Basic Statistical Mechanics
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Lecture - 34
Phase Transition and Landau Theory (Part 1)

Good morning. So what we will do today is an important class, which is hardly taught in chemistry departments, at least nowhere in India, in chemistry department it is taught and so I insisted that these should be dealt in very elementary form and in detail and in the book Stat Math book, there I have devoted 5 chapters of 30 to 5 chapters, so that kind of tells you so how much importance I give on the phase transition.

I told in the last class, when you did the Mayer's theory. So Mayer's theory is one of those 5 chapters. In Mayer's theory, Mayer was the first to do a theory starting from interaction. As I told you ideal gases, they do not have phase transition. Ideal gases do not become liquid; they do not become crystal. They are in good reference systems, but they cannot explain the real world. What you and me exist and the phase transition happens because of molecules and atoms interact.

And one of the most dramatic consequence of the molecules interact is the phase transition and however, the understanding of phase transition is very tricky because the concepts are profound and deep and many of the things that we know in physical chemistry and physics even chemical kinetics as far field as chemical kinetics are derived from the basic idea, that phase transition give to us.

For example, concept of order parameter, concept of free energy landscape, the glass transition, ruggedness, all the things that we hear are multi-dimensional processes. Many of these things have their origin and this is beautiful and very profound and fundamental field of phase transition.

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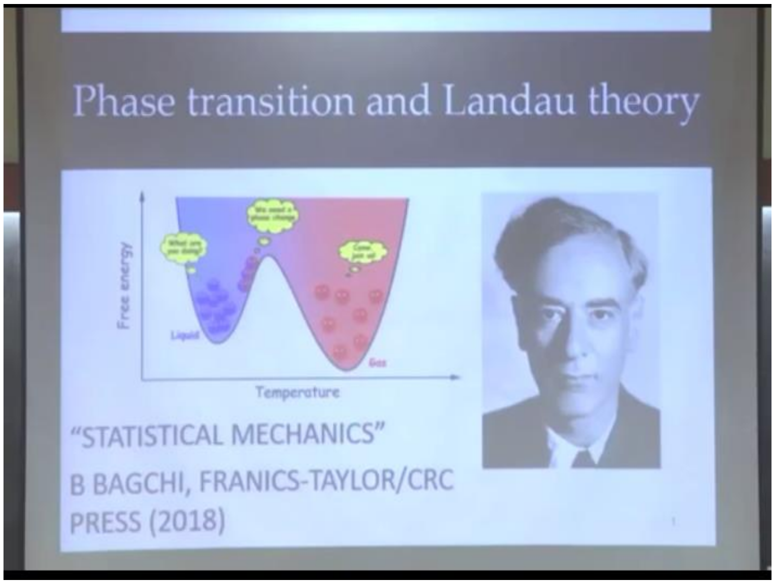

Phase transition and Landau theory

“STATISTICAL MECHANICS”
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So this is what we will be doing. Since though is the Landau phase transition, it will be lot more. So the main theory of this, so in 1937 and do you know these great Big Bang episode? That when Sheldon was teaching Penny physics and they warned somebody winning in Greece. I suddenly remembered with you know what I am going to say reminded me of Big Bang Theory. If you have not seen that particular episode, you should see that is really one of the most hilarious in Sheldon and Penny.

Now in 1937, you know much later than the Greece, there are two things happened in the same here. Joseph Mayer came out with the theory of condensation and which went on as I mentioned in the last class, our cluster, concept of cluster expansion representing interacting molecules as dots and lines between them, which gives to graph theoretical picture of physics that ultimately developed into Feynman’s integrals and all these things.

The representation of an integral in theoretical physics as the graphs started with Joseph Mayer, then it went on to become Mayer-Ursell cluster expansion in quantum mechanics and of course, over the Feynman’s quantum electrodynamics and we are talking of atoms and molecules and phase transitions. The same year 1937, Landau came up with a theory of his chains, you know which is the extremely simple and elementary.

But it captures very essence of many of the things that we will be talking today, but before I can do that, I will try to go through some very basics as I said because the generality of phase transition is not what a chemist usually used to see. We are used to specific properties of atoms and molecules that attract us. So when it comes to generally in general picture, this is not something that is our forte.

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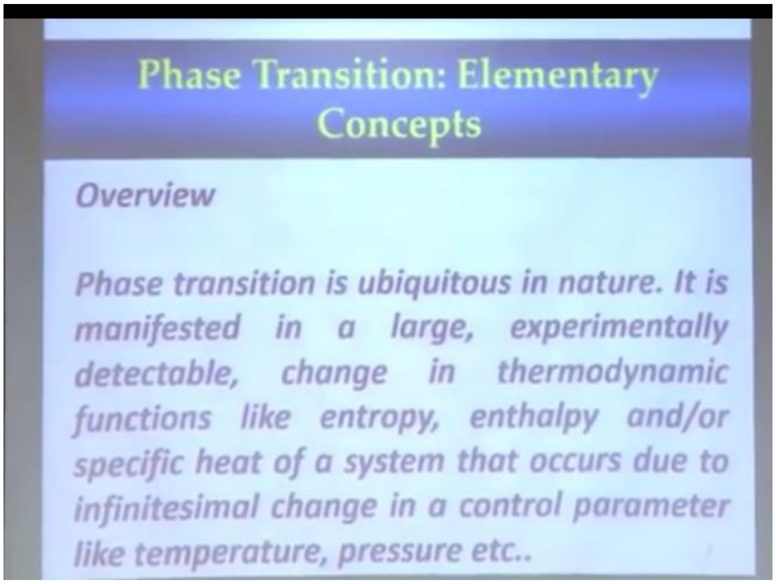

Phase Transition: Elementary Concepts

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..

So I have many elementary concepts basics chapters that will be there. You can just quickly read or I can read, but we will be not spending too much time on that. That is ubiquitous in nature. It is manifested in a large, experimentally detectable. The main thing is that there is infinitesimal change in a control parameter, like temperature, pressure or power order parameter. I will talk about it later. Infinitesimal change leads to a macroscopic change or thermodynamic change.

So you know, remember the concept of derivative. You put the change of your dependent variable in the numerator and your independent variable in the denominator. So we always think of change in terms of a derivative. So you can easily see, if I have an infinitesimal change in a control parameter and I have a macroscopic thermodynamic change, then that means we are talking essentially of a very peculiar phenomena, which is called singularity.

In much of the things that you read in your calculus are the ones with the functions that have called inter functions or their first or second derivatives exist. So that is how we work with them. If you have a singularity, you cannot do anything. So that is the first difficulty we will have.

