Basic Statistical Mechanics
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Lecture – 36
Phase Transition and Landau Theory (Part 3)

Welcome back and hope that to got some time to spend on the last class which is Mayer’s theory which is a formidable class, this is the second time we are doing it, first time we did little bit more detail but it is a very difficult thing and we; I decided to review it once more along with the revision of the atomic, monoatomic and diatomic and polyatomic gases because these are fairly new things to students of chemistry for whom these courses designed.

And so in chemistry, we do a large amount of body of work on phase transition, from the beginning of chemistry you know from Van der Waals theory of gases, from phase transition, gas to liquid transition, see now are even undergraduate chemistry, there is a big, big chapters and on phase equilibrium, phase transition and precipitation in chemistry, physical chemistry, organic chemistry laboratory we are all the time doing melting as a taste of purity and identification.

So, phase transition is very dear to physical chemist and physical chemist is mandated to explain these thing now, there is always this curiosity so why, how the raindrops form, how gas goes to liquid, then of course how ice melts and water goes into ice, what are the molecular processes; these are only present, they are all around us but it turned out explanation of them, understanding of them, challenged with the intellectual ability of man to a very high degree.

And the people and the scientist who are involved in doing these are some of the best minds of that we have produced in entire civilization, so I already described and I hope you spend some time and I encourage you to spend more time in understanding Mayer's theory, how intermolecular interactions entered the picture to mere a function which gives us Virial series.

And also tells us how one can envisage or picture gas to liquid transition as small, small clusters in the room, for instance inside in this room, small, small clusters coagulate together to form a gigantic big cluster almost the size of the total number of particles of the system which is the liquid phase, which is the correct picture, this is that exactly what happens that when a gas goes into liquid.

Then many, many clusters of smaller size, quite small size actually can be clusters of the size of only maybe 20, 30 molecules, not more than that but many, many of those clusters, most of them still monomer and dimer, they qualis together in a very short temperature span to form a gigantic cluster of Avogadro number of molecules, this happen in so sharply and in such a short temperature range that it we call it a singularity.

We call it that the properties; thermodynamic properties diverge for example, you calculate specific heat, it diverges so phase transition as then characteristics of these divergence that things just fantastic things happen but then how do I explain these fantastic things; Mayer's told us okay think in terms of small, small clusters and they suddenly come together to become big clusters.

But I told you the Mayer's theory however beautiful it is it breaks down because we do not get the cluster integrals, reliable cluster integrals, we told us how to do these things but those things are very difficult we cannot do, even now today we cannot calculate any useful cluster integrals for Lennard-Jones systems of something more than the size of the say for example, 10 particles together.

There is a huge number of graphs that come in which cannot be evaluated and 10 particles double connected will be 30 dimensional integral, it is just not possible actually people in Lennard-Jones have done only up to 6 that Benny and Hoover who did this beautiful work in a landmark work in about 30 years ago but nothing more here has been done after that.

However, at the 1937 target around the same time, when Mayer was developing his game changing theory of in terms of graph theory, in terms of clusters, in terms of cluster integrals, one brilliant physicist called Landau; Landau was developing a simple phenomenological theory to describe the phase transition and this is called order parameter theory that went on to become the main stream of phase transition study that went on to develop many languages.

And went on to give him probably to obtain 15 Nobel prizes in this area of phase transition, so we will briefly described and after you did it once before but I am going to do it again probably somewhat from different perspective and as I go on this way I will go, I will repeat things, once you go little advance then go back and then again go forward, so in that way as I said painting is a way to learn things.

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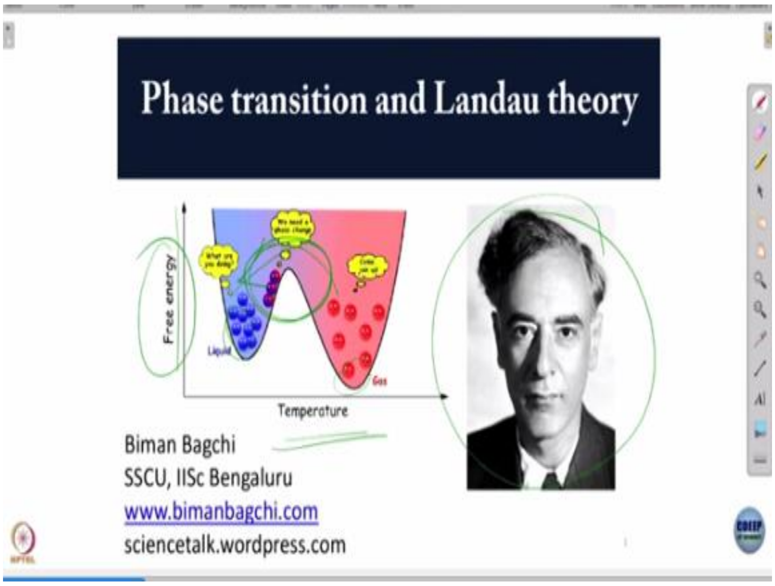

Phase transition and Landau theory

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So, this is a; this our picture of Landau, the great Landau and with many, many things and this is kind of a free energy diagram which came was inspired by Landau that if gas to liquid high temperature, if the temperature large, gas where molecules are far from each other but in a liquid the molecules are near, so this is the kind of droplet, the small clusters from Mayer's theory, this one gigantic cluster that forms and the phase transition.

But look at that there is a barrier, it has to go over the barrier and these free energy barrier; going around the free energy barrier is also a very difficult process but the appearance of this double minimum is the essence of the Landau theory and that this when plotting free energy against the appropriate quantity on the x axis with free energy y axis is called Landau's an energy landscape.

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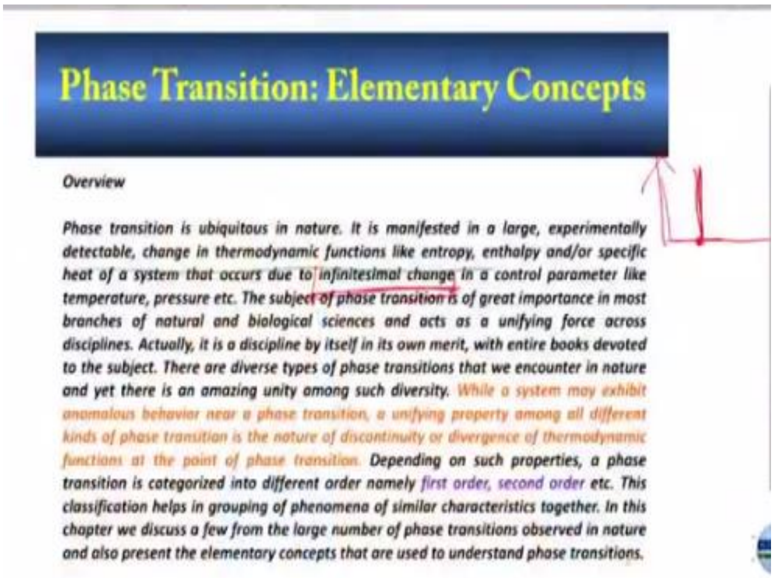

Phase Transition: Elementary Concepts

Overview

Phase transition is ubiquitous in nature. It is manifested in a large, experimentally detectable, change in thermodynamic functions like entropy, enthalpy and/or specific heat of a system that occurs due to infinitesimal change in a control parameter like temperature, pressure etc. The subject of phase transition is of great importance in most branches of natural and biological sciences and acts as a unifying force across disciplines. Actually, it is a discipline by itself in its own merit, with entire books devoted to the subject. There are diverse types of phase transitions that we encounter in nature and yet there is an amazing unity among such diversity. While a system may exhibit anomalous behavior near a phase transition, a unifying property among all different kinds of phase transition is the nature of discontinuity or divergence of thermodynamic functions at the point of phase transition. Depending on such properties, a phase transition is categorized into different order namely first order, second order etc. This classification helps in grouping of phenomena of similar characteristics together. In this chapter we discuss a few from the large number of phase transitions observed in nature and also present the elementary concepts that are used to understand phase transitions.

