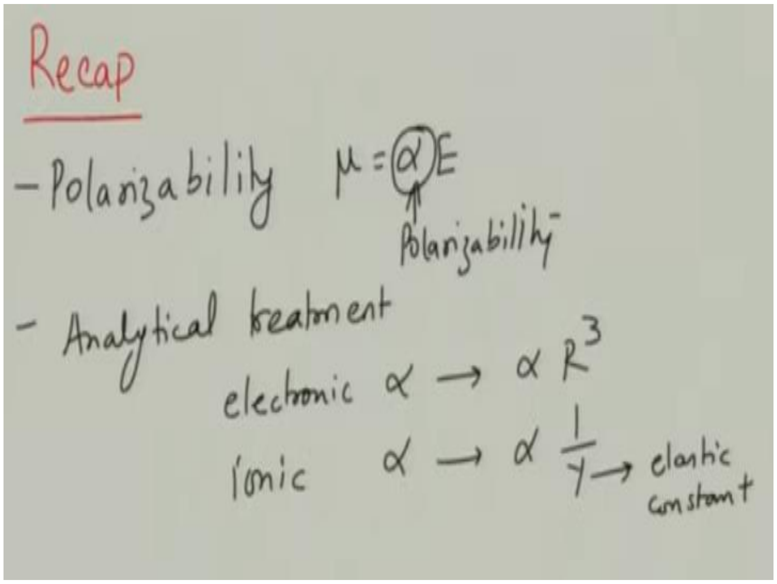
Fundamental and Applications of Dielectric Ceramics
Prof. Ashish Garg
Department of Materials Science & Engineering
Indian Institute of Technology – Kanpur

Module No # 04
Lecture No # 19
Dielectric Polarizability

So welcome again to the course fundamental and applications of dielectric ceramics so we will start with the new lecture today again let first recap the previous lecture.

(Refer Slide Time: 00:25)



Recap

- Polarizability $\mu = \boxed{\alpha} E$

$\uparrow$ Polarizability

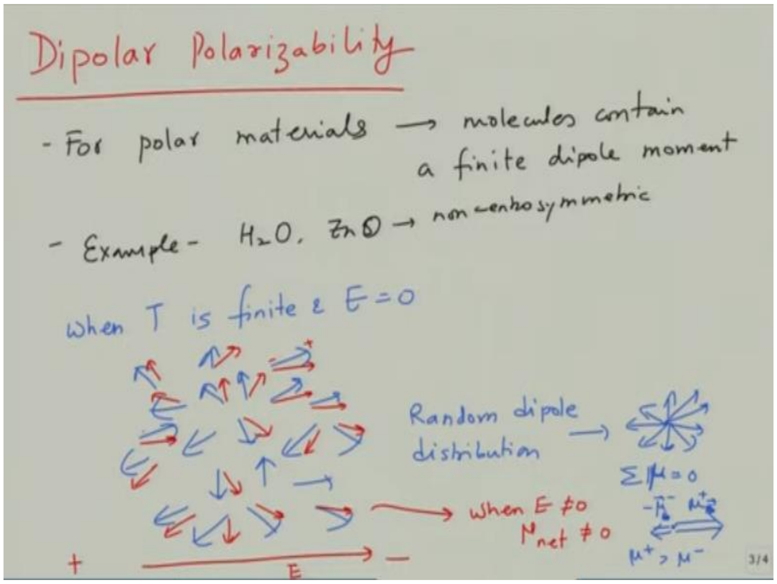
- Analytical treatment

electronic $\alpha \rightarrow \propto R^3$

ionic $\alpha \rightarrow \propto \frac{1}{Y} \rightarrow$ elastic constant

So in the previous lecture we learnt about the polarizability which is μ which relates with the dipole moment with the electric field so alpha is polarizability and we did analytical treatment of electronic polarizability and ionic polarizability and here we found that it is proportional to R cube which means bigger the atom is more polarizable it is and here it is inversely proportional to 1 over y which is the elastic constant. So more stiff the material is more the bond energy is lesser it is able to polarize which makes sense some in stronger materials do not get polarize very easily.

