Electroceramics
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Lecture - 19

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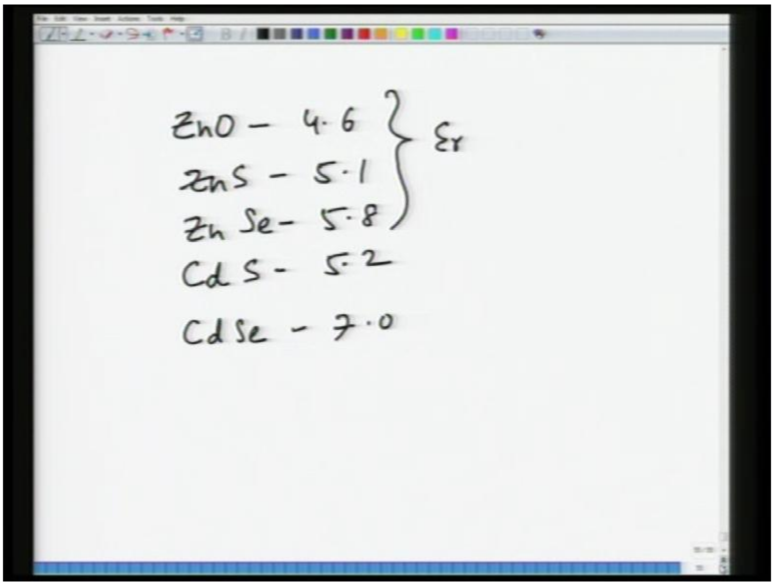

$$\left.\begin{array}{l} ZnO - 4.6 \\ ZnS - 5.1 \\ ZnSe - 5.8 \end{array}\right\} \varepsilon_r$$

$CdS - 5.2$

$CdSe - 7.0$

So, we are into now new lecture, what we will do is that first we will review the last lecture and then we will go through the new concepts.

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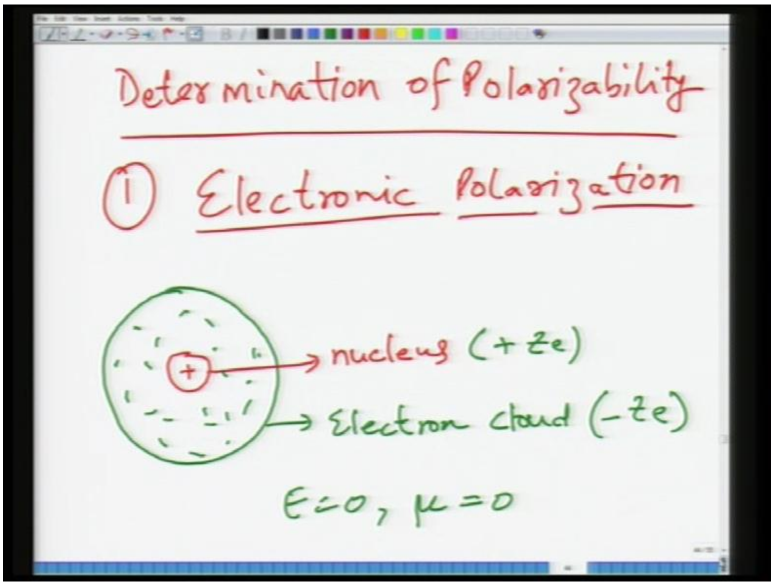

Determination of Polarizability

① Electronic Polarization

$E=0,\ \mu=0$

So, in the last lecture we started our analytical solution to the polarizability of dielectric materials and in this, first we took what was, first we took electronic polarization and there we looked at the effect of electric field on the electron cloud around the nucleus and shifting of centres of charges, which gives rise to and then which gives rise to, what is called as, electronic polarization.

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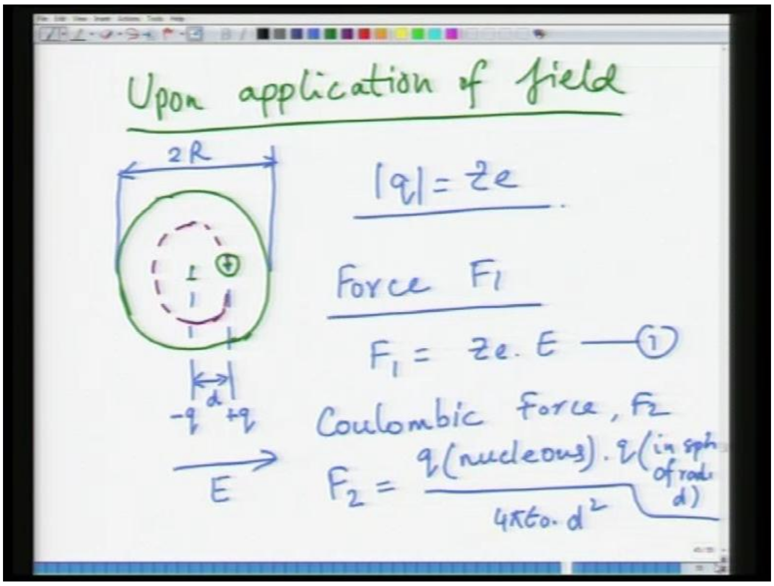