So, we will now do, so this is kind of thing from the book that phase transition ubiquitous in manifested large and very important thing of phase transition, large experimentally detectable change, large change, macroscopic change, so macroscopic change but the macroscopic change takes place in infinitesimal small change that means I change I something very small but something very big happens.

That means, this is a small change in a control parameter leads to huge change like the temperature at 100 °C, I just make it I reach 99.9 and make 100, that 0.1 degree centigrade leads to huge change similarly, ice; 0 °C, I make it 0.1 degree centigrade, ice melts, so the real thing to emphasize that note that that infinitesimal change leads to a macroscopic change in specific enthalpy, entropy of a parts of the system.

This is the subject of phase transition, this is great importance in most branches of natural and biological science like helix coil transition, DNA and protein, protein folding, these are kind of a cooperative phenomena. So, what is the language here that the classification, there is that many, many molecules kind of acting together collectively to give rise to this at a macroscopic change.

So, this is one of the most fascinating field of condensed matter science or natural science that how molecules talk with each other, the molecules collectively change over from one phase like gas phase to another phase like liquid phase. So, how do I understand that; Mayer try to understand from intermolecular potential that is detail that gives us some picture how things are happening.

But that fails to give us; fails to describe the generality of the phenomena, so we need a description which is simpler but which is general which captures the essence of this macroscopic change in the thermodynamic property due to microscopic change, infinitesimal change in a control parameter like temperature or density, so that is what Landau did.

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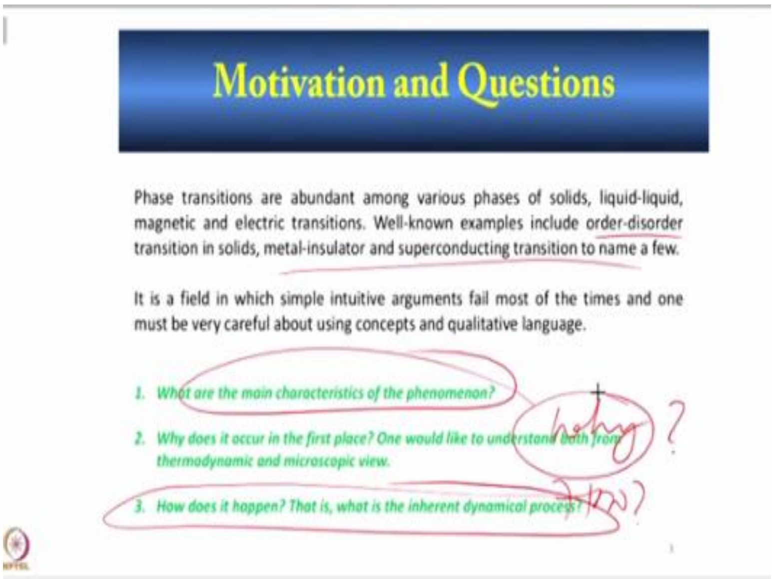

Motivation and Questions

Phase transitions are abundant among various phases of solids, liquid-liquid, magnetic and electric transitions. Well-known examples include order-disorder transition in solids, metal-insulator and superconducting transition to name a few.

It is a field in which simple intuitive arguments fail most of the times and one must be very careful about using concepts and qualitative language.

1. What are the main characteristics of the phenomenon?
2. Why does it occur in the first place? One would like to understand both from thermodynamic and microscopic view.
3. How does it happen? That is, what is the inherent dynamical process?

why ?

how ?

So, I described it before but I will describe it a little bit more physically this time, so phase transition had very common liquid-liquid, solid, magnetic transition, ferromagnetic paramagnetic transition, ferroelectric and all these things well known examples, or order, disorder, many, many phase transitions here. So, then we study then do you ask me 3 questions; what, why and how.

What are the characteristics of the phenomena, what is the phase transition, why does it happen, there is a why, how does it happen, so how essentially brings dynamics which we will do later not today and then we will describe why it happens, how do I describe in terms of phase transition, like I go back to Mayer’s theory, Mayer’s says cluster come together but how does it happen manifested in, how do I describe in free energy, this is what Landau did.

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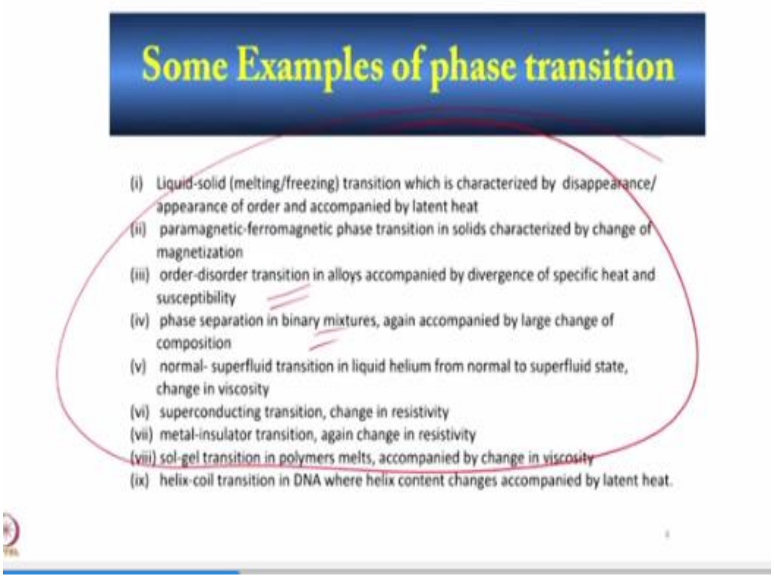

Some Examples of phase transition

(i) Liquid-solid (melting/freezing) transition which is characterized by disappearance/ appearance of order and accompanied by latent heat
(ii) paramagnetic-ferromagnetic phase transition in solids characterized by change of magnetization
(iii) order-disorder transition in alloys accompanied by divergence of specific heat and susceptibility
(iv) phase separation in binary mixtures, again accompanied by large change of composition
(v) normal- superfluid transition in liquid helium from normal to superfluid state, change in viscosity
(vi) superconducting transition, change in resistivity
(vii) metal-insulator transition, again change in resistivity
(viii) sol-gel transition in polymers melts, accompanied by change in viscosity
(ix) helix-coil transition in DNA where helix content changes accompanied by latent heat.

