Electroceramics
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Lecture - 22

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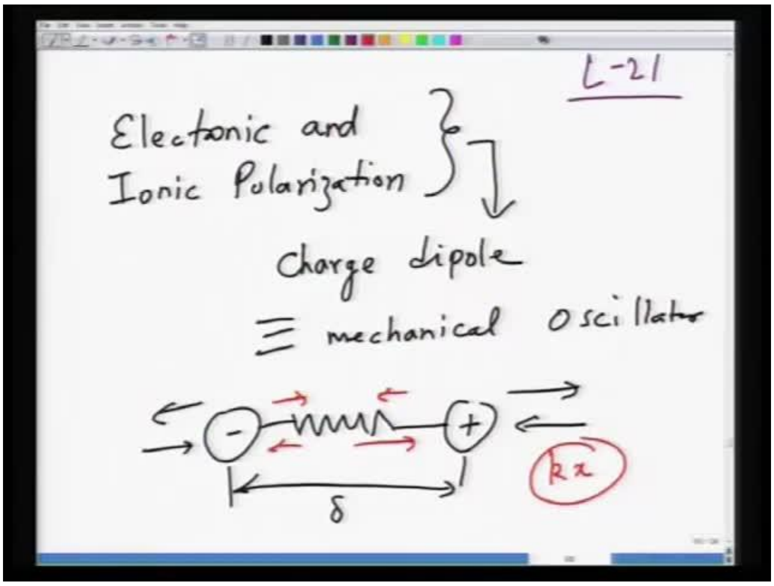

L-21

Electonic and Ionic Polarization → Charge dipole ≡ mechanical Oscillator

So, what we will do in this new lecture is to review the previous lecture first. And then go about the contents of this lecture. So, what we did in the last lecture was we started our analytical treatment of electronic and ionic polarization in the presence of AC field. That is important, because it is the AC field which which is useful for most of the practical applications and this is where and and and dielectrics are mostly used in at various frequencies of the applied field. So, it is essential to take this treatment. So, for electronic and ionic polarization where you know that charge where positives, center's of positive negative charges they separate away from each other giving rise to a permanent dipole, giving rise to a dipole moment upon the application of electric field.

Now, when the application, when the electric field is applied, the charge center separate giving rise to dipole moment and the electric field is removed, charge centers come back together to the concentric position giving rise to 0 dipole moment or in the symmetrical position to giving giving rise to 0 dipole moment.

Now, this can be treated. Now, in the in the case of, in the case of applied field which is AC alternating the field is changing its sign. So, fielding is going, field is for example, follow behavior of let us say a sin wave or cos wave. So, which means as time, it increases then decreases then goes back to other side of the time plot and so on and so forth, it keeps happening. So, what happens when the field switches back and forth like this? What happens to the, this charge dipole. Now, the best way to represent the behavior of this charge dipole is to consider this charge dipole like a mechanical oscillator.

So, when you apply field in this direction it stretches in this direction and the spring force which is k x tries to pull it back into this direction. So, the applied field is is is is balanced by acceleration force and spring and the and the spring force and there is a another term which is called as damping because most of the systems undergo damping because of inherent friction in the system. So, as a result this system which is nothing but a linear mechanical oscillator can be described by what is called as a equation of motion.

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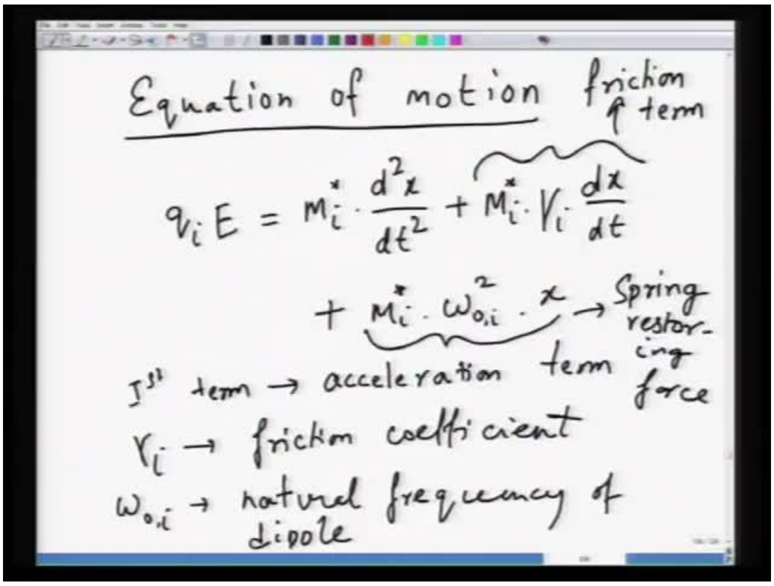

Equation of motion

$$q_i E = M_i^* \cdot \frac{d^2x}{dt^2} + \overbrace{M_i^* \cdot \gamma_i \cdot \frac{dx}{dt}}^{\text{friction term}} + \underbrace{M_i^* \cdot \omega_{0,i}^2}_{} \cdot x \rightarrow \text{Spring restoring force}$$

1st term → acceleration term

γ_i → friction coefficient

$\omega_{0,i}$ → natural frequency of dipole

So, here we saw that the field the force due to applied field equals the force due to acceleration plus force due to friction plus the force due to spring spring restoring force. Now, solving this equation gives you the displacement x in terms of frequency.

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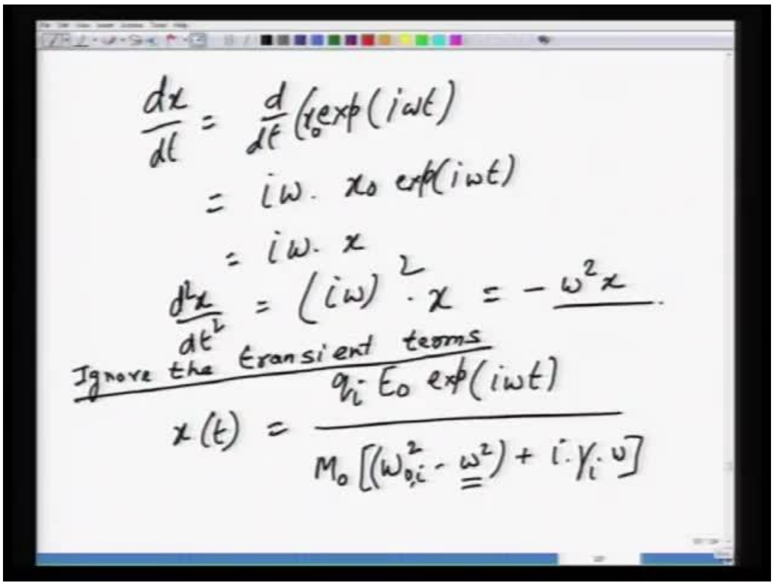

$$\frac{dx}{dt} = \frac{d}{dt}\left(x_0 \exp(i\omega t)\right)$$

$$= i\omega \cdot x_0 \exp(i\omega t)$$

$$= i\omega \cdot x$$

$$\frac{d^2x}{dt^2} = (i\omega)^2 \cdot x = \underline{-\omega^2 x}$$

Ignore the transient terms

$$x(t) = \frac{q_i E_0 \exp(i\omega t)}{M_0\left[(\omega_{0,i}^2 - \underline{\underline{\omega^2}}) + i \cdot \gamma_i \cdot \omega\right]}$$

So, we if you if you solve it for e is equal to E naught exponential i omega t you get the expression for x which is this. So, it has a dependence upon what is called as omega o i which is the, which is a resonant frequency for that given charge dipole depending upon the type of dipole. And since we consider this as a mechanical oscillator it has to undergo resonance. So, this is the resonant frequency, omega is the applied frequency and this is the field term on top.

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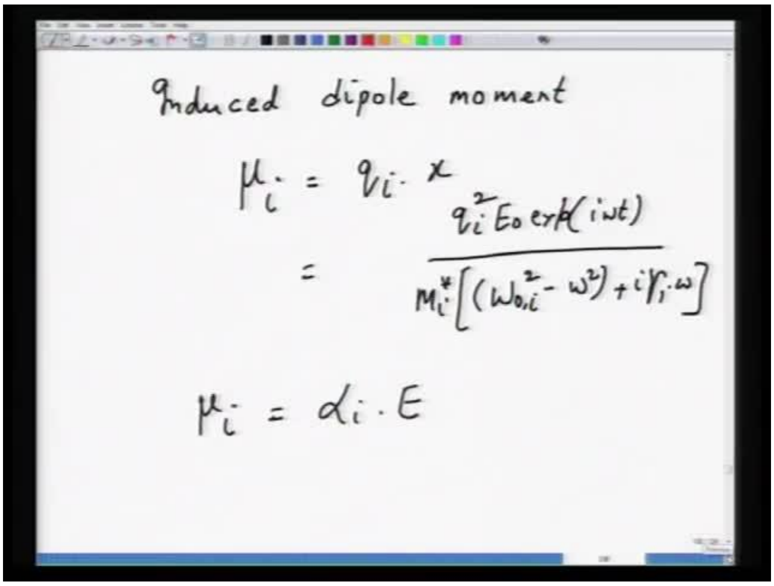

Induced dipole moment

$$\mu_i = q_i \cdot x$$

$$= \frac{q_i^2 E_0 \exp(i\omega t)}{M_i^*\left[(\omega_{0,i}^2 - \omega^2) + i\gamma_i \cdot \omega\right]}$$

$$\mu_i = \alpha_i \cdot E$$

This can be converted into, this can be put it, put back into the induced dipole moment which is nothing but charge multiplied by the displacement and as a result from that you can calculate what is called as polarizability. So, when you now look at the expression for polarizability.

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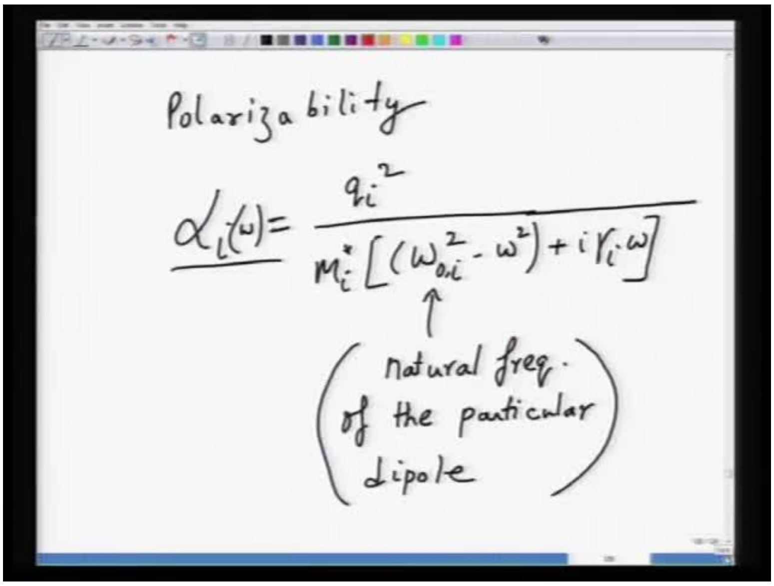

Polarizability

$$\underline{\alpha_i(\omega)} = \frac{q_i^2}{m_i^*\left[(\omega_{0i}^2 - \omega^2) + i\gamma_i\omega\right]}$$

(natural freq. of the particular dipole)

This polarizability expression has frequency dependence. So, this is this is there is something which is new which we haven't seen before I mean the earlier treatment which we took that was a very simple force balance model, but that did not have a frequency dependence because we considered there AC field.

So, here we have, what we have seen is there is a frequency dependence and this also explains if we earlier, if you earlier remember we we drew the plot between dielectric constant versus frequency and there was some anomalous regions specially for electronic and ionic polarization and this is explained by this frequency dependence.

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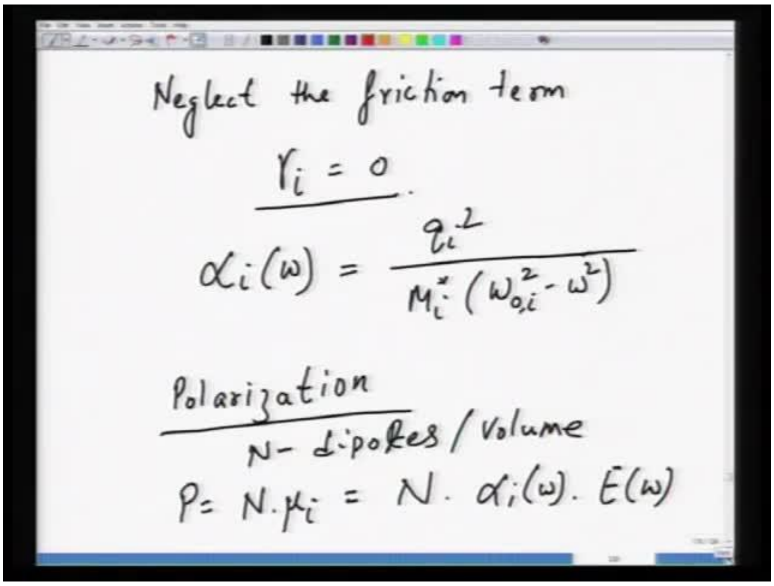

Neglect the friction term

$$\underline{\gamma_i = 0}$$

$$\alpha_i(\omega) = \frac{q_i^2}{M_i^*(\omega_{0,i}^2 - \omega^2)}$$

Polarization

N- dipoles / Volume

$$P = N.\mu_i = N.\alpha_i(\omega).E(\omega)$$

So, based on this you can calculate the polarization.