Upon application of field

$|q| = Ze$

Force F_1

$F_1 = Ze.E$ ①

Coulombic force, F_2

$$F_2 = \frac{q(\text{nucleous}).q(\text{in sph of radi } d)}{4\pi\epsilon_0 . d^2}$$

And then how do you work out the polarizability? You calculate the forces due to electronic field and the opposing force which would be Coulombic force and equate these two forces to find out what is the equilibrium separation or what is the equilibrium distance. And this gives rise to the dipole moment and from that we can find out what is electronic polarizability.

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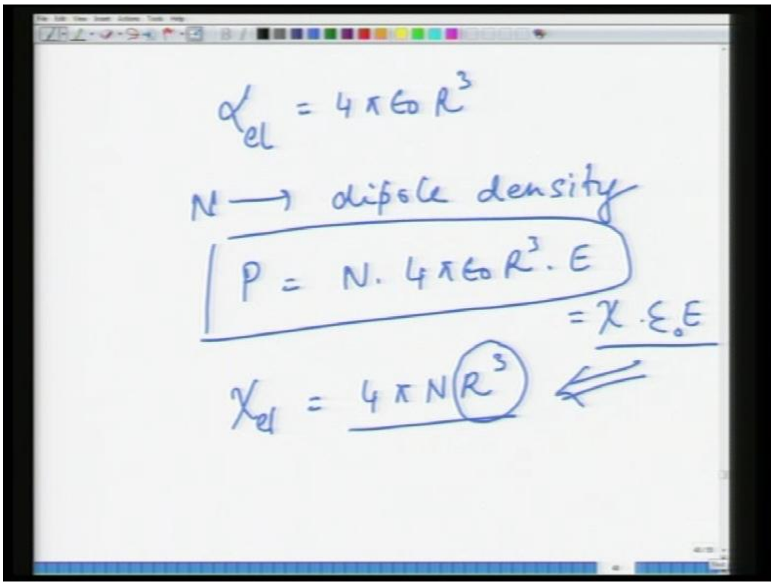

$\alpha_{el} = 4\pi\epsilon_0 R^3$

N → dipole density

$$\boxed{P = N \cdot 4\pi\epsilon_0 R^3 \cdot E} = \underline{\chi \cdot \epsilon_0 E}$$

$$\chi_{el} = \underline{4\pi N R^3} \Leftarrow$$

And the conclusion that we do from this exercise was as for larger the atom is, larger the polarizability is. So, larger atoms can be polarized more than small atoms can be.

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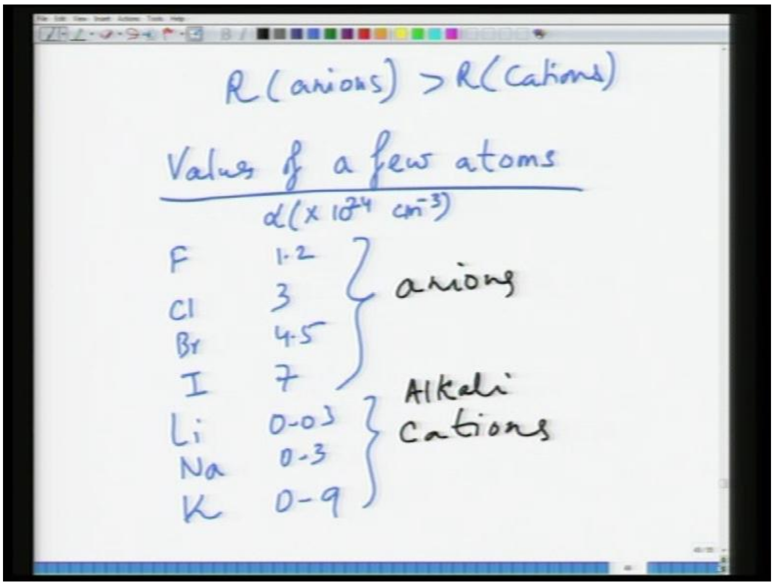

