Fundamentals and Applications of Dielectric Ceramics

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Lecture - 34
Second Order Phase Transition in Ferroelectric Materials

So welcome to the new lecture again for this course fundamentals and applications of dielectric ceramics. So, let us just briefly recap the last lecture.

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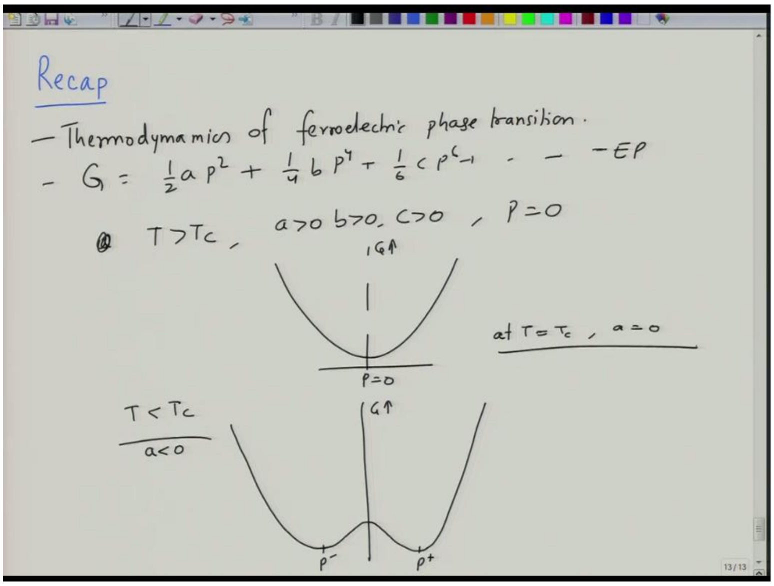

Recap

— Thermodynamics of ferroelectric phase transition.

— $G = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \ldots - EP$

@ $T > T_c$, $a > 0$ $b > 0$, $c > 0$, $P = 0$

at $T = T_c$, $a = 0$

$T < T_c$

$a < 0$

So, in the last lecture, we started doing thermodynamics of ferroelectric phase transition and for that we took a free energy expression and we rotate in terms of just polarization. So, it was given as:

$$G_p = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \ldots\ldots\ldots\ldots - E.P$$

and then we wanted to minimize this free energy as a function of, with respect to polarization.

So, for that we considered two conditions. We got two regimes, first is $T > T_c$ when $a > 0$, $b > 0$, $c > 0$. For that $P = 0$ happens to be a root. So, as a result we get a minima and free energy at $P = 0$, so this is G and then for $T < T_c$, the scenario changes. For $T < T_c$, the value of a becomes less than zero, so the free energy shows this kind of behaviour with roots at P^+ or P^- and in between there is a transition, when $T = T_c$, $a = 0$.

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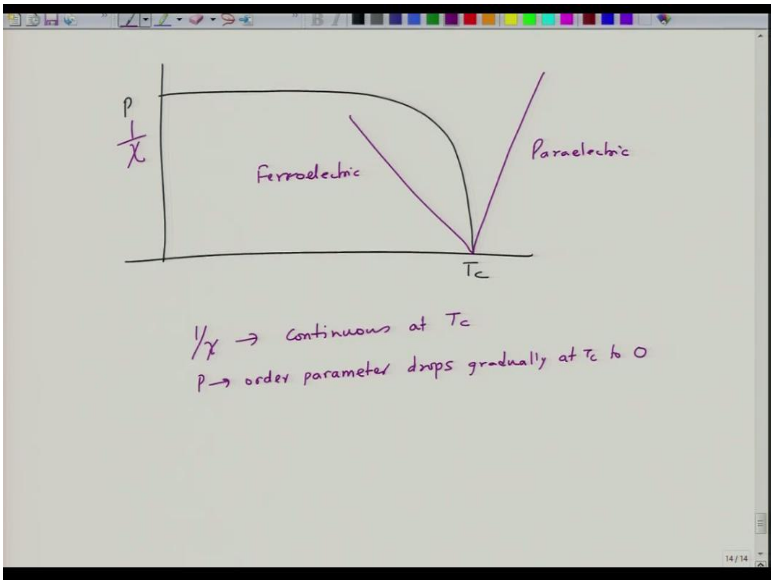

