Condensed Matter Physics
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Lecture - 17
Dispersion and Absorption of Electromagnetic Waves In Dielectric Media: Ferro-and Antiferroelectrics

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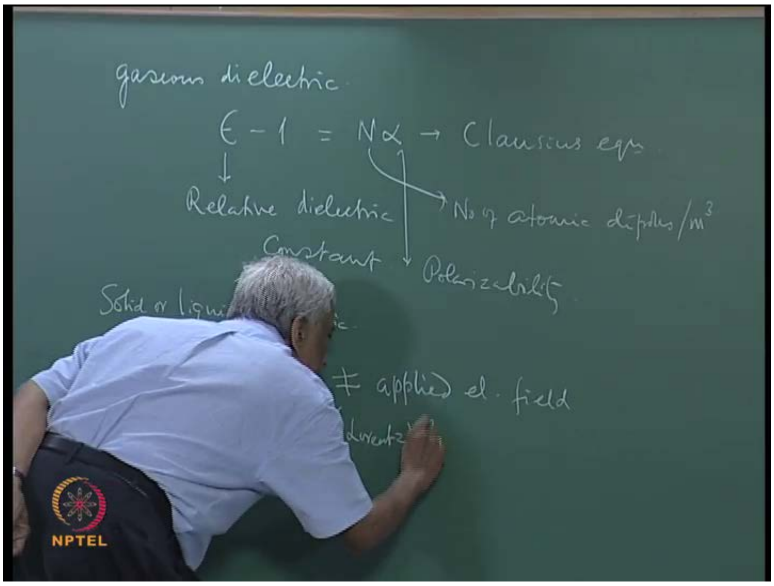

In the last lecture, we discussed the basic mechanism of polarization of a dielectric medium, and we saw that in the case of gaseous dielectric gases so we have the relation epsilon minus one equal to n alpha this is known as a Clausius equation. Here epsilon is the relative dielectric constant, n is the number of dipoles atomic or molecular dipoles per meter cube, and alpha is the polarisability. We also saw that when we come to a condensed phase like a solid or liquid, we saw that this equation is not valid anymore, because of the presence a local field which is not equal to the applied electric field because of the presence of an internal field which is also known as the Lorentz field.

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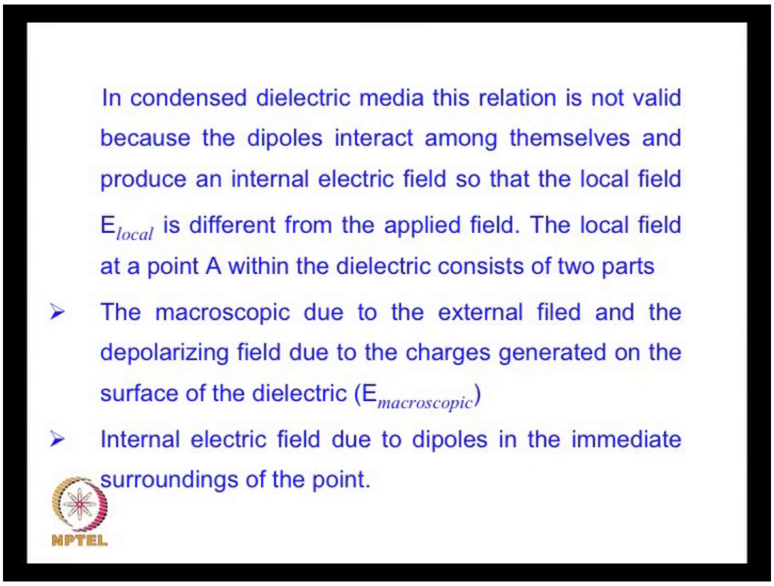

In condensed dielectric media this relation is not valid because the dipoles interact among themselves and produce an internal electric field so that the local field E_{local} is different from the applied field. The local field at a point A within the dielectric consists of two parts

- The macroscopic due to the external filed and the depolarizing field due to the charges generated on the surface of the dielectric ($E_{macroscopic}$)
- Internal electric field due to dipoles in the immediate surroundings of the point.

So, it is this E local which has to be used here in this equation, and this leads to a modification of the Clausius equation in the form and this is known as the Clausius-Mossotti equation and this is what is valid for solids and liquid dielectrics.

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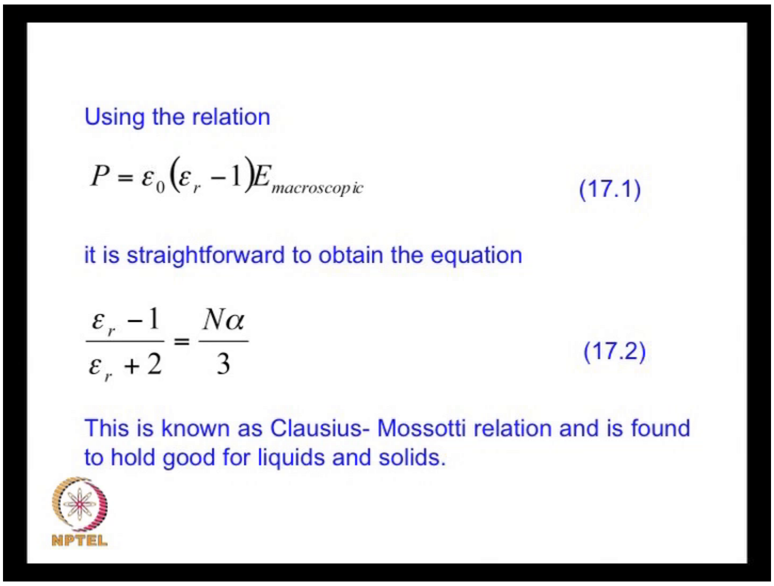

Using the relation

$$P = \varepsilon_0 (\varepsilon_r - 1) E_{macroscopic} \qquad (17.1)$$

it is straightforward to obtain the equation

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha}{3} \qquad (17.2)$$

This is known as Clausius- Mossotti relation and is found to hold good for liquids and solids.

So, this is the Clausius Mossotti equation which has to used for solid and liquid dielectric, and therefore of relevance class.

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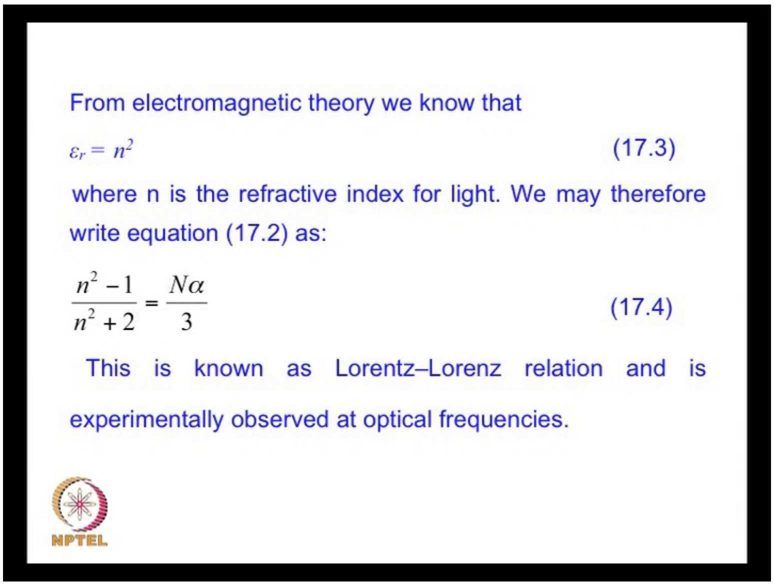

From electromagnetic theory we know that

$$\varepsilon_r = n^2 \quad (17.3)$$

where n is the refractive index for light. We may therefore write equation (17.2) as:

$$\frac{n^2-1}{n^2+2} = \frac{N\alpha}{3} \quad (17.4)$$

This is known as Lorentz–Lorenz relation and is experimentally observed at optical frequencies.

Since we also know that the dielectric constant is proportional to n square from em theory we can also write this as in this form this is known as the Lorentz relation.