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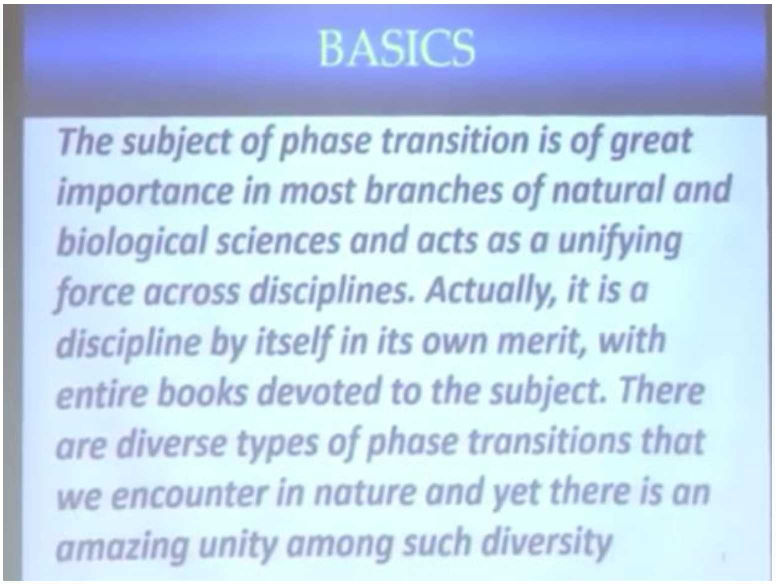

BASICS

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

So in many branches of natural and biological science like you know of late we had the protein folding that completely used the language of glass transition and folding funnel or Onuchic-Wolynes all these things that just completely come borrowed from phase transition or nowadays in many of the things with genomic studies and all this again from phase transition. So it is a discipline by its own merit with entire books devoted to phase transition like the book by Eugenie Stanley is on phase transition.

There is one by Balescu. There are many books just on phase transition by itself and I find people, I disdain people who do not find it interesting, very frankly. This is such a beautiful subject. It is a strong language, but I think sometimes you need this strong language, at least in India. So this is amazing, it has in different diverse types of phase transition that we encounter in nature, yet there is an amazing unity in such diversity. These are all lines from my own textbook and my own writing.

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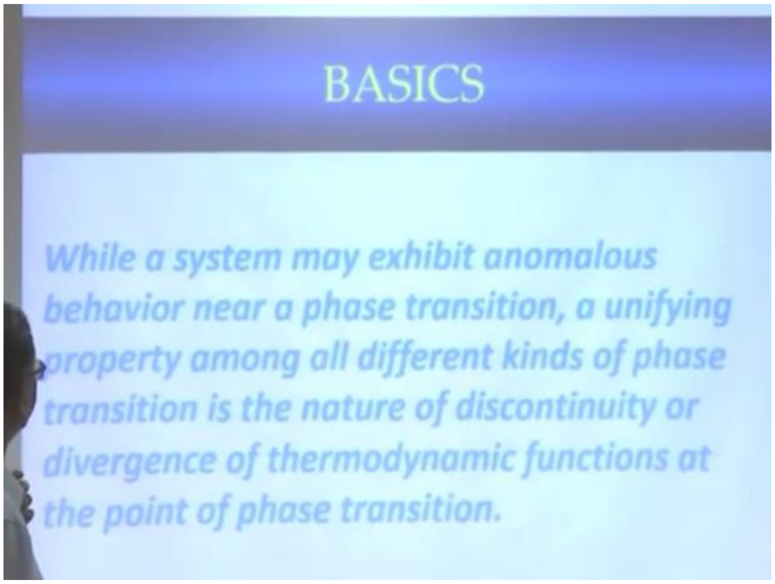

BASICS

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.

There is a unifying property among all the different kinds of phase transition, is the nature of discontinuity. So I can characterize a huge number of phase transitions by saying the various first order or second order. As soon I say it is a first order, then there is a huge number of phase transitions, which immediately become, you know that there certain characteristics which are common or universal.

When I say a second order phase transition again a huge number of phase transitions can be grouped together. So this characterization of faster second order phase transition, you know is possible and that brings this unity in diversity that I have been talking about.

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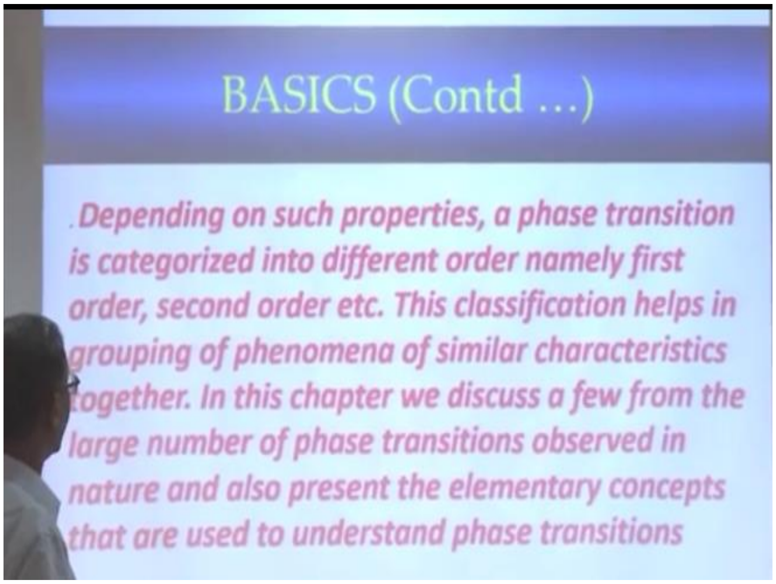

BASICS (Contd …)

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 depending on phase transition, this category should define order, namely first order, second order and classification is the grouping of phenomena in similar characteristics together and a few of them large number of phase transition observed, you know. So what did one is trying to do now characterization and it is a very powerful. For example, when it is a first order phase transition gas-liquid phase transition, liquid to crystal phase transition, many, many other phase transitions are there.

Magnetic phase transition in the presence of a magnetic field, electrical transition invincibility with a huge number of isotropic-nematic phase transition, nematic-smectic phase transition, liquid crystals the huge number of things in polymer. As soon as I say it is the faster of phase transition, they are all very similar. So I know what does mean by first order phase transition. Similarly, when I say second order phase transition, the order disorder transition, gas-liquid phase transition, critical point and huge number of transitions like that which this.

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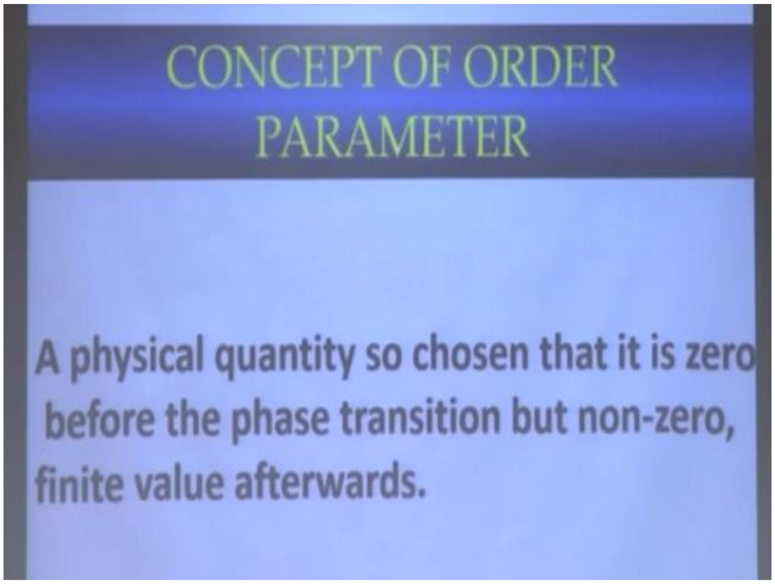

CONCEPT OF ORDER PARAMETER

A physical quantity so chosen that it is zero before the phase transition but non-zero, finite value afterwards.