(Refer Slide Time: 01:42)



Dipolar Polarizability

- For polar materials → molecules contain a finite dipole moment

- Example - H_2O, ZnO → non-centrosymmetric

when T is finite & $E = 0$

Random dipole distribution →

$\Sigma \mu = 0$

→ when $E \neq 0$ $\mu_{net} \neq 0$

$\mu^+ > \mu^-$

So today what we will do is that we will take a case of what we call as dipolar polarizability which is essentially a material which if contains for material which contains dipolar polarization let us so basically this treatment is valid from materials which are polar in nature which means molecules contain a finite dipole moment. So, this would be valid for examples like example would be H_2O molecule it is also to some extent valid for tends like zinc oxide which is the non-centro-symmetric structure.

So any solid which is polar in nature will have this is valid so the reason so what happens when you have this polar molecules on polar molecules sorry polar molecules is that when temperature is finite and electric field is equal to 0 then let us say that dipole moments are all over the place so these are the molecules which are present in the system and as a result of randomization.

So you have basically random dipole distribution and you can sum it as if these dipoles are pointing in such a manner so that μ is $\sum \mu = 0$. So, although each of the individual molecule as a finite dipole moment the system does not have dipole moment to show for because of thermal randomization lead to 0 dipole moment. Now what happens is that when you apply electric field.

So, let us say when you such a system and when you apply electric field so when you apply electric field to such a system now. So, let us say electric field is pointing from positive to negative which means dipole moments have to align so this which means dipole moments are from negative to positive okay. So, this positive of this has to align the negative of electric fields so if you have a parallel plate capacitor so negative charge will be in the plates and then positive charges will have to align with itself.

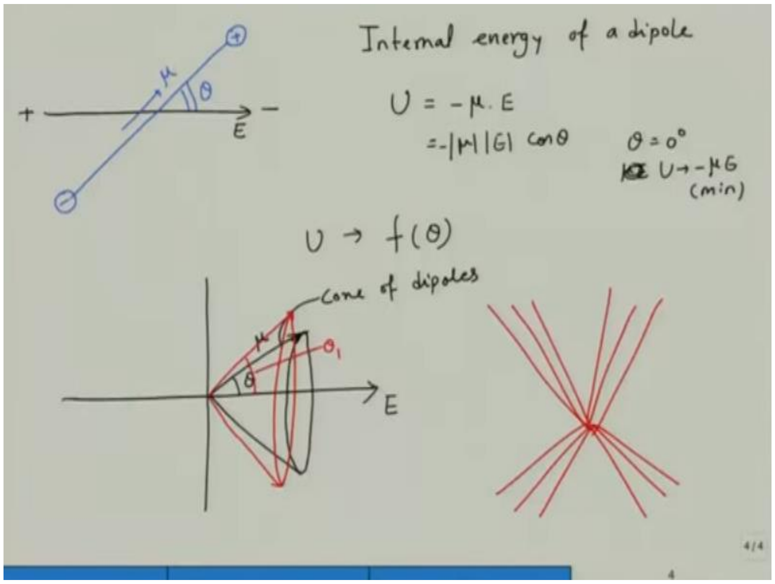
So, these have to now sort of tilt towards the applied electric field okay so this is already aligned this will come closer to be in. and so on and hence so forth. So basically the electric field will pull them towards some finite so that you have net dipole moment now in so now when E is not equal to 0 the Mu net is also not equal to 0 what it means is that in such a state your dipole moment in this direction is bigger and the dipole moment in this direction is smaller.

So, this is μ let us say E direction and this is μ, which is $-\mu$ right in this direction so this so let us not E but just say so μ so let us say positive negative. So, μ positive being greater than μ negative will give you net dipole moment. So, this is basically you will have to overcome so field strength in this case as to such that so that the field is able to overcome the applied the thermal energy.

So basically, you need to now find how much energy is required to orient this molecule to overcoming the thermal energy. So basically, this is a process which is thermally driven process so you need to apply sufficient amount of electric field to overcome this thermal randomization. So, if this is the case basically what it means is that we need to minimize the free energy of system and free energy consist of enthalpy and entropy terms so we need to balance out enthalpy and entropy but what will is such a system entropy is little difficult to calculate.

So instead of banking on the entropy we will take the help of Maxwell distribution Maxwell Boltzmann distribution to find out what is the probability of aligning certain number of dipole with certain amount of energy in the direction of applied field. So, we will in fact rely more on distribution function than on the entropy aspects of it.

