Fundamentals and Applications of Dielectric Ceramics
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Lecture No 24
Debye Equations for Dipolar Relaxation

Welcome to the new lecture of this course, Fundamentals and Applications of Dielectric Ceramics.

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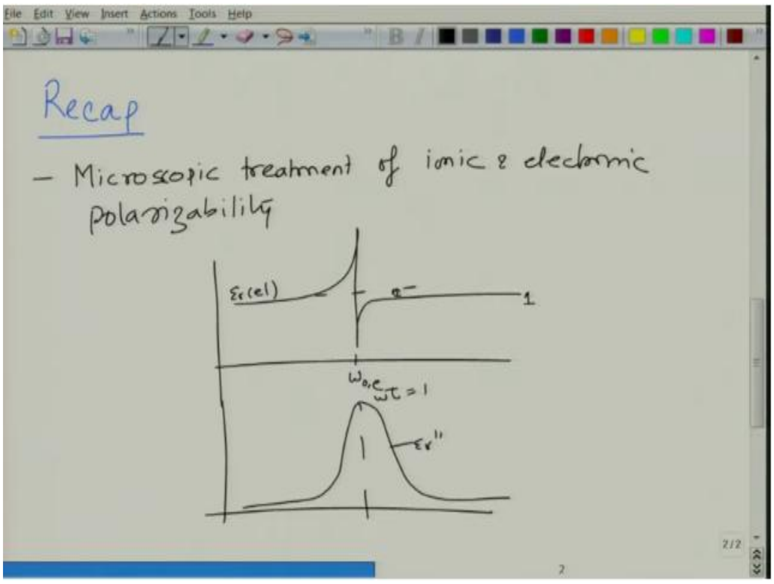

Recap

- Microscopic treatment of ionic & electronic polarizability

So, let us briefly recap. Earlier, we talked about the microscopic details of treatment of ionic and electronic polarizability in which we saw that, when you estimate the polarizability, and when you plot the dielectric constant, the dielectric constant shows a, sort of, resonance at a frequency ω. And this is the difference that you create. So, if $\omega\tau$ is 1, this would be ε(electronic) and this would be $\omega_{0,e}$ for instance.

And at the same time you will have a peak in ε_r''. So, this is ε_r''. So, this is where $\omega\tau = 1$. So, this is what we saw and we also started with a simple model for our dipolar relaxation or dipolar polarizability.

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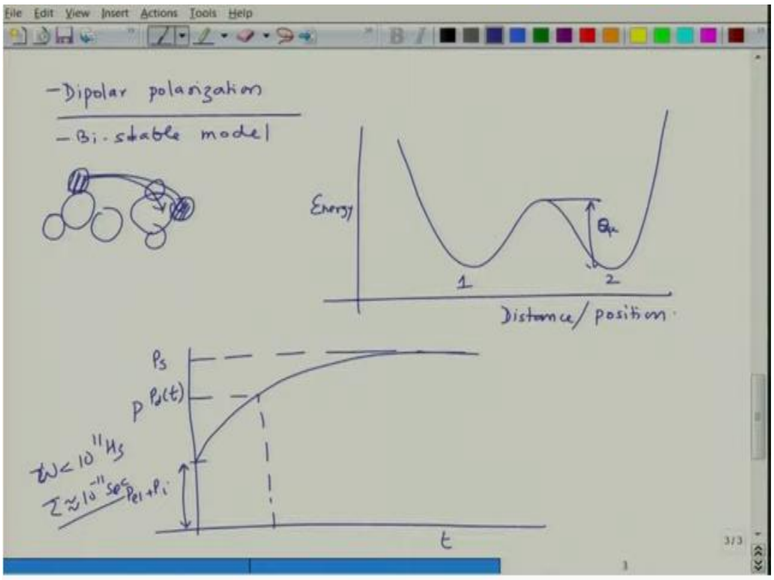

Where we said that, we are going to treat, so for dipolar polarizability or polaziation, we started with the bi-stable model, where we assume that you know you have a molecule let us say, like this. And this molecule, so it is connected in this fashion and this more molecule transverses to another position, which is, like this, let us say. So this atom is basically moving to this positions, from position one to position two. So you might consider this as a rotation of, let us say a molecule.

So, this could be a different atom altogether. So, basically what is happening is that if you plot the energy landscape, the molecule is shifting from one stable position to another stable positions. So, this is position one, this is position two. And it has to overcome energy barrier E_a or Q_a, let us say. So, this is energy and this is, let us say, distance or position. So it goes from one position to another position, and this happens by hopping.

And when the dipolar relaxation happens, basically when you plot polarization as a function of time, the evolution of electronic plus ionic component is almost instantaneous, because it happens at a frequency, which is below 10^{11} Hz. So, basically, timescale is the order 10^{-11} seconds and this happens extremely fast. So, your electronic and ionic polarization develops almost instantaneously and then dipolar polarization develops slowly.

Until it saturates and reaches a polarization called as saturation polarization that is P_s. And at any given point of time, this is represented by P.dt, the time dependent dipolar polarization. And this is what is dependent upon a model that we will discuss.

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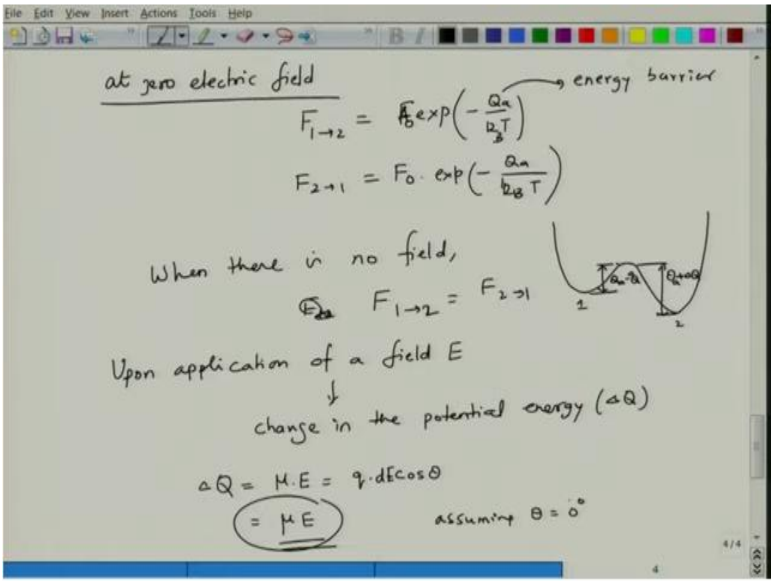