Now so we started off saying the order. Now before that, I tell what is it an order. Let me tell you, what we need to know something to characterize the phase transition. These have gone to the concept of order parameter. It is a physical quantity, so chosen that it is 0 before the phase transition, but becomes non-zero and acquires a finite value after the phase transition that the definition of order parameter, which is selected, which is chosen.

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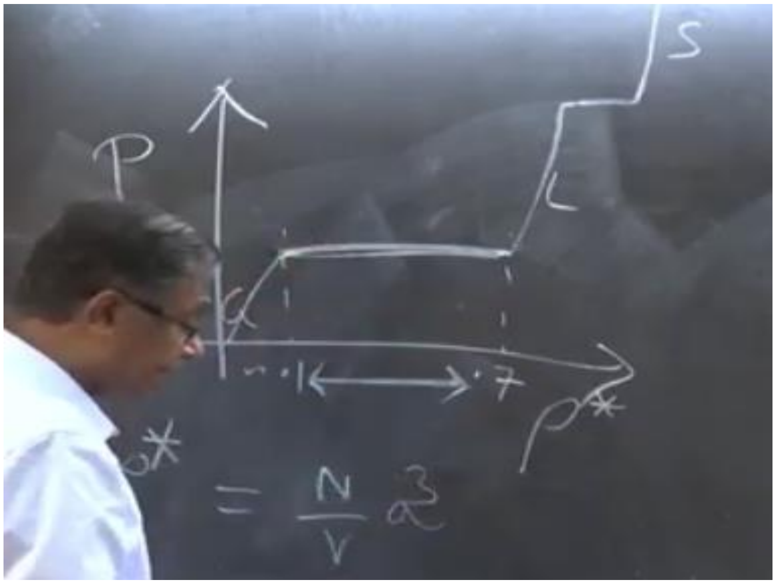

For example, if I have a gas to liquid transition, then so the canonical gas liquid we will see it many times pressure versus density, then this is the. So this is gas, this is liquid, this is crystal solid. So this is coexistence. Now the order parameter at a given temperature will be this change in density, that means density here $\rho_L - \rho_{gas}$ that will be order parameter. In a magnetic transition, it is magnetization that will be the order parameter.

Because that is 0 before the magnetic transition and non-zero afterwards, so these kind of identification is extremely important and that was the one that was implemented by Landau, because this change that I will be seeing here is which characterizes. So the whole idea is that if I want to understand how a phase transition takes place and why a phase transition takes place, these why and how will depend.

See if my understanding is proper or not, whether I can explain this change in density. For example, typically let us say as I described earlier that one of the very another unifying thing, we do is we introduce $\rho^* = \frac{N}{V}a^3$. The universality comes because all the liquids have very narrow range of ρ^*. They may have very different number density, like 10^{22} per cc, then 10^{23} per cc.

But in that, when you take the molecular diameter, the number density and multiply, you find they are all between 0.8 and 0.9. This is a wonderful. The most of the gases; they are widely different, but at the condensation typically not to, quite a bit lower than critical temperature, but not too low. This is typically between 0.05 and 0.1, less than 0.1. So now I suddenly have a fantastic with the carbon dioxide or methane or water or methanol, I have a fantastic unification, when I go to the dimensionless quantity.

Now as I was saying, I am just giving a number. This ρ^* is 0.1 and then liquid typically goes to 0.7 or 0.8. So I have to if I understand properly, I should be able to say why gas to liquid transition, density increases by a factor of 7 and what pressure it happens and I have to be able to say what are the other characteristics of the change like latent heat. So these are the kind of properties that one would like to know.

The whole understanding of this transition starts with the identifying an order parameter, which is as I said 0. So if I did $(\rho_L - \rho_L)$, so it is 0 order parameter, 0 just before that, then it jumps by a large number.

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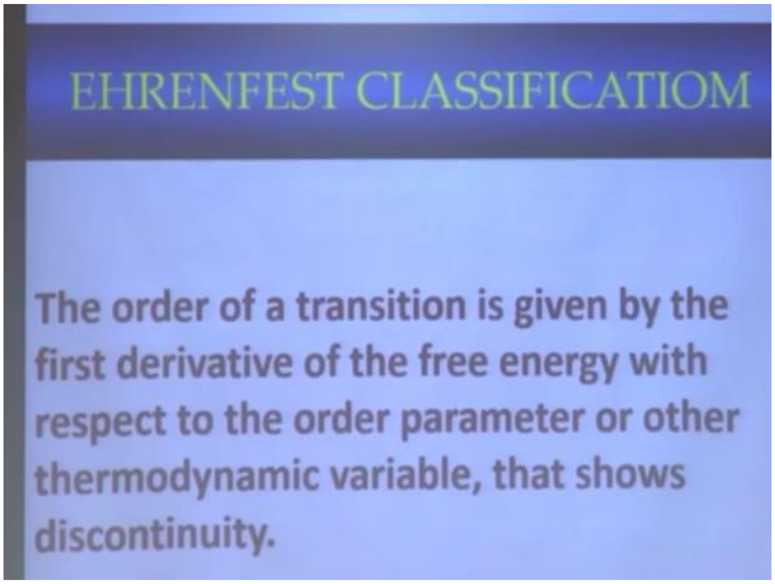

EHRENFEST CLASSIFICATIOM

The order of a transition is given by the first derivative of the free energy with respect to the order parameter or other thermodynamic variable, that shows discontinuity.

Now this was the very famous classification by Ehrenfest. Ehrenfest introduced this and this is the beginning order parameter and Ehrenfest classification is the beginning of our formal study of phase transition. So Ehrenfest defined the following way. He noticed that gas-liquid, liquid crystal, these two here and you know as I said magnetic transition in the presence of external magnetic field, all are characterized by finite change in a first order property.

First order property mean first derivative of free energy like entropy and then pressure or other $\frac{dA}{dP}$, you can get the density. So the first order properties change, then he noticed that there are cases where it is a like superconductivity. It is the second order property that is changing. Order disorder transition in metallic alloys, it is the second order property, like this specific heat, the susceptibility. Specific heat is second derivative of free energy.

Susceptibility is second derivative with respect to volume. So there is a class of phase transitions, which are characterized by first derivative discontinuity or singularity or anomaly, the first derivative of free energy and their properties, which are second derivative and this is suddenly you begin to say, okay then there are characteristics between liquid and nematic and smectic or gas and liquid, liquid and solid, all this is same.

Yes, they are all very similar and we will see their similarity even more. They all have the latent heat, while the second order phase transition, they have no latent heat. It is very important. They have no latent heat. They have a discontinuity, the second order property. So Ehrenfest classification at one shot allowed us to classify very different kind of phase transition, which apparently so different, but they are similar.

