Fundamentals and Applications of Dielectric Ceramics
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Lecture No. – 23
Dipolar Relaxation

Welcome to this new lecture of the course, fundamentals and applications of dielectric ceramics.

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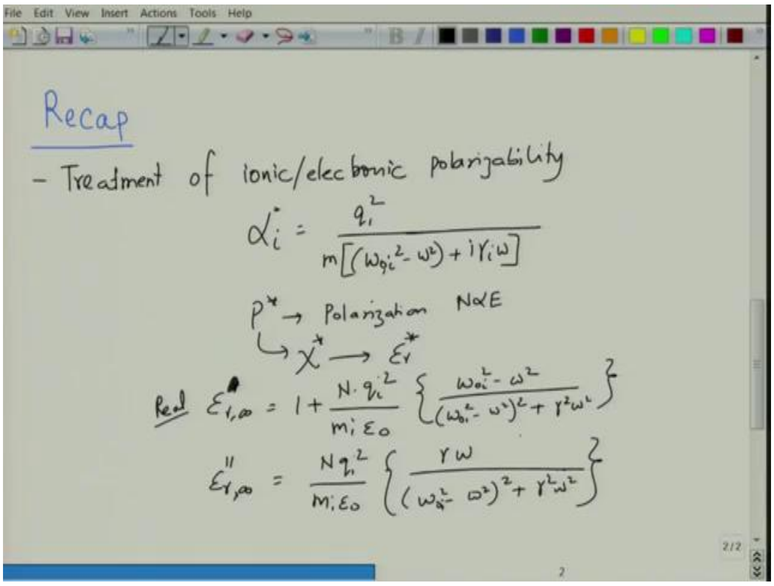

Recap

- Treatment of ionic/electronic polarizability

$$\alpha_i = \frac{q_i^2}{m[(\omega_{0i}^2 - \omega^2) + i\gamma_i\omega]}$$

$$P^* \rightarrow \text{Polarization} \quad N\alpha E$$

$$\hookrightarrow \chi^* \longrightarrow \varepsilon_r^*$$

Real $\varepsilon'_{r,\infty} = 1 + \frac{N \cdot q_i^2}{m_i \varepsilon_0} \left\{ \frac{\omega_{0i}^2 - \omega^2}{(\omega_{0i}^2 - \omega^2)^2 + \gamma^2\omega^2} \right\}$

$$\varepsilon''_{r,\infty} = \frac{N q_i^2}{m_i \varepsilon_0} \left\{ \frac{\gamma\omega}{(\omega_{0i}^2 - \omega^2)^2 + \gamma^2\omega^2} \right\}$$

Let us just briefly recap what we did in the last class. In the last class, we did a treatment of ionic or electronic polarisability. The first treatment that we did, in that we found that, you know, ionic and electronic polarisabilities are temperature independent. And we also did not look at the frequency dependence. We just did it under dc conditions. We saw that electronic polarisability is proportional to r^3, that is the size of ionic species, size of the atom, and then ionic polarisability is inversely proportional to the modulus.

But then, we took a step further and we did frequency dependence by applying a sinusoidally varying electric field and considering the electron cloud and the nucleus or the ions as connected through a spring in the form of a simple harmonic oscillator. As a result, we wrote the equation of motion and then we solved it for a displacement x, and then, based on that we calculated what is the polarisability.

So, polarisability was worked out as:

$$\alpha^*{}_i = \frac{q_i^2}{m_i^*[(\omega_{0,i}^2 - \omega^2) + i\gamma_i\omega]}$$

This is what we worked out. And from this one can work out what is the polarisation. Of course, it is a complex quantity. So, we can work out what is polarisation. Polarisation will be:

$$P = N\alpha E$$

where N is the number of dipoles per unit volume.