at zero electric field

$$F_{1\to 2} = F_0 \exp\left(-\frac{Q_a}{k_B T}\right) \rightarrow \text{energy barrier}$$

$$F_{2\to 1} = F_0 \cdot \exp\left(-\frac{Q_a}{k_B T}\right)$$

When there is no field,

$$F_{1\to 2} = F_{2\to 1}$$

Upon application of a field E

↓

change in the potential energy (ΔQ)

$$\Delta Q = \mu \cdot E = q \cdot dE\cos\theta$$

$$\boxed{= \mu E} \quad \text{assuming } \theta = 0^\circ$$

So, let us say, we so we were talking about the probabilities of jump. So, when you have zero electric field, then probability of jump from one to two will be equal to:

$$F_{1\to 2} = F_0 e^{\left(-\frac{Q_a}{k_B T}\right)}$$

Q_a is basically energy barrier. It being Arrhenius process and this is the thermal energy k_BT. So, you might have similar and so for one to two this is the frequency. Similarly, for two to one, the jump probability will be:

$$F_{2\to 1} = F_0 e^{\left(-\frac{Q_a}{k_B T}\right)}$$

And these will be sort of equivalent at equilibrium. So, when there is no field, then

$$F_{1\to 2} = F_{2\to 1}$$

So, there are equal energy barriers from both sides as a result. So, and when you apply a field, upon application of a field E, the potential energy of two sides changes. So, this changes the ΔQ amount. So, what will happen is that, this energy barrier on one side will become smaller and other side will become larger.

So, let us say this is one this is two. So, on this side, you will have deduction from **(Q_a - ΔQ)** and from this side, you will have increase from **(Q_a + ΔQ)**. And this ΔQ will basically correspond to:

$$\Delta Q = \mu . E = q.dE\cos\theta$$

So, assuming that cos θ is equal to, they are co-linear. So, essentially we will say that this energy is nothing but **μE** for complete alignment.

So this is the change in the energy that happens when you apply the electric field. So assuming that, $\theta = 0^0$. So if this is the case, let us build upon further.

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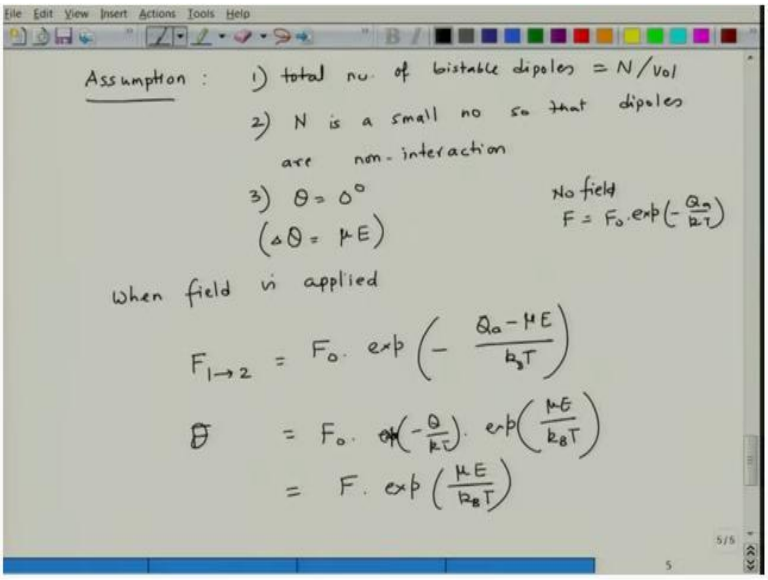

Assumption : 1) total nu. of bistable dipoles = N/Vol

2) N is a small no so that dipoles are non-interaction

3) $\theta = 0^\circ$

$(\Delta\theta = \mu E)$

No field

$F = F_0 . \exp\left(-\frac{Q_a}{kT}\right)$

when field is applied

$$F_{1\to 2} = F_0 . \exp\left(-\frac{Q_a - \mu E}{k_B T}\right)$$

$$= F_0 . \cancel{ex}\left(-\frac{Q}{kT}\right) . \exp\left(\frac{\mu E}{k_B T}\right)$$

$$= F . \exp\left(\frac{\mu E}{k_B T}\right)$$

So assuming that we have, so first assumption is that we have total number of bistable dipoles are equal to N per unit volume. And N is a small number so that type roles are non-interacting. So, non-interacting means, there are no internal electric fields that set in. And third is we assume that $\theta = 0^0$. So, when $\theta = 0^0$, then $\Delta Q = \mu E$.

So, when you apply a field, then:

$$F_{1\to 2} = F_0 e^{\left(-\frac{Q_a - \mu E}{k_B T}\right)}$$

And similarly, and if you just break it up, this will become:

$$F_{1\to 2} = F_0 e^{\left(-\frac{Q_a}{k_B T}\right)} e^{\left(\frac{\mu E}{k_B T}\right)}$$

$$F_{1\to 2} = F e^{\left(\frac{\mu E}{k_B T}\right)}$$

Here,

$$F = F_0 e^{\left(-\frac{Q_a}{k_B T}\right)}$$

So when we have no field F will be same as the expression just above.

So basically, it is saying that the site where the energy barrier has lowered, the probability has increased by the amount **$\exp(\mu E K_B T)$**. So the flow to one direction has increased, but flow from other direction will correspondingly decrease.