$1/\chi \rightarrow$ continuous at T_c

$P \rightarrow$ order parameter drops gradually at T_c to 0

And this we termed as second order transition in which the polarization gradually drops to temperature at T_c and susceptibility, if you write susceptibility $1/\chi$ then it decreases to T_c before rising further below T_c and in this state this ferroelectric below T_c and above T_c, it becomes paraelectric and this analysis was valid for small values of polarization and as a result and only in the vicinity of T_c we can do that.

And this is also reflected, so you can see that the value of $1/\chi$ is not discontinuous. So, $1/\chi$ is continuous at T_c polarization which is called as order parameter drops gradually at T_c to zero and then it is the second derivative of free energy which is discontinuous but not the first derivative that is. So, in this case, in this kind of transition, there is no evolution of latent heat and it is only the second derivative of free energy that is discontinuous as second derivative of free energy is nothing but your specific heat.

Now, let us look at little bit detailed analysis of second order phase transition as to how do we progress it. So, for the second order transition, we wrote the energy or maybe we will do the analytical treatment later because let us first do what we call as the first order phase transition scenario.

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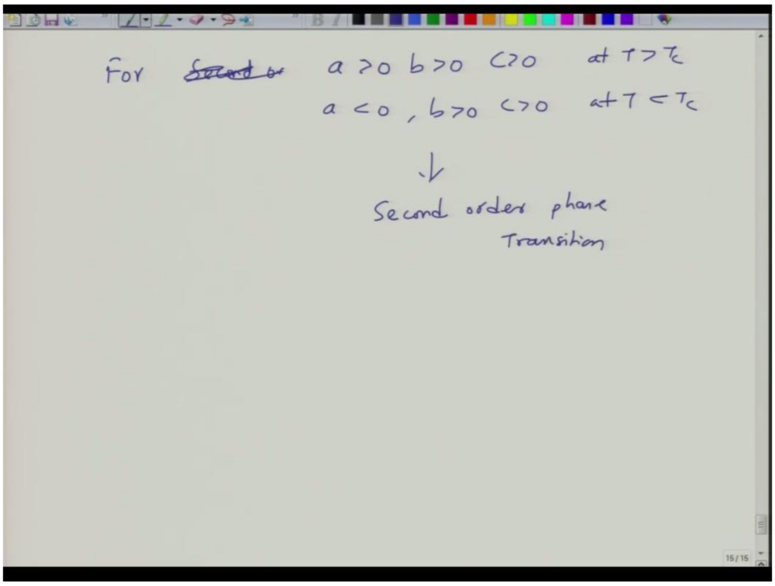

For ~~Second or~~ $a > 0$ $b > 0$ $c > 0$ at $T > T_c$

$a < 0$, $b > 0$ $c > 0$ at $T < T_c$

↓

Second order phase Transition

So, first in the previous part, we considered that for second order for the condition when a is > 0, b > 0, c > 0 at T > Tc and a < 0, b > 0, c > 0 at T < Tc, we termed it as a signature of second order phase transition. Now, let us say what happens if we consider a different scenario.