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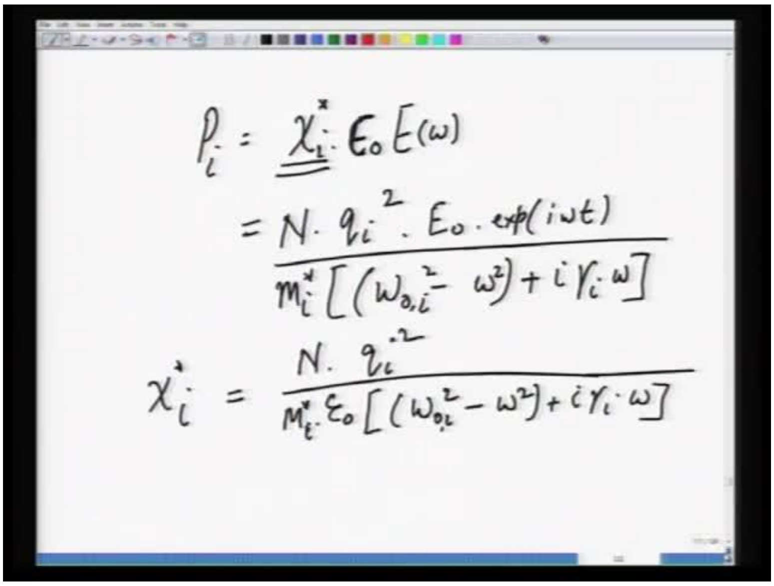

$$P_i = \underline{\underline{\chi_i^*}}.\varepsilon_0 E(\omega)$$

$$= \frac{N.q_i^2.E_0.\exp(i\omega t)}{m_i^*[(\omega_{0,i}^2 - \omega^2) + i\gamma_i\omega]}$$

$$\chi_i^* = \frac{N.q_i^2}{M_i^*.\varepsilon_0[(\omega_{0,i}^2 - \omega^2) + i\gamma_i.\omega]}$$

And and from that you can extract what is called as susceptibility which again is a complex quantity has a frequency dependence.

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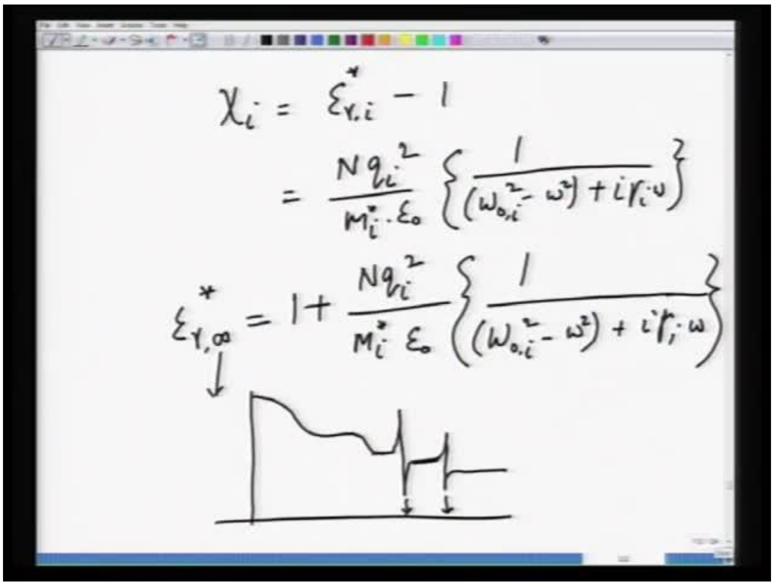

$$\chi_i = \varepsilon^*_{r,i} - 1$$

$$= \frac{N q_i^2}{M_i^* \cdot \varepsilon_o} \left\{ \frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma_i \omega} \right\}$$

$$\varepsilon^*_{r,\infty} = 1 + \frac{N q_i^2}{M_i^* \varepsilon_o} \left\{ \frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma_i \omega} \right\}$$

And from this we are able to determine what is the dielectric constant and this dielectric constant as you can see is nothing but epsilon r infinity which is a static dielectric constant is 1 plus N q i square divided by M i star epsilon naught into 1 divided by omega o i square minus omega square plus i gamma i omega and it is the dependence of this electric constant on these on on omega here which gives rise to these peaks here.

So, depending upon whether you are talking about electronic polarization or ionic polarization this mass will change but not only the mass will change but also omega o i will change which is a resonant frequency. So, for electronic polarization the resonant frequency will be on the righter side which is about roughly 10 to power 15 hertz and for ionic polarization when dipole gets heavier then omega o i is lower approximately 10 to the power 12, 13 hertz.

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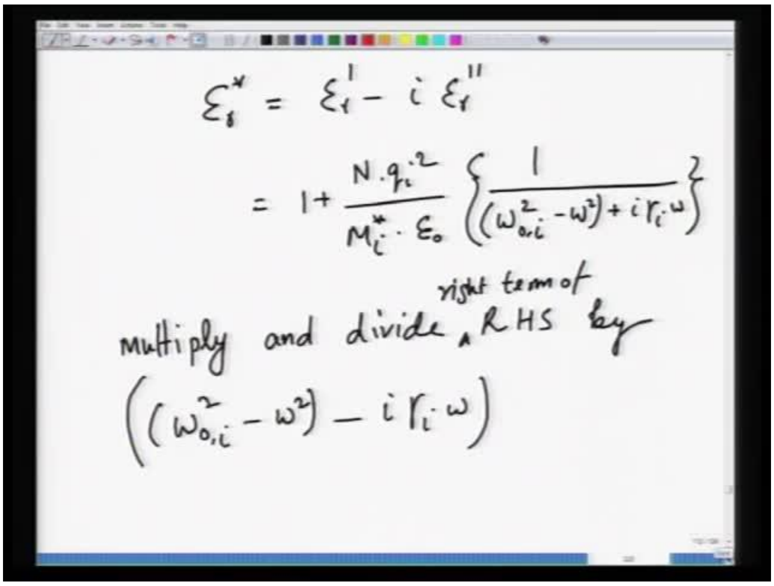

$$\varepsilon_r^* = \varepsilon_r' - i\,\varepsilon_r''$$

$$= 1 + \frac{N.q_i^2}{M_i^* \cdot \varepsilon_0}\left\{\frac{1}{(\omega_{0,i}^2 - \omega^2) + i\gamma_i \omega}\right\}$$

multiply and divide right term of RHS by

$$\left((\omega_{0,i}^2 - \omega^2) - i\gamma_i \omega\right)$$

And from this you can also extract the real and imaginary part of a dielectric constant and you can have a look in terms of the dependence on omega i omega.

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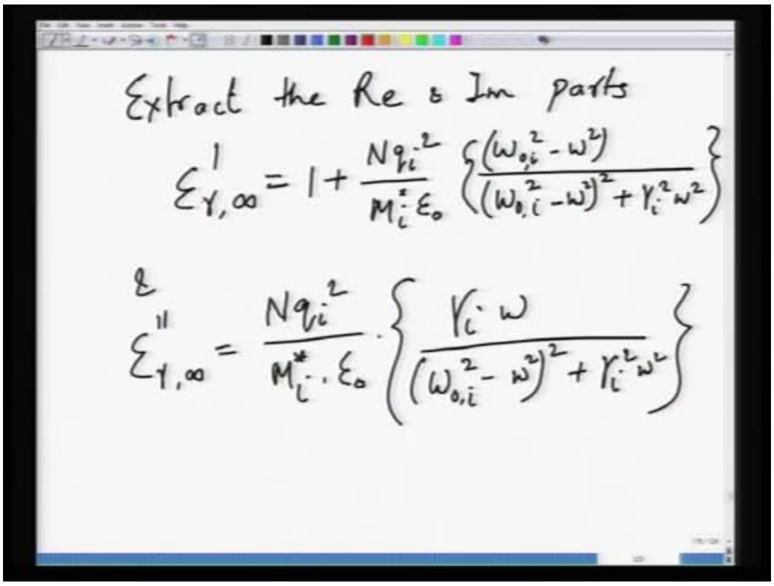

Extract the Re & Im parts

$$\varepsilon_{r,\infty}' = 1 + \frac{Nq_i^2}{M_i^* \varepsilon_0}\left\{\frac{(\omega_{0,i}^2 - \omega^2)}{(\omega_{0,i}^2 - \omega^2)^2 + \gamma_i^2 \omega^2}\right\}$$

&

$$\varepsilon_{r,\infty}'' = \frac{Nq_i^2}{M_i^* \cdot \varepsilon_0} \cdot \left\{\frac{\gamma_i \omega}{(\omega_{0,i}^2 - \omega^2)^2 + \gamma_i^2 \omega^2}\right\}$$

And if I go to next slide so this is the expression for omega r prime, this is the expression for omega r double prime and based on these two expressions you can make a plot of dielectric constant versus frequency.

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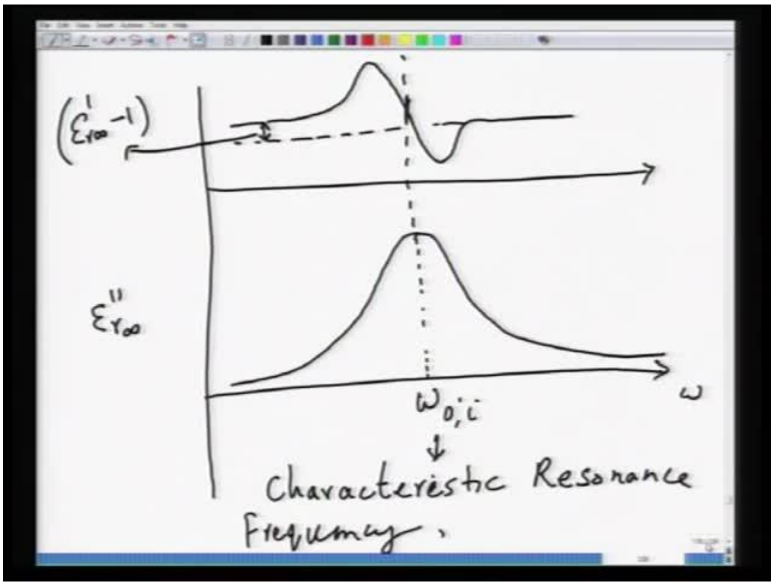

And you can see that when you plot a static dielectric constant versus frequency, it has this anomalous region and in this region at omega naught o i the charges are completely, the charges resonate with the applied field.

So, when the resonance occurs the loss is maximum epsilon r double prime goes under undergoes through a maxima. In order for any the particular polarization mechanism to be active the omega that you apply has to be smaller than omega o i. So, for instance for electronic polarization omega has to be smaller than omega o i. So, that you get electronic contribution to the polarization and for ionic contribution to occur you have to apply omega which is smaller than omega naught for ionic polarization. So, this is what we learnt in the in the previous lecture.

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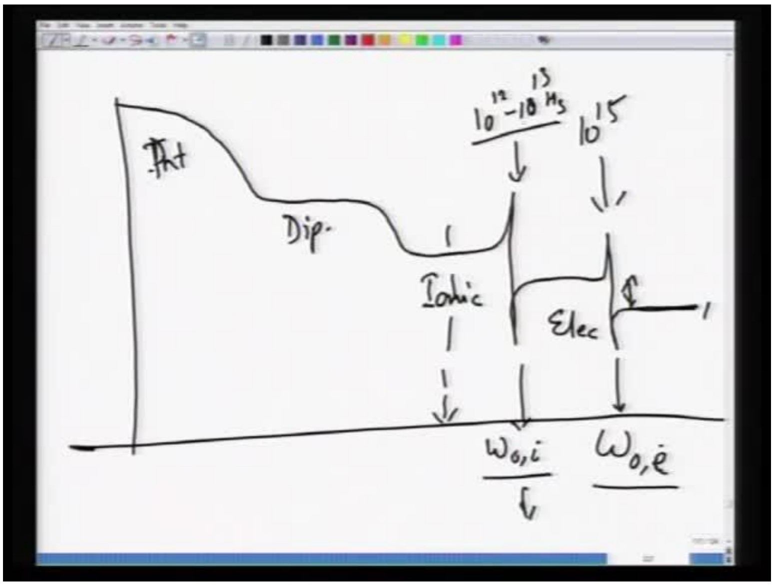

And so you can explain the the origin of these two peaks, which are nothing but due to resonance.