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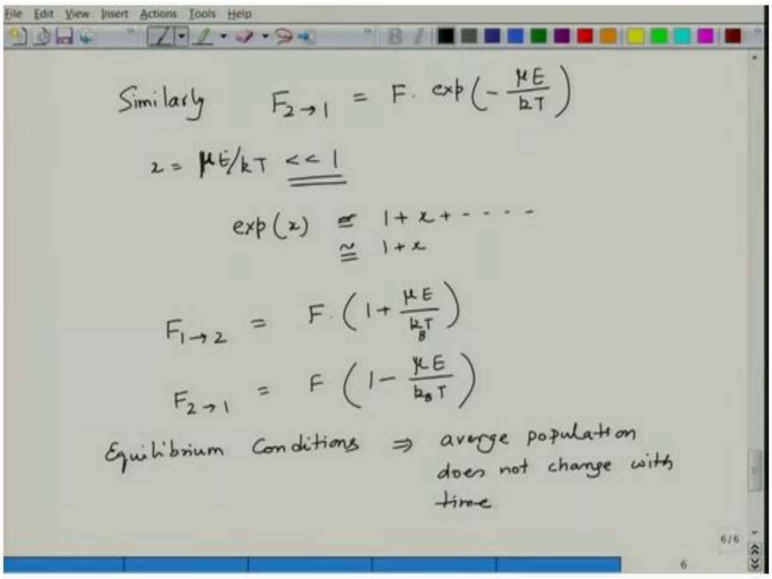

Similarly $F_{2\to 1} = F \cdot \exp\left(-\frac{\mu E}{kT}\right)$

$x = \mu E/kT \ll 1$

$\exp(x) \cong 1 + x + \cdots$

$\cong 1 + x$

$F_{1\to 2} = F \cdot \left(1 + \frac{\mu E}{k_B T}\right)$

$F_{2\to 1} = F \left(1 - \frac{\mu E}{k_B T}\right)$

Equilibrium Conditions ⇒ averge population does not change with time

So similarly, when you talk of $F_{2\to 1}$

$$F_{2\to 1} = Fe^{\left(\frac{\mu E}{k_B T}\right)}$$

So, from one side, there will be more diapers moving to another side, whereas from another side, there will be lesser number of dipoles moving to the first side because of the increase in energy barrier. However we say that **$\mu E K_B T$** is sufficiently small and this is verifiable. You can choose the values of μ, which is nothing but Q.D. So if you put in there some approximate magnitude of μ, Q and D.

And then the value of E, then this is smaller than:

$$x = {}^{\mu E}\!\big/_{k_B T} \ll 1$$

So, for all practical purposes, x is smaller than one. So, we can approximate exponential x for smaller values, then we can write:

$$e^x = 1 + x + {}^{x^2}\!\big/_{2!} + {}^{x^3}\!\big/_{3!} + \ldots\ldots\ldots$$

$$e^x \cong 1 + x$$

So, as a result we can write:

$$F_{1\rightarrow 2} = F\left(1 + \frac{\mu E}{k_B T}\right)$$

And,

$$F_{2\rightarrow 1} = F\left(1 - \frac{\mu E}{k_B T}\right)$$

So this is the approximation that we make.

Now, under equilibrium, let us say, we have equilibrium conditions, that will mean that, average population does not change with time, right. Average population at a given side will not change with time.

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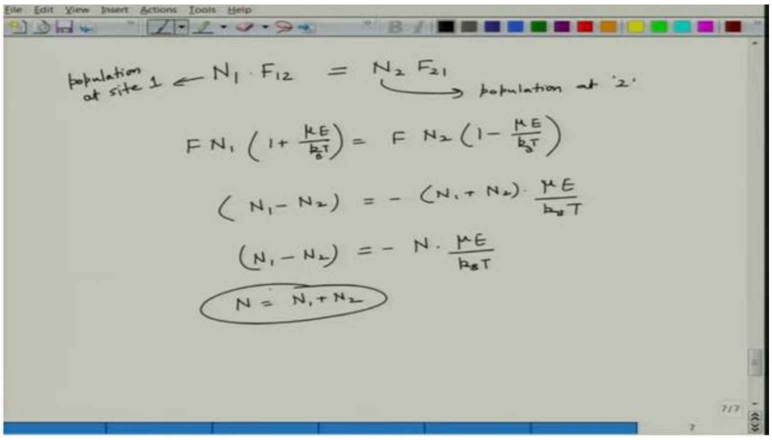

population at site 1 $\leftarrow N_1 \cdot F_{12} = N_2 F_{21}$ $\rightarrow$ population at '2'

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

$$(N_1 - N_2) = -(N_1 + N_2) \cdot \frac{\mu E}{k_B T}$$

$$(N_1 - N_2) = -N \cdot \frac{\mu E}{k_B T}$$

$$\boxed{N = N_1 + N_2}$$

What will it mean is that, so outflow from 1 that is **N_1 $F_{1\rightarrow 2}$**. N_1 is the population at site one. $F_{1\rightarrow 2}$ is the probability of jump from one to two. So this will be the number of dipoles or number of atoms or number of species leaving the site one. This will be equal to **N_2 $F_{2\rightarrow 1}$** and this will be population at site, at two, whereas $F_{1\rightarrow 2}$ and $F_{2\rightarrow 1}$ will be the probabilities. So, we can say that this is equal to:

$$N_1 F_{12} = N_2 F_{21}$$

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

So, if we now do the mathematics, simple maths here:

$$(N_1 - N_2) = -(N_1 + N_2)\frac{\mu E}{k_B T}$$

So, this is first relation, we get:

$$\left(N_1 - N_2\right) = -N\frac{\mu E}{k_B T}$$

because,

$$N = N_1 + N_2$$

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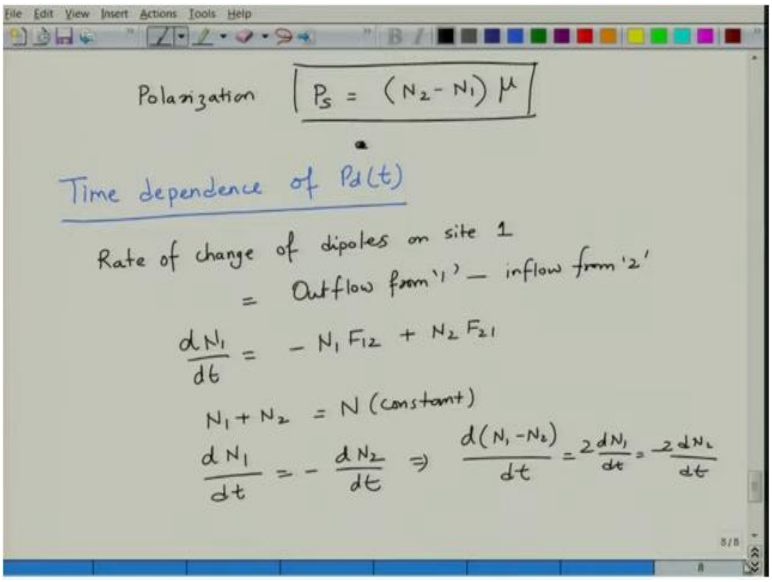