(Refer Slide Time: 07: 17)



So let us say we have a picture like this so we have a dipole we have an electric field which is pointing like this from positive to negative then we have a dipole which is pointing from negative to positive okay this is your μ this is E this μ is attracted towards E so this is the angle theta between the 2. So basically, the internal energy of a dipole can be written as let us see U and this U basically is written as$U = -\mu \cdot E$.

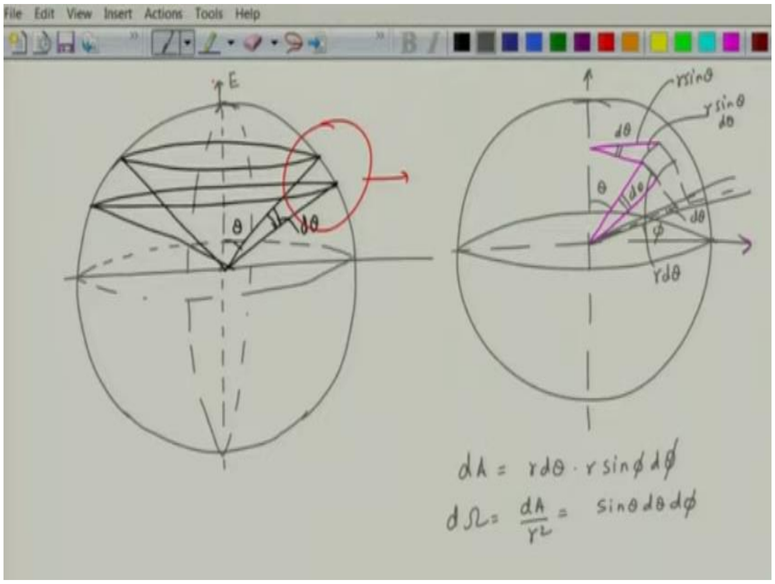
So, if you take E in the opposite direction as we conventionally take then you have to write it at $+\mu \cdot E$ because then $cos\theta$ will have so basically this will become $\mu \cdot Ecos\theta$. So, in this case when the θ is minus $\mu \cdot Ecos\theta$ when θ is equal to 0 degree then $\mu \cdot E$ would be thus U would be negative $\mu \cdot E$ that is minimum okay. Alternatively, if you take the electric field direction opposite just talking about the do not represent these charges then you have to take it as $+\mu \cdot E$.

So, you have to be careful with the sign as to how you applied the field and how you depict the field. So basically, the orient this U is basically you can see the function of theta okay so we are saying now we have multiple dipole in the system and we have the electric field applied. So basically, we can depict them as if we have let us say this direction so let us say this is the direction of E for what basically will mean is that we will have in 3 dimension a cone of dipole’s.

So, this is the cone of dipoles at an angle theta with these respect to E so this is μ this is E so this is basically a cones of dipoles at different θ will be present now. So, this is one cone of dipole at one θ you might have another cone of this is another θ let us say this is θ_1 and so on and hence so forth. So, what you basically will have in 3D you will have if you put it vertically you will have 1 cone you will have an another cone and so on and hence so forth and this will also be true in the other direction okay.

Because not all the dipoles are going to be orientated in one directions so you will have this kind of situations as well. So basically, you if you now consider these multiple cones together it will be as if you have the spherical surface created by these cones putting put altogether so which means you need to carry out integration from all the angles alright. So now let us consider in such a situation a spherical case so where we have the situation like this.

(Refer Slide Time: 10:42)



$$dA = r d\theta \cdot r \sin\phi \, d\phi$$

$$d\Omega = \frac{dA}{r^2} = \sin\theta \, d\theta \, d\phi$$

So, we draw a okay right so this is the vector E so this is let us say the first cone at certain angle theta and then you have another cone let us say an angle $d\theta$ okay. And so, you have these first cone here so this is what is let us just put up it all and then we have another cone here okay this angle would be the angle d theta and if you now project it on a surface of a sphere. So, it was if you make it little 3 dimension in nature.

So basically, you will be projecting a sort of now zoom this up so let us zoom this up on the surface of this sphere okay. So on this surface of this sphere we will have an element like this okay which will have these lines connecting right and so this is let us say one direction this is let us say one direction from so let us say this angle is θ this is $d\theta$ but in this plane in the horizontal plane here it will have projection let us say we will have one line here and another line here so this angle will be φ and this angle $d\varphi$ okay.