And so Landau, he said this will be given to you there is a large number of examples, paramagnetic ferromagnetic phase transition, liquid solid, gas liquid order disorder, in a very common in solid phase like alloys, binary mixtures again, the separate polymers, in superconductivity, in super fluidity, sol-gel, helix coil, there are just phase transitions all around us.

And you have to give proper importance to phase transition, not just because it is all around us but phase transition brings in introduces some of the most common and most useful language to physical science, this is something we learn from like the concept of order parameter, the concept of singularity and this language is free energy expansion, free energy landscape.

The all the language you routinely use they started in this field of phase transition, so I am talking a very elementary language but those were the newcomers this is a; I must emphasize this is a very, very important thing, so these are the examples of phase transition, let me go through.

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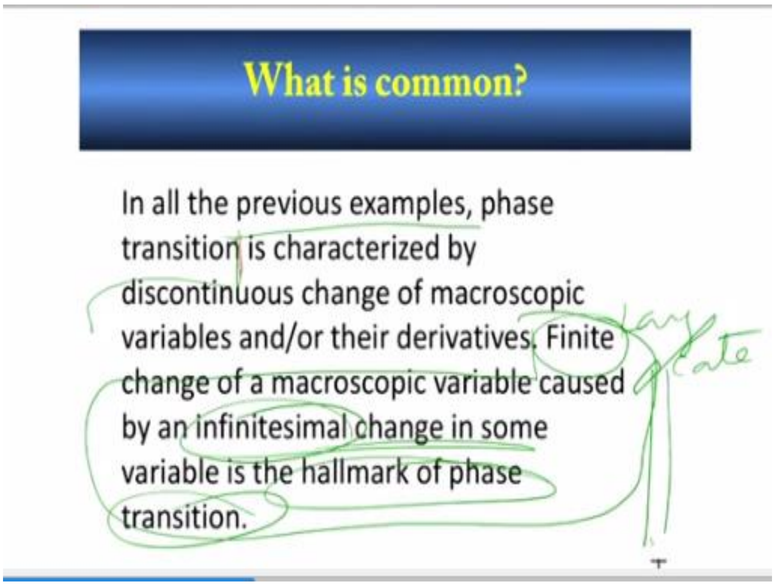

What is common?

In all the previous examples, phase transition is characterized by discontinuous change of macroscopic variables and/or their derivatives. Finite change of a macroscopic variable caused by an infinitesimal change in some variable is the hallmark of phase transition.

large scale

So, the all these examples, this is my favourite is huge is this is characterized by discontinuous change of macroscopic variables that is finite change of a macroscopic variable due to infinitesimal change, so the thing to know finite large scale change due to infinitesimal change, small change in some variable and this is the hallmark of phase transition. So, if you say what is the phase transition, then this is the phase transition, what?

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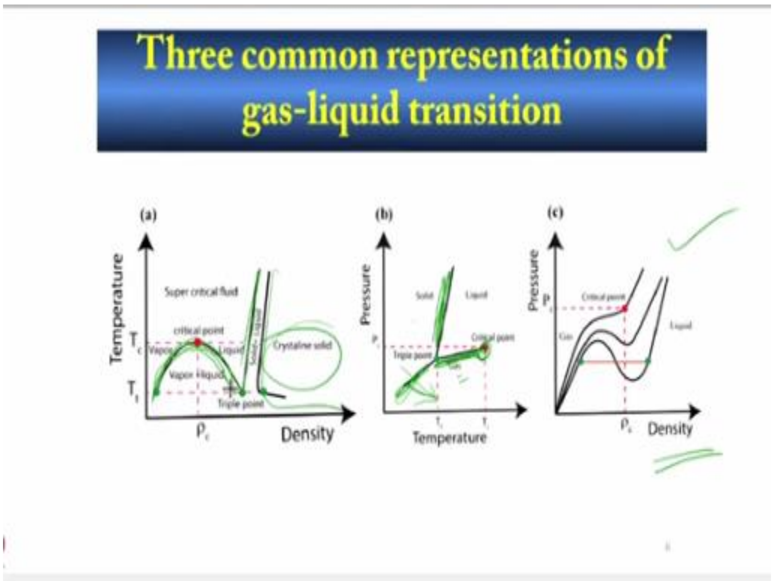

Three common representations of gas-liquid transition

This is the definition of a phase transition, what; now these are the examples; we already did pressure against density in Mayer's theory, you know these, then we always ask this in the our interview of undergraduate students and then we ask pressure plot; plot pressure versus temperature plane and this is solid, liquid and gas; gas here and in our classroom we find really very interesting things where students put gas here, solid here and liquid here and all kinds of things they do but this is the phase diagram.

So, this pressure temperature, this is the triple point and this is the critical point, you know all these things, then the another representation; so there are 3 representation, these temperature against density, then these another temperature; so this is the gas liquid coexistence and then this beautiful way goes, so this is the solid. So, I can describe the same phenomenon in 3 ways, it says something very interesting and new.

Like here, it says when this kind of Van der Waals loop or the kind of spinodal and stability here it because these are the coexistence line, these are the ley lines along with gas and liquid coexist, liquid and solid coexist, solid and gas sublimation across that that coexist and here it says how gas liquid crystals are showing together in a beautiful way including this parabolic shape which showing you the Bell shape which showing you the critical point and all these thing. So, these are the 3 representations, so phase transition deals with this kind of graph, this is for gas liquid, this is simple thing, I can draw identical thing for almost magnetic systems.

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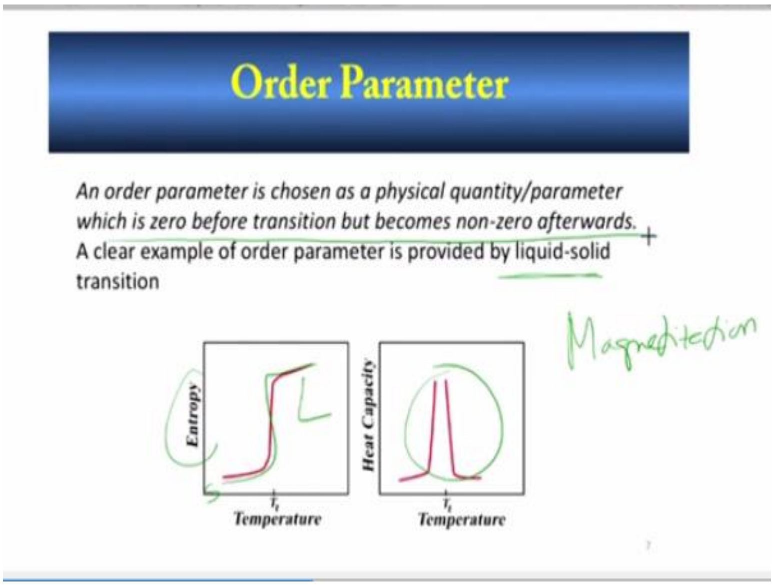

Order Parameter

An order parameter is chosen as a physical quantity/parameter which is zero before transition but becomes non-zero afterwards.

A clear example of order parameter is provided by liquid-solid transition

Magnetization

Now, as I said one a very important contribution of the phase transition that goes on to many different fields of condensed matter science or even protein folding or any other things, the order parameter. What is an order parameter? An order parameter is chosen as a quantity which is 0 before the transition but becomes nonzero afterwards, a clear example is provided by liquid solid transition, where is the order also magnetic transition that is the magnetization, it is an order parameter.