Polarization $\boxed{P_s = (N_2 - N_1)\,\mu}$

Time dependence of Pd(t)

Rate of change of dipoles on site 1

= Outflow from '1' − inflow from '2'

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

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

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

Second thing the polarization can be written as, polarization P$_s$ can be written as, change in the number of jumps that is **(N_2 – N_1)**, more have reached N$_2$, few have reached N$_1$ because of change in the energy barrier. So, total number, which has shifted, change in the dipole density multiplied by change in the number of dipoles per unit volume multiplied by the dipole movement. So this will be equal to, basically you can say, let us take it at as this right now.

Now let us see, so this is the another relation that we have:

$$P_s = \left(N_2 - N_1\right)\mu$$

Now, let us work out what is the time dependence of P.dT. So let us say, first we want to work out what is rate of change of dipoles, let us say on site one. This is equal to outflow from one minus inflow from two. So, basically this is:

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

So this is the rate of change of dipoles on site one. We also know that:

$$N = N_1 + N_2$$

which is constant.

So, if we now differentiate, so this is constant, but N1 and N2 are changing right.

So,

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

So, as a result we can write as:

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

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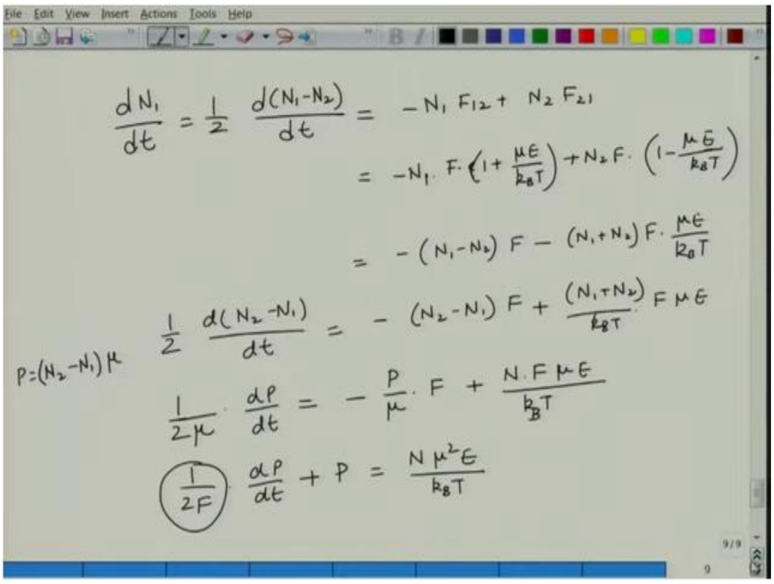

$$\frac{dN_1}{dt} = \frac{1}{2}\frac{d(N_1-N_2)}{dt} = -N_1F_{12} + N_2F_{21}$$

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

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

$$\frac{1}{2}\frac{d(N_2-N_1)}{dt} = -(N_2-N_1)F + \frac{(N_1+N_2)}{k_BT}F\mu E$$

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

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

$$\boxed{\frac{1}{2F}}\frac{dP}{dt} + P = \frac{N\mu^2 E}{k_BT}$$

Now let us go back to our previous this thing, basically we are saying that:

$$\frac{dN_1}{dt} = \frac{1}{2}.\frac{d(N_1 - N_2)}{dt}$$

So, if you now do the, just some substitutions here, you will get:

$$\frac{dN_1}{dt} = -N_1F\left(1 + \frac{\mu E}{k_BT}\right) + N_2F\left(1 - \frac{\mu E}{k_BT}\right)$$

$$\frac{dN_1}{dt} = -(N_1 - N_2)F + (N_1 + N_2)F\frac{\mu E}{k_BT}$$

We have just changed the minus sign, just multiplied by a minus sign everywhere. Now, what is this, this is nothing but one over, we said that:

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

So, we replaced this, so, this becomes:

$$\frac{1}{2\mu}.\frac{dP}{dt} = -\frac{P}{\mu}F + NF\frac{\mu E}{k_B T}$$

$$\frac{1}{2F}.\frac{dP}{dt} + P = N\frac{\mu^2 E}{k_B T}$$

So, one over and F is the jump probability, which is in per second, right, frequency.

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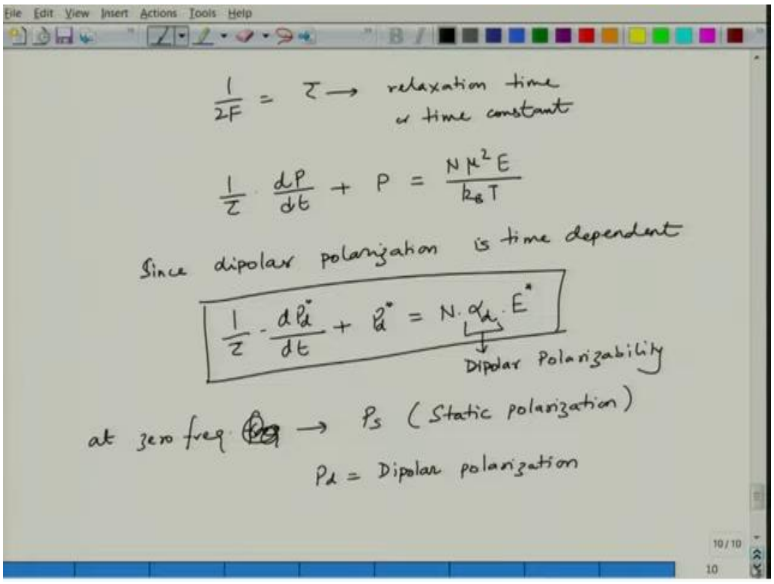

$\frac{1}{2F} = \tau \rightarrow$ relaxation time or time constant

$$\frac{1}{\tau} \cdot \frac{dP}{dt} + P = \frac{N\mu^2 E}{k_B T}$$

Since dipolar polarization is time dependent

$$\boxed{\frac{1}{\tau} \cdot \frac{dP_d^*}{dt} + P_d^* = N.\underbrace{\alpha_d}_{\text{Dipolar Polarizability}}.E^*}$$

at zero freq $\rightarrow$ P_s (Static polarization)

P_d = Dipolar polarization

So this F can be approximated now as:

$$\frac{1}{2F} = \tau$$

So, we can write this as:

$$\frac{1}{\tau}.\frac{dP_d^*}{dt} + P_d^* = N.\alpha_d.E^*$$

So, now, writing this in terms of polarization, which is time dependent polarization. So, among the polarization components if you see, the time dependent part is the dipolar part.