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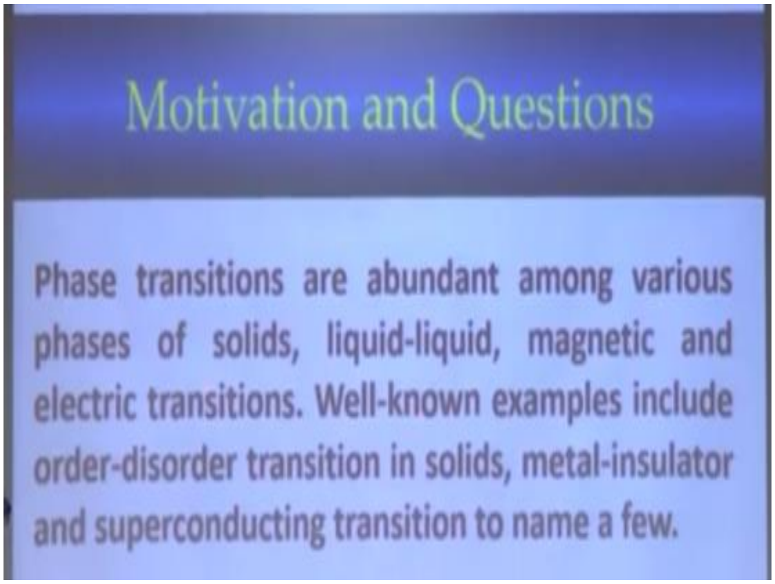

Motivation and Questions

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.

Again motivation and questions, I have said that these I have said in various phases of solid, liquid, magnetic include order disorder transition, metal, insulator transition superconducting transitions, solid gel transition, liquid crystal all these things.

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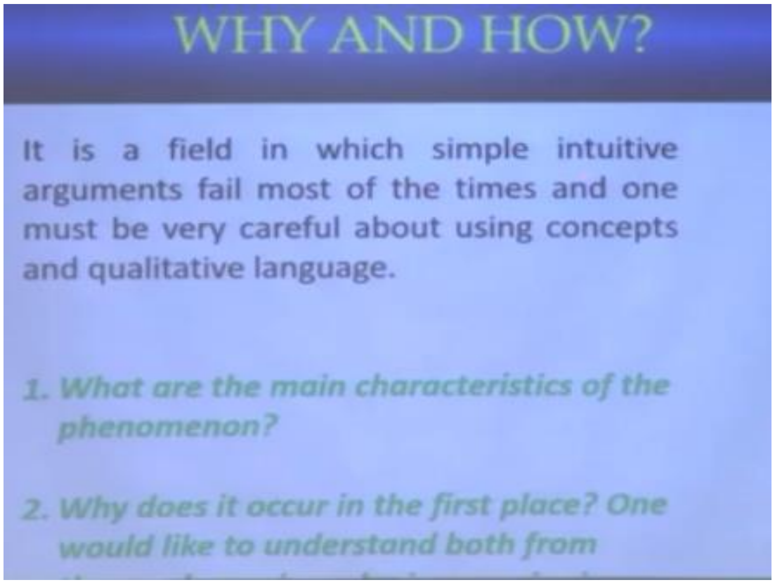

WHY AND HOW?

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*

Now one very important thing, I should point out that it is a field simple intuitive arguments fail miserably and this is one of the reason the theories are held, so highly regarded and I will say how it does not work, like one of the most important thing is the second order phase transition, which was solved in 1971 by KD Wilson by using individual innovation group, which is one of the most formidable thing that has been created by our mental things, on a human beings our intellectual feet.

Now so what we have to say, as I say always why and how. Why you study? I just said you and what are the main characteristics of the phenomena? Why does it occur in the first place? One would like to understand both from microscopic. It is not here microscopic and from macroscopic, both from fundamental and phenomenological point of view. So if there are many examples I said.

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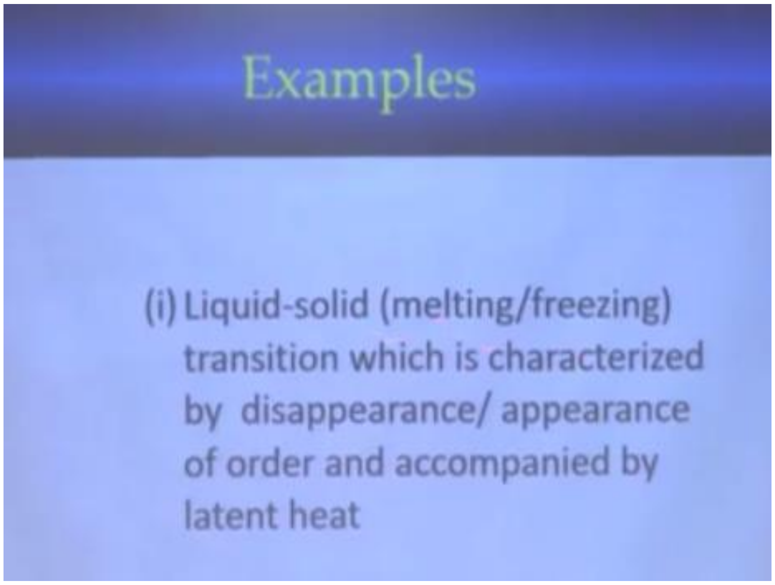

Examples

(i) Liquid-solid (melting/freezing) transition which is characterized by disappearance/ appearance of order and accompanied by latent heat

Let us go through them. This is one of the most common things we see every day life and the famous paper come from India of T.V. Ramakrishnan of Kanpur IIT that one of the highly cited paper is the freezing transition. The first line of the beautiful paper was that freezing is the most ubiquitous of all the phase transitions. Great line they started with.

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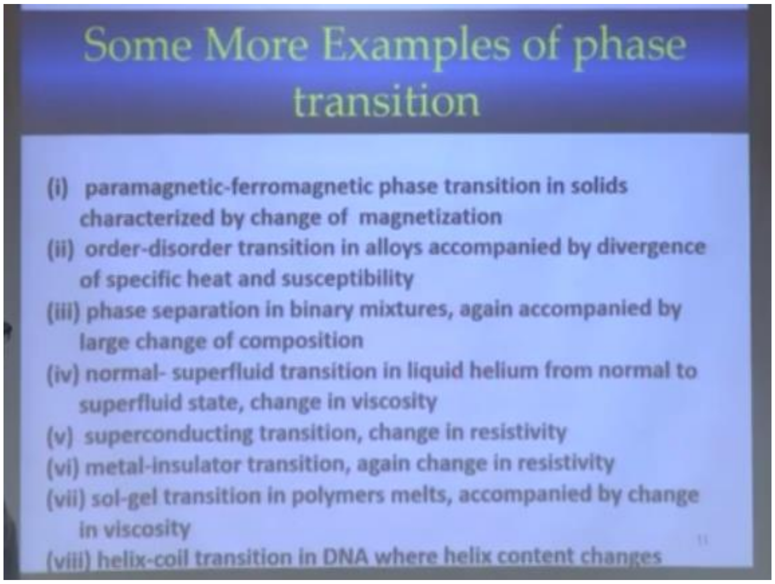

Some More Examples of phase transition

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

Then paramagnetic-ferromagnetic phase transition, order-disorder phase transition, binary mixture, large change of composition, normal-superfluid transition, liquid helium taking to superconductivity, super fluidity, then metal insulator transition again change in resistivity, solid-gel, helix-coil transition, DNA protein folding, list goes on.