The 2 lines that will be coming from top so this angle is $d\varphi$ this angle will also be $d\varphi$ okay. So now if you take the projection this distance will become $rsin\theta$ so this will become $rsin\theta$ into $d\varphi$ and this will be $rd\varphi$. So, the solid so dA for this small element will be $dA = rd\theta \cdot rsin\varphi d\varphi$. So, what is the solid angle going to be? So solid angle will be

$$d\Omega = \frac{dA}{r^2}$$

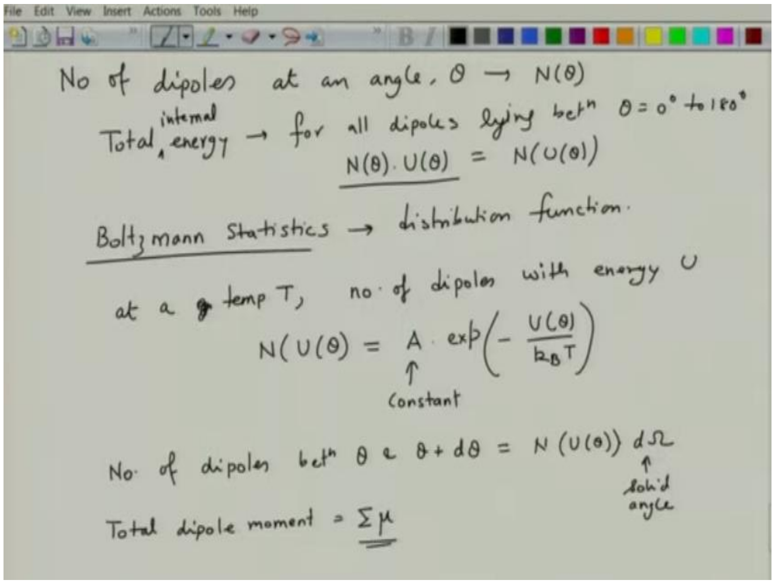
this will be

$$d\Omega = sin\theta d\theta d\varphi$$

okay.

So, this is the distance $rsin\theta d\theta$ this is the distance $rd\theta$ take them together a product of these 2 consistent that small element is square in size or rectangle in size the area of that will be $rsin\theta d\theta$. So now a basically what we are going to do is that this is the case where we need to consider the number of dipole first we need to consider so this is the schematic diagram that we have drawn here.

(Refer Slide Time: 14:42)



No of dipoles at an angle, $\theta \rightarrow N(\theta)$

Total internal energy → for all dipoles lying betn $\theta = 0^\circ$ to 180°

$$\underline{N(\theta) \cdot U(\theta)} = N(U(\theta))$$

Boltzmann Statistics → distribution function.

at a temp T, no. of dipoles with energy U

$$N(U(\theta) = \underset{\substack{\uparrow \\ \text{Constant}}}{A} \cdot \exp\left(-\frac{U(\theta)}{k_B T}\right)$$

No. of dipoles betn θ & $\theta + d\theta = N(U(\theta)) \underset{\substack{\uparrow \\ \text{solid} \\ \text{angle}}}{d\Omega}$

Total dipole moment = $\underline{\underline{\Sigma \mu}}$

Now we need to consider first number of dipoles at an angle θ which are equal to $N(\theta)$ and they will also be carrying some energy. So, these are the number of dipoles at an angle θ carrying some energy corresponding to that angle because angle is energy is angle dependent right. So, because we have seen it $\mu E cos\theta$ so basically, we need to integrate them all the angles starting from 0 to 180 degrees.

So this will give us the total internal energy so total internal energy will be for all dipoles line between θ = 0 degree to 180 you take from the south pole and go to the north pole right and this is for all the so this is for basically n theta into u theta so this is for 1 set of angles and then you need to integrate it from 0 to 180 to carry out to get the all energy completely. So now let us use the Boltzmann statistics which allows us to basically minimize the free energy using a distribution function.