Whereas, the ionic and electronic parts are nearly time independent. Dipolar polarization is time dependent. So, here we say, that at zero frequency, so, this is the expression that we get. So, what is this **NαE**, so we can see that this is the dipolar polarization, this is time variation of bipolar polarization.

Which means, this should be the net polarization or saturation polarization that we should obtain after sufficiently long times. So, here we define that, let us say, at zero frequency, we achieve a polarization of P_s, right. When the frequency is very small, all the mechanisms are contributing, then what we get is, let us say, static polarization. That is the maximum we can obtain. And then we also define and then P_d is nothing but dipolar polarization.

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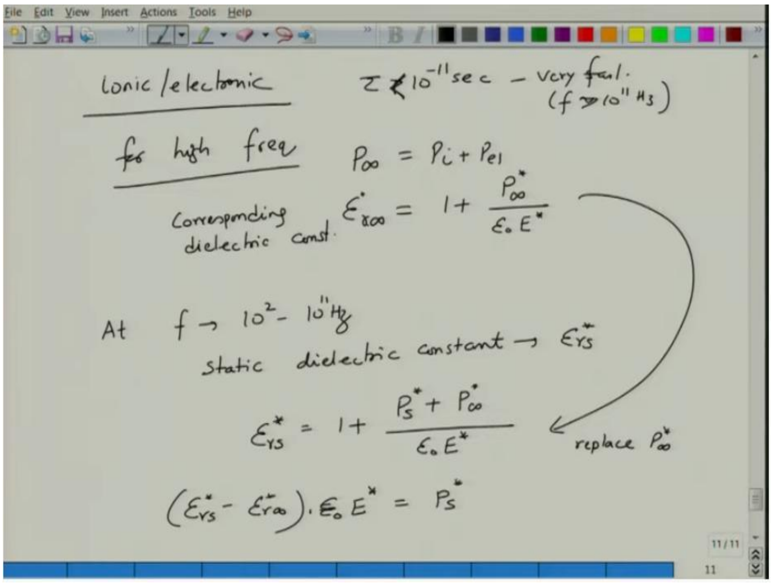

Ionic/electronic $\tau \nless 10^{-11}$ sec – very fast.
$(f \gg 10^{11}$ Hz$)$

for high freq $P_\infty = P_i + P_{el}$

Corresponding dielectric const. $\varepsilon^*_{r\infty} = 1 + \frac{P^*_\infty}{\varepsilon_0 E^*}$

At $f \rightarrow 10^2 - 10^{11}$ Hz
static dielectric constant $\rightarrow \varepsilon^*_{rs}$

$\varepsilon^*_{rs} = 1 + \frac{P^*_s + P^*_\infty}{\varepsilon_0 E^*}$ replace P^*_∞

$(\varepsilon^*_{rs} - \varepsilon^*_{r\infty}) \cdot \varepsilon_0 E^* = P^*_s$

So, if we simplify these steps, so there so of course to solve this you need to do some simplifications. So, let us say, that for ionic and electronic, your timescale is faster than this. So, basically time scales are very fast. In fact, we can say timescales are smaller than this actually. So, they are very fast time scales, hence for high frequencies we can write a component:

$$P_\infty = P_i + P_e$$

Correspondingly, so for high frequency polarization is this.

And we define a dielectric constant as $\varepsilon_{r,\infty}$. So, corresponding dielectric constant will be:

$$\varepsilon^*_{r,\infty} = 1 + \frac{P^*_\infty}{\varepsilon_0 E^*}$$

So, this is the high frequency part. So, this is also complex. And at frequencies between 10^2 to 10^{11} Hz, which is now lower than this frequency, because this frequency is bigger than 10^{11} Hz. So, lower than this frequency, we have another contribution, which we call as static dielectric constant, which is $\varepsilon^*_{r,s}$.

So, $\varepsilon^*_{r,s}$ can be written as:

$$\varepsilon^*_{r,s} = 1 + \frac{P^*_s + P^*_\infty}{\varepsilon_0 E^*}$$

This is the saturation polarization that you are going to obtain after the depolarization saturates. And this is the contribution from higher frequency, which is from ionic and electronic polarization. So, if you now replace the value of P^*_∞ here, you will obtain. So replacing this value here, P^*_∞ and rearranging the terms:

$$\left(\varepsilon^*_{r,s} - \varepsilon^*_{r,\infty}\right).\varepsilon_0 E^* = P^*_s$$

So, basically the saturation polarization that you will obtain because of saturation or dipolar polarization is nothing but, the difference between the static dielectric constant and high frequency dielectric constant.

So, basically $\Delta\varepsilon$ multiplied by $\varepsilon_0.E$. And this is expected, right, this is what is dipolar contribution that you get.