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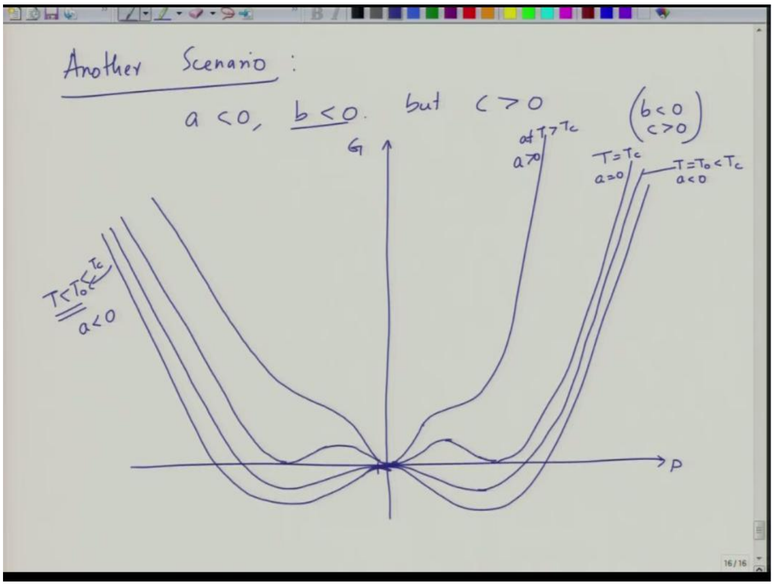

Another Scenario :

$a < 0$, $b < 0$. but $c > 0$

So, the different another scenario is a < 0, b < 0 but c > 0. Now, in this case what happens is that when you plot the free energy versus polarization. In this case, what happens is at temperature T, at temperature let say very low temperatures, let say at a temperature something. So, this is let say a temperature T less than the temperature called as T_0 which is less than T_c.

This is where we have a free energy, if we draw the line little bit here that is not appropriate and this is polarization. At very high temperature, when we are at a temperature $T > T_c$ then our situation is something like this, the free energy change sort of, so this is at $T > T_c$ and at this value so here we are saying that $b < 0$, $c > 0$ and we are looking at a change in the sign of 'a'.

So, for this $a > 0$ and at this point what happens is that $a \leq 0$ which means in between some change happens. The change that happens is in such a fashion so that we have a change like this. So, at $T = T_c$, we have $a = 0$; at $T > Tc$ we have $a > 0$ and let say at a temperature, so this is at a temperature $T = T_0$ which is lower than T_c. At this temperature, 'a' is negative.

So, 'b' is the quadratic coefficient. So, with the quadratic coefficient being negative even if $T >T_0$, so T_0 is the lower temperature than T_c. So, in the previous case, we saw that we have termed this temperature as T_c. Now, consider this T_c as T_0 at present. So, even if T is greater than that particular T_0 with this 'b' being negative, the free energy plot has some subsidiary minima as against in the previous case.

So, what happened in this case is at $T \leq T_0$, we have this minima which is fine which is the ferroelectric state. At $T = T_0$, we again have a similar state but at $T = T_c$ which is higher than T_0, at higher than T_0 in the previous case, it would have been just one minima but what we have in this case is the transition temperature is sort of little weird here. So, in the previous case, T_0 would have been that transition temperature.

Because you have a situation like this and then you have a single well but in between what we observe at a temperature called as T_c that we have this sort of subsidiary minima at $P = 0$ also, instead of having a maxima, we have a minima. This kind of transition basically is called as first order transition where we have a sort of you can say transition state at $T = T_c$ where we find three minimas and these three minimas gradually shift to two minimas as the transition temperature is lowered a little bit.