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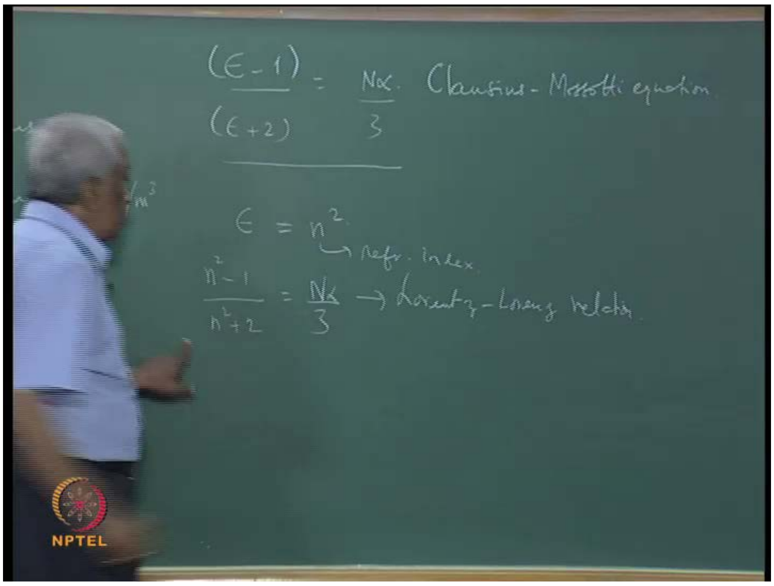

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} = \frac{N\alpha}{3}$$ Clausius-Mossotti equation

$$\epsilon = n^2 \rightarrow \text{Refr. index}$$

$$\frac{n^2-1}{n^2+2} = \frac{N\alpha}{3} \rightarrow \text{Lorentz-Lorenz relation}$$

So, if you measure the refractive index n, this is the reflective index, you can use this equation at optical frequencies.

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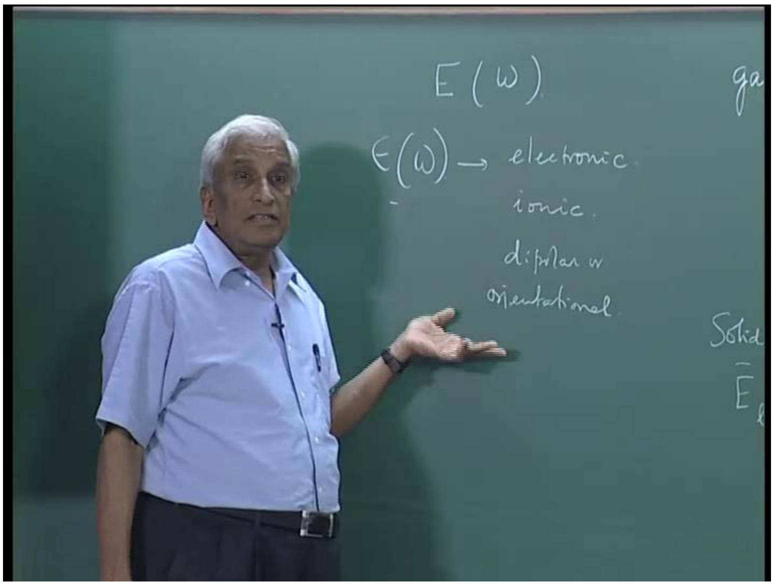

So, this is the overall situation and we also saw how when we go from the static to the dynamic situation where the applied field is a function of omega the frequency, so it is an alternative field for example, ((Refer Time: 04:36)) field. Then you have the frequency dependent dielectric constant, which is basically because of the polarization of various entities in the medium. The mechanism of polarizations can be different electronic, ionic and dipolar or orientation. Last time we discuss these with specific reference to examples such as sodium chloride and water and so on. Sodium chloride is the ionic material and the ionic contribution will not be able to keep phase, will not be able to follow the past frequency variations of the applied dielectric field. And therefore, it will not contribute to the polarization at high frequencies.

Whereas, the electronic polarization will go all the way will be able to follow the polarizations follows the field variations right up to the ultraviolet across the visible spectrum. And for example, if you have a polar molecule like water in which there is a permanent electric dipole moment then there is an orientation of these dipoles in the applied electric field and this also has a certain time constant. And therefore, depending on the relaxation of these dipoles, this will also contribute only up to a certain frequency such as microwaves.

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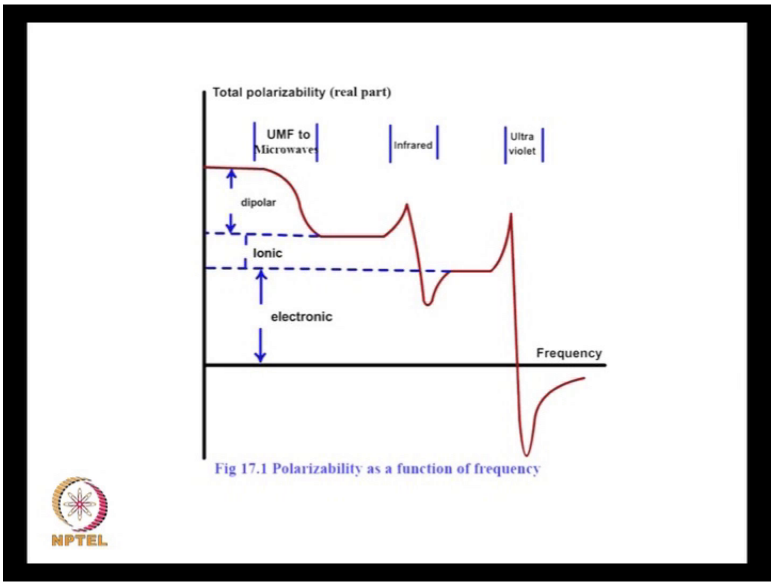

Fig 17.1 Polarizability as a function of frequency

So, this is what we saw last time, and all these three together are illustrated in the next figure, where we have plotted the polarisability as a function of frequency. Now what we see is that at low frequencies, you have the dipolar mechanism, so you have something like this.

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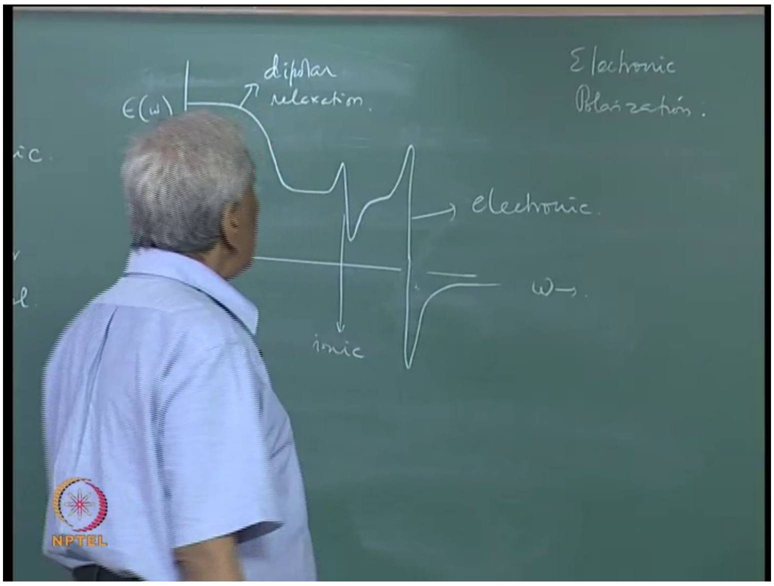

So, the epsilon omega function of omega starts from this zero static value and goes down and then there is the region here and then region here. So, that is the overall shape of the polarisability as a function of frequency. So, this is the dipolar region, dipolar relaxation this is the ionic and this is the electronic, so that is the overall behavior of the polarized ability and we will consider these in some detail next.

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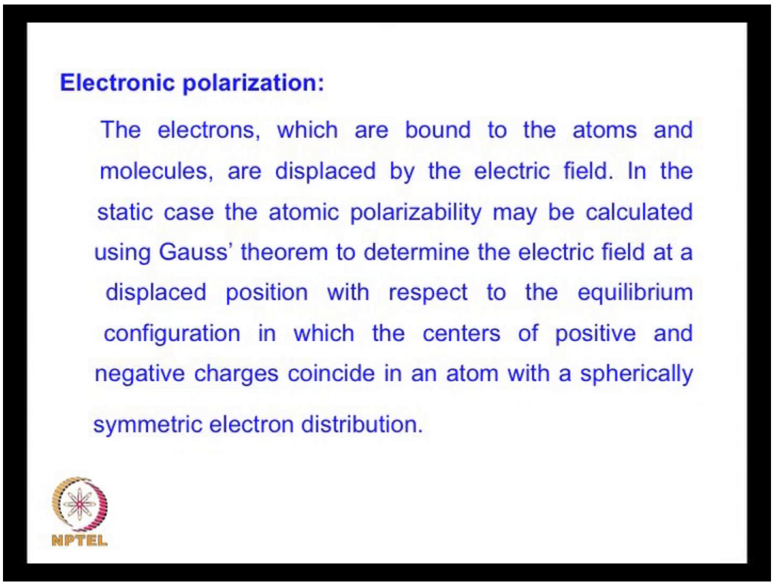

Electronic polarization:

The electrons, which are bound to the atoms and molecules, are displaced by the electric field. In the static case the atomic polarizability may be calculated using Gauss' theorem to determine the electric field at a displaced position with respect to the equilibrium configuration in which the centers of positive and negative charges coincide in an atom with a spherically symmetric electron distribution.

So, let us consider electronic polarization. So, we have a medium in which there are bound electrons, the electrons are not free in a dielectric like unlike in a metal. So, they are bound electron. So, when the electric field is acts upon them the electrons are only slightly displaced by the electric field. So, first let us see how this polarisability may be calculated in the static case.

