered. So this is a flat free energy interface. There are inside it, gas-like and liquid-like, but those are microscopic or mesoscopic domain. They are essential ingredient for the large scale fluctuations. We call the exact language these large scale fluctuations, but those large scale fluctuations are affecting the thermodynamic properties, but there is no macroscopic interface.

This is a very important question that you asked and the very essence of a critical phenomena and so I go over, take care of those fluctuations in this term and then get a huge amount of difficulty that comes in, cannot be solved and that is what comes an important way how to go to next step and that first thing was done by Kadanoff; he introduced how the length scale diverges. That is called Kadanoff transformation.

There is a beautiful book by Shang-keng Ma Dynamical innovation book, Dynamics of Critical Phenomena. He described the beautifully kind of and there is a wonderful review article for high school students essentially, but first year PhD students called Mattice and Kadanoff Physics Today 1979 or 78, wonderful that is the best of critical phenomena that I know of. Kadanoff and Mattice or Mattice and Kadanoff, both were at Brown and they wrote together and we got the print.

Everything was done in one dimension which is done in that particular article or almost into in my book, the critical phenomena. So doing that was dance step by step. Kadanoff did the Kadanoff transformation says how to treat the emerging correlations, long length correlations that happens, things become correlated over long, because the fluctuations become correlated that because here if I have a liquid-like region, then I has to have a gas-like region.

This is called fluctuations getting correlated, then one of the most powerful theory of modern times KD Wilson in 1970 or 71 did the innovation, which is lot of fun with that. I did that once. I was happy to, I was very lucky in Chicago to work with one guy called Yoshi Ono, we did the donation group calculations of polymers, but it was the amazing theory.