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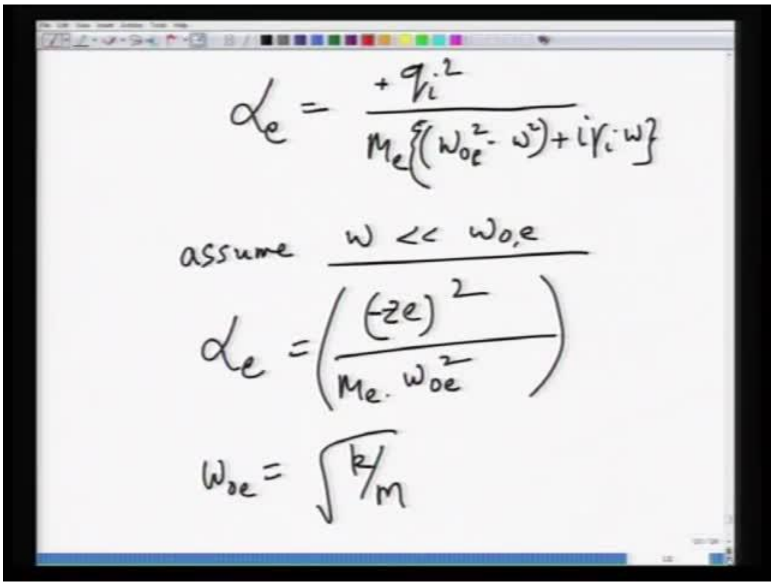

$$\alpha_e = \frac{+q_i^2}{M_e\{(\omega_{oe}^2 - \omega^2) + i\gamma_i\omega\}}$$

assume $\omega << \omega_{o,e}$

$$\alpha_e = \left(\frac{(-ze)^2}{M_e \cdot \omega_{oe}^2}\right)$$

$$\omega_{oe} = \sqrt{k/m}$$

And you can also simplify this equation again bringing it, bringing back to what we learnt earlier how we derived by using just a force balanced model. So, if you just make this let us say for a static values omega is much smaller then omega o e you can simplify this equation as minus z e square divided by M omega e square and if that was true and omega o e can be related to your spring constant which is root and which is also omega o e is equal to root k k by M.

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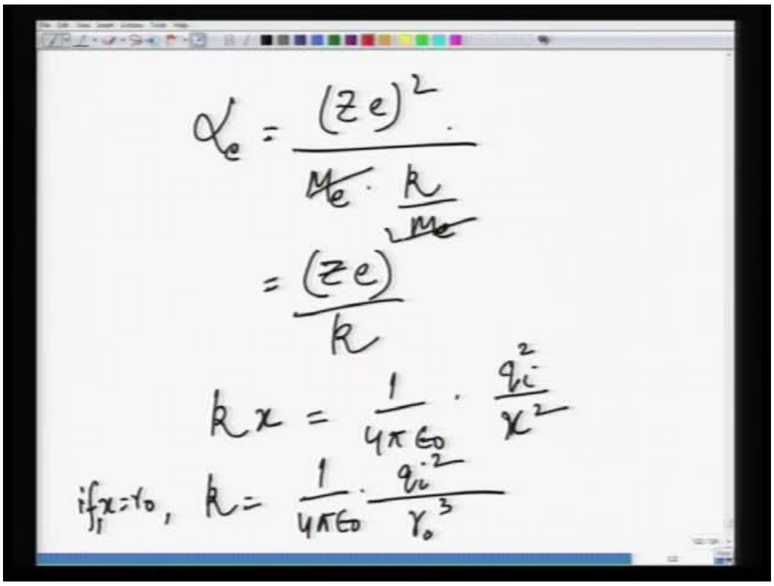

$$\alpha_e = \frac{(ze)^2}{\cancel{M_e} \cdot \frac{k}{\cancel{M_e}}}$$

$$= \frac{(ze)}{k}$$

$$kx = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_i^2}{x^2}$$

$$\text{if } x = r_0, \quad k = \frac{1}{4\pi\epsilon_0} \cdot \frac{q_i^2}{r_0^3}$$

And if you just make the substitutions alpha becomes equal to z e square divided by k and from the force balance you can write k x is equal to 1 by 4 pi epsilon naught q i square divided by x square, x is nothing but r naught. So, k becomes equal to 1 by 4 pi epsilon naught into q i square divided by r naught q.

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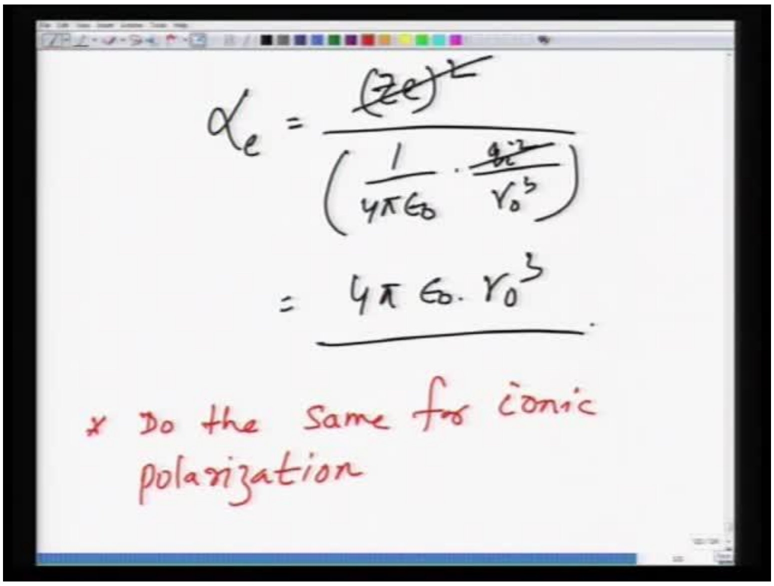

$$\alpha_e = \frac{\cancel{(ze)^2}}{\left(\frac{1}{4\pi\epsilon_0} \cdot \frac{\cancel{q_i^2}}{r_0^3}\right)}$$

$$= \underline{4\pi\epsilon_0 \cdot r_0^3}$$

x Do the same for ionic polarization

And if you make the substitution you get the value of alpha which is nothing but 4 pi epsilon naught r naught q. So, this explains that the model that we have adopted now is nothing wrong with this model, it is just that this model takes a frequency dependence into the picture and if you if you if you get rid of that frequency you get back to the same equation that we derived earlier. And if you do the same thing for ionic polarization you will again retrieve the same equation that we derived earlier.

So, basically what we did we derived expressions for electronic and ionic polarizabilities, incorporating the frequency dependence by taking into account the application of AC electric field. So, what what we will do now is to look at the dipolar polarization where the mechanism is rather different.

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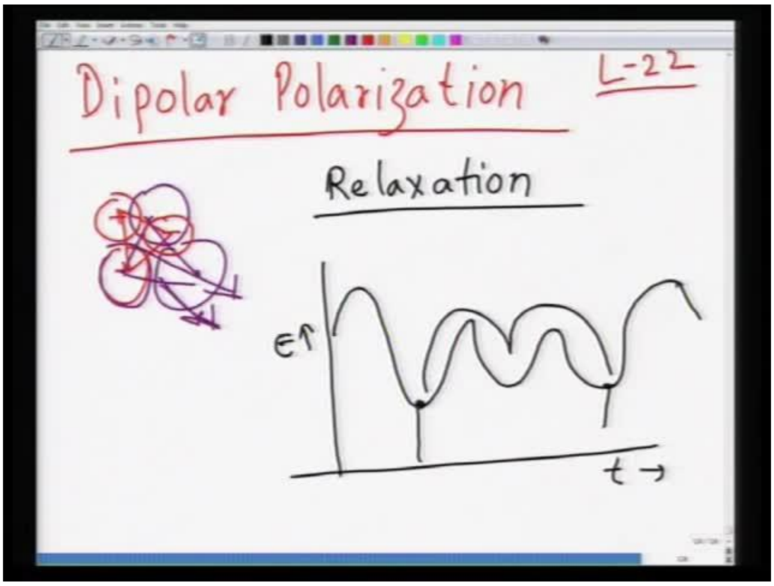

So, so we will look at this dipolar polarization. Now, this dipolar polarization is rather different because what happens here is first of all dipolar polarization occurs in solid which already have a permanent dipolar moment. So, for instance you can have, I am always taking this example of water molecule which is a simplest. So, this water molecule has a built in dipole moment because of asymmetry associated with the molecule. So, as a result this, the vertical components cancel each other the horizontal components survives.

So, this has a permanent dipole moment. When this has a permanent dipole moment what happens is now within within the space this molecule will have several sorry if you if you put this molecule in this, this situation, this is one situation you can turn it back. When you apply field let us say in this direction this molecule rotates itself in such a manner so that so that now the dipole moment aligns in the direction of applied field. So, as a result this new position becomes the more, the new equilibrium position. When you remove the field this does not necessarily go back to this position rather it might adopt some other equilibrium position.

So, since this is a heavy molecule you can see that this molecule has to turn back or move back into the some equilibrium position and this movement requires time and that is why this phenomena of dipolar polarization is associated with what we call as relaxation. And this relaxation, basically relaxation the molecule relaxes back to the equilibrium position and this relaxation process is very commonly found in most of the ceramics and ionic solids and especially in glasses and and this happens typically in the low frequency region where where if you apply this damped oscillator model that does not work very well so you have to start with the new model all together.

Now, this movement of atom from one position to another is is a is a is a phenomena which is which is diffusional in nature. As you know from the earlier lectures diffusion is a process which is thermally activated phenomena. Similarly, this processes is also very say very strongly temperature dependent just like diffusion. So, since diffusion is slow process again this relaxation process takes reasonably long time so that redistribution of charges can occur upon the application or removal of electric field.

So, essentially you can describe this in such manner. So, you have this energy plot here versus time and let us say these are various states. So, if you have let us say the atom hops from this position to that position. So, it has to go from this position to that position by hopping and this hopping is nothing but a temperature dependent phenomena. So, as a result the energy required in this case is high and you have to operate in the low frequency region. This is typically a low frequency phenomena which happens upon the application of electric field. So, what we can do is that.

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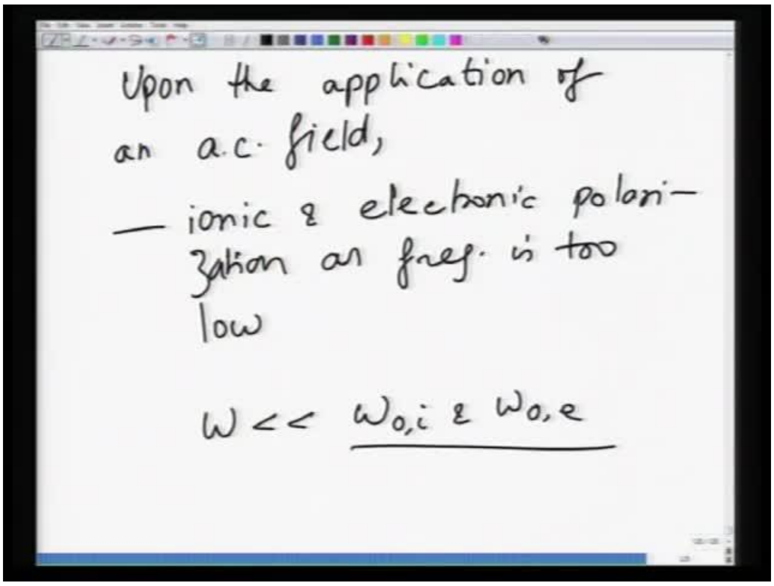

Upon the application of an a.c. field,

— ionic & electronic polarization as freq. is too low

$\omega << \underline{\omega_{o,i} \; \& \; \omega_{o,e}}$

So, let us take the, so let us, so when you when you apply field upon the application of field and upon the application of AC field what happens is that the polarization develops. So, you have now when the frequency decreases certain values you have a inbuilt polarization mechanism so you will have of course, have ionic and electronic polarization occurring as frequency is too low. So, omega in this case will be much smaller than omega o i and omega o e. So, both of these phenomena’s will occur in any case.