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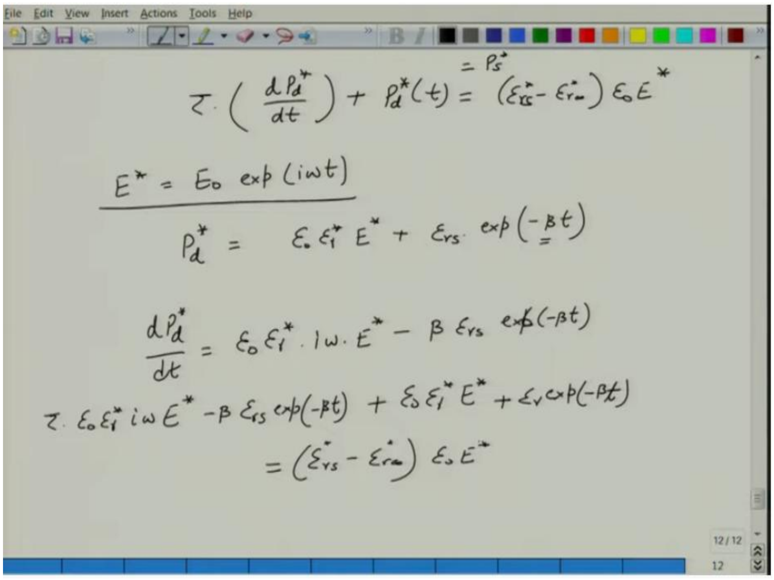

$$\tau.\left(\frac{dP^*_d}{dt}\right) + P^*_d(t) = \overset{= P^*_s}{\left(\varepsilon^*_{rs} - \varepsilon^*_{r\infty}\right)\varepsilon_0 E^*}$$

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

$$P^*_d = \varepsilon_0 \varepsilon^*_1 E^* + \varepsilon_{rs} \cdot \exp(-\underline{\underline{\beta}} t)$$

$$\frac{dP^*_d}{dt} = \varepsilon_0 \varepsilon^*_1 . i\omega . E^* - \beta \varepsilon_{rs} \exp(-\beta t)$$

$$\tau . \varepsilon_0 \varepsilon^*_1 i\omega E^* - \beta \varepsilon_{rs} \exp(-\beta t) + \varepsilon_0 \varepsilon^*_1 E^* + \varepsilon_r \exp(-\beta t)$$
$$= \left(\varepsilon^*_{rs} - \varepsilon^*_{r\infty}\right) \varepsilon_0 E^*$$

So, this is the saturation you get. So, you can now modify our expression as:

$$\tau.\left(\frac{dP^*_d}{dt}\right) + P^*_d(t) = \left(\varepsilon^*_{r,s} - \varepsilon^*_{r,\infty}\right)\varepsilon_0 E^*$$

Because this was equal to P_s star. So, this is the term that we get for P_s.

$$\tau.\left(\frac{dP^*_d}{dt}\right) + P^*_d(t) = \left(\varepsilon^*_{r,s} - \varepsilon^*_{r,\infty}\right)\varepsilon_0 E^* = P^*_s$$

So, assuming now we know that E^* has a relation:

$$E^* = E_0 e^{i\omega t}$$

So since field is varying, it has a time dependence. We might expect the solution of P is also time dependent. So, we can write a solution, so, let us say, we say that P$_d$ star can be written in the form:

$$P_d^* = \varepsilon_0 \varepsilon_r^* E^* + \varepsilon_{r,s} e^{(-\beta t)}$$

It has some sort of form, which is like this and we want to determine here what β is. So, if β is like this, what we do is that, first if we say that this is the solution, we differentiate this d(P$_d$) with respect to time and what we obtain is:

$$\frac{dP_d^*}{dt} = \varepsilon_0 \varepsilon_r^* i\omega E^* - \beta \varepsilon_{r,s} e^{(-\beta t)}$$

This can be expanded using above expressions as:

$$\tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \beta \varepsilon_{r,s} e^{(-\beta t)} + \varepsilon_0 \varepsilon_r^* E^* + \varepsilon_r e^{(-\beta t)} = \left(\varepsilon_{r,s}^* - \varepsilon_{r,\infty}^*\right) \varepsilon_0 E^*$$

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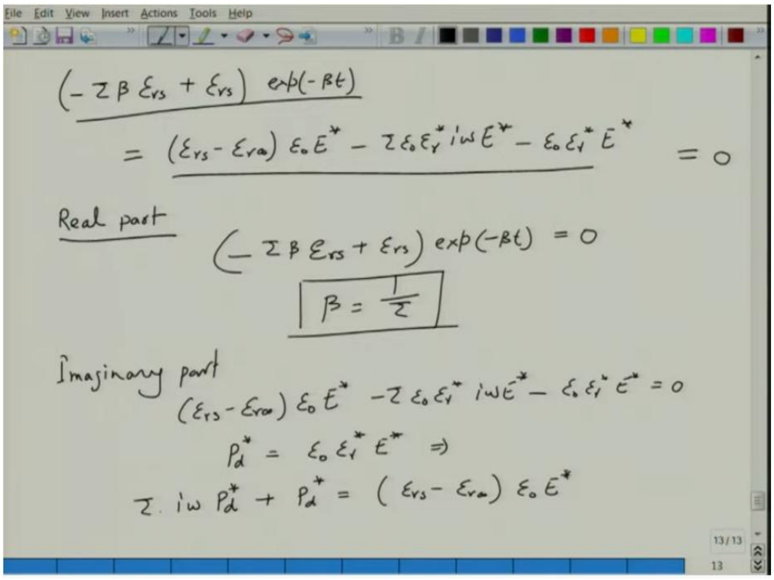

$$\underline{(-\tau\beta \varepsilon_{rs} + \varepsilon_{rs}) \exp(-\beta t)}$$

$$= \underline{(\varepsilon_{rs} - \varepsilon_{r\infty}) \varepsilon_0 E^* - \tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \varepsilon_0 \varepsilon_r^* E^*} = 0$$

Real part

$$(-\tau\beta \varepsilon_{rs} + \varepsilon_{rs}) \exp(-\beta t) = 0$$

$$\boxed{\beta = \frac{1}{\tau}}$$

Imaginary part

$$(\varepsilon_{rs} - \varepsilon_{r\infty}) \varepsilon_0 E^* - \tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \varepsilon_0 \varepsilon_r^* E^* = 0$$

$$P_d^* = \varepsilon_0 \varepsilon_r^* E^* \Rightarrow$$

$$\tau . i\omega P_d^* + P_d^* = (\varepsilon_{rs} - \varepsilon_{r\infty}) \varepsilon_0 E^*$$

Now, what we get is, we can separate, the frequency dependent part and non frequency dependent part on two sides. So this part will become:

$$\left(-\tau\beta \varepsilon_{r,s} + \varepsilon_{r,s}\right) e^{(-\beta t)} = \left(\varepsilon_{r,s}^* - \varepsilon_{r,\infty}^*\right) \varepsilon_0 E^* - \tau \varepsilon_0 \varepsilon_r^* i\omega E^* - \varepsilon_0 \varepsilon_r^* E^* = 0$$

So, now since these two sides are equal to each other, they must be called to some constant and it turns out that constant is equal to zero.