So, this allows this gives the distribution functions and what is this distribution function basically this distribution function is at a given temperature at a temperature T. Number of dipoles with energy U will be $N[U(\theta)]$ so this will be,

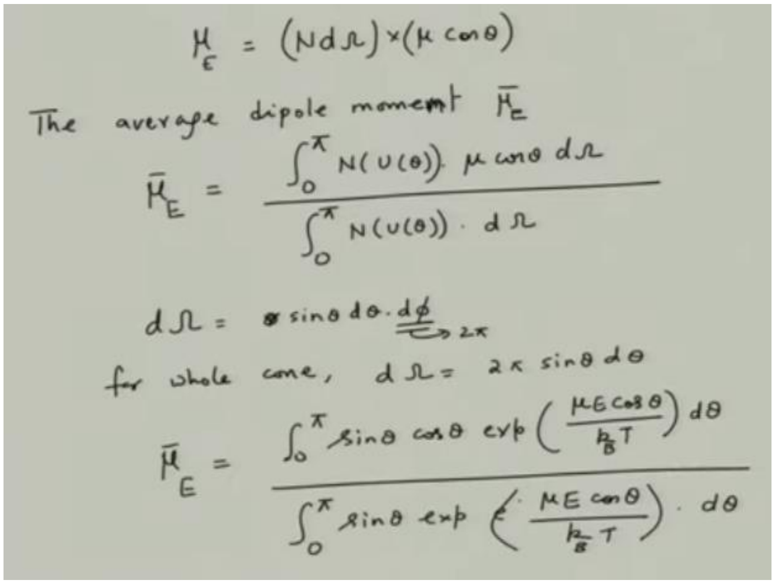
$$N[U(\theta)] = A \cdot exp\left(-\frac{U(\theta)}{k_B T}\right)$$

, $k_B T$ which is thermal energy and these are so this is basically probability of having so many dipoles of energy $U(\theta)$ with respect to $Q(\theta)$okay.

So, A*exp of so if this is a case so A is the constant here and rest is you know k_B is Boltzmann constant so this Boltzmann function so this equation will provide the number of dipoles within a given cone N number of dipoles with energy $U(\theta)$ at an angle θ. So now let us calculate the component of the dipole moment that is parallel to the applied field for this we will have to use the solid angle we have just calculate that is $d\Omega$ if you consider sphere as a unit is sphere as the angle range θ to $\theta + d\theta$ and then we integrate it from 0 to 180 degree for θ degree θ value.

So, φ is within the plane of the sphere which is from 0 to 360 degree that is 2π whereas θ goes from 0 to 180 degree from one side to another side. So, let us do that now so what we do is now number of dipoles, number of dipoles between θ and $\theta + d\theta$, are = $N[U(\theta)] \cdot d\Omega$ this is the solid angle right. So, the total dipole is moment is now is equal to $\sum \mu$ which are pointed along the direction of E so let us see how do we do that.

(Refer Slide Time: 19:02)



$$\mu_E = (N d\Omega) \times (\mu \cos\theta)$$

The average dipole moment $\bar{\mu}_E$

$$\bar{\mu}_E = \frac{\int_0^{\pi} N(U(\theta)) \cdot \mu \cos\theta \, d\Omega}{\int_0^{\pi} N(U(\theta)) \cdot d\Omega}$$

$$d\Omega = \sin\theta \, d\theta \cdot \underset{\to 2\pi}{d\phi}$$

for whole cone, $d\Omega = 2\pi \sin\theta \, d\theta$

$$\bar{\mu}_E = \frac{\int_0^{\pi} \sin\theta \cos\theta \exp\left(\frac{\mu E \cos\theta}{k_B T}\right) d\theta}{\int_0^{\pi} \sin\theta \exp\left(\frac{\mu E \cos\theta}{k_B T}\right) \cdot d\theta}$$

So, this μ_E we know is equal to which is aligned in the direction of applied field is

$$\mu_E = (Nd\Omega) \times (\mu cos\theta)$$

and so this is for one particular angle now we average it out. Now the average let us say $\overline{\mu_E}$ this $\overline{\mu_E}$ is calculated as,

$$\overline{\mu_E} = \frac{\int_0^{\pi} N[U(\theta)] \cdot \mu cos\theta d\Omega}{\int_0^{\pi} N[U(\theta)] \cdot d\Omega}$$

So, this is the total dipole moment for all that dipoles divided by the number of dipoles that will give you the average dipole moment so this is again from $\int_0^{\pi} N[U(\theta)] \cdot d\Omega$.