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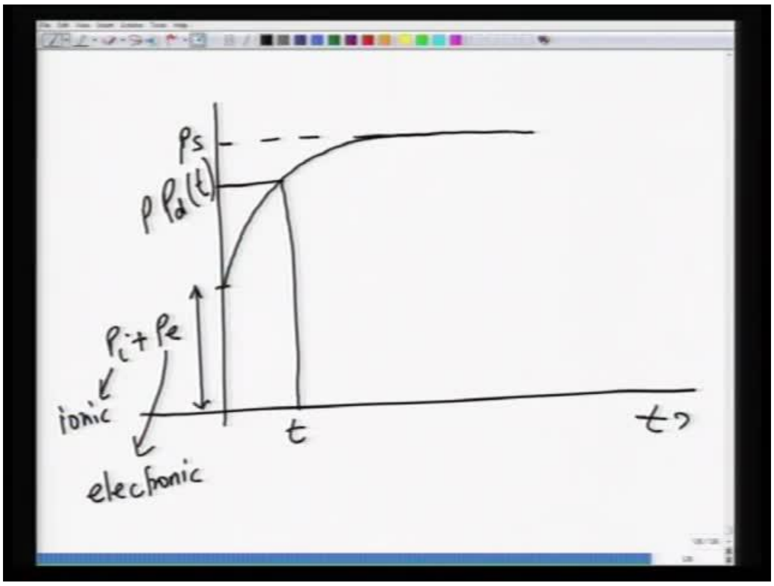

Now, as a function of time what will happen is upon the application of electric field when you plot this polarization versus time. So, P is the polarization t is the time. So, you have almost inbuilt polarization which is nothing but sum of P i plus P e where i is the ionic component, ionic polarization component and this is due to electronic and then slowly this develops into what is called as a saturation polarization P s and polarization at any time t is defined as P d t. This is the dipolar polarization which eventually converts into P s and P s is the saturation polarization when all the dipoles have aligned themselves into the direction of applied field, but since this molecules are heavier they take time, they do not respond to the applied field immediately.

So, as a result there is a strong dependence on the frequency and time and typically it happens to be a low frequency phenomena because of longer times required for migration to occur from one position to another.

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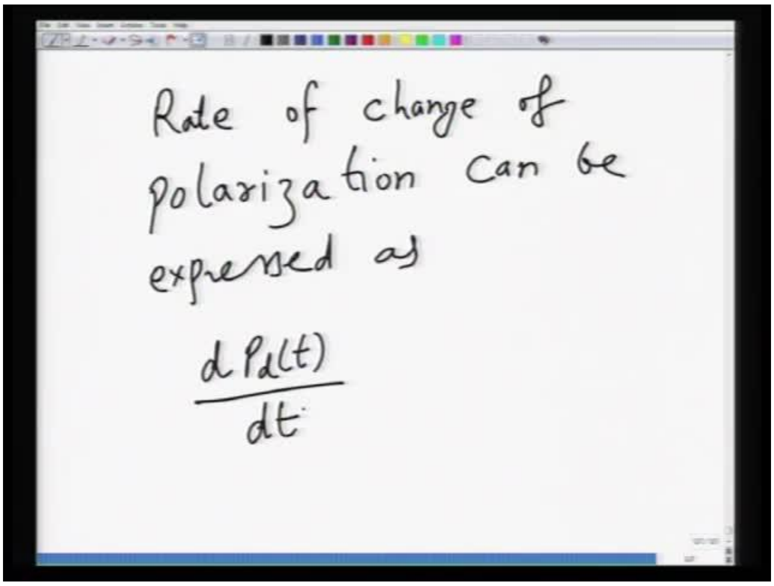

Rate of change of polarization can be expressed as

$$\frac{d P_d(t)}{dt}$$

And this rate of change of polarization, so can be expressed as d P d t by d t.

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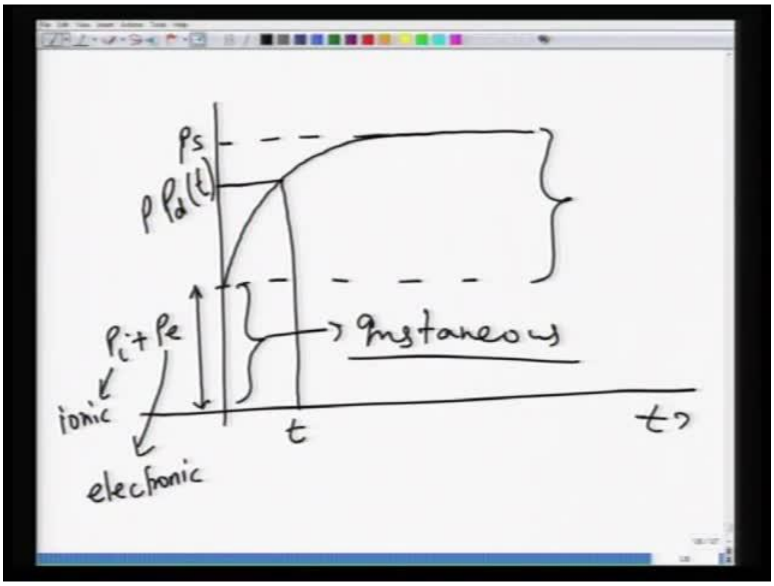

So, rate of change of basically we are talking in the regime which is if you go to the previous plot we are talking of the, this regime basically. So this is the instantaneous polarization you can say and this instantaneous polarization is because of ionic and electronic mechanisms and since they are too fast they almost develop instantaneously, but then for the dipolar polarization to occur it takes time.

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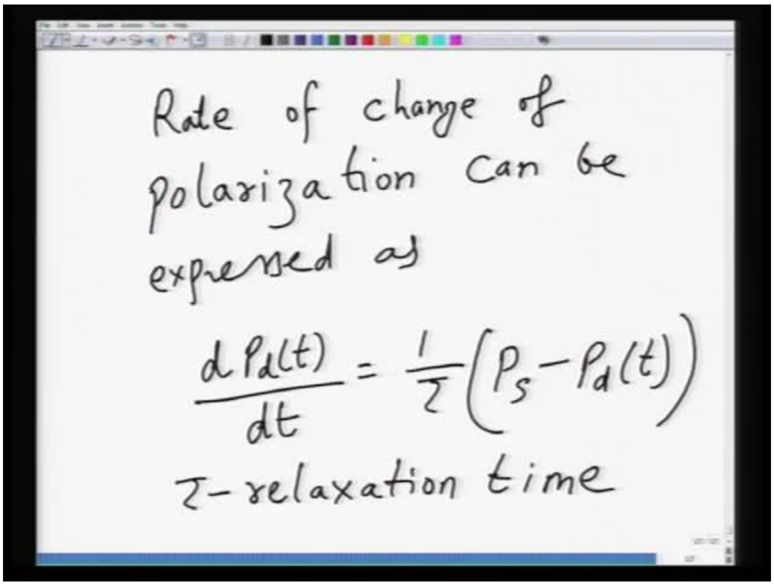

Rate of change of polarization can be expressed as

$$\frac{dP_d(t)}{dt} = \frac{1}{\tau}\left(P_s - P_d(t)\right)$$

τ – relaxation time

So, this rate of change of dipolar polarization can be expressed as d P d by d t is equal to 1 over tau into P s which is a saturation polarization minus P d t. So, this is a basic equation which governs the development of this dipolar polarization.

Now, how do we arrive at this situation? How do we arrive at this equation? We will look at it in a while and if we have tau is the relaxation time or you can say 1 by tau is nothing but your proportionality constant which gives rise to tau as a relaxation time. So, what we will do now is we will look at how this equation comes about? So, so what we will do is that let us take let us take a hypothetical picture.

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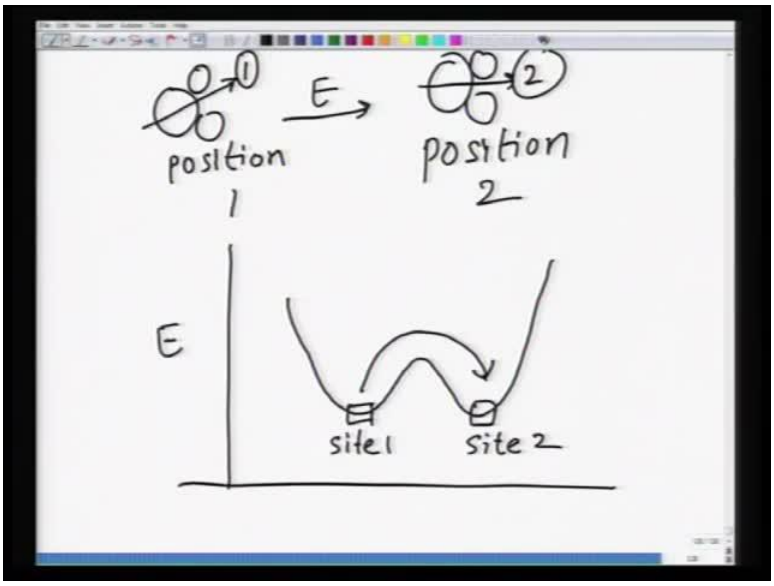

So, we have this molecule with let us say dipole vector in this direction. So, this is let us say is position 1 and when you apply field in this direction it comes back to, it comes to this position so this is mu 1, this is mu 2. Well mu is same, it is just that let us say, let us not confuse. So, let us say just this is 1 and this is 2. So, this is called as position 2. So, when you apply field this is how it happens. So, how do you represent this in terms of energy? So, if you draw energy then it goes from site 1, site 2. So, this is site 1, this is site 2. So, it has to hop from this position to that position and this is for instance you can call about you can you can you can imagine.

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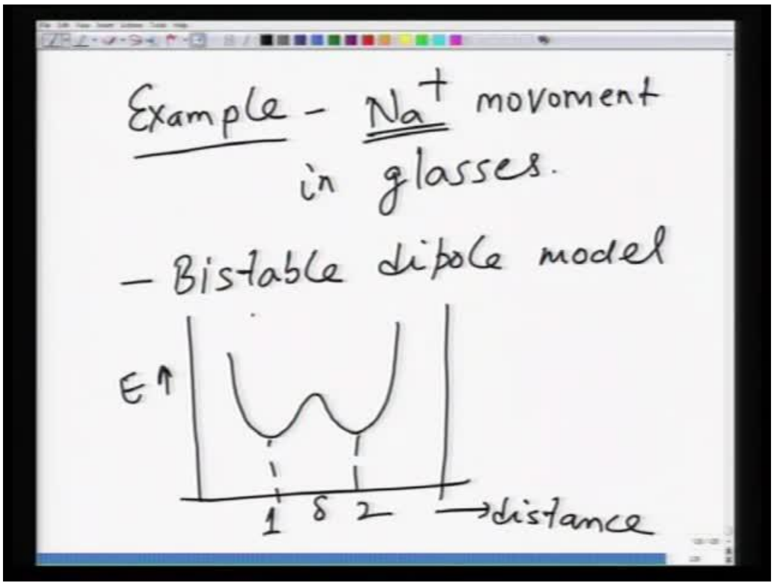

Example - Na^+ movoment in glasses.

- Bistable dipole model

So, example can be sodium plus. Now, sodium is an ion which is present in, which is the mobile ion in glasses and fast ionic conductors. So, sodium plus movement in glasses, so this is the mobile ion. So, now how do you, we will we will we will do a little bit more analytical treatment. So, consider what is called as a bistable dipole model and so sodium ion is moving from left to right. Again we draw this picture. So, we have this distance called as delta from 1 to 2 and this is again energy. So, as a sodium atom moves from left to right there is a change in the coordinate, but at any given temperature above 0 K there is a finite probability of hopping either to this site or to other site. So, whether to left or whether to right there is a finite probability of hopping.

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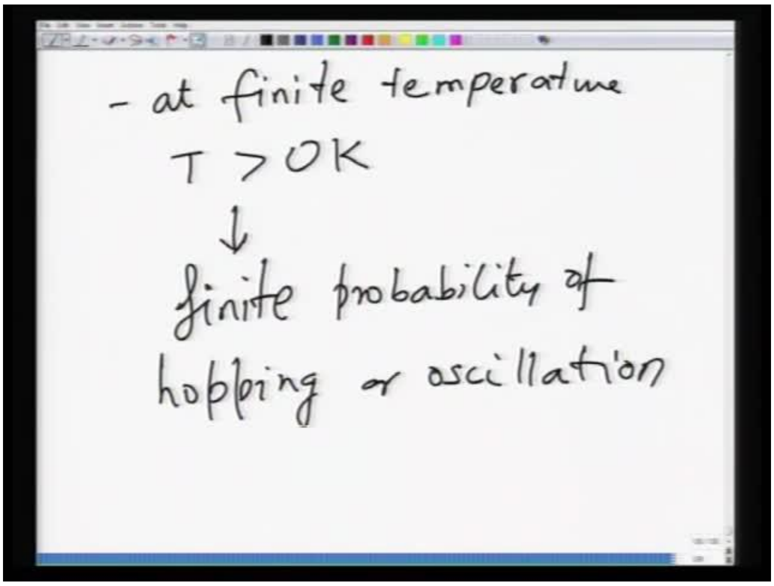

- at finite temperature

$T > 0K$

↓

finite probability of

hopping or oscillation

So, this hopping probability, so at finite temperature T above 0 K is a finite probability of hopping or you can say oscillation and how do you calculate this probability?