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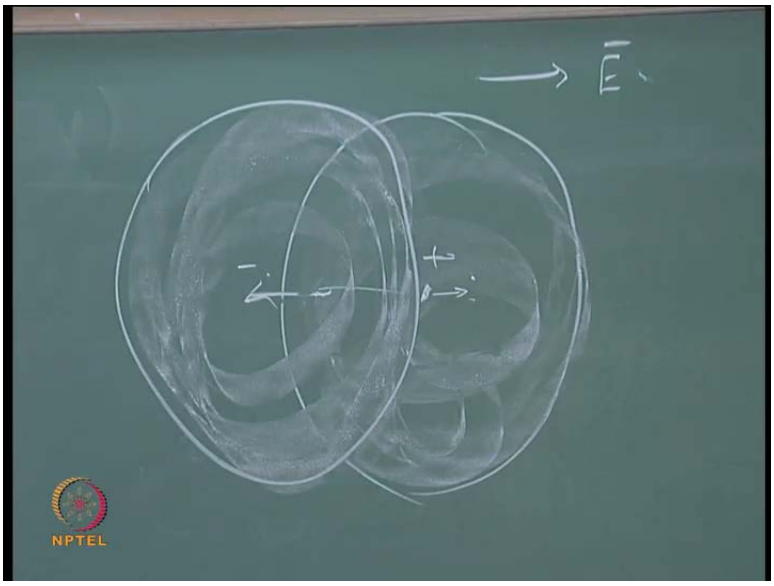

So, this can be done because we have already seen how in the presence of an applied electric field in the case of spherical atom the electronic cloud with the nucleus, the nucleus in the presence of an applied electric field how is the nucleus gets displaced slightly while the electronic cloud is replaced much more. And so there is the rigid shift of this electronic cloud. So, the centers of positive and negative chargers are displaced relative to each other say by an amount x. So, now, we can use Gauss theorem to calculate the polarisability.

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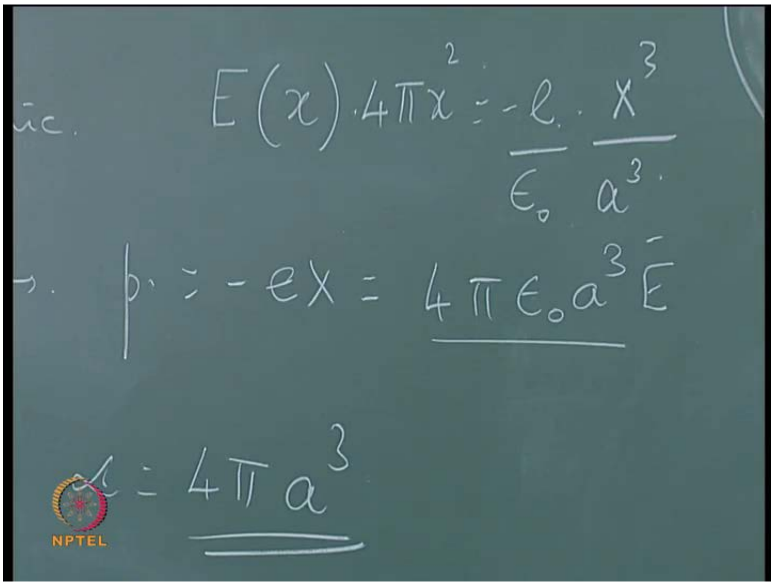

$$E(x) \cdot 4\pi x^2 = \frac{-e}{\epsilon_0} \cdot \frac{x^3}{a^3}$$

$$p = -ex = \underline{4\pi\epsilon_0 a^3} \bar{E}$$

$$\alpha = \underline{4\pi a^3}$$

Because Gauss theorem say that is the flux due to an electric field and that is equal to the charge which is minus e is the electronic charge times x cube by a cube. Because in both cases will be four-third pi x cube and four third pi a cube I am writing four third pi cancels of and this is all we are left with. So there we have e x equal to 4 pi epsilon naught a cube E, and this is what we call the dipole moment induce dipole moment. And therefore, we can see from the definitions of the polarisability that the polarisability alpha is four pi a cube, so it is proportional to the atomic volume, this is of course, in the static situation.

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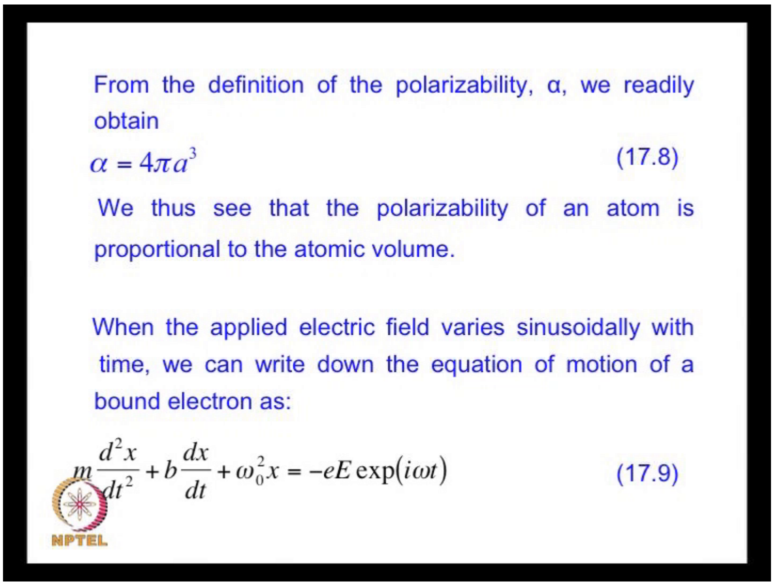

From the definition of the polarizability, α, we readily obtain

$$\alpha = 4\pi a^3 \qquad (17.8)$$

We thus see that the polarizability of an atom is proportional to the atomic volume.

When the applied electric field varies sinusoidally with time, we can write down the equation of motion of a bound electron as:

$$m\frac{d^2x}{dt^2} + b\frac{dx}{dt} + \omega_0^2 x = -eE\exp(i\omega t) \qquad (17.9)$$

But when there is a time dependent or an oscillating electric field the response of the electron a given electron can be written using the equation of motion which is m d square x y d t square that the Mossotti acceleration by Newton’s law plus b times d x by dt. This is because the electronic motion always experiences a resistance for its motion. And this resist the force by unit moss is the taken to be proportions to this speed or velocity then the bound electron has it is bound with a kind of elastically or to the atom with a kind of force which can be represented in the simple approximation.

The simplest model by harmonic oscillators of natural frequency x omega naught, so that I can write omega naught square x equal to minus v e e to the power of i omega t, so that is the equation of motion which is to be solved and be assume, since I am writing only the time-dependent here. So, i has so assume that the displacement also has a form e to the power i omega d, so that there might be a full shift, but we will just consider this omega naught square here is just the k by m where k is the time force constant.

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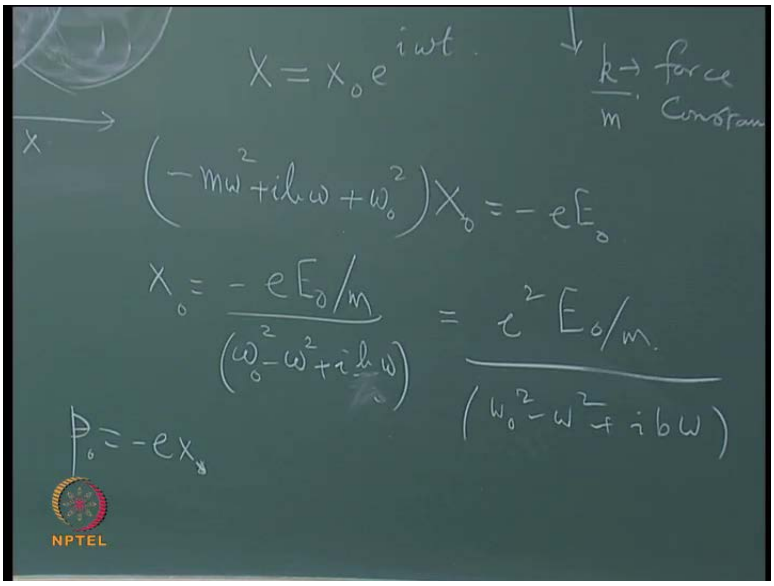

$$X = x_0 e^{i\omega t}$$

$\frac{k}{m}$ → force constant

$$\left(-m\omega^2 + ib\omega + \omega_0^2\right) X_0 = -eE_0$$

$$X_0 = \frac{-eE_0/m}{\left(\omega_0^2 - \omega^2 + i b\omega\right)} = \frac{e^2 E_0/m}{\left(\omega_0^2 - \omega^2 + ib\omega\right)}$$

$$p_0 = -e x_0$$

So, using the, we can immediately write m omega square plus be omega i plus omega naught square times x naught equal to minus e naught. So, that x can be written it is not in written as well we will write a b by m as b you will just define this by the damping per unit moss, so that the simpler left with this. So, immediately we can calculate the dipole moment because the dipole moment in this case is minus e x naught at the amplitude of the oscillating dipole moment and therefore, this will be and since we have the dipole moment the protocol polarization is just n times p.