R(anions) > R(Cations)

Values of a few atoms

	$\alpha (\times 10^{-24}\ cm^{-3})$	
F	1.2	anions
Cl	3	
Br	4.5	
I	7	
Li	0.03	Alkali cations
Na	0.3	
K	0.9	

And this is also seen as a difference in anions and cations because anions, typically, tend to have larger radius as compared to cations. So, for example, you see in case of fluorine, chlorine, bromine iodine, as the size of the ion is going, going to increase, the alpha value, which is the polarizability value also increases. And similarly for cations, as the, as we go from lithium to sodium to potassium, the value of polarizability also increases.

However, if you compare these, so these are your anions and these are your cations, so if we compare and that too, these are alkali cations, so if we compare these alkali cations with these halogens you can, you can see, that polarizability in case of cations is much more smaller and this is again due to, typically due to size of the smaller, size of the cations.

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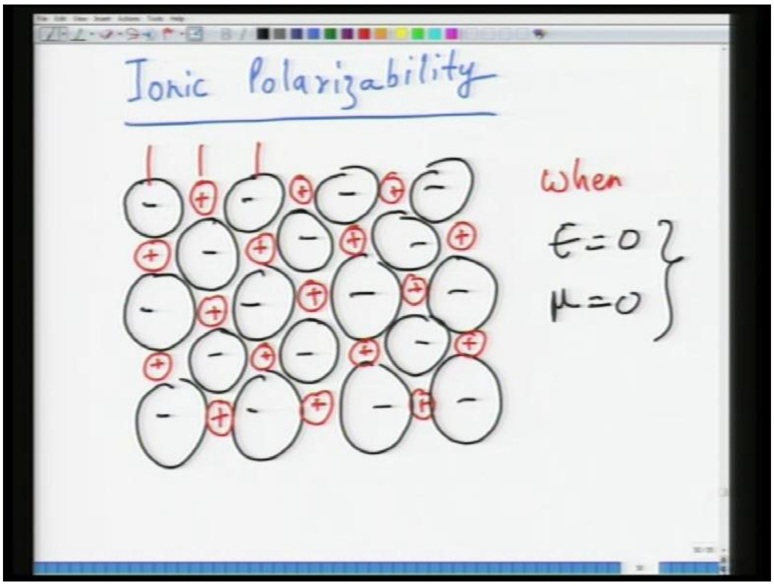

Now, the next thing that we discussed was ionic polarizability. Now, this, this arises from what we learnt earlier was ionic polarization. So, we know what ionic polarization is, we just took a case of sodium chloride and when the field is 0, then all the atoms are sitting in, their all the ions are sitting in their equilibrium positions. As a result, whatever dipole moment components are there, they cancel each other because the symmetry of the lattice and hence, the net dipole moment is equal to 0.

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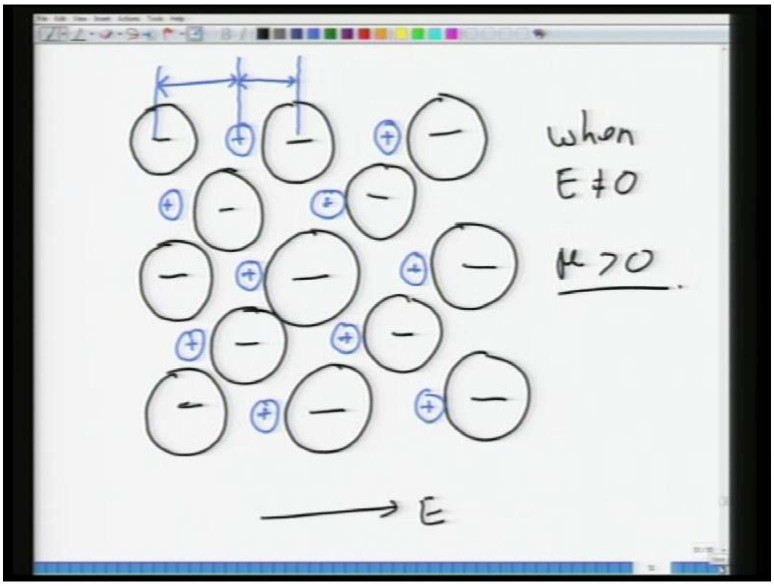

When you applied field, then there is a relative displacement of ions with respect to each other. So, for instance, in this schematic diagram, the anions, the cations are all shifted towards right, which means, they are closer to their right anion in anion neighbour as compared to their left anion neighbour.