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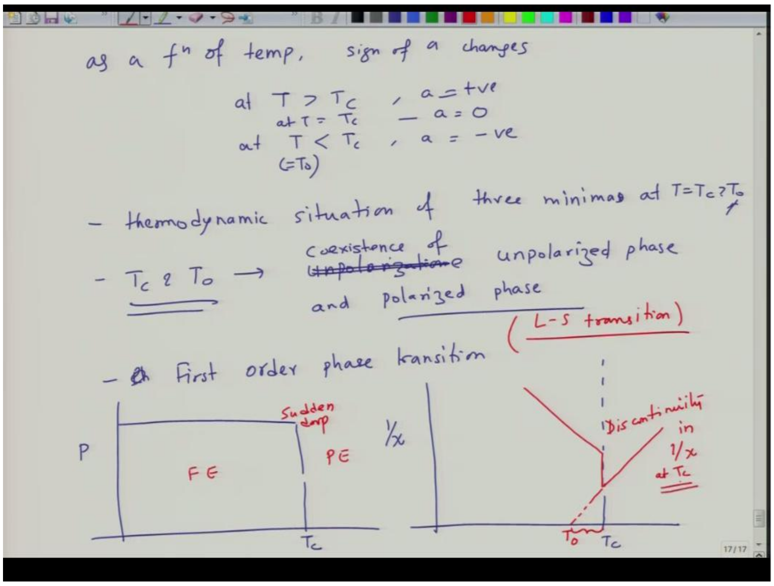

as a f^n of temp, sign of a changes

at $T > T_c$, $a = +ve$
at $T = T_c$ — $a = 0$
at $T < T_c$ $(=T_0)$, $a = -ve$

- thermodynamic situation of three minimas at $T = T_c > T_0$
- T_c & T_0 → coexistence of ~~unpolarizatione~~ unpolarized phase and polarized phase (L-S transition)
- First order phase transition

So, T = T$_c$ is somewhat you can say funny state, something weird happens there. So, what happens is that as you reduce, so as a function of temperature, we can see that sign of a changes right. So:

$$
\begin{aligned}
T > T_c \quad & a = +ive \\
T = T_c \quad & a = 0 \\
T < T_c \quad & a = -ive
\end{aligned}
$$

It is similar fashion but polarization but the change in free energy curve is rather different.

So, in the previous case, what we obtained was a behaviour like this. Here, the free energy shape is sort of different, it does not show a perfect minima. It has a sort of change in slope at a point and then a minima and then at T = T$_c$ instead of having just one minimum you have three minimum with one subsidiary minimum.

So, basically as a function of temperature, as you change the sign of ‘a’ , so basically we have a thermodynamic situation of three minimas at T = T$_c$ and this T$_c$ is higher than the T$_0$ at which you would have otherwise seen at the well. So, just below the temperature at which you see the double well, you sort of see a triple well and the triple well is basically, so you can say that between T$_c$ and T$_0$ something funny happens.

And basically you can say the unpolarized state; basically what happens is that you can see that these two minima’s belong to polarized state. This minima belongs to unpolarized state which means between T_c and T_0 we have a coexistence of unpolarized state and polarized state. So, this is what happens in this case the coexistence of unpolarized phase and polarized phase. This is more like liquid-solid transition.

When you transform liquid into a solid right, all of the liquid does not convert into solid altogether or all of the solid does not convert into liquid altogether. There is a range of temperature when liquid and solid coexist. You can explain this in case of solidification on the basis of under cooling and energy required to create you know critical size and so on and so forth.

Perhaps, similar explanations can be given here that to nucleate a stable polar phase, you need to wait for some time, some under cooling is required probably similar sort of arguments can be made but nevertheless what happens this funny state of free energy well that you see a triple well between temperatures T_c and T_0 is basically suggest that you have coexistence of two phases and this kind of phase transition is called as 1st order.

And when you make measurement of such a material, the polarization sort of goes and then drops boom at T_c and if you measure susceptibility, it shows a funny kind of behaviour. Susceptibility shows a discontinuity at this temperature and if you extend this below, this is the temperature T_0, the extrapolation of susceptibility on the right hand side makes a intercept on the temperature axis at a temperature T_0.

And between these two temperatures, we have coexistence of polar and nonpolar phases, very similar to what we can say solidification in which liquid and solid coexist despite being a pure metal. Pure metal does last as a liquid solid region because of need to nucleate stable nuclei. Similarly, probably here you have a region between T_0 and T_c when the material has these three minimas.