And then, when you do the separation of real and imaginary parts then we can relate polarisation to susceptibility. Susceptibility can give rise to ε_r, and we found expressions for a ε_r:

$$\varepsilon'_{r,\infty} = 1 + \frac{N.q_i^2}{m_i\varepsilon_0}\left\{\frac{\omega_{0,i}^2 - \omega^2}{(\omega_{0,i}^2 - \omega^2)^2 + \gamma^2\omega^2}\right\}$$

This was the real part. And the imaginary part was:

$$\varepsilon''_{r,\infty} = \frac{N.q_i^2}{m_i\varepsilon_0}\left\{\frac{\gamma\omega}{(\omega_{0,i}^2 - \omega^2)^2 + \gamma^2\omega^2}\right\}$$

So, this was the expression that we got and basically this suggests that in the denominator you have this term **($\omega^2_{0,i}$ - ω^2)**. So, the resonance will happen when **$\omega = \omega_{0,i}$**.

So, your dielectric constant has to be measured at frequencies which are lower than this **$\omega_{0,i}$**. The moment frequency is higher than the **$\omega_{0,i}$**, the corresponding dipoles do not respond to the frequency. As a result, they do not contribute to dielectric constant.

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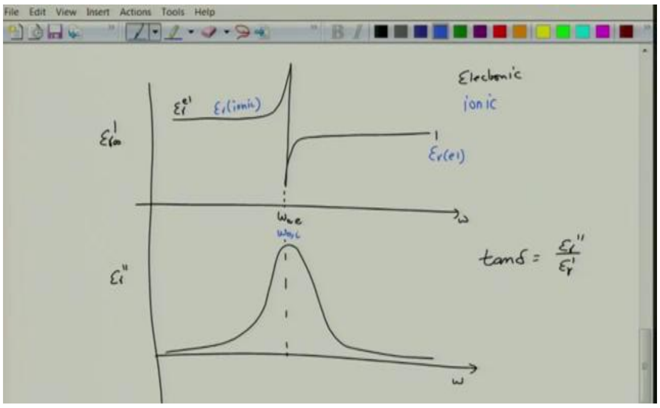

So, when you plot these dielectric constants, when you plot this ε_r' as a function of frequency, then we see something like that. So, if it is for electronic, then this would be one and this would be **$\varepsilon_{r\,(\text{electronic})}$**, and this frequency would be **$\omega_{0,e}$** correspondingly. And at this point we will have the maximum and the ε_r''.

And, correspondingly, if you plot tan δ which is equal to $\varepsilon_r''/\varepsilon_r'$, you will see a peak in tan δ as well. So, basically what happens is that above this frequency **$\omega_{0,e}$**, the dipoles are not able to keep pace with the frequency of the applied field, as a result, they do not respond. So, you have to go to frequencies below **$\omega_{0,e}$** for electronic dipoles to respond, then only they will be able to contribute to the dielectric constant.

Similarly, when you go below this, for ionic, if we now make similar plot in the blue color as ionic, this frequency would be **$\omega_{0,i}$** and here it would be **$\varepsilon_{r\,(\text{electronic})}$** and here it would be **$\varepsilon_{r\,(\text{ionic})}$** So, this is how it will change as a function of frequency when you measure this dielectric constant.

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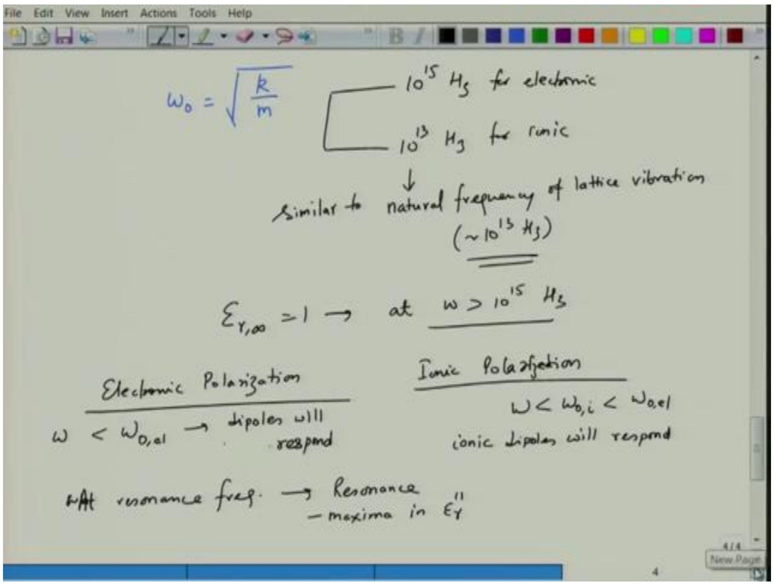