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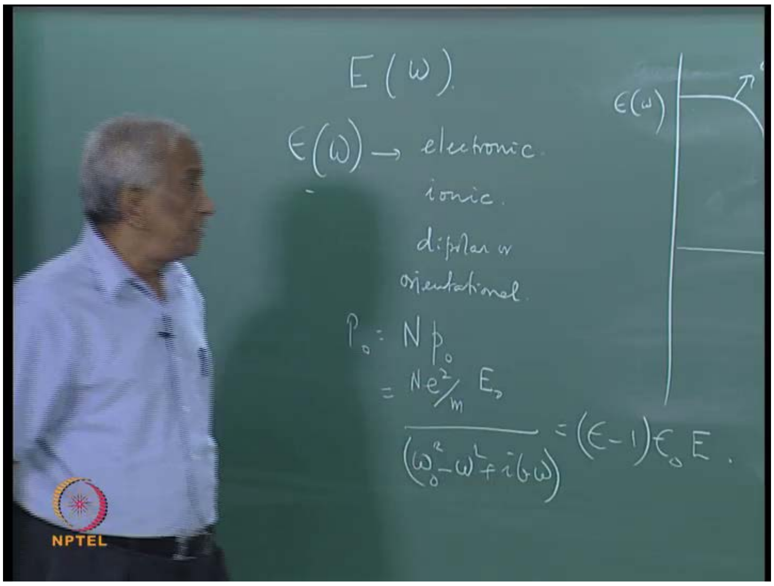

$E(\omega)$

$\epsilon(\omega)$ → electronic
ionic
dipolar or
orientational

$$P_0 = N p_0 = \frac{Ne^2/m \, E_0}{\left(\omega_0^2 - \omega^2 + ib\omega\right)} = (\epsilon - 1)\epsilon_0 E$$

So, this is the naught and therefore, this will simply be n is square by m e naught by omega holes square minus omega square plus i b omega and therefore, since the relation between this is what gives you the epsilon. So this can be written as epsilon minus one, so that we get the directory constant and because of this factor, i here this becomes a complex quantity and therefore, the epsilon is in general complex.

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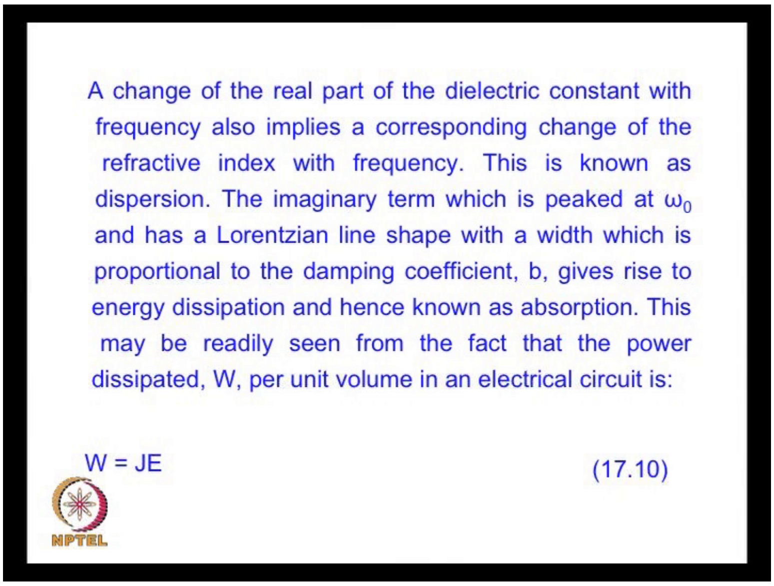

A change of the real part of the dielectric constant with frequency also implies a corresponding change of the refractive index with frequency. This is known as dispersion. The imaginary term which is peaked at ω_0 and has a Lorentzian line shape with a width which is proportional to the damping coefficient, b, gives rise to energy dissipation and hence known as absorption. This may be readily seen from the fact that the power dissipated, W, per unit volume in an electrical circuit is:

$$W = JE \qquad (17.10)$$

So, let us write it as epsilon prime plus i epsilon double i. So, we have the complex dielectric constant. So, the real and imaginary parts are there. So, it can be separated into real and imaginary part and we have these are plotted here.

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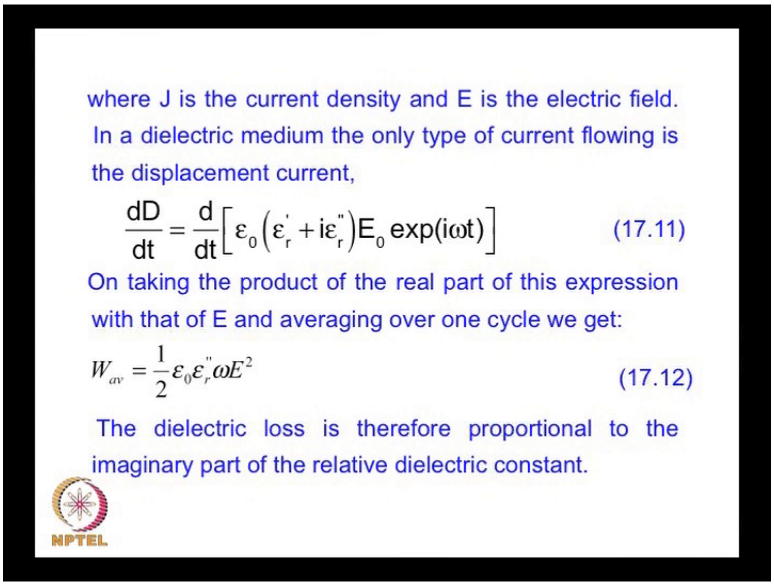

where J is the current density and E is the electric field. In a dielectric medium the only type of current flowing is the displacement current,

$$\frac{dD}{dt} = \frac{d}{dt}\left[\varepsilon_0\left(\varepsilon_r' + i\varepsilon_r''\right)E_0 \exp(i\omega t)\right] \qquad (17.11)$$

On taking the product of the real part of this expression with that of E and averaging over one cycle we get:

$$W_{av} = \frac{1}{2}\varepsilon_0\varepsilon_r''\omega E^2 \qquad (17.12)$$

The dielectric loss is therefore proportional to the imaginary part of the relative dielectric constant.

They are given the real and imaginary parts are given in the equation here and therefore, you can see that they are plotted here the real and imaginary parts of the direct constant as a function of frequency.

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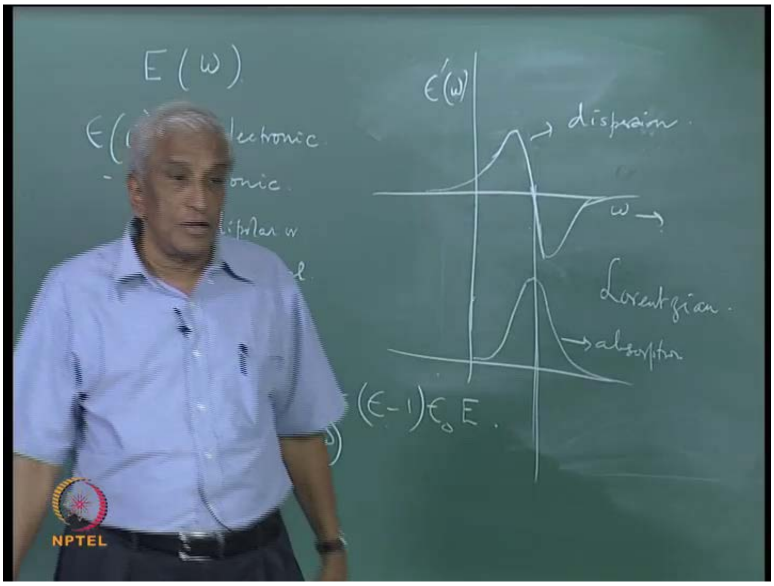

So, the real and imaginary parts look like this. So, I take epsilon prime omega as a function of frequency in the neighborhood a resonances then I have something like. So, that is the kind of response. So, this is real part of the dielectric constant while imaginary part below. So, these two so the imaginary part is the maximum. So, this is what is known as a Lorentzian, because these the dispersion part and this is the absorption. So, dispersion and absorption the real part in the dielectric constant is a associated with dispersion while the imaginary part of the dielectric constant is relative to the absorption. Now we saw that there are several other mechanism will not consider the ionic in detail. Now we will instead go to the other case where there are permanent dipoles in the system.