So, basically we make first for the real part:

$$\left(-\tau\beta\varepsilon_{r,s} + \varepsilon_{r,s}\right)e^{(-\beta t)} = 0$$

So from this, one can see that:

$$\beta = \frac{1}{\tau}$$

This is the first thing that we get. And now we do the same thing for imaginary part. So, basically we have made them equal to zero. And imaginary part if we do the same thing, then:

$$\left(\varepsilon^*_{r,s} - \varepsilon^*_{r,\infty}\right)\varepsilon_0 E^* - \tau\varepsilon_0\varepsilon^*_r i\omega E^* - \varepsilon_0\varepsilon^*_r E^* = 0$$

So, if you say that, if:

$$P^*_d = \varepsilon_0\varepsilon^*_r E^*$$

So, if you do the substitution, what we will get is:

$$\tau i\omega P^*_d - P^*_d = \left(\varepsilon_{r,s} - \varepsilon_{r,\infty}\right)\varepsilon_0 E^*$$

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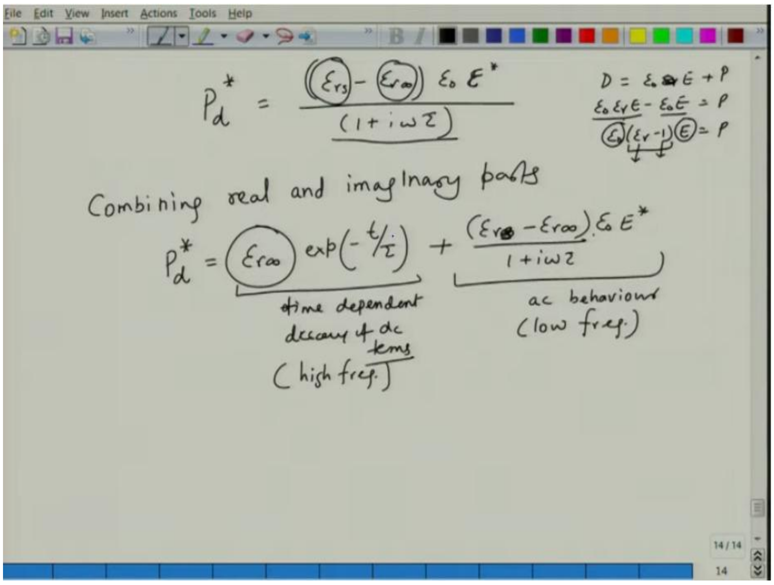

$$P_d^* = \frac{(\varepsilon_{rs} - \varepsilon_{r\infty})\,\varepsilon_0 E^*}{(1 + i\omega\tau)}$$

$D = \varepsilon_0 E + P$

$\varepsilon_0\varepsilon_r E - \varepsilon_0 E = P$

$\varepsilon_0(\varepsilon_r - 1)E = P$

Combining real and imaginary parts

$$P_d^* = \underbrace{\varepsilon_{r\infty}\exp\left(-t/\tau\right)}_{\substack{\text{time dependent}\\ \text{decay of dc terms}\\ \text{(high freq.)}}} + \underbrace{\frac{(\varepsilon_{r} - \varepsilon_{r\infty})\,\varepsilon_0 E^*}{1 + i\omega\tau}}_{\substack{\text{ac behaviour}\\ \text{(low freq.)}}}$$

So, P_d^* becomes:

$$P^*_d = \frac{\left(\varepsilon_{r,s} - \varepsilon_{r,\infty}\right)\varepsilon_0 E^*}{\left(1 + i\omega\tau\right)}$$

If you look at this expression, it is fairly similar.

Essentially, earlier we took dielectric displacement after inserting a dielectric, minus the dielectric displacement without the dielectric that was equal to polarization, induced polarization. Here also it is the same. So, here we are taking macroscopic values, maximum dielectric constant minus one. One was when we did not have a dielectric.

ε_r was the one when you had dielectric. Here we are comparing two relative values, one is the high frequency contribution, another is the low frequency or nearly zero frequency contribution. Difference between the two is the dipolar part. So here, we are now not looking at the total polarization, we are only looking at the dipolar contribution. Additionally what we have in denominator is a term which is the frequency dependent term.

So, if you make $\omega = 0$, this becomes basically 1. So, it becomes similar to what we have seen earlier. So, there is nothing too magical here, it is just that now, we have done frequency dependent analysis. Now, if we combine real and imaginary part, what we get is:

$$P_d^* = \varepsilon_{r,\infty} e^{\left(-t/\tau\right)} + \frac{\left(\varepsilon_{r,s} - \varepsilon_{r,\infty}\right)\varepsilon_0 E^*}{\left(1 + i\omega\tau\right)}$$

This is the frequency independent term, this is the d.c term basically.

We can say time dependent dc term. So time dependent decay of, let us say, because this $\exp(-t/\tau)$, so how does the d.c contribution decays as a function of time. So time dependent decay of nearly dc term. Basically you cannot say it is particularly d.c, because you have $\varepsilon_{r,\infty}$, there is a frequency dependence there, but it is at very high frequencies. For all practical purposes, you can consider this to be frequency independent.

So time dependent decay of the independent term and then we have this another term which is basically the ac behavior at low frequencies. So, this is basically the low frequency, this is ultra-high frequency, which is nearly a constant term how it decays with the polarization. So, essentially this contribution is going to be extremely small to dipolar polarization and that is why most of the times we ignore that part.