So a system in zero magnetization non-magnetic before the transition, after the magnetic it become ferromagnetic, a magnetization goes up large, so gas liquid or liquid solid, the entropy is; so this is solid, this is liquid entropy diverging then you look at specific heat that is diverging, so order parameter is a quantity that is zero before the transition becomes non zero.

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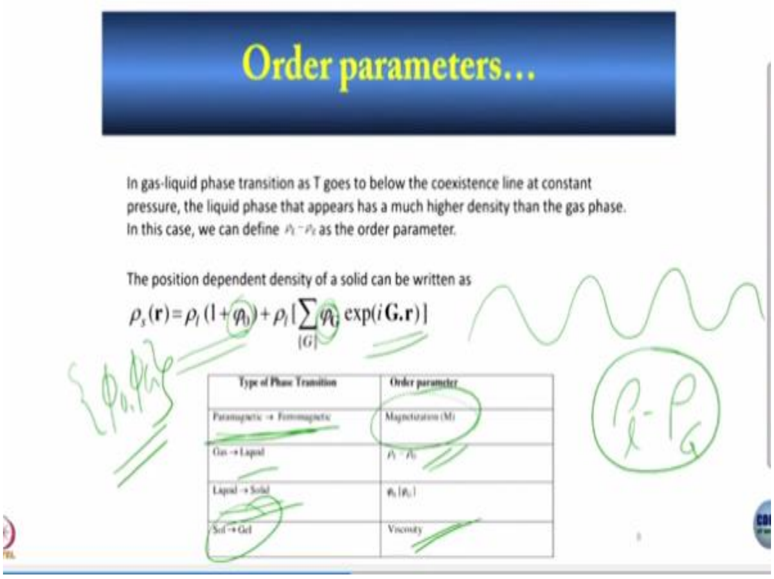

Order parameters…

In gas-liquid phase transition as T goes to below the coexistence line at constant pressure, the liquid phase that appears has a much higher density than the gas phase. In this case, we can define $\rho_l - \rho_g$ as the order parameter.

The position dependent density of a solid can be written as

$$\rho_s(\mathbf{r}) = \rho_l(1+\varphi_0) + \rho_l[\sum_{\{G\}} \varphi_G \exp(i\mathbf{G.r})]$$

Type of Phase Transition	Order parameter
Paramagnetic → Ferromagnetic	Magnetization (M)
Gas → Liquid	$\rho_l - \rho_g$
Liquid → Solid	$\varphi_0\ (\varphi_G)$
Sol → Gel	Viscosity

In solids we have some more examples there, for example if I show liquid solid, so there is a random system then that becomes periodic and periodic I can expand it any reciprocal that is vectors, you know these expansion and these are fractional density change and these quantities are the corrected factors but these are the order parameter. So, in this example ϕ_0, ϕ_G are the order parameters.

Then in the gas-liquid transition is 0, liquid minus rho gas that is the order parameter, magnetic and ferromagnetic transition, magnetization is order parameter, gas liquid is these difference, liquid solid ϕ_0, ϕ_G are the order parameters, sol-gel viscosity is order parameter, so it is a quantity which is zero before the transition becomes non zero after the transition, this was Landau's equation.

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Ehrenfest Classification of Phase Transition

Under this scheme phase transitions are labeled by the lowest derivative of the free energy that is discontinuous at the transition.

The Ehrenfest scheme cannot be regarded as an accurate method of classifying phase transitions, as it does not take into account the case where a derivative of free energy diverges. For instance, in the ferromagnetic transition at zero magnetic field, the heat capacity diverges to infinity.

First Order Phase Transition: Phase transition which involves a latent heat. The most robust example is the liquid-solid transition.

Continuous/ Second Order Phase Transition: These have no associated latent heat. The most robust example is the ferromagnetic transition at zero magnetic field.

The *true second order transition of Ehrenfest is exceedingly rare*. It is probably true to say that for physically interacting systems there is only one transition, that is the superconducting transition.

Now, why did Landau define it, okay Landau defined it because Landau have in mind to describe a phase transition, so Landau was looking for a quantity, see in physics, when you want to describe a change, we want to quantify the change, why we want to quantify the change, why? Because if I have described a free energy then I want a smallest parameter, this smallest parameter is the one that I can expand free energy above.

And that smallest parameter is the order parameter; it is something which is zero and then become nonzero, so I can do a Taylor expansion in the smallest parameter. So, order parameter becomes a smallest parameter in my Taylor expansion and that was the idea of Landau and that is the very beautiful idea that now, there was when this was done, it is another brilliant physicist name is Ehrenfest.

Ehrenfest came up with a; he noticed something very interesting, he noticed that, that the there are some phase transitions where entropy undergoes a jump like melting and then liquid solid transition away from the critical; gas liquid transition away from the critical point, there is a jar, like you know in water pipe, 40 kcal/mole; kilo per gram for gas liquid, 80 kcal/gram per; calorie gram or kilo gram, I do not know, but they are finite set.

However, when you go to critical point then specific heat diverges not change in latent heat and then magnetic transition, parametric, ferromagnetic transition, the absence of a magnetic field is a transition which is again continuous but has this divergence, peculiar behaviour, super fluidity has this peculiar transition. Then order, disorder transition solids like brass has shows these characteristics.

This show the characteristics where second order properties of free energy undergoes divergence but in the melting is the first order property is entropy, the first derivative of free energy, so first order property means when you have an order parameter and a control parameter, I change that control parameter, first derivative of free energy becomes discontinuous.

So Ehrenfest said, let me now define capture this universality across the phase transitions, the first order phase transition and those phase transitions were first derivative of the free energy is discontinuous and second order was the second derivative of the free energy, they expect order parameter or control parameter become discontinuous, suddenly everything kind of falls in place oh, now I say, when I say first order phase transition, I know the characteristic for first order phase transition whatever that material is the gas liquid transition away from the critical point or melting or magnetic transition in the presence of a magnetic field, all have the same characteristics.

Similarly, in a second order phase transition it is second derivative of free energy but most of the second order phase transition actually continuous transition like the critical point and superfluid transition except one, there is one truly second order phase transition in Ehrenfest sense, the second derivative which shows discontinuity and that is the most important transition is a superconductivity. But however, there are all these little trollification here and there but Ehrenfest introduced a very powerful paradigm, saying the order of a phase transition following all the definition of order.