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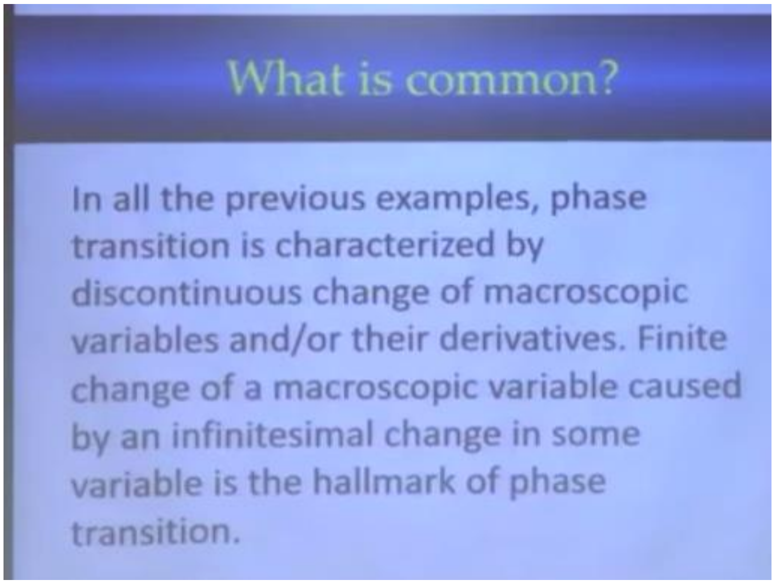

What is common?

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.

No, very good question. Many of them are second order like superconducting transition is second order. Super conducting is very unique. I will talk on super conductivity. Helix-coil transition is a first order phase transition, protein folding is considered also first order phase transition, but the change is very small. Helix-coil transition order parameter is; we use the helical pitch. Yeah, exactly and this theory if you are interested please take a note.

It was done by Zimm and Bragg in 1959, two pages next to each other, both one and a half page or even less than that and other by my adviser Gibbs and de Marzio and Julian Gibbs and it is beautiful theory. They would easily become first order; it is very nice. See, as we will discuss the second order phase transition, particularly the order-disorder, gas-liquid at critical point, they are characterized by large scale fluctuations and so huge density fluctuation near gas-liquid transition.

The compressibility goes to 0 in gas-liquid transition. Order-disorder transition again your composition is hugely changing that is the composition that is out of parameter that first order phase transitions are characterized by the new needed inflation. That means it is not characterized by that kind of huge fluctuations. So when helix-coil transition takes place, if you want a DNA helix to be broken into coil, then you have to first break the 3 hydrogen bonds.

You break the first hydrogen bond, you do not get, second, you break the third one, then it starts rotating. You get the rotational entropy. So that is the essential mutilation phenomena in that. We would not be able to I understand everything today in this one lecture. As I told you, full semester course is given on phase transition, but the idea here is to introduce the universality and the grandeur of the field.

And the concepts like order parameter in first and second order phase transition, which I said that is the first order, it is determined by the derivative of the free energy where it becomes discontinuous. That means this is the Ehrenfest classification, the order of a transition is given by the first derivative of the free energy with respect order parameter or other thing control parameter that shows discontinuity.

So in second order phase transition, first derivative like density, entropy, they are not discontinuous, but in the first order phase tension is the entropy. That is what you call latent heat, that is discontinuity. So heat contained entropy jumps from crystal to liquid, entropy jumps and entropy is the first derivative of free energy. That is why melting freezing are first order phase transition.

This I said this continuous change in microscopic derivatives, finite change of a macroscopic variable caused by infinitesimal change I said, but it is very important that infinitesimal change in a variable, but if macroscopic change in a variable is the hallmark of a phase transition. That is the uniqueness and the beauty of the phase transition.

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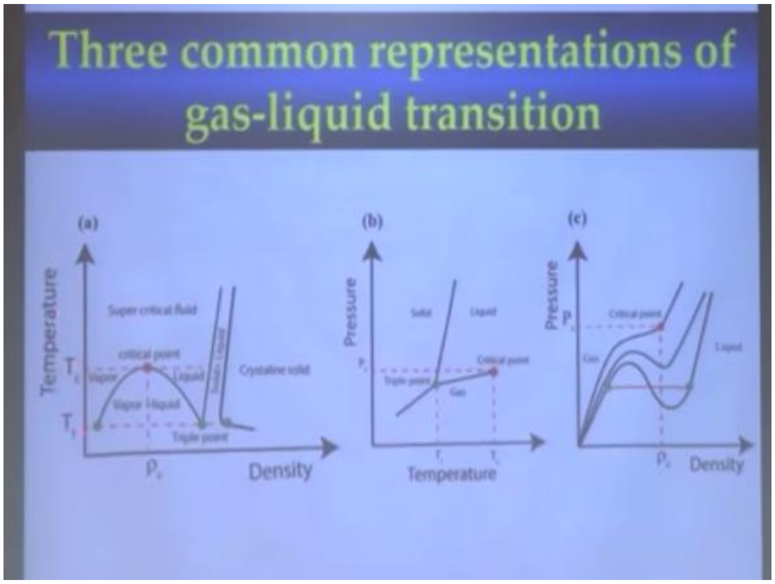

Three common representations of gas-liquid transition

These are many of these things. This is the famous temperature-density plane. So this is the vapor, this is the liquid and this is the critical point and this is the coexistence. All across coexistence, we get a phase transition. Here we get condensation, here we get boiling and this is the coexistence with liquid and crystal and here you get the phase transition, a lot of interesting things happen and lot of study going on now in this supercritical fluid.

And you also know we asked in our interview and about 80% students cannot answer any of them. I have done statistics 80% of the student cannot boot. They are coming for doing PhD. Pressure versus temperature plane, they cannot do. You can ask this question. It is very interesting they will put solid here, liquid here and so it is a kind of a Rubik's cube, we make them do, but here it is a first order phase transition, liquid solid melting.

Here sublimation in the first order phase transition. Gas-liquid is the first order phase transition, but it is only here, it is at the critical point nature of the transition changes, it becomes a second order phase transition and that second order phase transition is like this. So I have drawn the van Der Waals loop also to try this Maxwell construction, pressure versus density, you have seen in your first year and again you do it.

And in the first year undergraduate books, there is a great, great section which is the law of corresponding states that is done in a huge way. Now it is time for you to ask a question. What is the law of corresponding states and why it is so unique? Absolutely, this is our first in physical chemistry or physics the first A with the universality that I can P/P_C, V/V_C, and T/T_C and I get an equation for van Der Waals.