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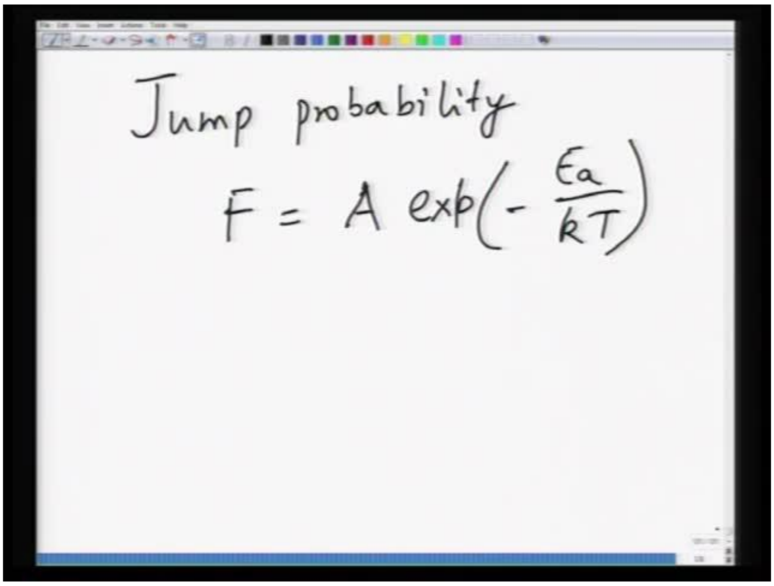

Jump probability

$$F = A \exp\left(-\frac{E_a}{kT}\right)$$

This probability is given as so this jump probability let us say F is defined as A into exponential minus of E a divided by k T where what is E a here? So, this is my like a Arrhenius equation.

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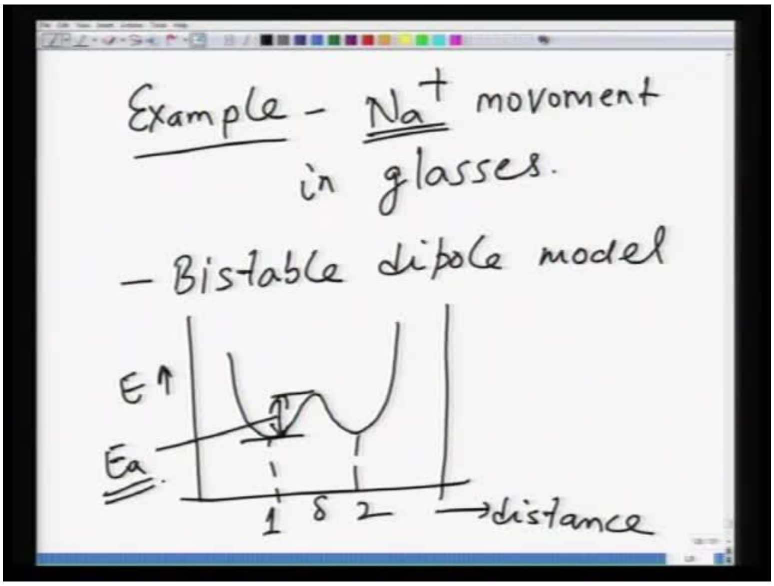

Example – Na^+ movoment in glasses.

– Bistable dipole model

So, this E a is nothing but this. So, this is E a, the energy barrier which needs to be overcome for ion to move from position 1 to position 2. So, we go from position 1 to position 2 there is a finite probability, it can it can do that in reverse direction as well. So, there is so when when you do not have any field there is a random probability of jumping, there is a probability of jumping in random directions. So, as a result net there is that the material does not show any kind of polarization even though it has a finite dipole moment because of this randomness associated with the jumps.

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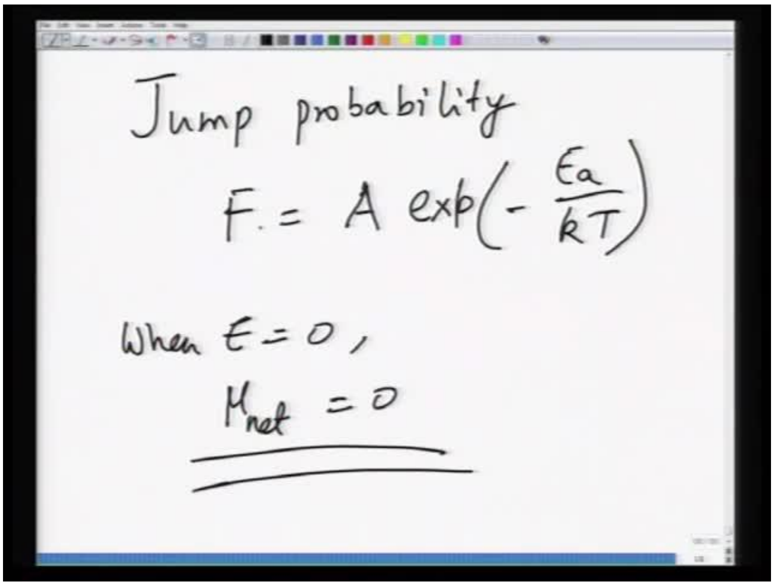

Jump probability

$$F. = A \exp\left(-\frac{E_a}{kT}\right)$$

When $E = 0$,

$$\mu_{net} = 0$$

Now, what happens when you apply electric field? So, when E is 0 even for a polar material like water the mu net is equal to 0 since there is randomness associated with this jump.

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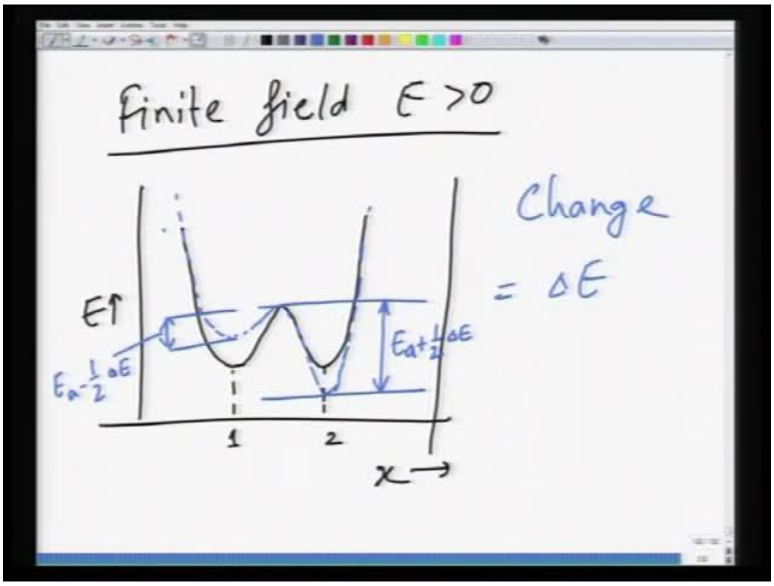

Now, when you apply a finite amount of field, so finite field E greater than 0 what happens in this case upon the application of field when you again draw this energy well diagram. So, this is E versus x. Now, so the initial picture was let us say this picture and these two are equivalent sides 1 and 2. When you apply field then the situation changes little bit. So, what happens is the energy will on one side increase in height as compared to energy wells on other side.

So, this and the magnitude of this energy is so this or rather let us say so this magnitude of change would be so delta E would be equal to z e. So, it would be z e E so let us say I will I will give you the value of this delta E little later, but let us say this is so change let us say is equal to delta E. So, what happens is that energy on this side increases by a magnitude E a plus half delta E and energy on this side becomes E a minus half delta E upon the application of electric field.

So, the probability, now, so when you have this kind of situation the energy wells on one side as are decreasing in depth, another side they are raising in height. So, as a result the barrier on one side becomes smaller, another side becomes lower the the the the probability on jump to both the side also changes.

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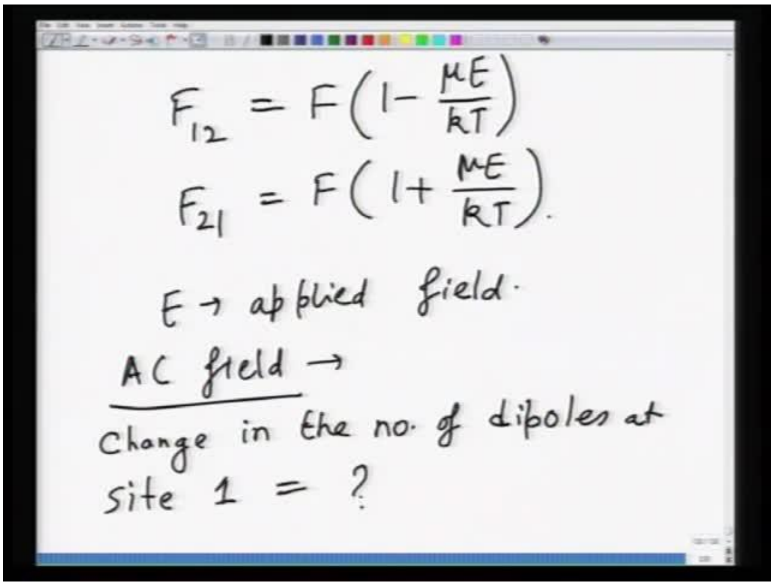

$$F_{12} = F\left(1 - \frac{\mu E}{kT}\right)$$

$$F_{21} = F\left(1 + \frac{\mu E}{kT}\right).$$

$E \rightarrow$ applied field.

AC field →

Change in the no. of dipoles at site 1 = ?

So, so when you apply field then F 1 2 which is the probability from 1 to 2 will be F multiplied by 1 minus mu E by k T and mu E as you know is the energy, if you if you recall the module module 4 and when we did the calculation of dipolar polarizability so mu E defines the dipole the the potential energy. So, since the potential energy of this potential energy well of ionic movement from 1 to 2 has increased decreased so as a result there is a probability of moving from 1 to 2 is F into 1 minus mu E by k T, on the other hand probability of moving from 2 to 1 F 2 1 becomes 1 plus mu E by k T.

So, where E is this applied field. Now, under AC field when you apply AC field, so when you have probability. Now, I am not saying at the moment which probability is more, which probability is less that you can determine from the magnitude of these probabilities by taking equation into account. So, when this kind of situation happens when the probability of movement in one direction is different from other direction in that case there is a net change in the number of the charge or dipoles at any given site. So, let us say change in the number of dipoles at site 1. So, we are interested in calculating this. So, what is this equal to?

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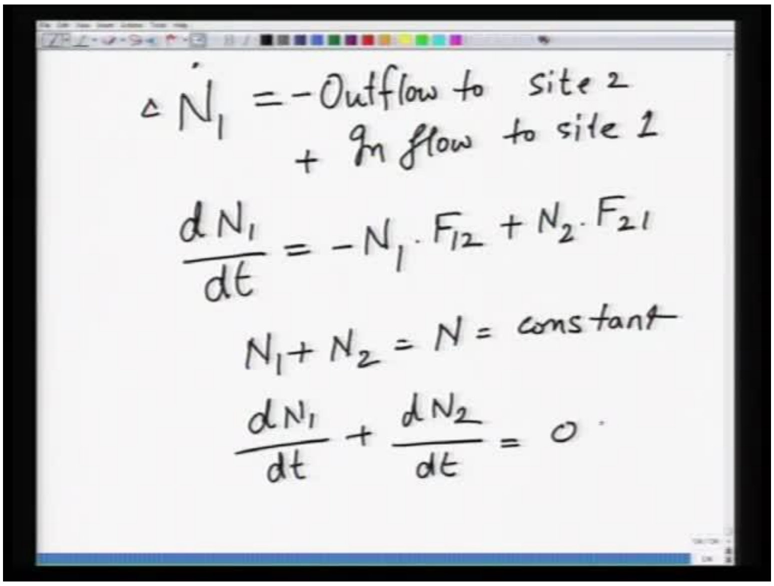

$\Delta \dot{N}_1 = -$ Outflow to site 2 + In flow to site 1

$$\frac{dN_1}{dt} = -N_1 \cdot F_{12} + N_2 \cdot F_{21}$$

$$N_1 + N_2 = N = \text{constant}$$

$$\frac{dN_1}{dt} + \frac{dN_2}{dt} = 0$$

So, let us say this change. So, so we define this as delta N 1. So, delta N 1 is equal to let us what will be this equal to? Outflow to site 2 minus inflow to site 1 because not only there is outward movement from site 1 to site 2 or any other site, but there is also inward movement since we are considering only site 1 and site 2. So, the net change in the dipole density or number of dipoles at site 1 will be equal to whatever has moved out from site site 1 to site 2 minus of whatever whatever has come to site 1 from site 2. So, this can be determined as, this can be written as so we can say so delta N dot because we are taking rate of change here.