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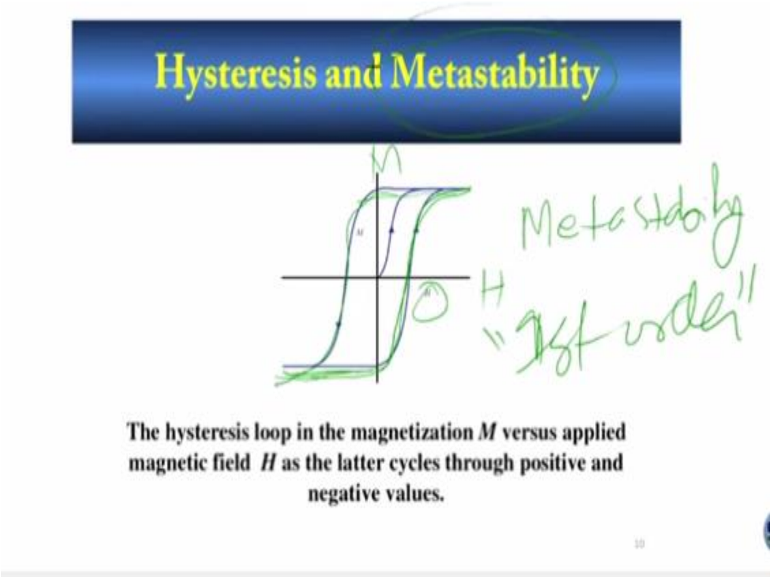

Hysteresis and Metastability

The hysteresis loop in the magnetization M versus applied magnetic field H as the latter cycles through positive and negative values.

Now, Landau theory comes in beautifully, Landau said okay, I now know, I know I can describe the free energy and I can describe the; so this is the hysteresis and metastability, then what shows in the presence of magnetic field. So, H is the magnetic field and is the magnetization m, I change that however, behold that I am switching the sides but even after switching it does not reverse immediately, it hang on and then go while the other way around it take a long time.

So, this hanging on the old phase is called metastability and hysteresis and this is the trademark of first order phase transition. Second order phase transitions never show metastability or hysteresis, this is very, very important and this is what let Landau to develop a beautiful theory.

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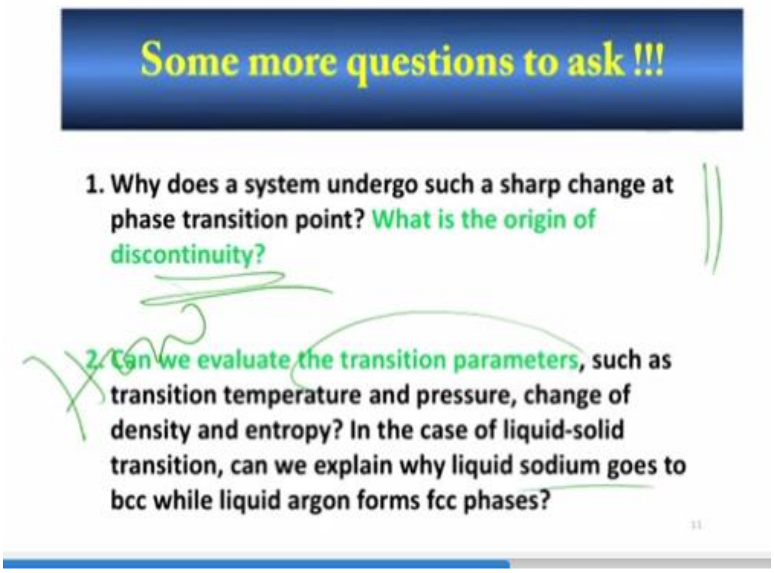

Some more questions to ask !!!

1. Why does a system undergo such a sharp change at phase transition point? What is the origin of discontinuity?
2. Can we evaluate the transition parameters, such as transition temperature and pressure, change of density and entropy? In the case of liquid-solid transition, can we explain why liquid sodium goes to bcc while liquid argon forms fcc phases?

So, again come back why does the system so such short change, what is the origin of discontinuity, then how can we calculate, how can we evaluate the transition parameters like latent heat, what are the order parameters, then why liquid sodium goes to bcc and while argon goes to fcc, these are the questions one would like to answer.

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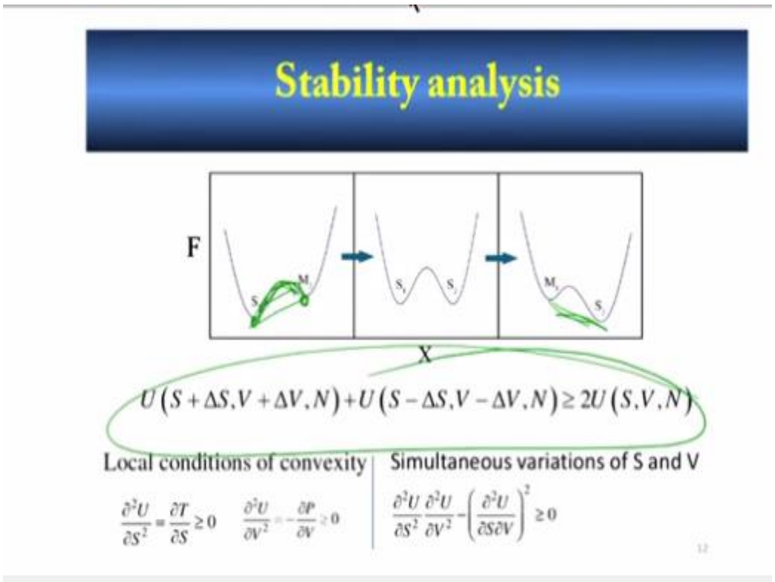

Stability analysis

$$U(S+\Delta S, V+\Delta V, N)+U(S-\Delta S, V-\Delta V, N)\geq 2U(S,V,N)$$

Local conditions of convexity

$$\frac{\partial^2 U}{\partial S^2}=\frac{\partial T}{\partial S}\geq 0 \qquad \frac{\partial^2 U}{\partial V^2}=-\frac{\partial P}{\partial V}\geq 0$$

Simultaneous variations of S and V

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2}-\left(\frac{\partial^2 U}{\partial S\partial V}\right)^2\geq 0$$

This is where Landau now came in Landau; these are the stability analysis that when does one system becomes stable and one talks upon convexity and concavity like for example, I draw the line between the 2 minima, then if the curved line ever then it is convex, however if it lies below then it is concave, so from stability to metastable; the stable phase to metastable you will have everywhere this convexity but however, the other all you have the concavity. So, these kind of things analysis done in terms of first and second derivatives as the energy is done here but that is very interesting.

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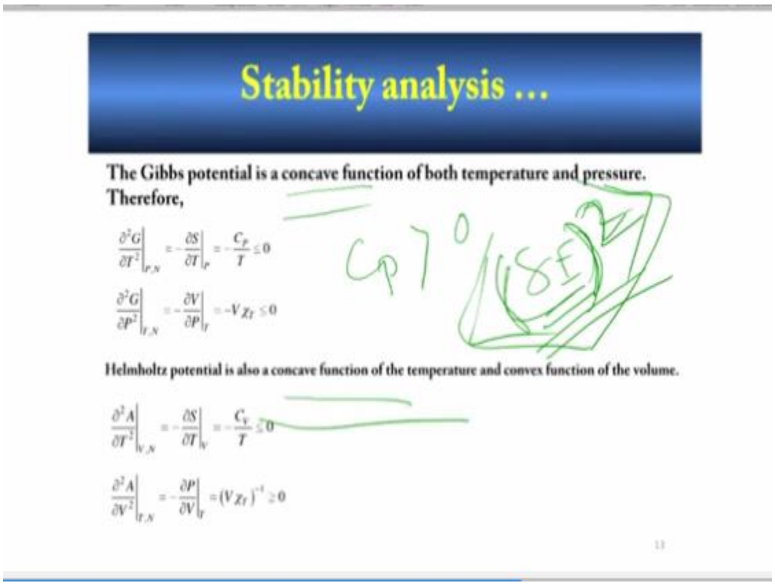