What it means is that out of these three minimas, two belong to the ferroelectric state and one belongs to the unpolarized state and these two states polarized and unpolarized states coexist between T_0 and T_c. So, this kind of first order phase transition is very similar to, you can say liquid to solid transition where we see a sudden drop of polarization below at T_c. So, you can see this is ferroelectric, this is paraelectric and you have sudden drop.

So, polarization is decreasing but it is not decreasing as gradually decreases and then boom goes to zero and sudden drop and then you have a discontinuity in $1/\chi$ at T_c. So, this is the fundamental difference in the 1st order transition.

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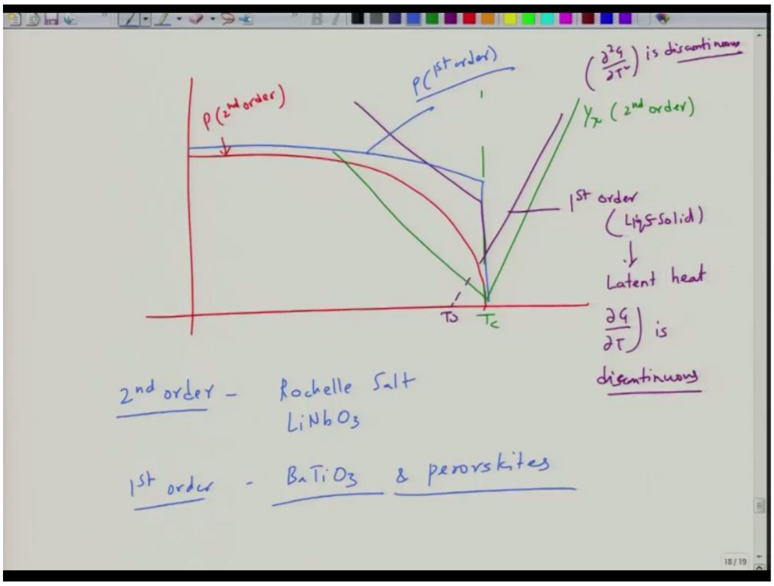

In the 2nd order transition if you now plot, at T_c, the susceptibility goes as like as shown, this is $1/\chi$ for second order but for first order what we have is something like this, this is 1st order. So, in some sense, the second order transition is more gentle, it happens gradually. That is the first order transition is abrupt sudden, so this is very similar to what we call as liquid to solid.

Because the whole structure has to be rearranged, the complete breaking of bones and then complete so there is a sudden change in for example enthalpy you have latent heat of evolution. So, first order transition is depicted by latent heat whereas in second order there is a gradual change as a result there is no latent heat. So, here in first order what you see is the first derivative of free energy is discontinuous whereas in case of second order, we see that is 2nd order.

So, here $\partial G/\partial T$ is discontinuous right and in this case $\partial^2 G$ is, this is the classic difference between the first order and second order. So and in case of polarization, so polarization in the second order will go in this fashion, this is second order and in case of first order, it will go boom. This is P first order and polarization is nothing but the order parameter right which can be related to free energy.

So, basically as we say that the first derivative is discontinuous, so you can see that here the first derivative is discontinuous and in this case the second derivative will be discontinuous. So, that is the fundamental difference between the two phase transitions, the first order and second order and there are quite a few ferroelectrics which show this first order phase transition.

But second order as we said earlier is shown by materials such as Rochelle salt etc whereas and also for example lithium niobate, it shows second order phase transition whereas first order transition is shown by material such as barium titanate and many other perovskites show a first order phase transition. So, this is what it is and this is also manifested in the other thermodynamic parameters.

So, we have not gone into entropy and specific heat and so on and so forth but for the sake of understanding, you may think that for the first order phase transition, the polarization is discontinuous, it drop suddenly at $T = T_c$, susceptibility show the discontinuity at $T = T_c$. For the second order, polarization drops gradually to zero at T_c whereas susceptibility is continuous, $1/\chi$ goes to zero and then again increases below T_c.