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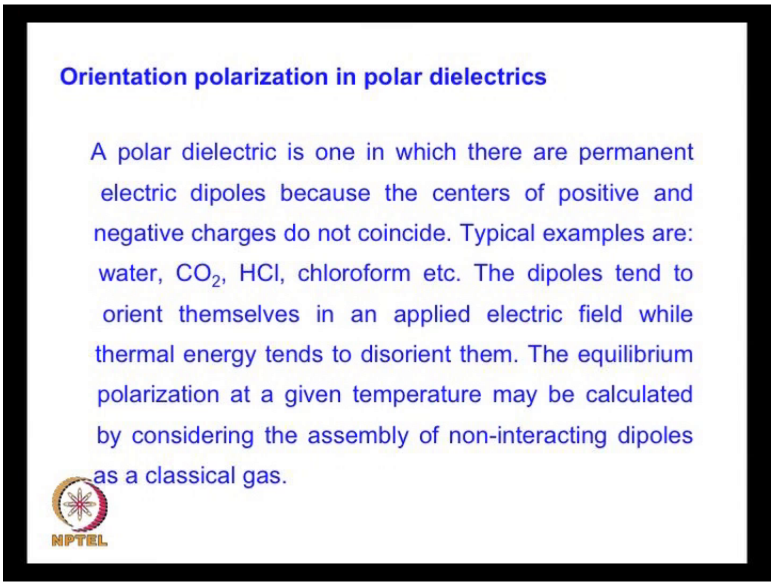

Orientation polarization in polar dielectrics

A polar dielectric is one in which there are permanent electric dipoles because the centers of positive and negative charges do not coincide. Typical examples are: water, CO_2, HCl, chloroform etc. The dipoles tend to orient themselves in an applied electric field while thermal energy tends to disorient them. The equilibrium polarization at a given temperature may be calculated by considering the assembly of non-interacting dipoles as a classical gas.

So, the medium in the dielectric medium is what is called the polar dielectric for example, water water has a large dipole moment.

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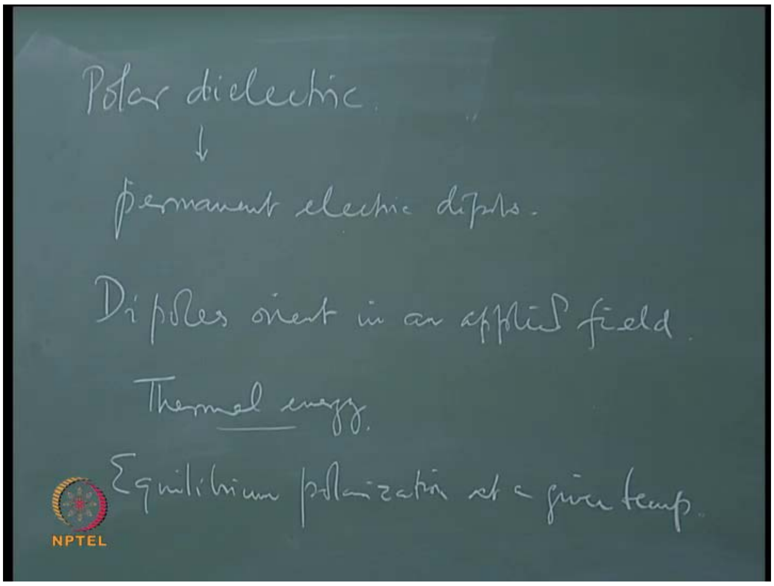

Polar dielectric

↓

permanent electric dipoles.

Dipoles orient in an applied field.

Thermal energy.

Equilibrium polarization at a given temp.

So, if you have a polar electric this means that there are permanent electric dipole moment as the distinct from induce electric dipoles which persist only as long as there is an applied electric field, for example, some typical is abstractions are water carbon dioxide. So, a hydrogen chloride chloroform etcetera they are all highly polar dielectric. So, what happens is that these dipole tend to orient themselves orient in an applied field. So, it is this orientation which gives you the polarization. In this cases because if do orient more as a orient more and more like get aligned alone the electric field there is the the polarization increases. Now this orientation tendency is opposed by the thermal energy this is some as thermal energy which tends to restoral the disorder, which tends to thermal energy is always lens leads to disorder the dipoles.

So, there is a ordering influence due to the applied field and which completes with these this ordering influence the equilibrium polarization at any given temperature at a given temperature that is what determine the dielectric constant. So, this can be easily calculated and this is the temperature dependent process unlike the induce dipole mechanism or the electronic ionic mechanism. So, this is the temperature dependent because the thermal energies more. So, there is a temperature dependence for the orientational polarized ability. So, this is now the orientational contribution to the polarized ability can be separated from the electronic for ionic contribution because you measure the dielectric constant as a function of temperature a different temperature and then the temperature dependent part comes from the orientation of mechanism. So, let us consider this mechanism, we have let us write down what is the polarization.

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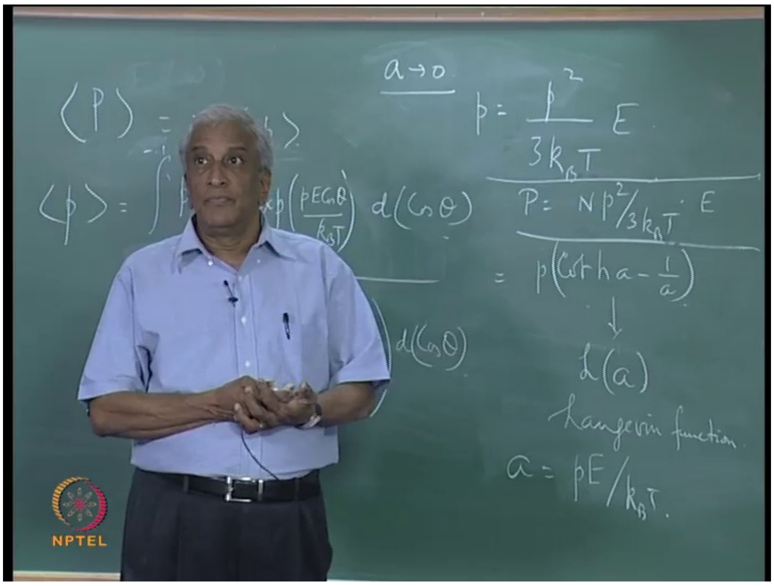

The polarization is P - it is a thermal average statistical average which is n times the individual average of the individual dipole moment. Where this average p is integral p cos theta, this is the projection of the dipole moment of the permanent dipole in the direction of the applied field times. There is the usual Maxwell Boltzmann factor statistical factor times b f cos theta zero to pi zero to one minus one point to minus one exponential p e cos theta by k b t and d of cos theta.

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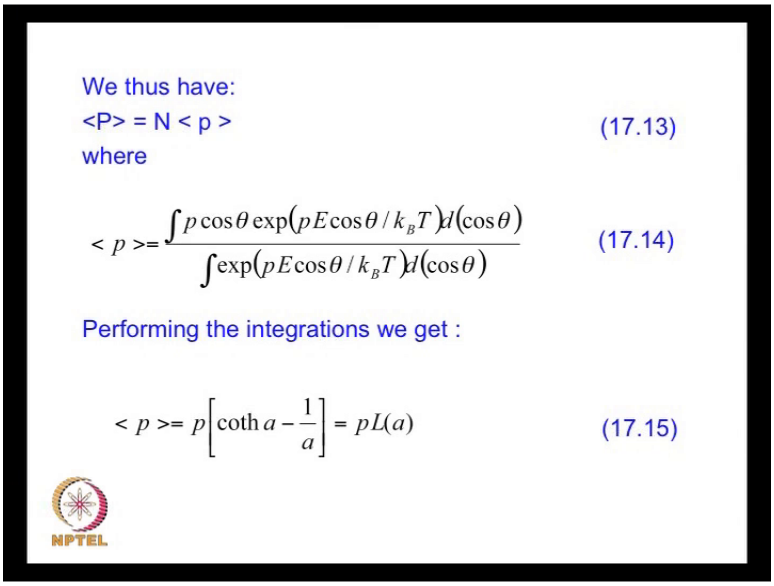

We thus have:

$<P> = N < p >$ (17.13)

where

$$< p >= \frac{\int p\cos\theta \exp\left(pE\cos\theta / k_B T\right) d(\cos\theta)}{\int \exp\left(pE\cos\theta / k_B T\right) d(\cos\theta)} \qquad (17.14)$$

Performing the integrations we get :

$$< p >= p\left[\coth a - \frac{1}{a}\right] = pL(a) \qquad (17.15)$$

Now this can be evaluated you get this as this is the functional dependent this function is usually known as the langevin function l of a.