So, we can write this as d N 1 by d t as equal to now outflow to site 1 would be minus of N 1 because this is something which is going down. So, minus of N 1 the dipole density on site 1 multiplied by the jump probability that is the F 1 2 and this inflow would be, this is something which is adding this would be N 2 multiplied by so basically let us say so here you must be little confused at at the moment. Why, why do I have taken the signs, so let us for the sake of the clarity. So, outflow let us take as sign which is minus and inflow let let us take the sign which is plus. So, this is now the inflow would be N 2 which is the dipole density at site 2 multiplied by the jump probability from 2 to 1 which is F 2 1 okay.

So, now we know that in real for for a given material N 1 is plus N 2 is equal to N which is constant because N 1 and N 2 does not change because nothing is coming from outside, nothing is going out. So, as a result we can write this d N 1 by d t plus d N 2 by d t is equal to 0.

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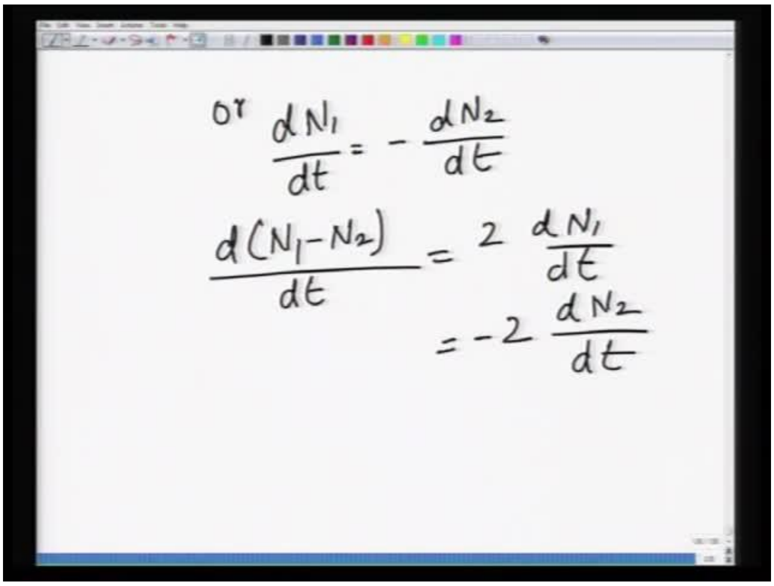

or $\frac{dN_1}{dt} = -\frac{dN_2}{dt}$

$$\frac{d(N_1-N_2)}{dt} = 2\frac{dN_1}{dt}$$
$$= -2\frac{dN_2}{dt}$$

Because N is constant or or d N 1 by d t is equal to minus of d N 2 by d t. Now, if you alternatively we can also write d into N 1 minus N 2 divided by d t, this can be written as 2 d N 1. So, this is just nothing, just nothing but manipulation of what we have written earlier 2 into d N 1 by d t is equal to minus of 2 into d N 2 by d t. So, we have not done anything miraculous here just manipulated the previous equations.

So, now to take it forward so what we do is that we we replace this d N 1 by d t in the above equation. So, this equation that we wrote here, excuse me; so the equation that we wrote here d N 1 by d t is equal to minus n 1 F 1 2 plus N 2 into F 2 1 and so we just replace this d N 1 by d t here from this equation.

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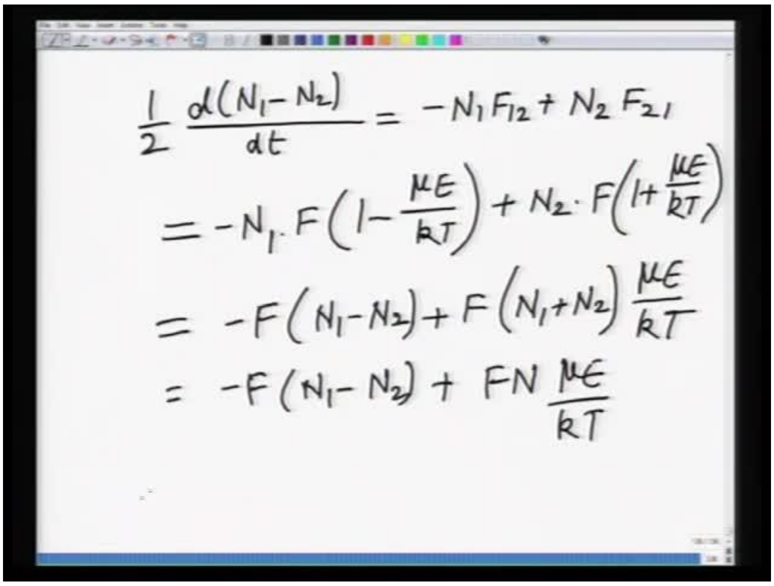

$$\frac{1}{2}\frac{d(N_1-N_2)}{dt} = -N_1F_{12}+N_2F_{21}$$

$$= -N_1\cdot F\left(1-\frac{\mu E}{kT}\right)+N_2\cdot F\left(1+\frac{\mu E}{kT}\right)$$

$$= -F(N_1-N_2)+F(N_1+N_2)\frac{\mu E}{kT}$$

$$= -F(N_1-N_2)+FN\frac{\mu E}{kT}$$

So, this becomes half of d N 1 minus N 2 divided by d t and this is equal to minus of N 1 F 1 2 plus N 2 F 2 1. Now, we know what F 1 2 and F 2 1 are, we just make a replacement so these becomes equal to, so this becomes equal to minus of N 1 into F into 1 minus mu E by k T plus N 2 into F 1 plus mu E by k T. And we can again rearrange these terms so this becomes minus F into N 1 minus N 2 plus capital plus F into N 1 plus N 2 multiplied by mu E by k T.

So, so you can see that now this is we have expressed this N 1 minus N 2 in terms of N 1 minus N 2 and then N 1 plus N 2, this is capital N itself. So, this becomes minus of F into N 1 minus N 2 plus F N mu E by k T. Now, how can you express the polarization? So, polarization now this net movement of charge which is the net build up or net depletion of charge can be related to what is called as polarization or dipole moment.

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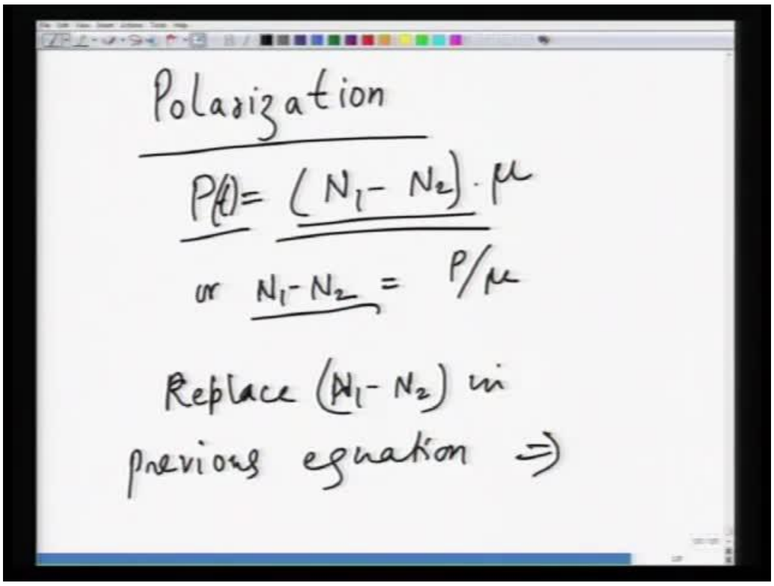

Polarization

$P(t) = (N_1 - N_2) \cdot \mu$

or $N_1 - N_2 = P/\mu$

Replace $(N_1 - N_2)$ in previous equation $\Rightarrow$

So, this, so we can this polarization P can be expressed as N 1 minus N 2 which is the net change in the density multiplied by the dipole moment which we know for each molecule is equal to mu, and and now we can replace this value of N 1 minus N 2 into the previous equation.

So, previous equation we know was equal to half d N minus d N 1 minus N 2 d t is equal to minus F N 1 minus N 2 plus F N mu E by mu mu E divided by k T. So, we replace this N 1 minus N 2 is equal to P divided by mu and this is also going to be a function of time because N 1 and N 2 are also going to change, because N 1 and N 2 have, they change because of jump from one to other place. So, as a result so what you do is that replace N 1 minus N 2 in previous equation to achieve what we call, what we write as …

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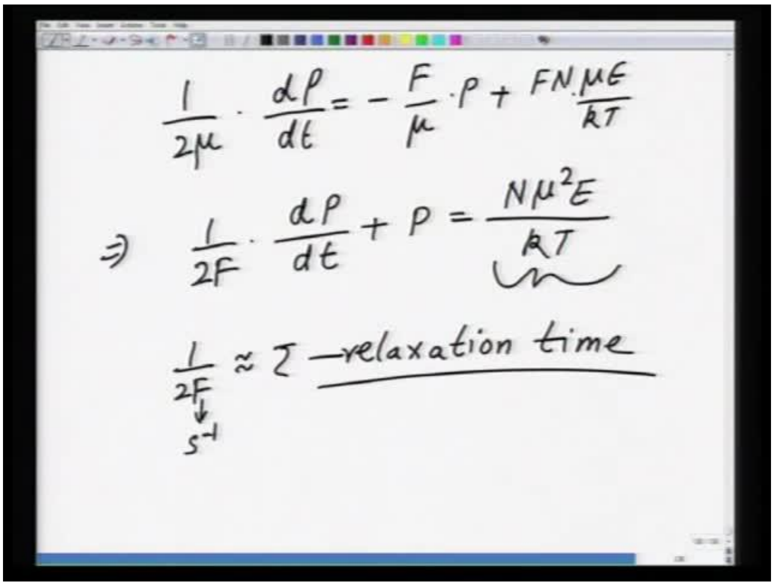

$$\frac{1}{2\mu} \cdot \frac{dP}{dt} = -\frac{F}{\mu} \cdot P + FN \cdot \frac{\mu E}{kT}$$

$$\Rightarrow \frac{1}{2F} \cdot \frac{dP}{dt} + P = \frac{N\mu^2 E}{kT}$$

$$\underset{\substack{\downarrow \\ s^{-1}}}{\frac{1}{2F}} \approx \tau \text{ — relaxation time}$$

1 over 2 mu into d P by d t is equal to minus F divided by mu into P plus F N mu E divided by k T or alternatively we can write this as again rearrange 1 divided by 2 F multiplied by d P by d t plus P to be equal to N mu square E divided by k T and now you must be familiar with this term. This term that we derived earlier, this was dipolar polarizability and and here 1 by 2 F. Now, F is nothing but probability per second so this has a unit of per second. So, 1 divided by 2 F is called as relaxation time tau, relaxation time and this is a characteristic of a system. So, this question can be rearranged in the following form.

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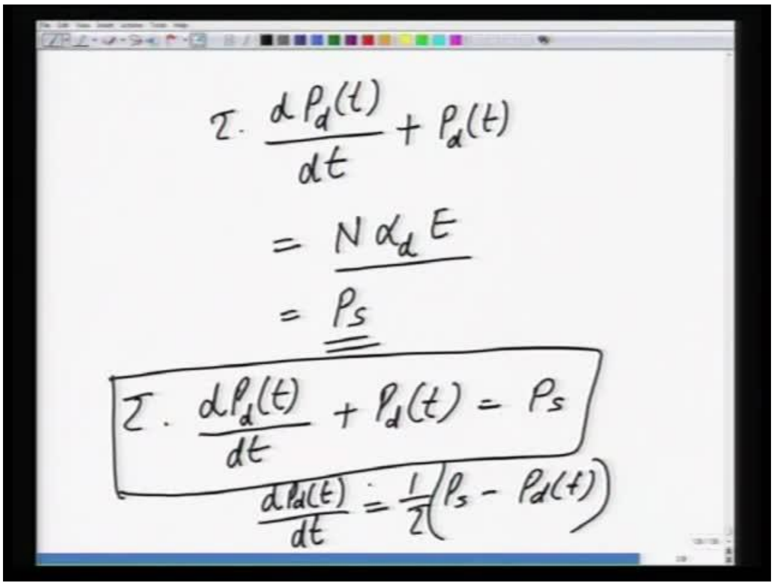

$$\tau \cdot \frac{dP_d(t)}{dt} + P_d(t)$$

$$= \underline{N \alpha_d E}$$

$$= \underline{\underline{P_s}}$$

$$\boxed{\tau \cdot \frac{dP_d(t)}{dt} + P_d(t) = P_s}$$

$$\frac{dP_d(t)}{dt} = \frac{1}{\tau}\left(P_s - P_d(t)\right)$$

So, we can write this equation as tau and this P is nothing but P d. So, tau d P d t by d t plus P d t is equal to N alpha d E and this is equal to N alpha d E will be equal to P s saturation polarization. So, what you have come across now is tau d P d t d t plus P d t is equal to P s and if you remember this is what we should earlier, the change in or you can write this you know in the previous form which is d P d t by d t is equal to P s minus P d t into 1 over tau. And this is what we wrote earlier.