$\omega_0 = \sqrt{\frac{k}{m}}$

10^{15} Hz for electronic

10^{13} Hz for ionic

$\downarrow$

Similar to natural frequency of lattice vibration ($\sim 10^{13}$ Hz)

$\varepsilon_{r,\infty} = 1 \rightarrow$ at $\omega > 10^{15}$ Hz

Electronic Polarization

$\omega < \omega_{0,el} \rightarrow$ dipoles will respond

Ionic Polarization

$\omega < \omega_{0,i} < \omega_{0,el}$

ionic dipoles will respond

At resonance freq. $\rightarrow$ Resonance – maxima in ε_r''

And another simple argument that one can look at is this vibrational frequency. So, frequency can be written as:

$$\omega_0 = \sqrt{\frac{k}{m}}$$

This is from classical mechanics. So, basically, if you balance the force that is inducing the movement and the restoring force, you will get the value of spring constant.

And this $\boldsymbol{\omega_0}$ works out to about, if you just consider it as spring simple harmonic oscillator with a certain value of **k**, $\boldsymbol{\omega_0}$ can be determined to be about 10^{15} Hz for electronic polarisation and then about 10^{13} Hz for ionic polarisation. And that sort of makes sense because the mass of electrons is far lower than the mass of ions put together.

So, as a result, the frequency is down and since this is a square root you can see that it must be about few orders of magnitude smaller. And another thing that you noticed is that the frequency here for ionic polarisation is about 10^{13} Hz which is similar to basically natural frequency of vibrations that is vibrations about, so ions vibrating means lattices vibrating, so this is about 10^{13} Hz for lattice vibration.

So, basically this shows that whatever we have done is fairly right. And as you go to very high frequencies naturally dipoles do not respond. As a result, $\boldsymbol{\varepsilon_{r,\infty}} = 1$ at frequencies greater than 10^{15} Hz because none of the polarisation mechanism is able to keep pace with the applied electric field, as a result, you have zero contribution from them.

So, essentially, basically, you can summarise this part as that for electronic polarisation critical frequency, the resonance frequency is $\boldsymbol{\omega_{0,e}}$. So, as long as your frequency is lower than this frequency your dipoles will respond. And for ionic polarisation your frequency is lower than $\boldsymbol{\omega_{0,i}}$ which is lower than $\boldsymbol{\omega_{0,e}}$. What this means is that your ionic dipoles will respond and correspondingly at the resonance frequency we will see a maximum in the $\boldsymbol{\varepsilon_r}$, that is ε_r''.

So, you will have resonance and maxima in ε_r''. So, this is a simple analysis for electronic and ionic polarisation given their frequency dependence. And you can also convert these equations to find out what happens when $\boldsymbol{\omega} = 0$. When it is equal to zero you should be able to convert them to similar dc equations that we worked out earlier. So, basically, α electronics should reduced to $\mathbf{4\pi\varepsilon_0 rq}$. So, that is what it should happen.