Remember is on the right hand side 8/3r and you get that equation now describes everything. Suddenly you get a master curve, when you plot pressure versus density everything is different. You cannot even plot them on the same graph paper, because density is so different; pressure is so different, but suddenly when I plot P/P_C and V/V_C or ρ/ρ_C, suddenly everything collapses. You get a master curve.

When van Der Waals did that he of course knew and van Der Waals did enormous, as I mentioned once before that he is one of the underrated scientists. This huge amount of work he has done. So these laws of corresponding states first told us that there is something very interesting, very fundamental going on. I do not have a slide on law of corresponding states. I should have had, but I forgot.

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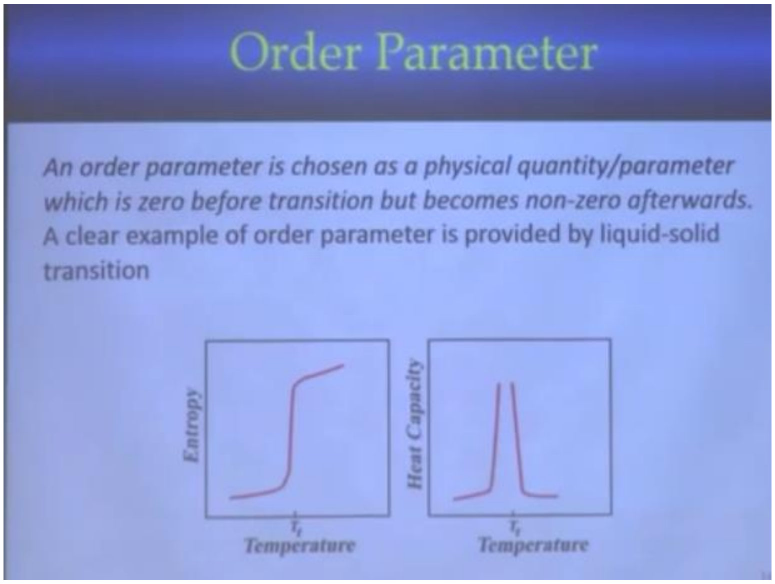

Order Parameter

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

Now an order parameter is chosen physical quantity as it is zero before the transition, becomes non-zero afterwards and that provided by liquid-solid transition, a clear example that we will go to, but here I have said entropy versus temperature. This is the first order phase transition; however, in a second order phase transition, of course this is, but it is specific heat that diverges.

All of us know that. There is only one truly second order phase transition in Ehrenfest sense, only one that we know and that is the superconductivity.

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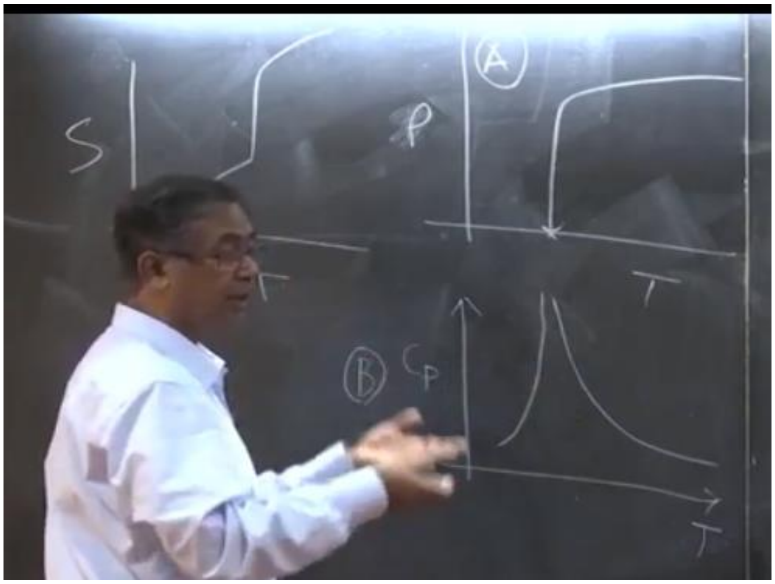

So if entropy goes, there are lot of things on that, because this has to be a positive because ds dt is specific heat. Those are the things we will do a little bit, then resistivity against temperature. This is the only, this is the superconductivity, but most of the second order phase transition that we call two kinds of phase transition estimation is N presence, other one where lambda transition in superfluidity.

So you guys have seen that, these figures, teachers, I think everywhere professors or whoever teach it or write books, they are all excited about this amazing thing that is here and this itself has given rise to huge amount of theories, understanding, papers, Nobel prizes and as I said it is highly regarded. I happened to do my PhD, started a few years after Kenneth Wilson's famous innovation book calculations and there are still so much excitement going on.

Leo Kadanoff who started some of the things was a brown and Leon Cooper who did the superconductivity Cooper pair was a brown. So it was a lot of fun to seeing the people who created physics around you. So this is the example of Ehrenfest first order phase transition, this one Ehrenfest first order phase transition, Ehrenfest second order phase transition. This we call continuous transition. Ehrenfest second order phase transition of the continuous type, that the little bit we do.

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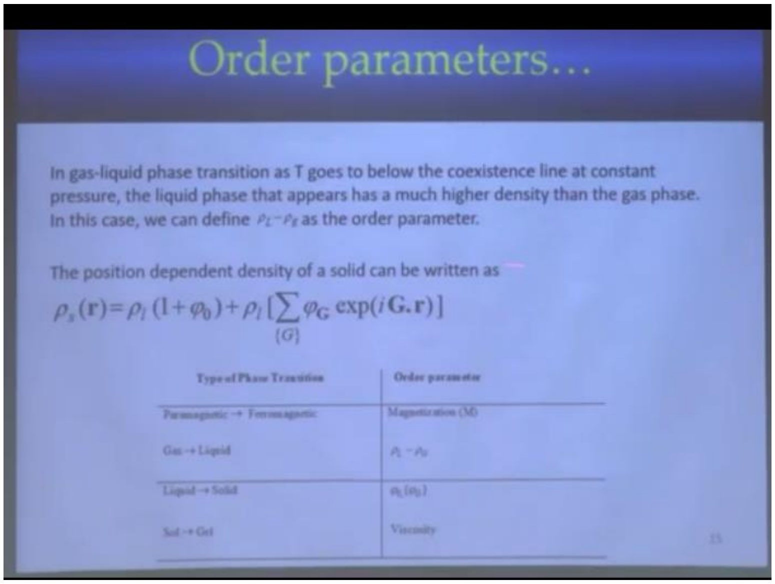

Order parameters…

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

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

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

As I said, some of the things will be elementary. I have to introduce people to nomenclature. Now one thing as I said, I always teach because this has come out from India, though the first one that by Kirkwood and Monroe in 1941, but that was not successful, for reasons I cannot go here, but the first successful theory of freezing was done by Ramakrishnan and Yussouff in 19s, paper written in 1977 came out in 1979 in physical review.

What they did and I teach it, because it is a wonderful example of order parameter. So this is the density of the solid, which is in homogeneous position dependent density. Liquid is homogeneous. There is no position dependence. That is average density is ρ_L. If you have read Kittel or any Solid State Physics books, then the density of solid is written in an expansion, where G is the reciprocal lattice vectors. So you do the x-ray, you get reflection of this planes.