So, this is what the main difference between the two polarization mechanisms. So, now what we do is that we will do little bit of analysis of second order transition first.

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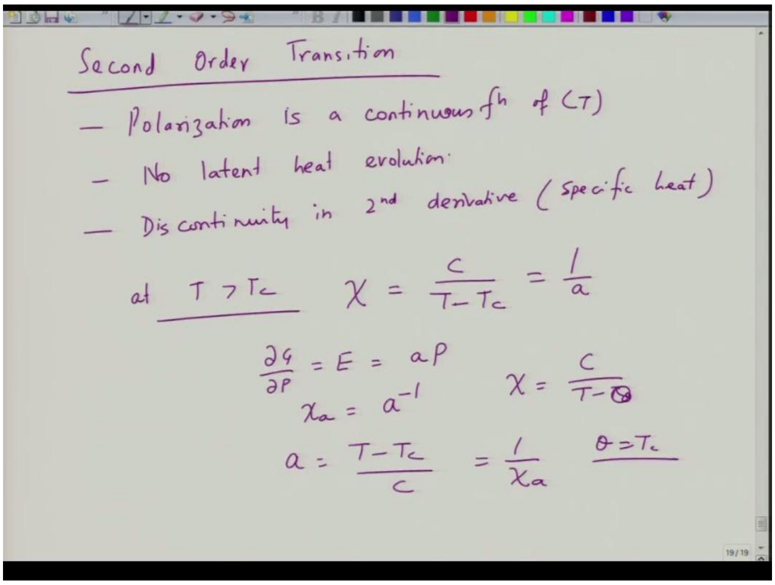

Second Order Transition

- Polarization is a continuous f^n of (T)
- No latent heat evolution.
- Discontinuity in 2^{nd} derivative (Specific heat)

at $T > T_c$ $\quad \chi = \frac{C}{T - T_c} = \frac{1}{a}$

$$\frac{\partial G}{\partial P} = E = aP \qquad \chi = \frac{C}{T - \Theta}$$

$$\chi_a = a^{-1}$$

$$a = \frac{T - T_c}{C} = \frac{1}{\chi_a} \qquad \Theta = T_c$$

So, in case of second order transition, if you look at the free energy specificity, so we can say for the second order transition, polarization is a continuous function of temperature, as a result there is no latent heat evolution but there is a discontinuity in second derivative which is nothing but specific heat, this is for the second order and in the second order case, at let us see if we can give you the expressions for susceptibility.

So, for susceptibility at T > Tc, we can write the susceptibility as:

$$\chi = \frac{C}{T - T_c} = \frac{1}{a}$$

$$a = \frac{T - T_c}{C} = \frac{1}{\chi_a}$$

and this can be proven easily because we can write this:

$$\frac{\partial G}{\partial P} = E = aP$$

ignoring the higher order terms.

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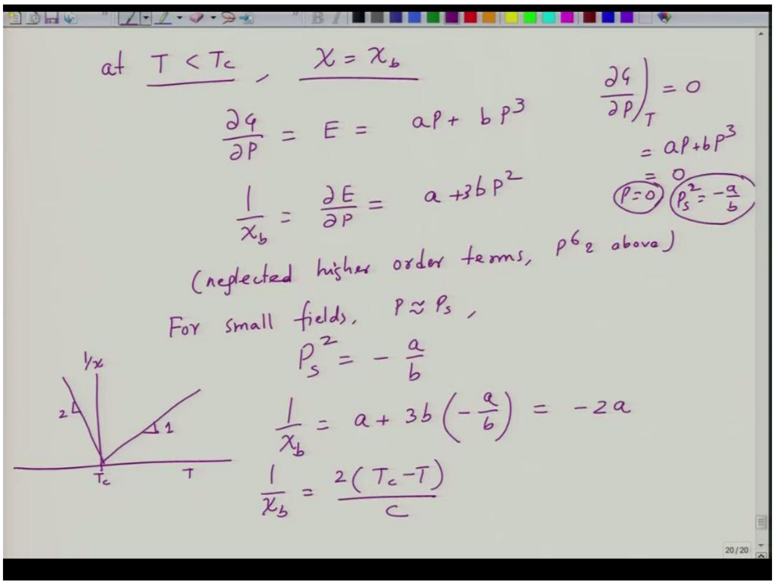