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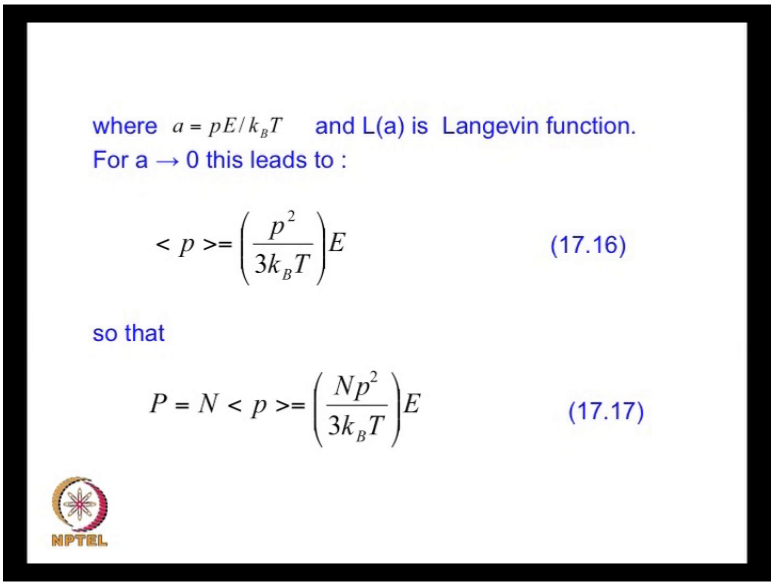

where $a = pE/k_B T$ and L(a) is Langevin function.

For a → 0 this leads to :

$$< p >= \left(\frac{p^2}{3k_B T}\right)E \qquad (17.16)$$

so that

$$P = N < p >= \left(\frac{Np^2}{3k_B T}\right)E \qquad (17.17)$$

Now, a is p E by k B T for a tend into zero that is p E by k B T tends to zero that is in small applied fields at very high temperatures P goes to p square by 3 k B T times E. So, the orientation of all receptivity is just is square by 3 k B T. And therefore, the total polarization is p equals. So, that is why orientational polarization as of and it has an inverse temperature of one temperature dependence for the absolute temperature T. So, you have a dielectric susceptibility which varies inversely with the temperature and like the electronic ionic contribution.

So, if you measure the dielectric constant as a function of temperature and plot it as of versus 1 by T, you will get a straight line for the orientational contribution which may therefore, be separate. Now this alignment, which we talk about these the equilibrium alignment of the dipoles is not of course, an instantaneous process and is govern by a relaxation time. So, there is a time dependent polarization which is due to the alignment of these dipoles this time dependence can be written.

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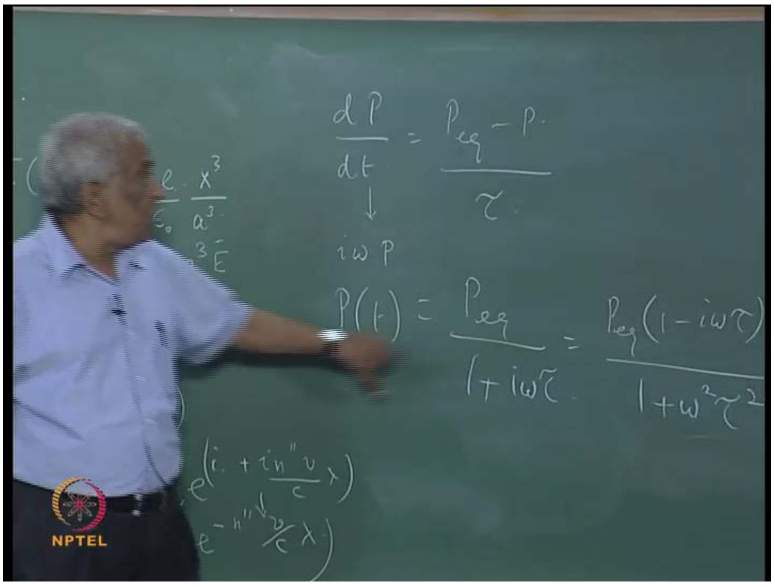

In terms of the time dependence of the polarization can be written as p equilibrium minus p by tau where tau is a characteristic relaxation time for the dipoles to get align and p equilibrium the equilibrium polarization. So, if you have this we can write this as i omega p therefore, this give you the rate equation which is p equal to p equilibrium by one minus i tau. And so one plus and this is p equilibrium one minus i omega tau by one plus omega square holes square. So, again you can see that the equilibrium polarization is complex and therefore, the relative dielectric constant due to this mechanism is also a complex quantity again the real part of which is the dispersive part and the imaginary part is the absorption. So, this is the contribution which we showed in the figures.

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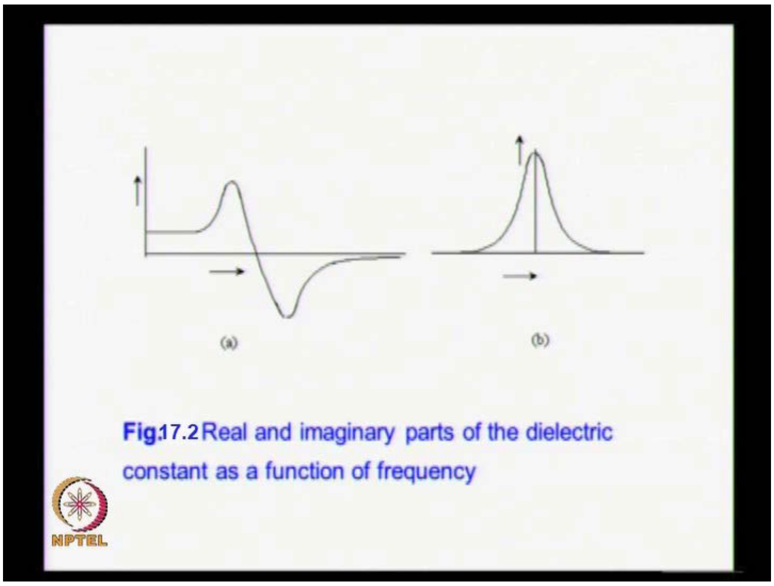

Fig.17.2 Real and imaginary parts of the dielectric constant as a function of frequency

We now come to a very important related concept namely that of ferroelectric phase transition. We talk at the beginning of this lecture course about thermodynamic phase transition such as the gas to liquid transition and then the liquid to solid phase transitions.

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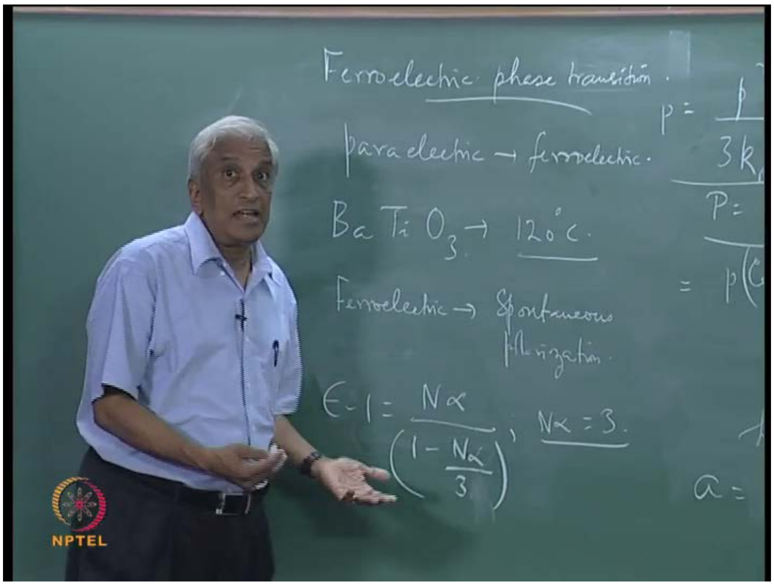

We are going to talk about another kind of phase transition, which takes place in the dielectric material which is known as the ferroelectric phase transition. So, an important this is an important class of phase transitions which go which take the material from a para electric to a ferroelectric this at low-temperature. For example, variant barium titanate is a very well-known ferroelectric material which has a ferroelectric phase transition temperature in the neighborhood of 120 degrees Celsius. So, belong hundred and twenty degrees Celsius it is ferroelectric about this it is a paraelectric. What do you mean by a ferroelectric material a ferroelectric material is characterized by existence of what is known as a spontaneous polarization there is a spontaneous polarization normally till now we have been talking about situation where an applied electric field.

Hence to create a polarization induce a polarization or orient the dipoles to produce a polarization net polarization. So, here these an entirely different situation where even in the absence of an applied electric field there is a polarization a polarization is present even when there is no applied electric field. So, it is call spontaneous polarization ferroelectrics are materials which are characterized with the existence of a spontaneous polarization whereas, a para electric is one in the there is no spontaneous polarization and you need an applied electric field in or at create a polarization now this ferroelectric behavior may be qualitatively understood from the Clausius Mossotti relationship.