These are the sharp peaks; however, the solid will not show that unless this factor is in front. This is a ϕ_G, this is the order parameter that becomes non-zero when liquid becomes crystal and phi naught is the fractional density change between liquid and crystal, like when I go to liquid to water twice, then this phi naught is negative, but most of the other cases sodium and all other molecular liquids, this is positive, because density increases.

Phi naught and ϕ_G are one of the best examples of the order parameter. So there are certain things given a parameter magnetization some other examples gas to liquid density as I said (ρ_L - ρ_G) and liquid to crystal, then phi naught and phi G and there is a bunch of them, because you have a bunch of reciprocal lattice vectors. In principle, you need to take all of them, but in practice we find couple of them.

It describes the theory and they get a very good agreement with these one of the most successful theories of phase transition. It is actually also called Landau theory, for reasons I will explain a little bit. So this is a very important slide where one gets examples of the order parameter. Now I want to tell you and if you can tell me, it will be even better, why we give so much importance on order parameter?

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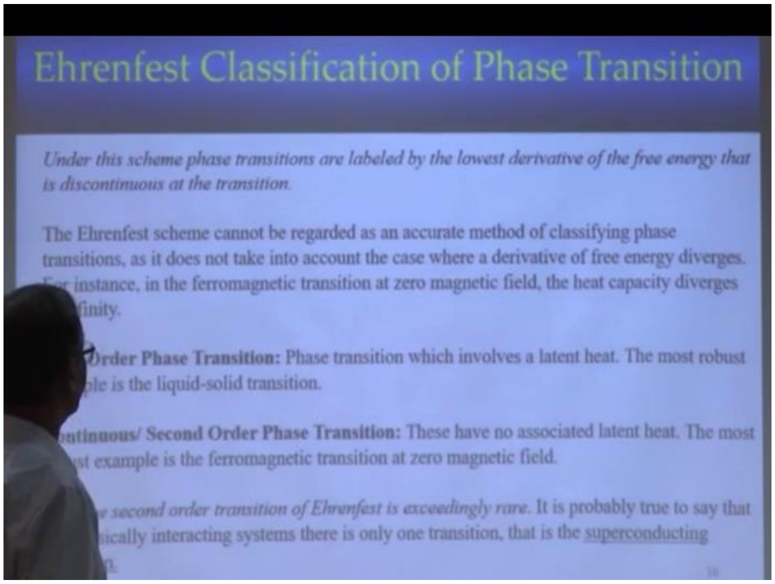

Ehrenfest Classification of Phase Transition

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. instance, in the ferromagnetic transition at zero magnetic field, the heat capacity diverges finity.

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

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

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

So this is again the same thing a phase transition labeled by lowest derivative of the free energy with classifying, but then first order phase transition continues as second order phase, true phase transition is superconducting transition is the true phase transition is exceedingly rare. We know only one case.

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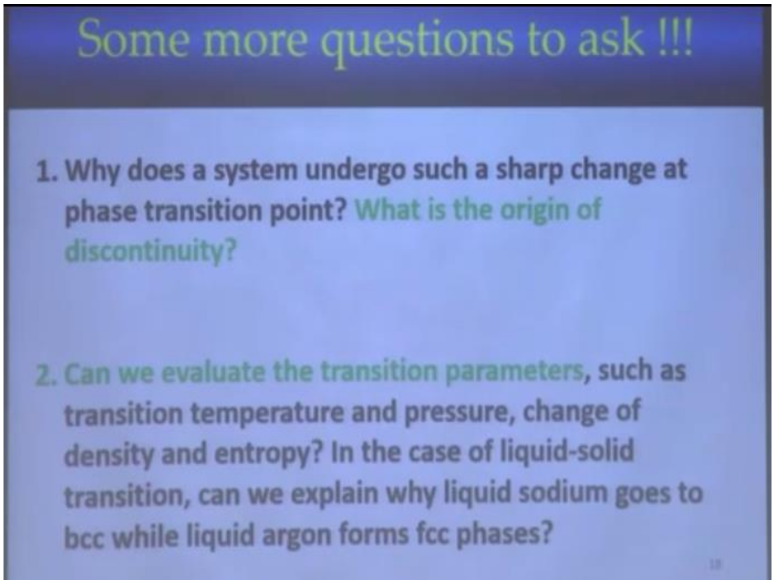

Some more questions to ask !!!

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 now some of the questions we need to ask, as I said why and how. Why does the system undergo such a sharp change of a phase transition point? What is the origin of discontinuity? Can we evaluate the transition parameters? So as I said these are the things, I wrote today morning to make it really simple to bring home the point. Now I have to ask you a question like last question corresponding state was very good.

Now Kailash or somebody again tell me why we need order parameter? Well, one is of course the unification. One is order of a transition, then unity among diversity, all this beautiful stuff, but there is one technical reason. Why Landau made it or introduced it and made it so famous? There is a practical view, you know the scientists are very pragmatic practical people. Theoreticians are even more practical; they may go around with air.

They are not practical but theoreticians are often very practical people, because we do what we can. Yes, access control parameter, correct, but I am asking what? Yeah, that is a practical side. I am saying theoretically Landau was a theoretician. He built this theory and he is the one who actually introduced all these things, the order parameters and all these things. The reason is that we do all these things, the reason is that we need to have a theory. Now let us think, we need to have a theory and what do we really need for the theory?

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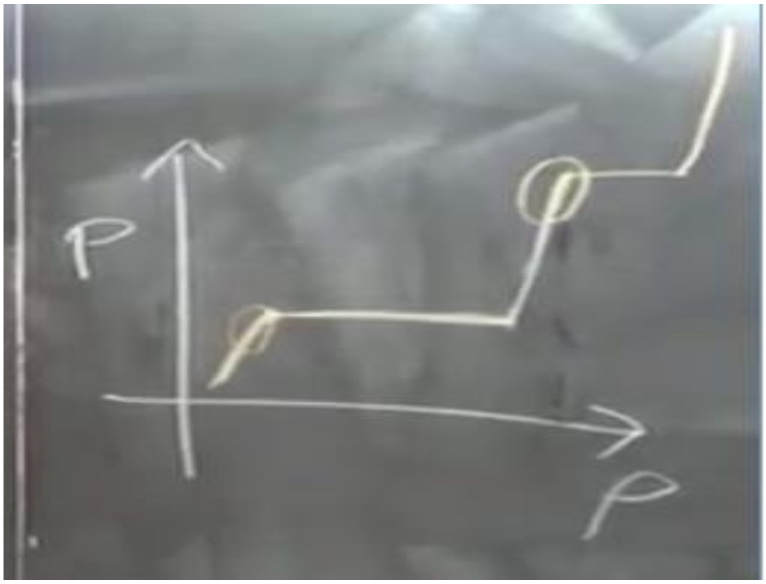

What is that this thing or what is the question? The question is that it reaches here, it goes over to liquid or reaches 0 degree centigrade water in your refrigerator, it becomes ice and so when I ask why? What exactly is that question why means? Why means that there are certain characteristics in this branch, certain characteristics which manifest itself, which kind of initiates or motivates the transition. One very simple answer, you could give and I expect you to give, what is the thermodynamic answer? Why water becomes ice? Absolutely, so free energy becomes minimum.