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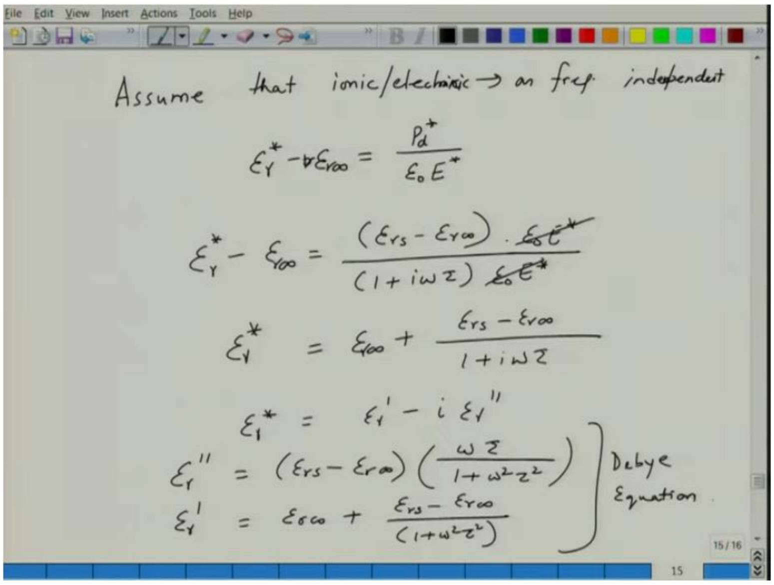

Assume that ionic/electronic → as freq. independent

$$\varepsilon_r^* - \varepsilon_{r\infty} = \frac{P_d^*}{\varepsilon_0 E^*}$$

$$\varepsilon_r^* - \varepsilon_{r\infty} = \frac{(\varepsilon_{rs} - \varepsilon_{r\infty}) \cdot \cancel{\varepsilon_0 E^*}}{(1 + i\omega\tau)\cancel{\varepsilon_0 E^*}}$$

$$\varepsilon_r^* = \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{1 + i\omega\tau}$$

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

$$\left.\begin{aligned} \varepsilon_r'' &= (\varepsilon_{rs} - \varepsilon_{r\infty})\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) \\ \varepsilon_r' &= \varepsilon_{r\infty} + \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{(1+\omega^2\tau^2)} \end{aligned}\right\} \text{Debye Equation}$$

So, assuming that ionic electronic contributions as frequency independent. We can write this:

$$\varepsilon_{r,s}^* - \varepsilon_{r,\infty}^* = \frac{P_s^*}{\varepsilon_0 E^*}$$

So, what we have done is, we have just taken the frequency independent of polarization. So, this becomes equal to essentially:

$$\varepsilon_r^* - \varepsilon_{r,\infty} = \frac{(\varepsilon_{r,s} - \varepsilon_{r,\infty})}{(1 + i\omega\tau)}$$

And we know that:

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

So, if we separate the real and imaginary part, what we will get is:

$$\varepsilon_r'' = (\varepsilon_{r,s} - \varepsilon_{r,\infty}).\left(\frac{\omega\tau}{1 + \omega^2\tau^2}\right)$$

And,

$$\varepsilon_r' = \varepsilon_{r,\infty} + \left(\frac{\varepsilon_{r,s} - \varepsilon_{r,\infty}}{1 + \omega^2\tau^2}\right)$$

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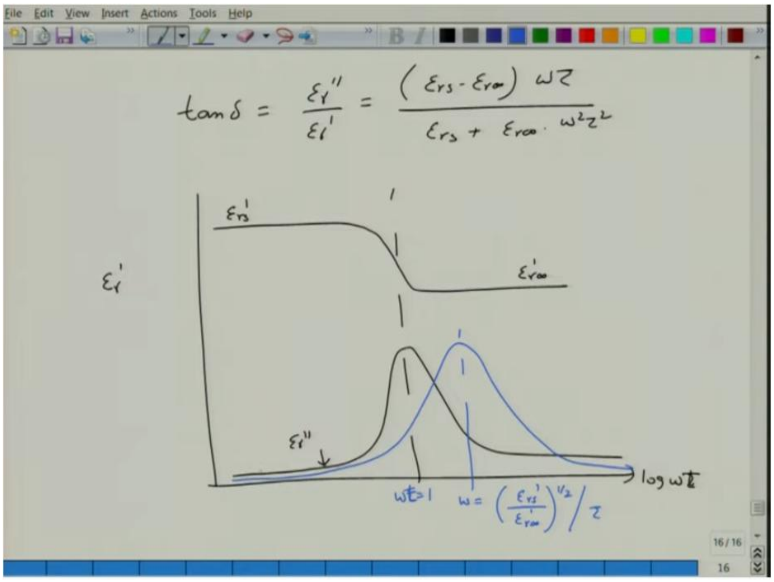

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} = \frac{(\varepsilon_{rs} - \varepsilon_{r\infty})\,\omega\tau}{\varepsilon_{rs} + \varepsilon_{r\infty}\cdot\omega^2\tau^2}$$

And tan delta will be equal to correspondingly:

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} = \frac{(\varepsilon_{r,s} - \varepsilon_{r,\infty})\omega\tau}{\varepsilon_{r,s} + \varepsilon_{r,\infty}.\omega^2\tau^2}$$

So this is what is the analysis that we have done and these equations are called as Debye equations. So these are called as Debye equation. And when you plot this dielectric constant as a function of frequency now, so ε_r'.

Let us say first, so there is a frequency. So, let us say we plot log(ωτ). So, at a value of ωτ=1, you have resonance that is occurring. So, this goes from $\varepsilon_{r,s}'$ to $\varepsilon_{r,\infty}'$. And this is ε_r'', it undergoes a maximum. And the tan δ maximize, so this is for ε_r''. The tan δ maxima has shifted to slightly higher frequencies. So, for tan δ you can plot maxima like this.

And this occurs at:

$$\omega = \frac{\left(\varepsilon_{r,s}' \big/ \varepsilon_{r,\infty}'\right)^{\frac{1}{2}}}{\tau}$$

So, we can find out that easily, the maxima at which point. So, this is what dielectric relaxation is, there is no resonance. There is a gradual change in low frequency dielectric constant, that is static dielectric constant to high frequency dielectric constant, at a frequency, at which ωτ = 1. So, this is also critical frequency.

So, this is $\omega\tau = 1$ at this point. And at the same point, we have a maxima imaginary dielectric constant. Correspondingly, tan δ also shows a maxima at this frequency, which is close to the peak of tan. So, this is what is the dielectric relaxation, which is basically about slow change of dipolar polarization as a function of time. So, as a result, we do not see a resonance, we see a relaxation of dielectric constant to smaller values as a function of time.