So now what is solid angle? Solid angle we have just said is equal to $rsin\theta$ sorry

$$d\Omega = sin\theta d\theta \cdot d\varphi.$$

Now if you, $d\varphi$ is basically if you notice $d\varphi$ is going from it is this incremental angle now if you consider the whole cone what is the θ will become? This theta will become equal to 2π so this will be considered as 2π for the whole cone so for whole cone I can consider

$$d\Omega = 2\pi sin\theta d\theta$$

I mean you can also integrate for phi from 0 to 2π it is a saying that you are integrating from 0 to 2π which is will give you basically 2π right.

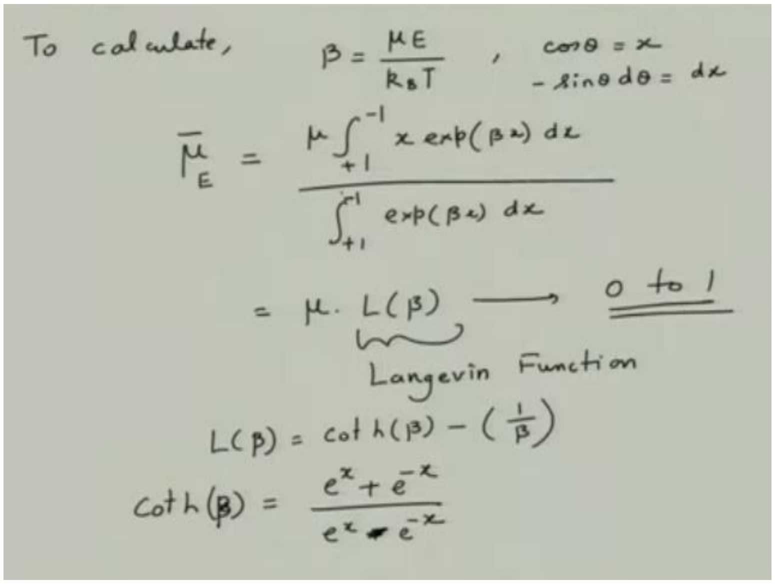
So, considering for all the dipole this is the for whole cone $d\Omega = 2\pi sin\theta d\theta$ so if you now write this equation again this

$$\overline{\mu_E} = \frac{\int_0^{\pi} sin\theta cos\theta exp\left(\frac{\mu E cos\theta}{k_B T}\right) d\theta}{\int_0^{\pi} sin\theta exp\left(\frac{\mu E cos\theta}{k_B T}\right) d\theta}$$

we have made a mistake of sign somewhere so this is minus of U(θ) what was U(θ) we wrote earlier U(θ) is minus of $\mu E cos\theta$.

So minus of μE minus-minus cancel each other so they will become plus okay so this is fine so now when you so this a little tricky to calculate sort of expression.

(Refer Slide Time: 22:38)



To calculate, $\beta = \frac{\mu E}{k_B T}$, $\cos\theta = x$

$-\sin\theta \, d\theta = dx$

$$\overline{\mu}_E = \frac{\mu \int_{+1}^{-1} x \exp(\beta x) \, dx}{\int_{+1}^{-1} \exp(\beta x) \, dx}$$

$$= \mu . \underbrace{L(\beta)}_{\text{Langevin Function}} \longrightarrow \underline{\underline{0 \text{ to } 1}}$$

$$L(\beta) = \cot h(\beta) - \left(\frac{1}{\beta}\right)$$

$$\cot h(\beta) = \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}}$$

So in this case let us say to calculate we make an estimation first let us assume constant β,

$$\beta = \frac{\mu E}{k_B T}$$

and we take $cos\theta = x$ so if you take this $cos\theta$ is equal to work x this will become $-sin\theta d\theta = dx$. So, if you make this substutions in the above equation we get

$$\overline{\mu_E} = \frac{\mu \int_{+1}^{-1} x exp(\beta x) dx}{\int_{+1}^{-1} exp(\beta x) dx}$$

so accordingly, the limits will also change so they will go from +1 to -1.