So, rate of change of dipolar polarization is nothing but 1 over tau multiplied by P s minus P d t. So, we have come, we have derived this form by taking up a bi-stable model of two diploes where dipoles are, where there is a jump of let us say atoms from one position to another and this jump is due to thermal phenomena and when the temperature is greater than 0 K in the absence of field these jumps are random, as a result there is no net dipole moment which develops.

But when you apply field these jumps become defined in in the direction of applied field or there is a net jump in the direction of applied field. So, when we take this bi-stable model of two dipoles from there is a net flow of, there is a net accumulation or depletion of charge at either position 1 or position 2 depending upon how the energy barrier is lowering or decreasing. And as a result you have this rate of change of dipolar polarization as a function of change of polarization as a function of time.

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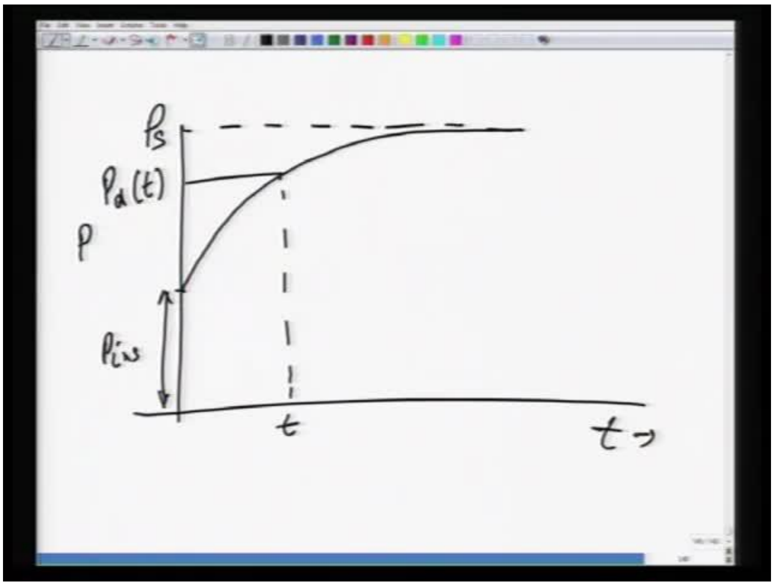

So, now what we do is that we need to solve this equation and before we do that let us just plot this. So, if we plot this P versus t, so we again, so this is your instantaneous polarization which is P instantaneous which is sum of ionic and electronic and then you have this variation of so this is your P s and this would be t P d t, and this P s is the saturation polarization whereas polarization cannot increase beyond this value after all the dipoles have aligned themselves.

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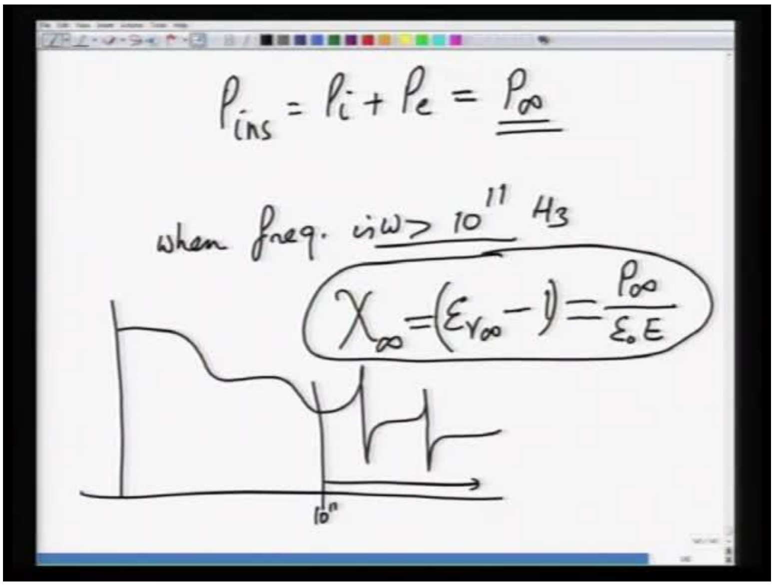

$P_{ins} = P_i + P_e = \underline{\underline{P_\infty}}$

when freq. is $\underline{\omega > 10^{11}}$ Hz

$\chi_\infty = (\varepsilon_{r\infty} - 1) = \frac{P_\infty}{\varepsilon_0 E}$

So, we write since the since the ionic and electronic polarization develop almost instantaneously and the sum of this. So, P instantaneous is equal to P i plus P e and this we write as often P infinity. So, as long as this applied frequency is below 10 to the power 13 hertz both of these polarizations are almost instantaneous develop and normally for this dipolar polarization, we are operating in frequencies below 10 to the power 6 hertz. So, as a result these two polarization mechanisms are automatically built in.

So, and when and we also know when frequency is let us say omega is greater than 10 to the power 11 hertz which means we are in the so if you look at this plot. So, when omega is beyond this limit. So, let us say this is 10 to the power 11 when you are in this frequency range then epsilon r infinity which is the static dielectric constant in the un relaxed condition. So, static high frequency un relaxed dielectric constant this is given as 1 plus P infinity divided by epsilon naught E and this is nothing but your basically you can write it in different manner. So, chi infinity is equal to epsilon r minus 1 and this is equal to nothing but the polarization developed at that particular point of time which is P infinity divided by epsilon naught E.

So, we have just followed the definition that we probably took in the beginning of this module. So, this again, so this chi infinity is equal to epsilon r infinity minus 1 divided is equal to P infinity divided by epsilon naught E when the frequencies are above 10 to the power 11 hertz with the operation of only two polarization mechanisms which are instantaneous in nature and the ionic polarization and the electronic polarization.

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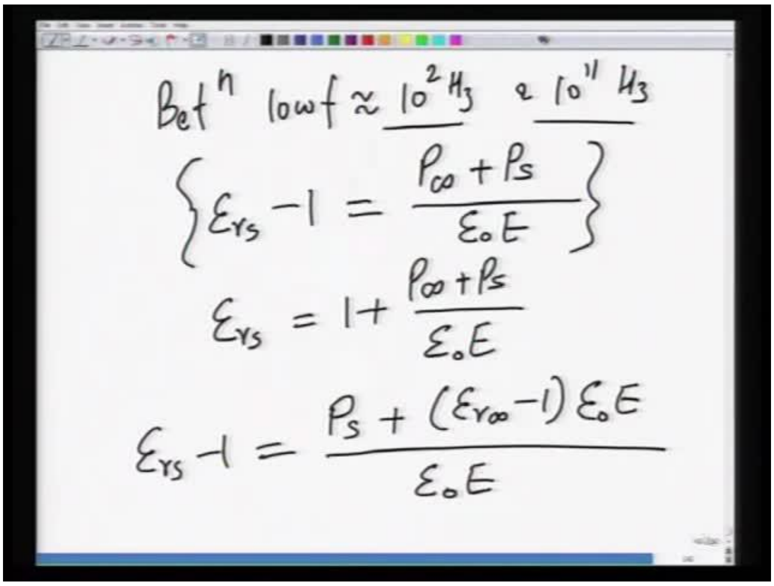

Bet^n low f ≈ $\underline{10^2 \text{ Hz}}$ & $\underline{10^{11} \text{ Hz}}$

$$\left\{ \varepsilon_{rs} - 1 = \frac{P_\infty + P_s}{\varepsilon_o E} \right\}$$

$$\varepsilon_{rs} = 1 + \frac{P_\infty + P_s}{\varepsilon_o E}$$

$$\varepsilon_{rs} - 1 = \frac{P_s + (\varepsilon_{r\infty} - 1)\varepsilon_o E}{\varepsilon_o E}$$

What happens between between let us say low frequency, enough let us say somewhere around 10 to power 2 hertz and 10 to the power 11 hertz. So, these numbers are just for for the sake of illustration, these numbers may vary depending upon the system, but typically they are like that. So, low frequency between 10 to the power 2 to 10 to the power 11 hertz dipolar polarization mechanism dominates and then you have this epsilon r low frequency again relaxed static dielectric constant is equal minus 1 is given as polarization which is P infinity plus P s and this is because of dipolar mechanism divided by epsilon naught E or epsilon r s is equal to 1 plus P infinity plus P s divided by epsilon naught E.

So, this equation is nothing but same as previous one, the susceptibility equation. So, and here we are not taking this local field into account here. So, so if we if we take use of these two equations, we can write this epsilon r s minus 1 to be equal to… Now, from the previous equation you can see what is P infinity? P infinity would be epsilon r infinity minus 1 multiplied by epsilon naught E. So, if we replace this P infinity in the next equation then we get P s plus epsilon r infinity minus 1 multiplied by epsilon naught E divided by epsilon naught E.

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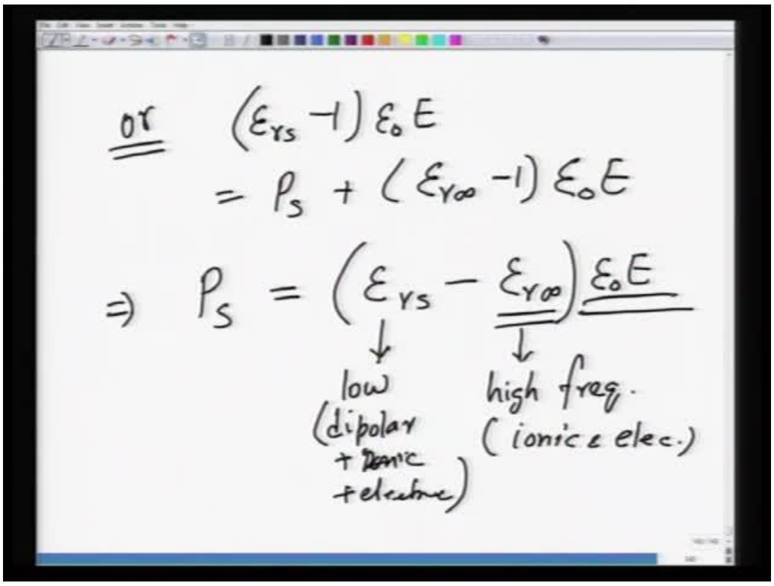

or $(\varepsilon_{rs} - 1)\varepsilon_0 E$

$$= P_s + (\varepsilon_{r\infty} - 1)\varepsilon_0 E$$

$$\Rightarrow P_s = \Big(\underset{\substack{\downarrow \\ \text{low} \\ (\text{dipolar} \\ +\text{ionic} \\ +\text{electronic})}}{\varepsilon_{rs}} - \underset{\substack{\downarrow \\ \text{high freq.} \\ (\text{ionic \& elec.})}}{\underline{\varepsilon_{r\infty}}}\Big)\underline{\varepsilon_0 E}$$

Or, if we again, so epsilon r s minus 1 into epsilon naught E is equal to P s plus epsilon r infinity minus 1 E. So, this gives rise to value of P s which is epsilon r s minus epsilon r infinity multiplied by epsilon naught E. And this kind of make sense because this is epsilon r infinity is for high frequency region taking care of ionic and electronic polarization mechanisms and this is low frequency and this takes care of dipolar plus these two ionic and electronic. So, the saturation polarization would be the difference of these two so that you get rid of these two effects. So, low frequency static dielectric constant minus the high frequency static dielectric constant the difference of these two multiplied by epsilon naught E will give you P s. So, and this E is again complex in nature which means it is a alternate dielectric field.

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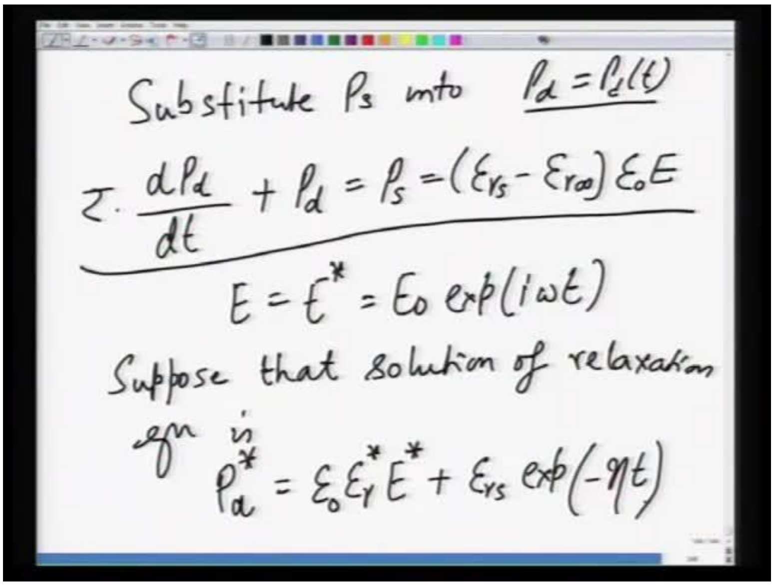

Substitute P_s into $\underline{P_d = P_d(t)}$

$$\tau \cdot \frac{dP_d}{dt} + P_d = P_s = (\varepsilon_{rs} - \varepsilon_{r\infty})\varepsilon_0 E$$

$$E = E^* = E_0 \exp(i\omega t)$$

Suppose that solution of relaxation eqn is

$$P_d^* = \varepsilon_0 \varepsilon_r^* E^* + \varepsilon_{rs} \exp(-\eta t)$$

Now, this substitutes this P into the equation that we derived earlier.