So, as a result, the distance between one side, distance between cation-anion on the one side is different as compared to the distance on the other side. And this results in net finite, net magnetic, net dipole moment. Excuse me, it is not magnetic, it is just dipole, electric dipole moment and this is finite and this happens when you apply electric field.

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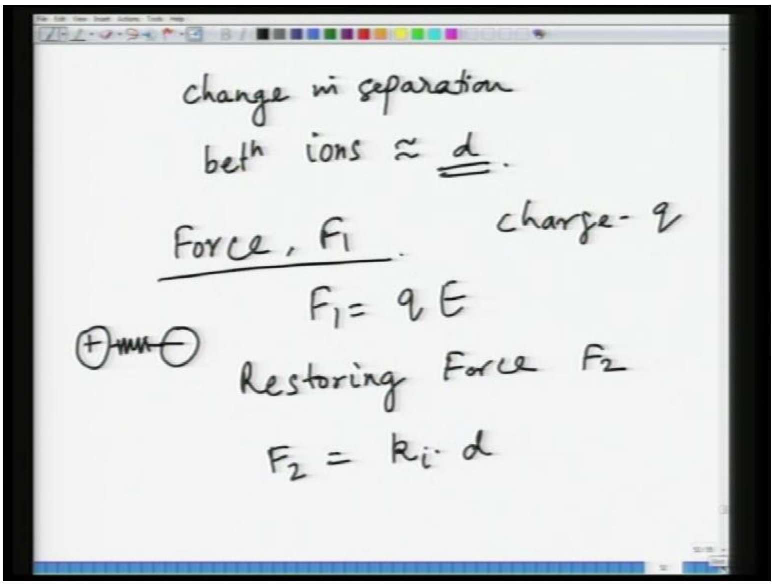

change in separation

betn ions $\approx \underline{\underline{d}}$.

Force, F_1 charge - q

$F_1 = q\,E$

Restoring Force F_2

$F_2 = k_i \cdot d$

So, again we, we, we, applied, we, we did the force balance, so the force, which is due to electric field is q E.

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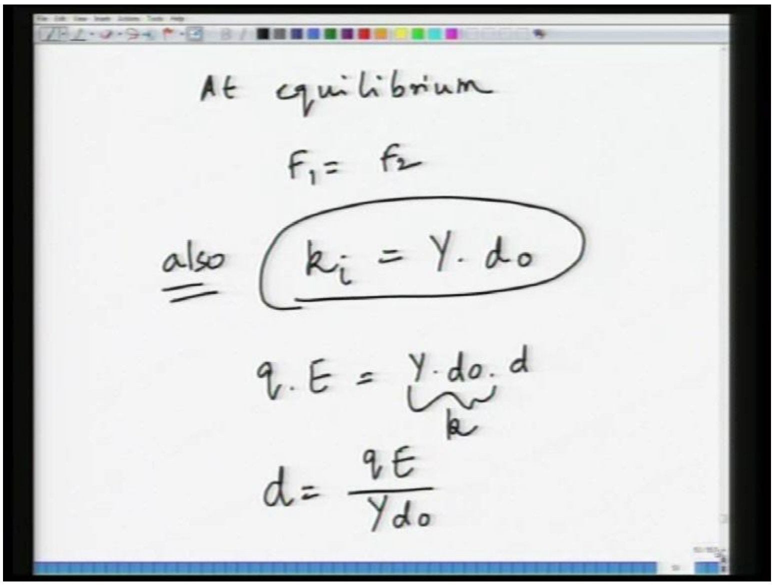

At equilibrium

$F_1 = F_2$

also $\boxed{k_i = Y \cdot d_o}$

$q \cdot E = \underbrace{Y \cdot d_o}_{k} \cdot d$

$d = \frac{qE}{Y d_o}$

And then the restoring forces k d, which is the, if you consider these bond between the ions as a spring, so based on that we find, found out what is the separate, what is the, what is the displacement d and this displacement d is given as q E divided by Y d naught.