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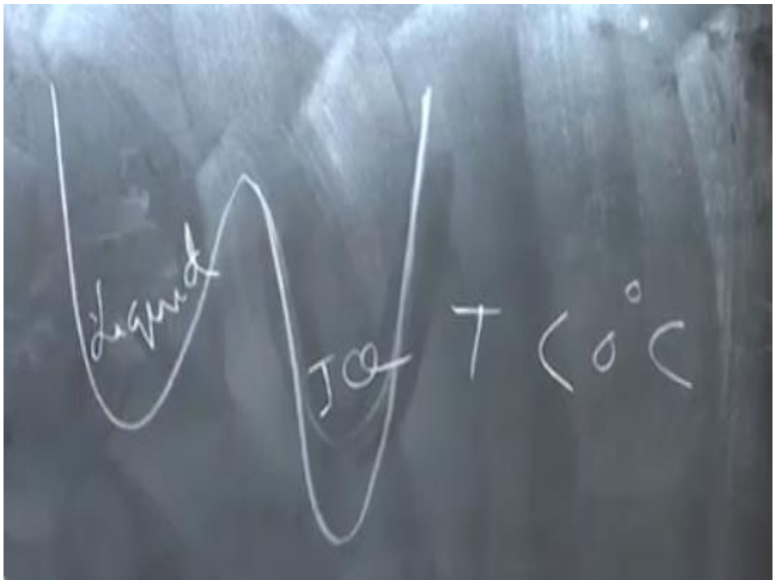

So if the free energy is like that, then that is a coexistence, but when free energy goes down, then this will be T below 0 degree centigrade and this will be ice and this will be liquid, water. So thermodynamic sense, we know the answer; that it is the free energy becomes low and so that was one of the first thing that people did not know and people knew it I think even into 19th century or 20th century. So this part is well understood.

That a phase transition takes place when the free energy, the system finds that it is more profitable free energy wise, to go over to the new phase. That is a valid and good answer. Now as I said here, why liquid sodium goes to bcc while argon goes to FCC. These are the kind of answer. If I want to know, then I have to look at the characteristics here, in this region that holds the key that it goes to bcc sodium.

Similarly, here is the characteristic that tells you how big the charm will be at a given pressure from gas to liquid. How do I describe that now? One of the things is that I calculate the free energy here. I calculate the free energy there, then I say okay I just whatever we did there, we compared the free energy and both will have minimum and then when this minimum goes down, then it system goes over to the this place.

That acts as an explanation at a level, which is a macroscopic level, but we want to know little bit more than that and we also want to know why the certain universal characteristics emerge in these kind of things and what allows us to calculate the transition parameters?

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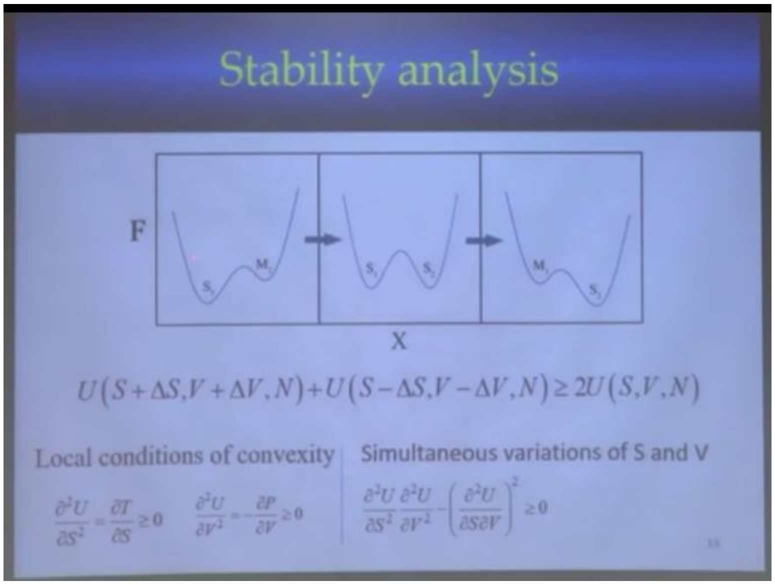

Stability analysis

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

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

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

So here certain things are there. We are not going to go too much into it. This is just what I said free energy stabilization. So free energy against an outer parameter X. It is like density or temperature, then here solid and melt, M is the melt, then here this is stable phase. So S is stable M is metastable, is stable and that lower free energy. At coexistence, they are both same free energy, both are stable.

But then when you lower the temperature or increase the density, then goes to the other things and there are certain stability conditions of convexity and concavity, which I do not think I will have time for that, but basically one says that if there is a maximum there, if I draw a line between these minima and this minima, then every point will lie above that cord. So these kind of things are maxima and minima or if it is a minima here, I draw a line from here and there. Then every point intervening lies below that cord. So that condition, simple condition is kind of stated here and that has certain consequences.

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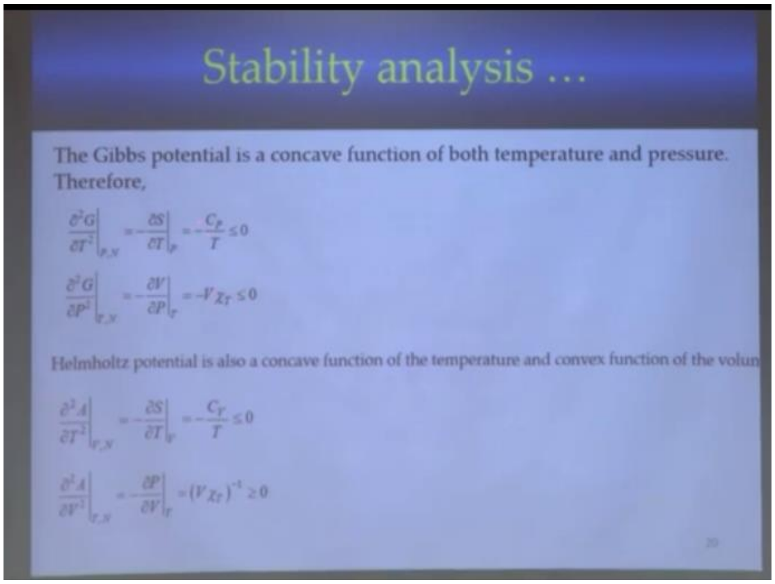

Stability analysis …

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 volun

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

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

And then another is that, for example Gibbs potential is a concave function and that means specific heat is positive. Concave function again means the compressibility is positive, there is a negative sign in front of it. So on the other hand, Helmholtz potential is a concave function of temperature and convex function of volume, which is given here. These are these slides I leave with this and I will not have time to go through these details of that, but these are essentially fundamental things telling you stability of a system, but that does not fully answer the questions that I am after here.