Stability analysis …

The Gibbs potential is a concave function of both temperature and pressure. Therefore,

$$\left.\frac{\partial^2 G}{\partial T^2}\right|_{P,N} = -\left.\frac{\partial S}{\partial T}\right|_{P} = -\frac{C_P}{T} \le 0$$

$$\left.\frac{\partial^2 G}{\partial P^2}\right|_{T,N} = -\left.\frac{\partial V}{\partial P}\right|_{T} = -V\chi_T \le 0$$

Helmholtz potential is also a concave function of the temperature and convex function of the volume.

$$\left.\frac{\partial^2 A}{\partial T^2}\right|_{V,N} = -\left.\frac{\partial S}{\partial T}\right|_{V} = -\frac{C_V}{T} \le 0$$

$$\left.\frac{\partial^2 A}{\partial V^2}\right|_{T,N} = -\left.\frac{\partial P}{\partial V}\right|_{T} = (V\chi_T)^{-1} \ge 0$$

$C_p > 0$

$\boxed{(\delta E)^2}$

But not the; this stability analysis then it essentially go back the specific heat has to be and I told you that specific heat is nothing but $\langle \delta E^2(0) \rangle$, this is the average of fluctuation and square of a fluctuation; fluctuation can be positive or negative but square has to be positive always, so specific heat has to be always, always positive quantity and that is a stability condition.

So, $-C_p/T = 0$, that means Cp must be positive, these are very; this concave function and concave function that I described here, you can read it in this and we have done it little bit before but you can read yourself.

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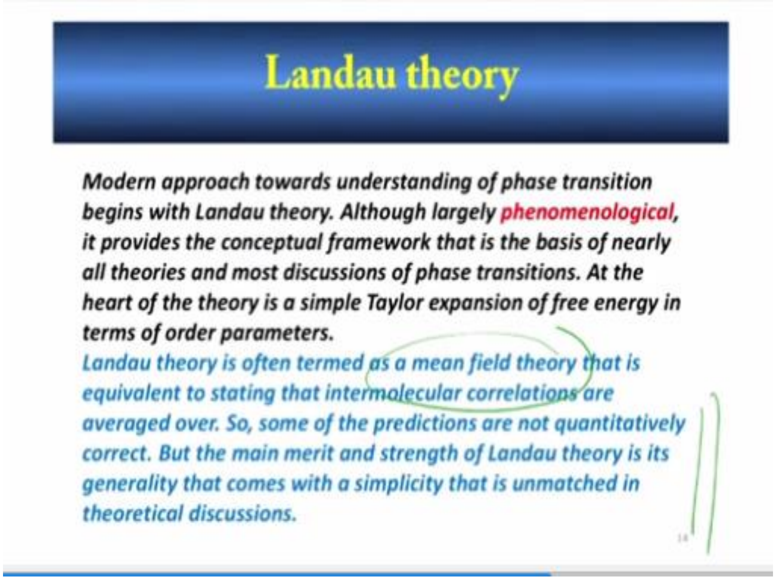

Landau theory

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.

But now, I go to Landau theory and in 5 or 10 minutes that I have I will just described Landau theory. Landau theory is a beautiful theory based on the order parameter, Landau theory is a free energy expansion in the order parameter, Landau theory is the basis of almost all theories, this is a phenomenological theory but it is a beautiful thing and so it is the mean; sometimes called mean field theory because some kind of fluctuations are neglected but it is; so main merit of the Landau theory that it taught us to think in terms of order parameter talk of the minimum free energy and free energy landscape.

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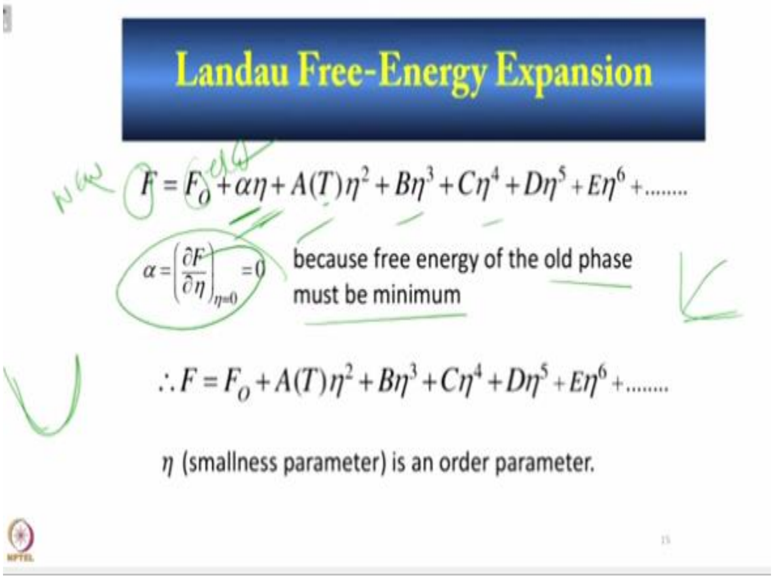

Landau Free-Energy Expansion

$$F = F_0 + \alpha\eta + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + ...$$

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

$$\therefore F = F_0 + A(T)\eta^2 + B\eta^3 + C\eta^4 + D\eta^5 + E\eta^6 + ...$$

η (smallness parameter) is an order parameter.

So, this is the Landau free energy expansion, so Landau said once we define the order parameter, Landau said okay now, I know I can expand free energy, so he went ahead and expand bring energy in terms of this order parameter, eta is the order parameter. He said okay and just a Taylor expansion, I want to describe this is the free energy of the new phase, this is the free energy of old phase, this is new, this is old and he wrote down a Taylor expansion then all of us know the Taylor expansion right, very simple Taylor expansion.

Now, we know Taylor expansion, we know now Taylor expansion if I have to get α, I will take $dF/d\eta$ at the old phase and I get α, the way we do the extrapolation, interpolation of the function but in my case that fast derivative of order parameter free energy but free energy has to be minimum because it has to be stable that is why we need all the stability analysis.

Then what does it mean; that mean these quantity cannot be there, alpha has to be 0 because a free energy of the old phase must be minimum but how do I; but that does not apply to these, so why can now get the secondary A(T), I can get A(T) by taking these second derivative of free energy and then evaluate it in the old phase that is what the Taylor expansion, we take the derivative but evaluate it in the old phase; O, A(T), B and all these quantities are temperature dependent and they are obtained in terms of the old phase free energy and now, so this is now Landau free energy by introducing this condition and it is my order parameter which is used as a smallest variable, this is just beautiful.