Now if you take this we have something like so this let you recall this this is the cloud of Clausius Mossotti relation and look at if you look at the denominator this denominator will become zero than n alpha equal to three then there’s become zero and therefore, the a dielectric constant singular it blows up. So, this means there would be a non- zero polarization even than the field is zero this is known as the polarization catastrophe where they are dielectric constant the polarization blows up and goes to infinity because of this behavior. So, when this condition is made.

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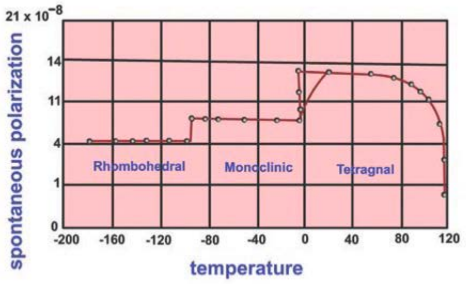

Fig 17.3 Ferroelectric phase transition in Barium Titanate

So, this behavior is illustrated in the next picture where the ferroelectric phase transition is shown in barium titanate at 120 degree Celsius. So, there is a polarization catastrophe.

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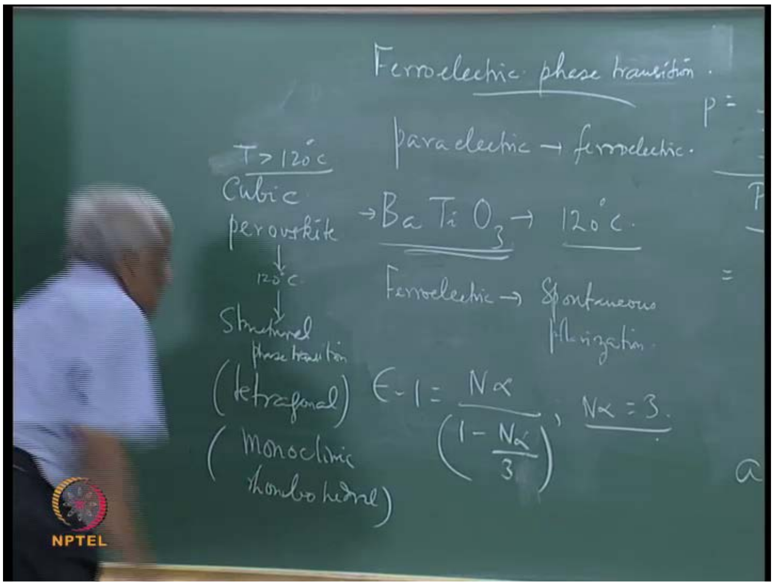

Ferroelectric phase transition.

paraelectric → ferroelectric.

T > 120°C

Cubic perovskite

↓ 120°C ↓

Structural phase transition

(tetragonal)

(Monoclinic rhombohedral)

→ $BaTiO_3$ → 120°C.

Ferroelectric → Spontaneous polarization.

$$\epsilon - 1 = \frac{N\alpha}{\left(1 - \frac{N\alpha}{3}\right)}, \quad N\alpha = 3.$$

So, above the transition temperature of a 120 degrees Celsius barium titanate exist in the cubic phase. This structure is a cubic structure which is known as the perovskite structure above where a conceive cool it below 120 degrees Celsius. There is a structural phase transition the structure the crystal structure changes along with the ferroelectric phase transition this becomes a tetragonal structure below 120 Celsius. So, and then subsequently becomes some monoclinic rhombohedral.

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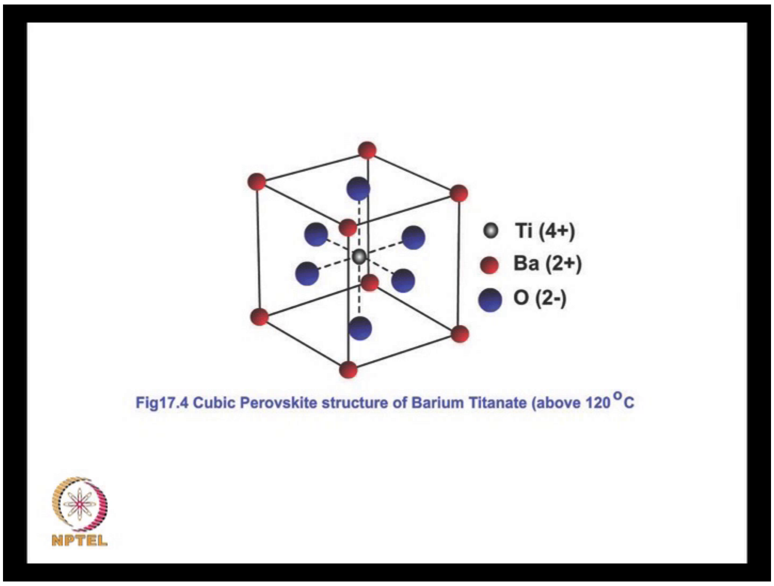

Fig17.4 Cubic Perovskite structure of Barium Titanate (above 120°C

So, this is shown in a this picture the cubic ferrite structure a barium titanate is shown in the figure. This is the structure of the barium titanate the titanium ions or at the centre of this cubic cell and surrounded by an oxygen atoms and then the barium atom occupy the corners of this cube.

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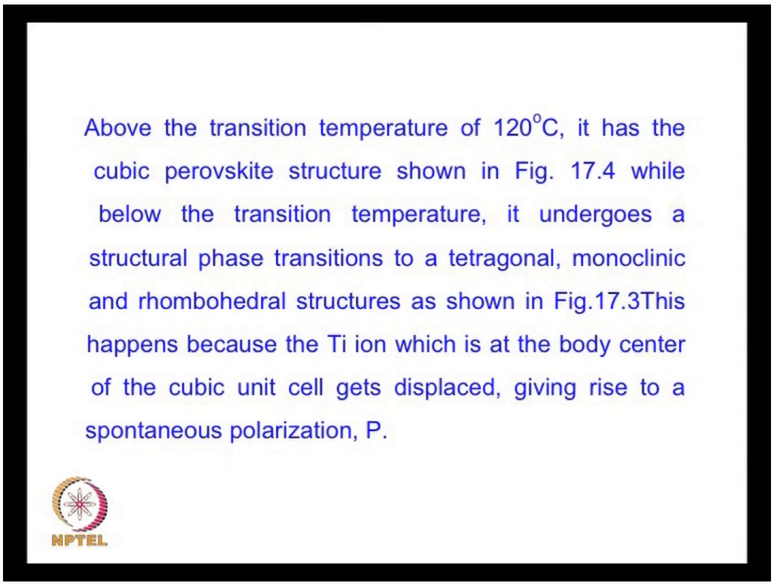

Above the transition temperature of 120°C, it has the cubic perovskite structure shown in Fig. 17.4 while below the transition temperature, it undergoes a structural phase transitions to a tetragonal, monoclinic and rhombohedral structures as shown in Fig.17.3This happens because the Ti ion which is at the body center of the cubic unit cell gets displaced, giving rise to a spontaneous polarization, P.

So, this is the structure at high temperatures, but once you cold the low 120 Celsius. This goes interior tetragonal structure because the titanium ion which is at the body centre of the cubic unit cell get displace and because of these displacement there is a spontaneous polarization this is the mechanism of the buildup of the spontaneous polarization in the ferroelectric.

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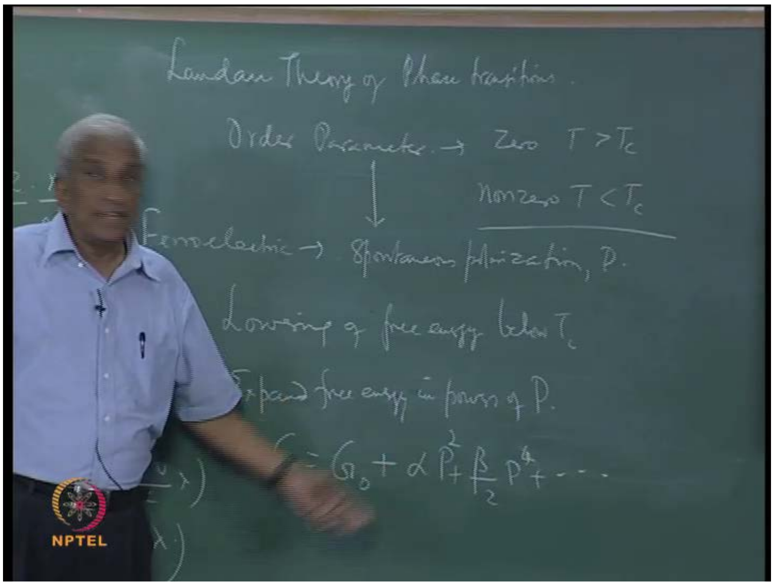

Landau Theory of Phase transitions.

Order Parameter → Zero $T > T_c$

↓ Nonzero $T < T_c$

Ferroelectric → Spontaneous polarization, P.