at $\underline{T < T_c}$, $\underline{\chi = \chi_b}$

$$\frac{\partial G}{\partial P} = E = aP + bP^3$$

$$\left.\frac{\partial G}{\partial P}\right)_T = 0$$

$$= aP + bP^3 = 0$$

$$\boxed{P = 0} \quad \boxed{P_s^2 = -\frac{a}{b}}$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3bP^2$$

(neglected higher order terms, P^6 & above)

For small fields, $P \approx P_s$,

$$P_s^2 = -\frac{a}{b}$$

$$\frac{1}{\chi_b} = a + 3b\left(-\frac{a}{b}\right) = -2a$$

$$\frac{1}{\chi_b} = \frac{2(T_c - T)}{C}$$

Now, at T < Tc, let us this define the susceptibility χ as χ_b, we first calculate ∂G/∂P which is equal to:

$$\frac{\partial G}{\partial P} = E = aP + bP^3$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3bP^2$$

We have neglected higher order terms that is P^6 and above, you can see here, we have only taken the P^2 and P^4 term. So, for small fields, we say that $P = P_s$ then in this region we can write this P^2_s can be equal to:

$$P_s^2 = -\frac{a}{b}$$

and this comes from basically the previous analysis of if you do $\partial G/\partial P$ at $T = 0$ if you do the minimization then we will get:

$$aP + bP^3 = 0$$

So, if you do the minimization, then we can so there is one at $P = 0$ the root but other thing will be P_s, which will be equal to negative of a/b from the free energy minimization. So, at constant temperature, if you take the derivative of free energy with respect to polarization for a stable equilibrium then we have the polarization values. So these are the nonzero values of polarization.

So, of course in the temperature lower than T_c, $P = 0$ is not a root that goes for maxima. So, what we have is the nonzero root at $T < Tc$ which is so:

$$P_s^2 = -\frac{a}{b}$$

$$\frac{1}{\chi_b} = a + 3b\left(-\frac{a}{b}\right) = -2a$$

$$\frac{1}{\chi_b} = \frac{2(T_c - T)}{C}$$

So, you can see that in the first case, $1/\chi$ is $(T - T_c)/C$, in the second case it is $2(T_c - T)/C$.

That is why when you look at the susceptibility at T_c, the slopes are different. So, you can see that $1/\chi$ has twice the slope. This will have slope of 1 and this will have slope of 2, $1/\chi$ versus temperature this is at T_c. These are very approximate analysis. They are not very accurate analysis but if you do accurate analysis, they will become complex.

So, but the simple analysis and the simple assumptions helps you to understand how the susceptibility varies as a function of temperature and what is its behaviour near T_c. So, this is what is about second order transition. We can do a simple analysis of the susceptibility for the first order transition as well which we will do in the next lecture.

So, what basically we have seen is the difference between the first and second order transition, the first order transition, qualitative analysis of first order phase transition as to how the free energy versus polarization varies across temperature and we see that the subsidiary minima at $P = 0$ between T_c and T_0 and this is basically reminiscent of coexistence of polarized phase with the unpolarized phase.

Because the two minimas belong to polarized phase which are nonzero, the minima that is at $P = 0$ it belongs to a unpolarized phase and they do coexist together. So, we will stop here. We will continue this in the next class with further discussion on ferroelectrics and then we will look at the application of three kinds of materials that we have discussed.