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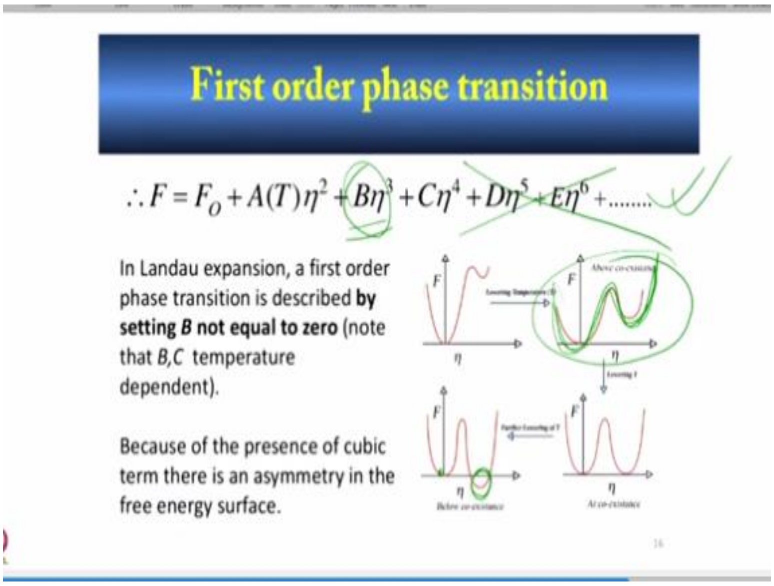

First order phase transition

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

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, what did Landau do now; okay, this again I am writing this thing, he did not said okay, let us we think of meta stability and let me think in terms of hysteresis. So, if there has to be hysteresis then I must be that when I am heating these, there should be a minimum, so it is getting stuck in the minimum and though I am; this new phase is more stable, old phase still remain a minimum, so that explain meta stability.

What does that mean? That means I have this kind of structure of free energy that means, I have one deeper minimum, one less deeper minimum, how do I get such a minimum; I can get such minimum by keeping the odd terms here however, so this is the first order phase transition where I need to have the odd terms, I will not talk of these things, I will just talk of this thing up to 4th power.

However, in a critical phenomena, there is no meta stability, there is no such, no hysteresis, so 2 minimum, then how does second order phase transition that is so important transitions in a critical phenomena, then magnetic transitions happens that that then he is argued very nicely he said okay, that happens in the following fashion.

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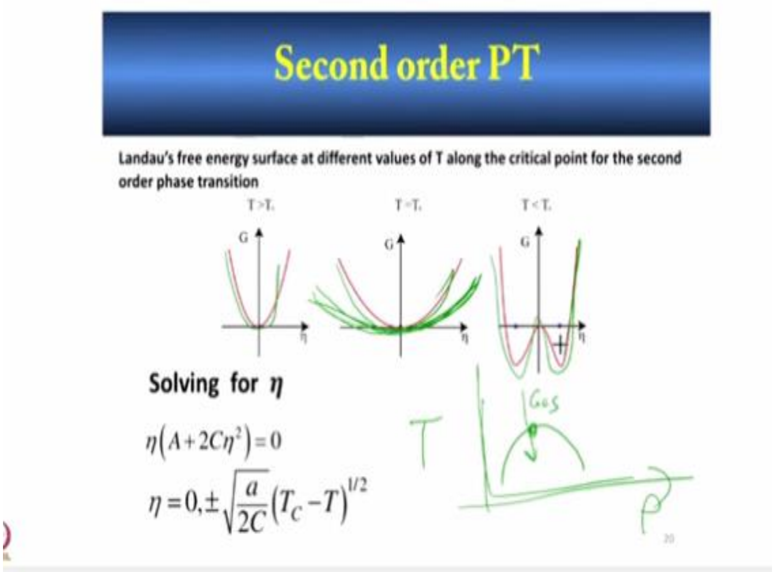

Second order PT

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

Solving for η

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

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

He said in that case, the one minima that becomes flat and it becomes increasingly flat and then it just becomes two phase the same, so if I go to this critical phenomena point temperature against density in gas liquid or binary mixture, I am coming down like that, then the minima in the gas phase there is a gas, minima in the gas phase is becoming flatter. Remember second derivative of free energy is the compressibility that diverges, it becomes infinitely compressible and that then suddenly when you go below the critical point, 2 minima appear that of the gas and the liquid, look at the symmetry this is called the symmetry breaking transition.

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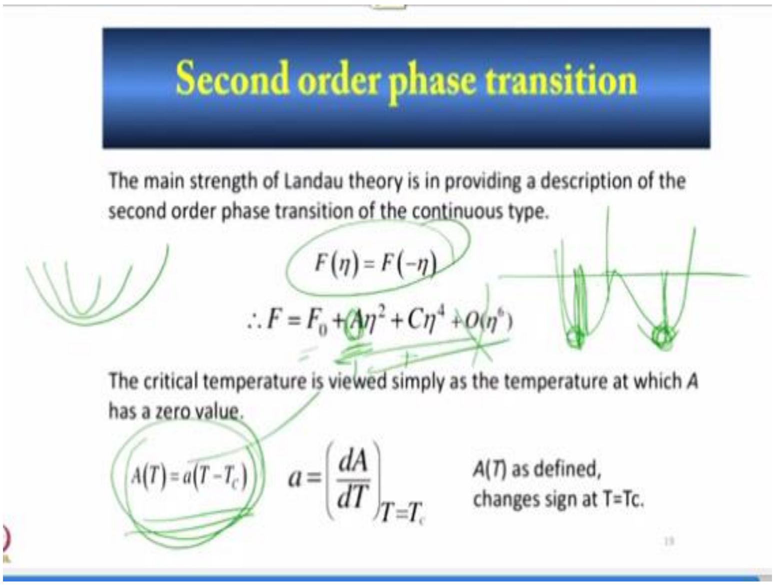

Second order phase transition

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.

So, how do I describe that now okay, in the second order phase transition I go back to my Landau theory of this expansion, I will come back this little bit later and then I say okay there is a the new phase I am going to describe as the symmetry that at +η and -η, free energy is the same, this is called parity, then this is the condition, when I said that odd terms disappear, it remain only the even terms.

And in the even terms, there is a very important quantity now, this is the free energy old term, A is the one that is the spring constant because this is the harmonic, this is the thing that gives rise to this 2 minima but before 2 minima, this is becoming flatter, my getting flatter who describes that this quantity describes the flat.

That means, these quantity which is the spring constant which holds the system together which is the second derivative of free energy is becoming smaller and smaller, how do I describe that and this is the brilliance of Landau, Landau said okay, let us assume that happens linearly that these A temperature dependence goes to 0 and critical temperature is approached and that goes will be assumed $(T-T_C)$ and this is given by the time derivative of the free energy, temperature derivative of the free energy okay.

Now, it changes sign in; these quantity now changes sign at TC this becomes, this is the second derivative of the order parameter but first derivative is the temperature, now because this quantity is compressible, so that is why it is a second order phase transition we are talking, so these quantity now is made to change sign. So, as soon as they have change sign it become minus and become plus that give rise to these things.

So, this is the Landau essentially, then one goes on and doing okay, then once solve for η, we take the if I these are 2 minima, then gets satisfies the minimum condition that the derivative of $dF/d\eta = 0$ and then do these this term this quantity, this quantity and I put $A = (T-T_C)$ and I take the derivative and I get this, an η equals to 0 is the maximum which is the solution, the trivial solution.

But then I get 2 values; one is for this one, another is this one, equal plus and minus, however the beauty is that this order parameter, these value; the value from here to here where the minima scales in this in a funny way $(T_C-T)^{1/2}$ this is the critical exponent or exponent of the critical exponent or Landau exponent or mean free exponent that is something more needs to be done.