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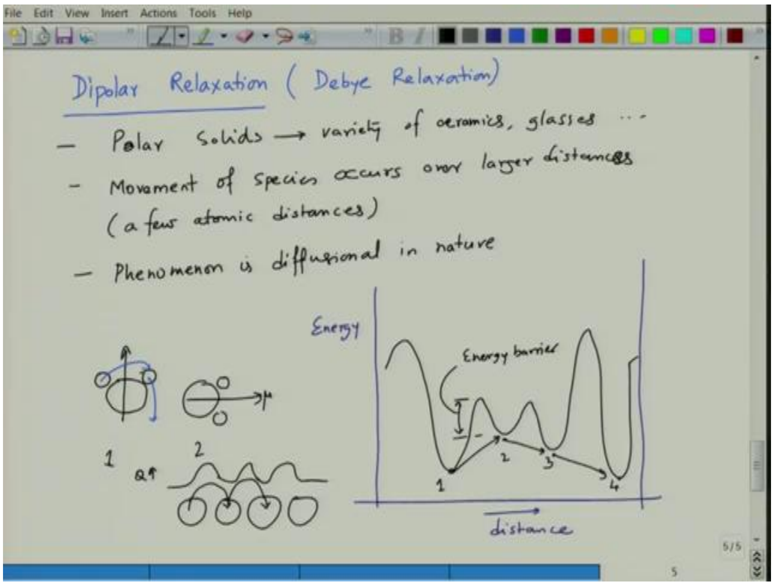

Dipolar Relaxation (Debye Relaxation)

- Polar Solids → variety of ceramics, glasses …
- Movement of species occurs over larger distances (a few atomic distances)
- Phenomenon is diffusional in nature

Now, let us look at the treatment of dipolar relaxation. Basically frequency dependence of dipolar relaxation and this is also called often as Debye relaxation in the name of Debye and this is valid for mainly we can say polar solids and this could be a variety of dielectric ceramics, glasses, and many other systems. So, here, we do not use that damped oscillator approach, rather, we use relaxation approach where some entity goes from one position to another position, relaxing from one to another.

So, here what we will say is that the movement of charges, the movement of a species let us say occurs over larger distances than as compared to electronic and ionic. So, it could be a few atomic distances and, as a result, the phenomena is diffusional in nature. Basically, suppose you have charged dipole like this, it was earlier in this fashion, now it has to move. So, this is the first position. Now, it has to move to this position.

Essentially it goes from this position to that position μ. So, all these atoms have to now hop from this position to, so this atom has to come from this position to this position. Correspondingly, this atom has to go from this position to that. So, everything has to rotate in a matrix and this could mean the translation of atoms could be fairly large of the order of atomic spacing or even higher.

So, basically, energetically speaking, you can represent this process as the species overcoming several energy barriers. So, when you plot this as a function of distance, and that is why these processes are diffusional in nature or they follow Arrhenius kind of relaxation.

So, here, you can plot this as, you can have scenarios like, so on and so forth. You might have transition, for example, from this state to this state.

You might have transition from this state to this state. You might have transition from this state to the state depending upon the type of solid, whether you have a glassy solid, whether you have a crystalline solid. In crystalline solid there will be more ordered movements. In glassy solid there will be more disordered movements. But, nevertheless, it goes from one metastable position to another metastable position.

These are all metastable position in the free energy landscape. As a result, for a species to change its configuration from let us 1 to 2. This is 1 let us say and this is 2, they have to overcome energy barrier. So, this is energy barrier which has to be overcome. So, when they go from 1 to 2 they cross this energy barrier, then 2 to 3 again there is energy barrier, and 3 to 4 again there is energy barrier.

As a result, there is a considerable slowness as compared to the previous because it has to diffuse from one place to another, another to another. Diffusion is basically Arrhenius phenomenal. So, if you look at the lattice, for example, when this atom moves from this place to another, basically it undergoes energy barrier because the transitions that takes place in the middle they dilate the lattice, as a result, there is a sort of temporary generation of strain in the lattice it has to overcome. So, it has to break one bond and form another bond.

As a result, there the activation energy, you can say Q that is needed for transition to occur. Similarly, in this fashion, it has to go from one position to another. As a result, the process is sort of diffusional in nature requiring activation of energy barrier to be crossed.