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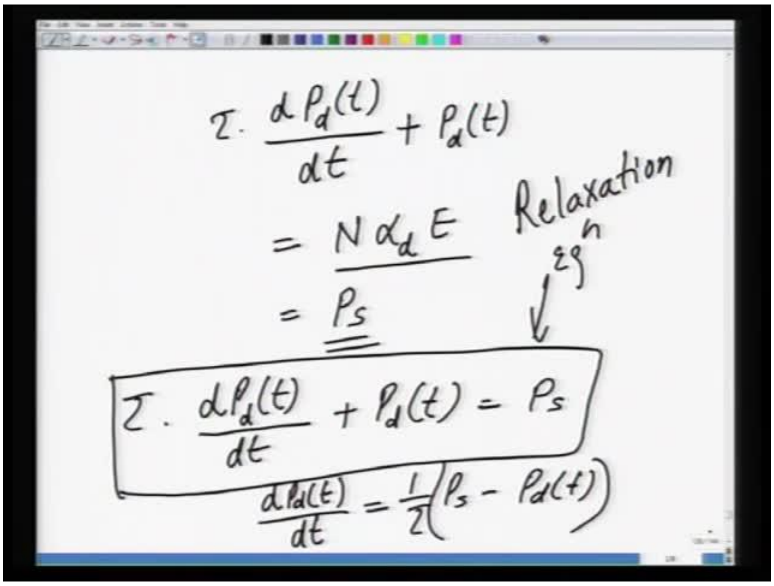

$$\tau \cdot \frac{dP_d(t)}{dt} + P_d(t) = \underline{N\alpha_d E} = \underline{\underline{P_s}}$$

Relaxation eq^n

$$\boxed{\tau \cdot \frac{dP_d(t)}{dt} + P_d(t) = P_s}$$

$$\frac{dP_d(t)}{dt} = \frac{1}{\tau}(P_s - P_d(t))$$

This equation which is also called as relaxation equation, so if we substitute this P s in this equation how does it look like? So, when we substitute this we get tau into d P d. So, we have taken this bracket in t off because P d is so basically P d is nothing but P d t. So, we so d P d by d t plus P d is equal to P s is equal to epsilon r s minus epsilon r infinity multiplied by epsilon naught E. Now, we know that E is equal to… Now, E is a complex quantity. So, E is equal to E star which is equal to E naught exponential of i omega t.

Now, now life is going to get little bit little bit more complex in solving this, specially when you substitute this there. So, what we do is that we assume a solution. So, assume that so suppose so we are solving for P d. So, suppose that solution of this equation the basically relaxation equation, equation is P d star we write a star because again since we are taking E as E star we have to take P as P star and everything converts into star because of complex nature. So, this becomes epsilon naught epsilon star E star plus epsilon r s into exponential of minus eta t. Suppose, this is a solution where where eta is some coefficient which is which is determined by the solution itself.

So, when you put this expression P d star is equal to epsilon naught epsilon r infinity epsilon r star sorry E star plus epsilon r s, epsilon r s exponential minus eta t into this equation, what you get?

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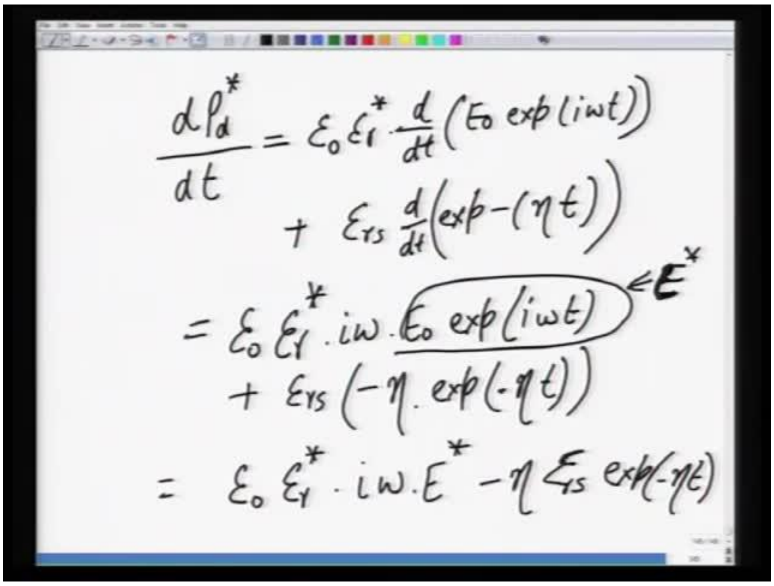

$$\frac{dP_d^*}{dt} = \varepsilon_0 \varepsilon_r^* \cdot \frac{d}{dt}\left(E_0 \exp(i\omega t)\right) + \varepsilon_{rs} \frac{d}{dt}\left(\exp-(\eta t)\right)$$

$$= \varepsilon_0 \varepsilon_r^* \cdot i\omega \cdot \boxed{E_0 \exp(i\omega t)} \leftarrow E^* + \varepsilon_{rs}\left(-\eta \cdot \exp(-\eta t)\right)$$

$$= \varepsilon_0 \varepsilon_r^* \cdot i\omega \cdot E^* - \eta \, \varepsilon_{rs} \exp(-\eta t)$$

So, you so if you just, first to do that let us differentiate d P d star. So, differentiate P d star with respect to time. So, d P d star by d t is equal to epsilon naught epsilon r star. So, what you are going to do is that d by d t E naught exponential of i omega t plus the other expression is epsilon r s epsilon r s into exponential of into d by d t exponential of minus eta t. So, when you do that this becomes epsilon naught epsilon r star and since E naught is a constant, so this becomes i omega comes out and again it becomes E naught exponential of i omega t plus epsilon r s multiplied by minus of eta into exponential minus eta t.

So, this becomes equal to epsilon naught epsilon r star into i omega into E star because this is again nothing but E star naught epsilon star E star minus eta epsilon r s into exponential of minus eta t. So, this is d P d star by d t. Now, this this is going to be substituted in the relaxation equation that we wrote earlier. So, if you do that the relaxation equation, so relaxation equation was again invoke the relaxation equation. So, relaxation equation is this which is…

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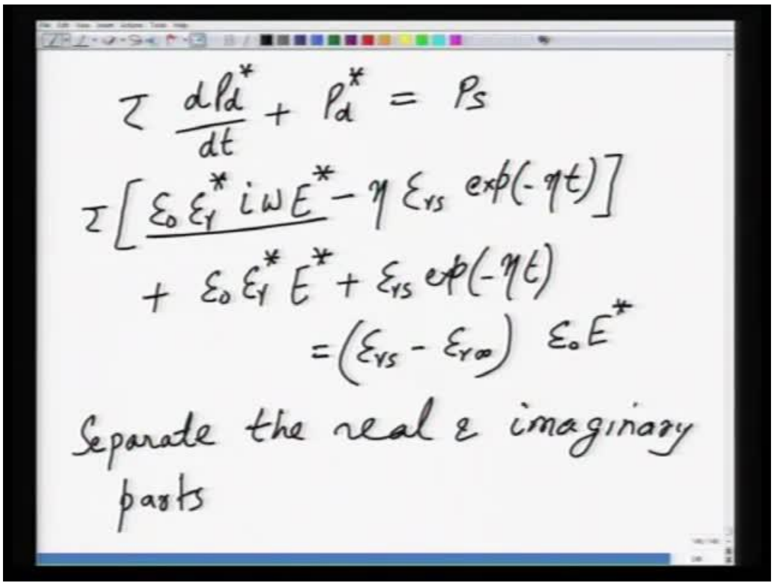

$$\tau \frac{dP_d^*}{dt} + P_d^* = P_s$$

$$\tau\left[\underline{\varepsilon_0 \varepsilon_r^* i\omega E^*} - \eta\, \varepsilon_{rs} \exp(-\eta t)\right] + \varepsilon_0 \varepsilon_r^* E^* + \varepsilon_{rs} \exp(-\eta t) = (\varepsilon_{rs} - \varepsilon_{r\infty})\, \varepsilon_0 E^*$$

Separate the real & imaginary parts

So, relaxation equation is tau d P d star by d t plus P d star is equal to P s. So, we are going to replace here. So, this is tau multiplied by epsilon naught epsilon r star i omega E star minus eta epsilon r s exponential of minus eta t plus P d star, P d star we have taken as we have assumed the solution so that we put as epsilon naught epsilon r star into E star plus epsilon r s exponential of minus eta t. That is equal to epsilon r s minus epsilon r infinity multiplied by epsilon naught E star. So, this is the complex equation that you get. So, what you do now is you have to separate the real and imaginary parts.

So, separate the real and imaginary parts of this equation. So, when you do the… So, basically where do you have a imaginary part, this is an imaginary part and now E star. So, let us do that now.

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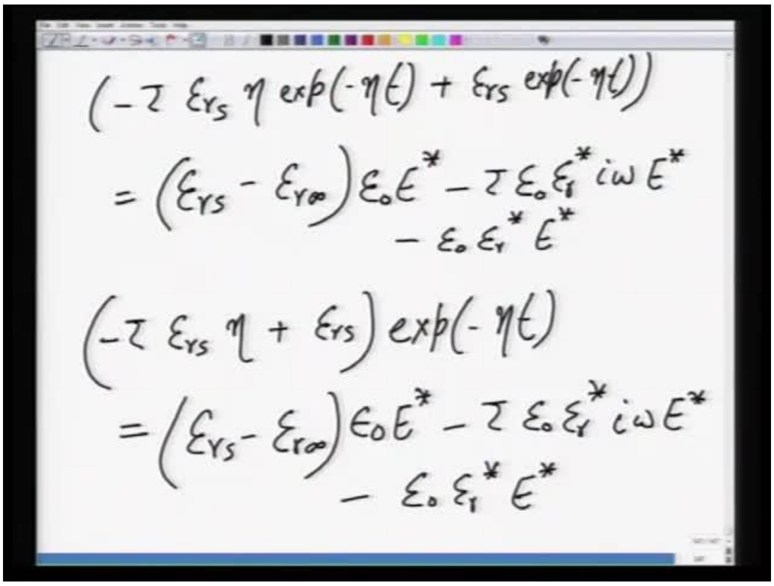

$$\left(-\tau \varepsilon_{rs} \eta \exp(-\eta t) + \varepsilon_{rs} \exp(-\eta t)\right)$$

$$= \left(\varepsilon_{rs} - \varepsilon_{r\infty}\right) \varepsilon_0 E^* - \tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \varepsilon_0 \varepsilon_r^* E^*$$

$$\left(-\tau \varepsilon_{rs} \eta + \varepsilon_{rs}\right) \exp(-\eta t)$$

$$= \left(\varepsilon_{rs} - \varepsilon_{r\infty}\right) \epsilon_0 E^* - \tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \varepsilon_0 \varepsilon_r^* E^*$$

So, when you do that, when we take minus of tau epsilon r s eta exponential of minus eta t this is the first part plus epsilon r s into exponential of minus eta t. This is the first part and this goes equal to epsilon r s minus epsilon r infinity into epsilon naught E star because this is a complex part minus of tau epsilon naught epsilon r star i omega E star minus of epsilon naught epsilon r star E star.

So, if you go to previous equation again. So, we have taken we have taken this term and we have taken this term out, because these are non non imaginary parts and this, this and this part on another side. So, that is how we have separated. So, this is the final equation. So, this can be written as minus of tau epsilon r s multiplied by eta plus epsilon r s into exponential of minus eta t. And this is equal to again very long equation. So, let us see what we can take out here. So, here, so basically this part I will I will not take out anything I will do that later epsilon naught E star minus tau epsilon naught epsilon r star i omega E star minus of epsilon naught epsilon r star E star.

So, now now we have to solve this equation which we do in the next class because not there is there is not enough time left. So, what we will do is that basically the both sides of this equation since looking at the equations since you have real part on some side, imaginary part on some side. So, in order to solve this equation both parts of this equation must be equal to some constant and that constant happens to be nothing but equal to 0. So, when you make this these two sides equal to 0 you arrive at some some more quantities which are of much more meaning.

So, we will do that in the next class. So, what we have done today is we have taken a bi-stable model for dipolar materials, shown material showing dipolar polarization where when the field is not applied that since the jump probability is random, jump, jumps are random as a result no dipole moment develops, but when you apply electric field these there is a finite jump probability in certain in the direction of applied field as a result you have dipolar polarization which is the function of time. And which is dependent upon the frequency of applied field. So, that and complete analysis of this we will do in the, follow in the next class.

Thank you.