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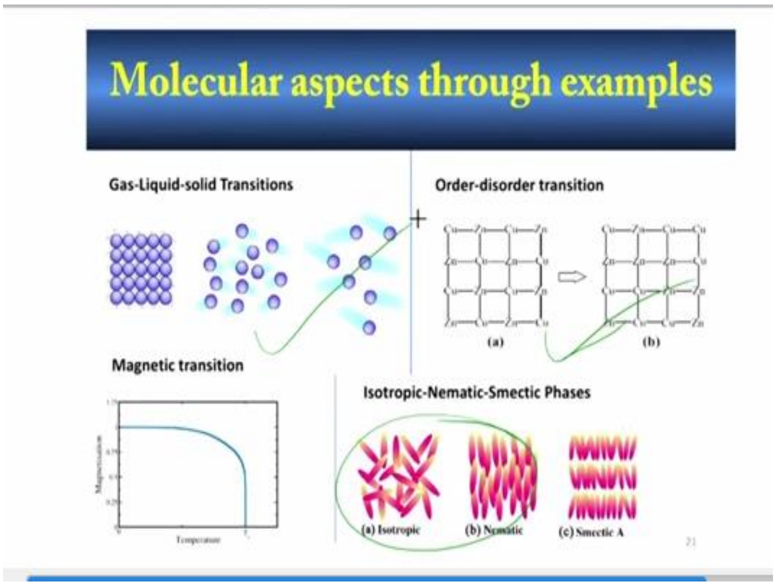

Molecular aspects through examples

Gas-Liquid-solid Transitions

Order-disorder transition

Magnetic transition

Isotropic-Nematic-Smectic Phases

So, this is Landau theory of critical phenomena then one can go on second order phase transition, one can many, many things are like that magnetic transition, weakly first order phase transition then superconductivity, Isotropic Nematics weakly first order almost second order phase transition, order disorder is a second order phase transition, gas liquid at critical point is a second order phase transition. The huge number of things that happens in the second order phase transition, sorry I have to now go back and do little bit, so this is the way second order phase.

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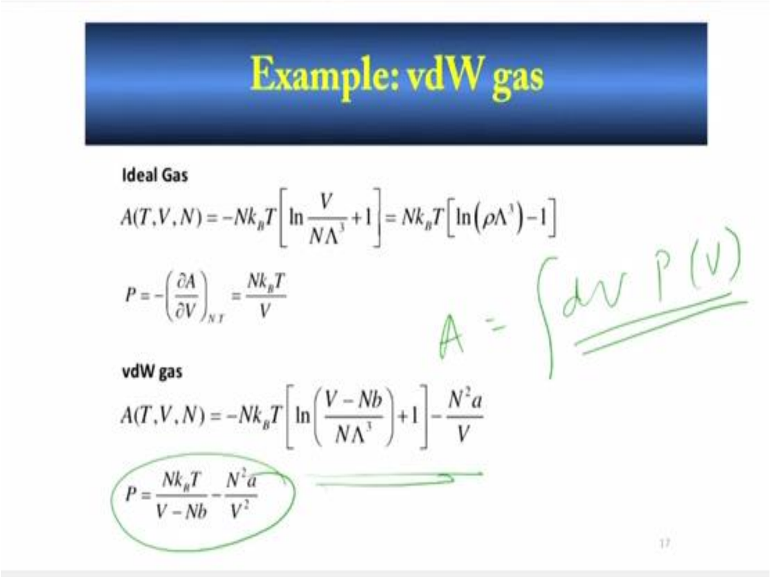

Example: vdW gas

Ideal Gas

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

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

$$A = \int dV\, P(V)$$

vdW gas

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

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

First order phase transition is terms like van der Waals, now we have, we cannot ignore the cubic term, we cannot ignore this term because that gives rise to meta stability and one can again go back and do one thing Van der Waals gas, we can do that, so this is the Van der

Waals equation, the free energy starting from this equation, I can integrate because free energy is dVP and put this then I can get the free energy and that is this quantity.

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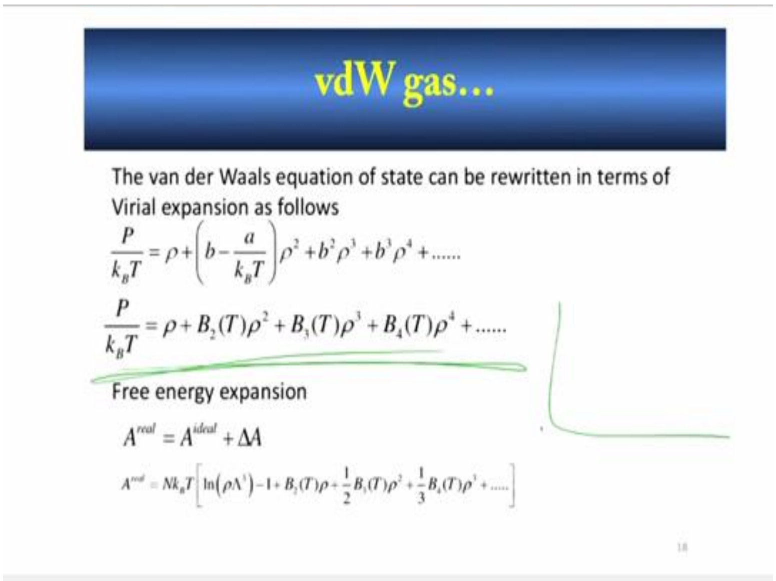

vdW gas…

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

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

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

Free energy expansion

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

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

Now, I do what Landau told us to do, I had one expansion in density, density is order parameter I told you gas liquid transition, then I get this beautiful thing which is nothing but Virial series and that now describes these phase transition and now describes the free energy that one can show that these essentially very much, this is the ideal gas part, this is the part that describes this free energy with one deeper than the other, the asymmetry in the first order phase transition from Landau; learning from Landau how to do it, go back to Van der Waals and we can describe that okay.

So, I think this is the; we will stop here today this beautiful area of phase transition, I have done it a little bit before, I did more now, many things I forgot into say in the first time to give you students more physical insight but now I have done it here a little bit more, so from now we will go on to doing few more things in phase transition in the next class, 1 or 2 more class will be on phase transition.

Then, we will go back again to do statistical mechanics of what we will do in phase transition essentially will be simple, will be phenomenological Landau theory because of the generality, it is so general, the things of phase transition that it is better to have a very general description that means, we need not talk of intermolecular interactions like Mayer did, when you talk of intermolecular interactions, we are demanding much more, we are doing so much more work, we need to then get the exactly the values of parameters like latent heat, what are the order parameter then it is okay, justify to do a very detailed calculation.

But then each calculation has to be for each phase transition, I want to do a melting transition, I have to do theory for melting, well, still Landau theory in the background, I have to do freezing that will be different from melting because of phenomena though they are thermodynamically or reverse of each other, stat mech, they are very different, liquids going to crystal is different from crystal going to liquid.

But if I want to do in terms of thermodynamics, the general parameter then again Landau theories comes in, then Mayer's theory as I show is for such details here, so the goal is different and our work is different, our these things are extremely connected to each other and a scientist, a physical chemist or physicist knows what he is trying and then develops the theory particular to the need of the time, the need of the moment okay, thank you, we will see you in the next class.