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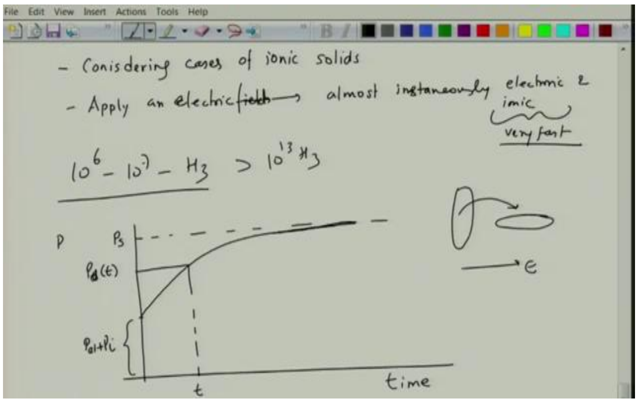

- Conisdering cases of ionic solids
- Apply an electric ~~field~~ → almost instaneously electronic & imic very fast

$10^6 - 10^7 - Hz > 10^{13}\ Hz$

So, here, let us say the case of ionic solids, considering cases of ionic solids, so when you apply electric field, now, as compared to this relaxation the frequency scale at which ionic and electronic polarisation will develop, will be very fast. So, basically, when you apply an electric field, you will develop almost instantaneously an electronic and ionic polarisation because they are very fast.

So, when you apply, let us say, a field of frequency 10^6 or 10^7 Hz which is very fast as compared to 10^{13} Hz. You can see that there is a magnitude of difference, seven orders of magnitude difference. So, when you apply frequency, electric field of this sort of frequency, then generation of electronic and ionic polarisation will be almost immediate.

So, when you now plot this polarisation as a function of, let us plot polarisation as a function of time, then almost instantaneously we have a contribution from electronic and ionic, let us say this is $P_{electronic} + P_{ionic}$ and the saturation polarisation then develops over a function of time. So, let us say, this is the value of saturation polarisation in a given system, the maximum value of polarisation that you can get, and this thing takes its own time to develop.

Eventually it does reach the value, but it takes time. And this is the dipolar polarisation which is time dependent polarisation, P.dt. As compared to electronic and ionic part this development is far more slower. So, molecules basically, you can say this is a molecule in this fashion, this molecule has to now rotate to go to this position. This you apply electric field, it has to come to this direction, but it has to rotate, it has to undergo a rotation in the matrix or in the structure.

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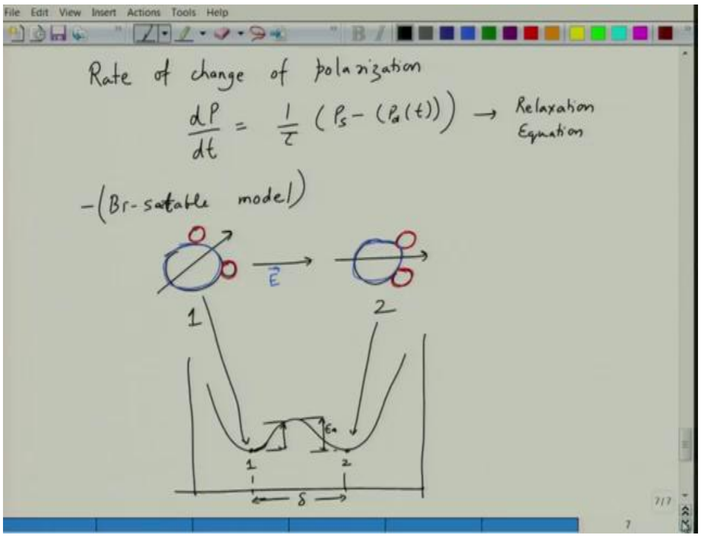

Rate of change of polarization

$$\frac{dP}{dt} = \frac{1}{\tau}\left(P_s - (P_d(t))\right) \rightarrow \text{Relaxation Equation}$$

-(Bi-stable model)

Correspondingly, if we assume this model to be true, then we write the rate of change of polarisation as:

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

Here, $1/\tau$ is basically a proportionality constant and this equation is called as relaxation equation or basically it will come to be as time constant tau which is proportionality constant. So, this model is sort of called as bi-stable model where you go from one stable state to another stable state.