Now this is expressed by something called as

$$\overline{\mu_E} = \mu \cdot L(\beta)$$

Where, $L(\beta)$ is called as Langevin function. So, this integration is little involved so we are going into details of Langevin function but Langevin function is defined as $L(\beta)$ is defined as

$$L(\beta) = \cot h(\beta) - \left(\frac{1}{\beta}\right)$$

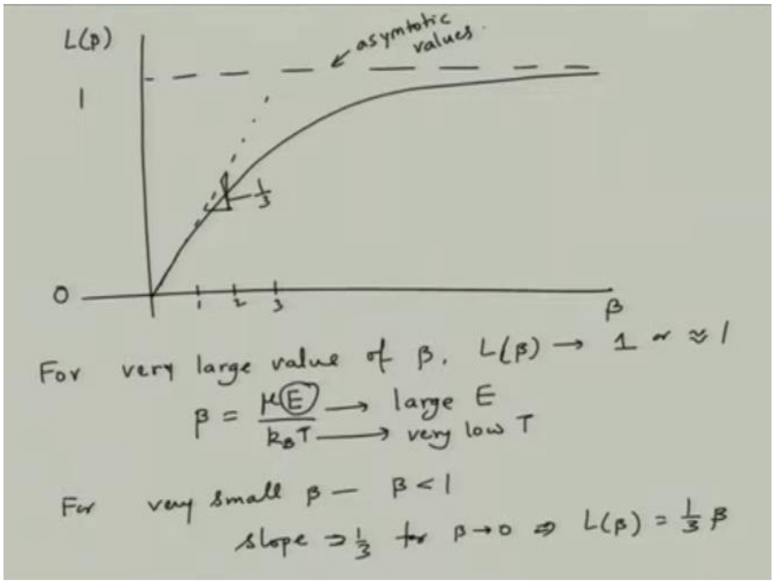
So if you want to get into derivation of it you can look at a Langevin function yourself but the analysis deriving this into Langevin function is less important but more important to an understand implication of this.

Now this $coth(\beta)$ is something you must be aware so $h(\beta)$ can be written as

$$\cot h(\beta) = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

So, we are not get into we are not going into detail of Langevin function but let us see the value of this Langevin function for our purposes lie between 0 to 1 and let us see what does it mean? What is the limit of +1? This is -1 plus into -1 so basically you had from o to π so for 0 *cosθ* will be equal to 1 for *cos* for π, *cosθ* will be equal to -1 sorry good that you reminded me now this should be -1 same as numerator.

(Refer Slide Time: 25:22)



For very large value of β, $L(\beta) \rightarrow 1 \sim \approx 1$

$$\beta = \frac{\mu \text{Ⓔ} \longrightarrow \text{large } E}{k_B T \longrightarrow \text{very low } T}$$

For very small β — $\beta < 1$

slope $\Rightarrow \frac{1}{3}$ for $\beta \rightarrow 0 \Rightarrow L(\beta) = \frac{1}{3}\beta$

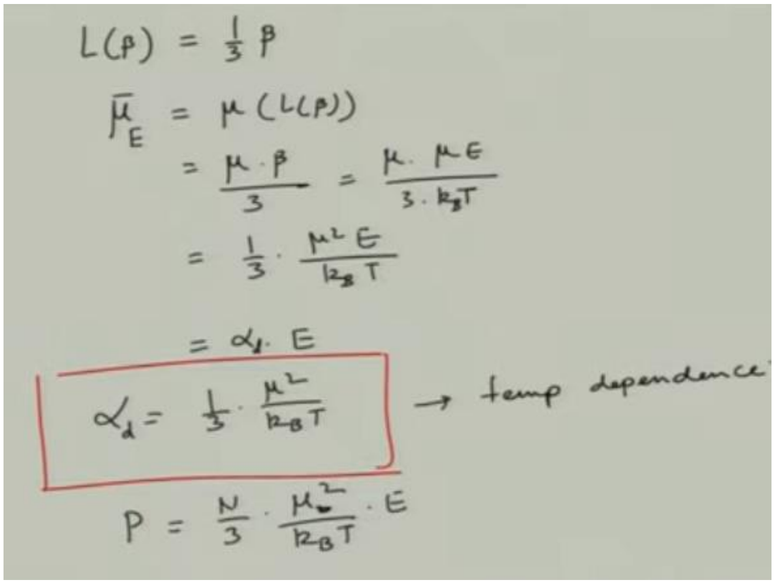
So now when we plot Langevin function is plotted as so we plot $L(\beta)$ as the function of β okay and you plot from 0 to 1 and the way this function goes is something like this okay. So, these values are basically we can say as asymptotic values okay so now let us see what is this function mean. So, for very large value of $L(\beta)$ that is β tends to be equal to 1 and what did we define β as β was equal to if you know $\frac{\mu E}{k_B T}$.