Lowering of free energy below T_c

Expand free energy in powers of P.

$G = G_0 + \alpha P^2 + \frac{\beta}{2} P^4 + \cdots$

Now, the general features of a ferroelectric phase transition understood in terms of landau theory of phase transition the general approach of landau theory is to define an order parameter. So, this is the crucial feature of the landau theory of phase transition defined an order parameter the order parameter can be any physical quantity which is zero or about the transition temperature and non-zero below. So, that the general definition of the order parameter in this presence case of a ferroelectric material the order parameter is the spontaneous polarization; obviously, the there is a no spontaneous polarization above t c the transition temperature and heat the spontaneous polarization existent therefore, is nonzero below t c. So, that is the order paramagnetic in this case the next step in the landau theory which is a thermodynamic theory.

This thermodynamic theory always says why should there be a phase transition, the phase transition takes place and the change there is a change in phase in this case the structural phase. And therefore, the ferroelectric phase because of a lowering of the free energy below T c. So, the free energy becomes lower in the order phase and therefore, this lowering as the free energy favors the existence of the order phase over the disorder phase. So, that is the basic explanation thermodynamic information given by the landau theory. So, how do you find this. So, you expand the free energy in powers of the order parameter in this case these spontaneous polarization.

So, we write this is the gift free energy g which is written as G naught plus alpha P plus beta by 2 p square plus etcetera P square meter the power four etcetera terms in p p cube etcetera do not exist because this as such as favorite state and central symmetry. And therefore, order powers will be vanished under the operation of the centre inversion therefore, only even powers p square p to the power four etcetera are there; all for beta are constants which have to be determine by the minimization of the ferroelectric.

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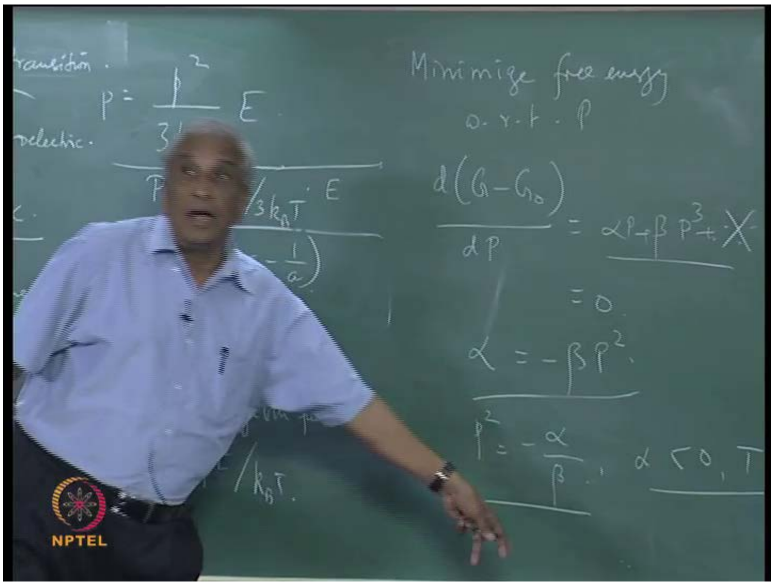

So, the entire exercise is to minimize this free energy with respect to variations in the order parameter changes in p. So, if i do that this is the free energy deference and this is minimize by taking the differential coefficient with respect to p and that will be alpha plus alpha p plus beta b cube neglecting the higher order terms was etcetera which are neglect. So, this is the derivative all the free energy difference with respect to p and we set this equal to zero for a minimum this give me alpha equal to minus beta p square or the square is minus alpha by beta. So, the minimum is characterized by a spontaneous polarization, which is minus alpha by beta. So, this is the order parameters. So, we expected to be zero above t c and nonzero below t c. So, in order that this should happen and p will be real. So, p square should be a positive definite quantity therefore, we take alpha to be less than zero for t less than t c alpha is negative, so that minus alpha by beta is positive when beta is also positive.

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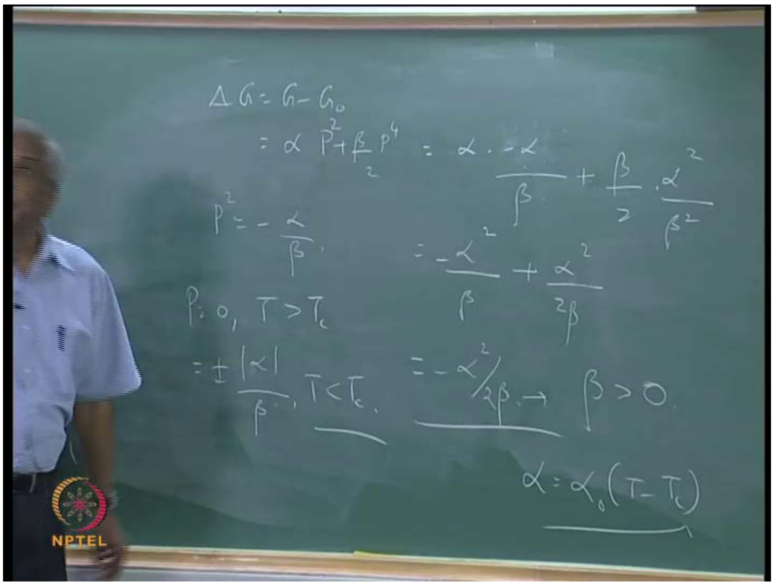

And the corresponding free energy difference when we substitute this delta G equal to G minus G naught equal to alpha P plus beta by 2 alpha P square plus beta by 2 P to the power 4. And substituting p square equal to minus alpha by beta for the minimization condition, we get this to be alpha time minus alpha or mod alpha by beta plus beta by two into alpha square by beta square. So, this gives me alpha square by beta minus plus this. So, this will be I can write this as alpha by 2 into minus alpha. So, this becomes minus alpha square plus alpha square by two beta which gives me minus alpha square by… So, one can see that there is a reduction in the free energy below T c. So, the free energy is lower we expect provided beta is positive and alpha now can be taken to be a function of T.

So, alpha can be written as alpha naught times T minus T c, so linear function of the temperature. So, we take these to be a alpha changes sign at t c and become positive making the para electric very energetically more stable at higher temperatures. So, the simplest analytical form is this and therefore, we have equal to zero for t equal to t c and p equal to zero for t greater than t c and equal to plus minus mode alpha by beta for t less than this to the power half taking square root for p square. So, the landau theory thus predicts a spontaneous polarization which goes as alpha to the power half or p goes as T minus T c or T c minus T, so half so the temperature dependence predicted by the landau theory for the spontaneous polarization.

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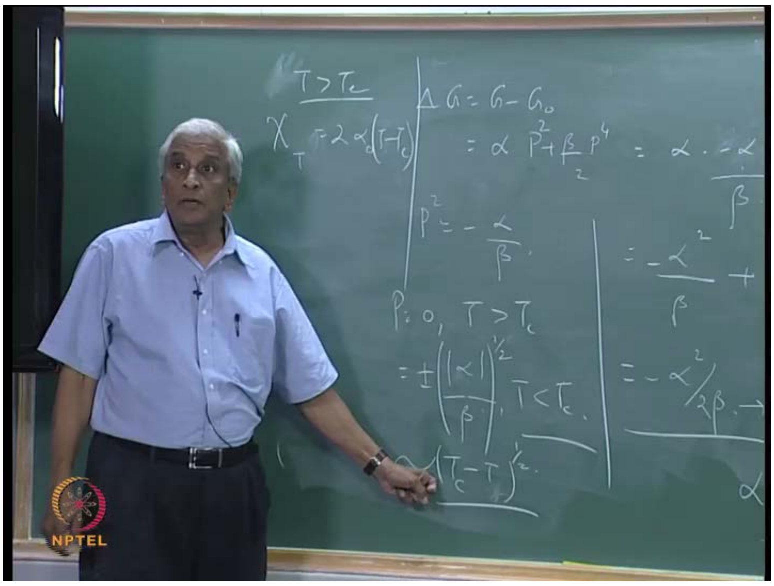

And above T c the para dielectric susceptibility goes as T greater than T c, the susceptibility goes as two alpha naught into T c, T minus T c as we conjunct readily. So, this is the temperature dependence for the susceptibility above the phase transition and this is the temperature dependence predicted for this spontaneous temperature dependence as the spontaneous polarization below T c. So, these are features which have been verify. Ferroelectric compounds in general fall into three main classes. One is the perovskite such as the barium, titanate, which you have discussed. Then there is another family, which is called the roselle salt type compound. And then a third class for which the prototype is the potassium dihydrogen phosphate type known as hydrogen bound it ferroelectrics. Dielectric in which adjacent dipoles are lined up not parallel to each other as in this case, but anti parallel to each other also exhibit a shop discontinuity in the relative dielectric constant at the transition temperature, these are known as anti ferroelectrics. In the next lecture, we will consider piezoelectric another important class of dielectric material.