So, basically, this change in polarisation is P_S - P_d. So, essentially you are looking at the rate of change of polarisation within this regime, and at any given time the polarisation is P.dt. And when you reach here, then of course, at very large times when $P_d = P_S$, then rate of change is equal to zero, the slope is equal to zero. We call this model as bi-stable stable model.

So, basically what we are saying is that you have a charged dipole like this whose orientation was like this and now this charge dipole changes its orientation. So, this is position 1, this is position 2. Let us say, if we make it a little coloured just for the sake of illustration, and this is where you apply electric field. So essentially we are considering the energy landscape can be plotted as, let us say this is position 1, this is some position 2, so this is position 1, this is position 2, and it has to overcome an energy barrier.

So, if you look from this side, the energy barrier will be this, E_a, and if you look from this side, then the energy barrier would be this much. And this distance between the two is equal to, let us say, δ. This is the distance between the two positions. So, this is position 1 corresponding to that and position 2 corresponding to this position. So, when you apply electric field to such a polar material, then ions hop from one position on the position.

This could be, for example, in glasses you have silver ion conductor, sodium ion conductor, etc., it could be dielectric, it could be ice structure of water molecules, various materials which are polar in nature will show similar kind of behavior.

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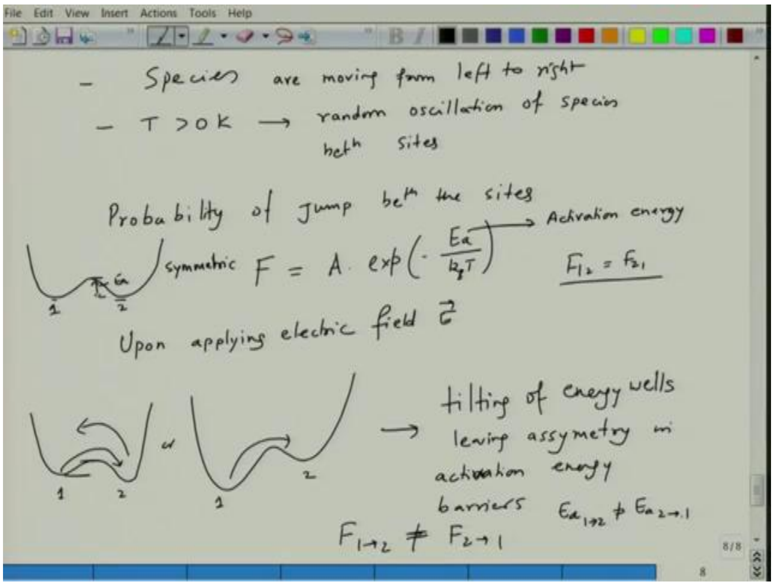

- Species are moving from left to right
- T > 0 K → random oscillation of species betn sites

Probability of Jump betn the sites

symmetric $F = A \cdot \exp\left(-\frac{E_a}{k_B T}\right) \rightarrow$ Activation energy

$F_{12} = F_{21}$

Upon applying electric field $\vec{E}$

→ tilting of energy wells leaving assymetry in activation energy barriers $E_{a_{1\to2}} \neq E_{a_{2\to1}}$

$F_{1\to2} \neq F_{2\to1}$

So, we can see in the previous image that cations are, let us say it is related to cations, so cations are moving from, instead of saying cations let us say species because it could be anything, so species are moving from left to right. And temperature is greater than zero. This is what we have to first see. So, when the temperature is greater than zero which means there is a random oscillation also of a species, because when your temperature is greater than zero degree centigrade the atoms or molecules will vibrate.

As a result, there will be a probability of rightward movement, there is a probability of leftward movement as well which is basically true for any solid. So, now, let us calculate what is the probability of jump between the sites. When we look at the probability of jump between the sites, let us define this as F:

$$F = A.e^{\left(-\frac{E_a}{k_B T}\right)}$$

We could have written as P, but P is something that we have defined for polarisation.
So, let us not confuse. Let us say for now the A is some sort of constant, and E_a is the activation energy or the barrier which species have to overcome to move from one position to another, k is the Boltzmann constant, T is the temperature, and A is the exponential factor.