So for a given system U is constant, μ is cannot be very large, k_BT is constant or given temperature it is basically what it means is that you have very large E so what it means is that when you have very large β when it is that large E okay what it could also mean is that very small it also means very low temperature okay. So, for a reasonably high temperature it could be very high field and for it could also mean very low temperature it could also be some combination of both of them.

So, for these values we see that $L(\beta)$ is tending to 1 or $L(\beta)$ is closer to 1 whereas for very small that is $\beta<1$. So, these values basically so here it may be little so at the very low values you tend to have sort of very sharp chain and slow so here you draw the values 1, 2, 3 so generally $L(\beta)$ is taken greater than 1 because of small values you cannot use that function for the purposes that want to use.

So, for beta less than 1 the that is for high temperatures we consider the slope as so in this line was drawn us for 1 the slope will be about 1/3. So this slope will be approximately it will be 1/3 for β tending to 0 and hence you are approximating this $L(\beta)$ as 1/3 beta. In general, we will consider beta which is much smaller than 1 but of course greater than 0 okay.

(Refer Slide Time: 28:33)



$$L(\beta) = \frac{1}{3}\beta$$

$$\bar{\mu}_E = \mu(L(\beta))$$

$$= \frac{\mu\cdot\beta}{3} = \frac{\mu\cdot\mu E}{3\cdot k_BT}$$

$$= \frac{1}{3}\cdot\frac{\mu^2 E}{k_B T}$$

$$= \alpha_d\cdot E$$

$$\boxed{\alpha_d = \frac{1}{3}\cdot\frac{\mu^2}{k_BT}} \rightarrow \text{temp dependence}$$

$$P = \frac{N}{3}\cdot\frac{\mu^2}{k_BT}\cdot E$$

So as a result, from this we consider so we have this for general cases of $L(\beta)$that is

$$L(\beta) = \frac{1}{3}\beta$$

somewhere less than 1 but greater than 0. So, L beta greater than $L(\beta)$ is equal to 1 over beta so $\overline{\mu_E}$ is now approximated as $\overline{\mu_E}$,

$$\overline{\mu_E} = \mu[L(\beta)]$$

So, this will be equal to

$$\overline{\mu_E} = \frac{\mu \cdot \beta}{3} = \frac{\mu \cdot \mu E}{3 \cdot k_B T}$$

so this becomes,

$$\overline{\mu_E} = \frac{\mu^2 E}{3 \cdot k_B T}$$

So here this is the first time that we have seen that di and this equal to $\alpha_d \cdot E$ so alpha will be equal to

$$\alpha_d = \frac{1}{3} \cdot \frac{\mu^2}{k_B T}$$

So here for the first time we have seen that the dipolar polarizability (α_d) of the system is inversely proportion to the temperature. So, this is alpha E basically α_d we can denominate it as $\alpha_d = \frac{1}{3} \cdot \frac{\mu^2}{k_B T}$ if you have N dipoles in the system then this will become

$$P = \frac{N}{3} \cdot \frac{\mu^2}{k_B T} \cdot E$$

of course, right N dipoles per unit volume.

So, this will be P value so basically what it tell what this equation is valid for this equation is valid for smaller value of dipole moment as well as electric field and large enough temperature. It is not very high temperature but not very low temperature as you see there so that is why we say that we are taking this regime which is the regime where $L(\beta)$ is equal to $\beta/3$ and this basically what it means is that for β smaller than one it means your temperatures are large but not very large temperature or it could be in small electric field or μ the dipole moment.

So, dipole moment for a given system will be for the molecule it will be fixed but your electric field will be smaller or temperature will be large enough to cause randomization. So, this is where the dipolar polarizability of a given system is inversely proportional to temperature and this make sense as the temperature increases that polarizability will reduce and basically you will have to spend more and more energy in the form of electric field to align the dipoles with the electric field.

So, this is the first case where you have temperature dependence as against electronic and ionic polarizability. So, this is sort of a simple analytical treatment of a dipolar polarizability based on classical mechanics Boltzmann distribution. So, we will further develop on this in the next lecture so where we will just summarize it and then move on to the next topic thank you.