So, when you apply electric field, this is symmetric, let us say you have a situation like this where the wells are symmetric. So, on both sides the energy barrier will be similar. So, this is symmetric to begin with, and when you go from 1 to 2 or 2 to 1 they have to face that similar E_a. So, as a result, you can see if you go from 2 to 1 or 1 to 2 the probability will be same.

Now, when you apply electric field, electric field will be in certain direction, as a result the wells will tilt. So, you might have a situation like this or you might have a situation like this. So, you can see that there is an asymmetry in the energy barrier. So, when you look at situations like this you can see for atoms to hop from this side to this side the energy barrier is lower, whereas from 2 to 1 the energy barrier is larger, or in the converse case, the hopping from 1 to 2 is more difficult, but 2 to 1 is easier because the energy barriers are low.

So, basically application of electric field leads to tilting of energy wells leaving asymmetry in activation energy barriers. Depending upon 1 to 2 and 2 to 1 when the magnitude of E_a has changed, which means the probability also has changed which means $F_{1\rightarrow2}$ will not be the same as $F_{2\rightarrow1}$. In this case when it is symmetric, then $F_{1\rightarrow2} = F_{2\rightarrow1}$. When there is no field it is the same probability, that is why you do not see overall diffusion.

But here, now that you have applied a force which is let us say electric force in this case, electrical force, then F_{12} is not equal to F_{21}. There is assymetry in E_a magnitude. As a result, $E_{a1\rightarrow2}$ is not equal to $E_{a2\rightarrow1}$ and this leads to a symmetry in the probability of jump. As a result, you will have a net flow of dipoles, net flow of species from one to another.

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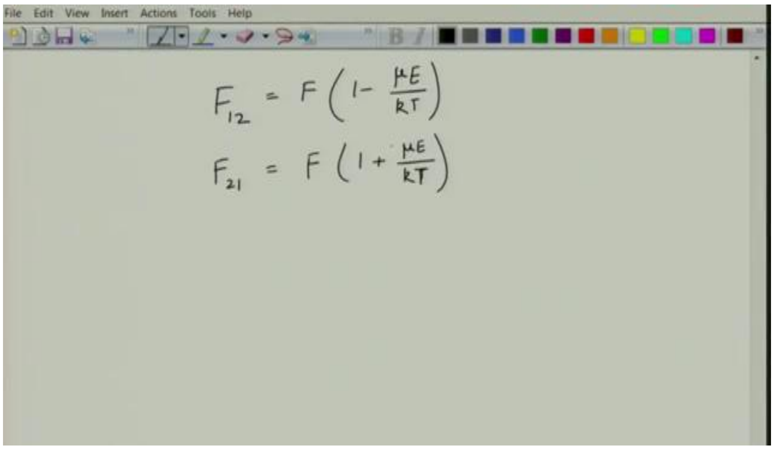

$$F_{12} = F\left(1 - \frac{\mu E}{kT}\right)$$

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

So, let us say we calculate this:

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

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

So, initial was F_{12} and F_{21} were equal to this. So, one of them will be plus and another would be minus. So, on one side you have added the energy, on the other side you have subtracted the energy. So, this is what we will take it further.

What we have done is we have just taken the simple bi-stable relaxation model where we are saying that when you apply electric field of certain frequencies the dipoles move from one position to another position. This is basically at lower frequencies. So, when you apply such low frequencies the electronic and ionic polarisation will develop almost instantaneously but the dipolar polarisation will be time dependent polarisation.

And this will happen on a much longer time scale. And why this happens is because you have a species moving from one position to another position and this process is called as relaxation. They have to overcome energy barrier. And since they are moving from one place to another place there is a possibility of back movement as well because the process is diffusional.

So, we need to calculate the probabilities of movement from one side to another, from 1 to 2 and 2 to 1 and we have to calculate a net flow of dipoles from 1 to 2 and 2 to 1. So, this is where we are right now. We will look at this a little later when we are in the next lecture.