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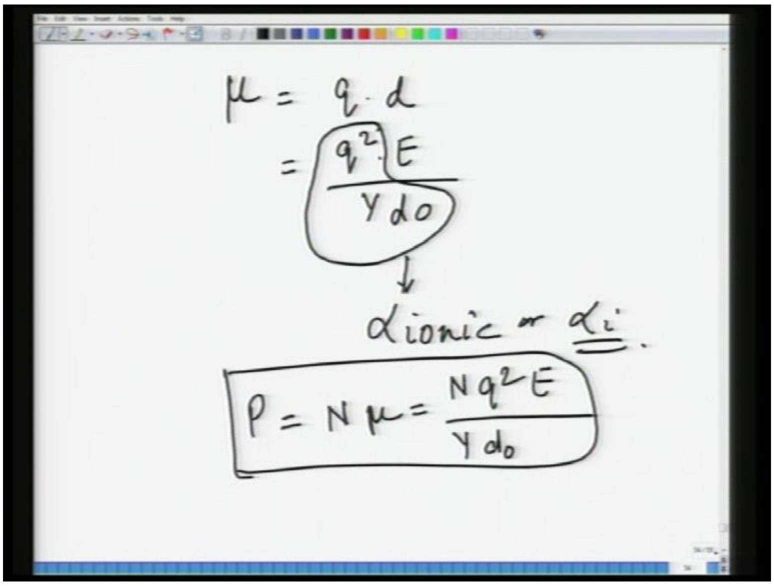

$$\mu = q \cdot d$$

$$= \frac{q^2 \cdot E}{Y d_o}$$

$$\downarrow$$

α_{ionic} or $\underline{\underline{\alpha_i}}$.

$$\boxed{P = N\mu = \frac{Nq^2E}{Y d_o}}$$

And from this you can work out what the dipole moment is and then and this gives you ionic polarizability alpha ionic, which is q square divided by Y d naught. So, what this expression tells you is, that larger this Y and Y is Young’s modulus, larger the Young’s modulus is, smaller the polarizability is. Similarly, larger the d naught is, smaller the polarizability is, which means, bigger unit cell where separation between the ions is much larger. There will be far less polarization and the more important thing is Y and this Y is Young’s modulus, which is and Young’s modulus higher or lower Young’s modulus is because of fundamental reasons such as bond strength.

So, higher the bond strength is, higher the modulus is and less the polarizability is. So, what it means is, that the materials, which have higher modulus or high stiffness, higher bond strength or higher melting point materials, they tend to have lower polarizability as compared to the ones with lower modulus. And this is true for, of course, the ionic systems where you have a group of cations and anions and mostly in case of symmetric lattices.

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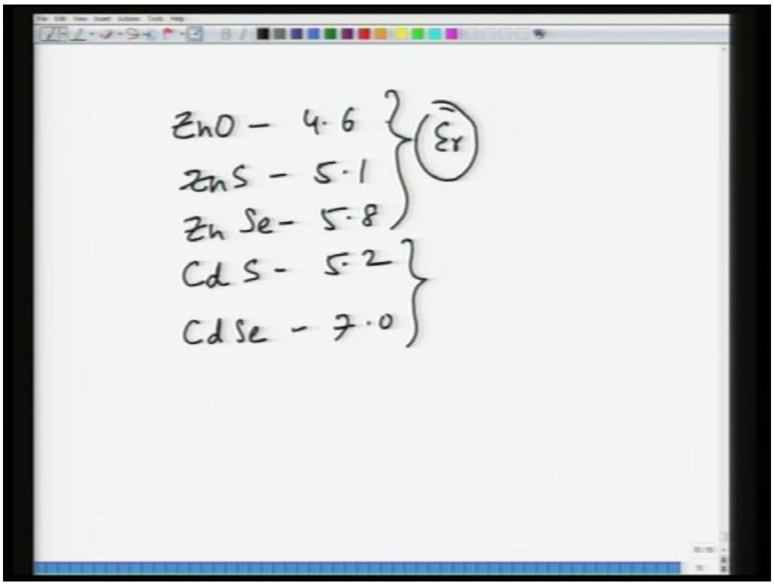

ZnO – 4.6
ZnS – 5.1
ZnSe – 5.8
CdS – 5.2
CdSe – 7.0

ε_r

So, when you look at some of the examples, the examples are, we can calculate, we can work out the values of directly constant for variety of materials. So, what I have taken here is a group of cadmium, zinc based materials and cadmium based materials. So, zinc oxide, zinc sulphide, zinc solenoid. So, as you as you go from zinc oxide to solenoid, the bonus strength, increases, decreases. As a result, the modulus in the melting point decrease, as a result the polarizability increases and as a result, diode electric constant increases. And same is true about cadmium sulphide and cadmium solenoid.

So, these two parts have given you some idea about the electronic and ionic polarization. So, what we are now going to take up is, we are not going to, now we are going to take up is what it called as dipolar polarization, the third part of the polarization.

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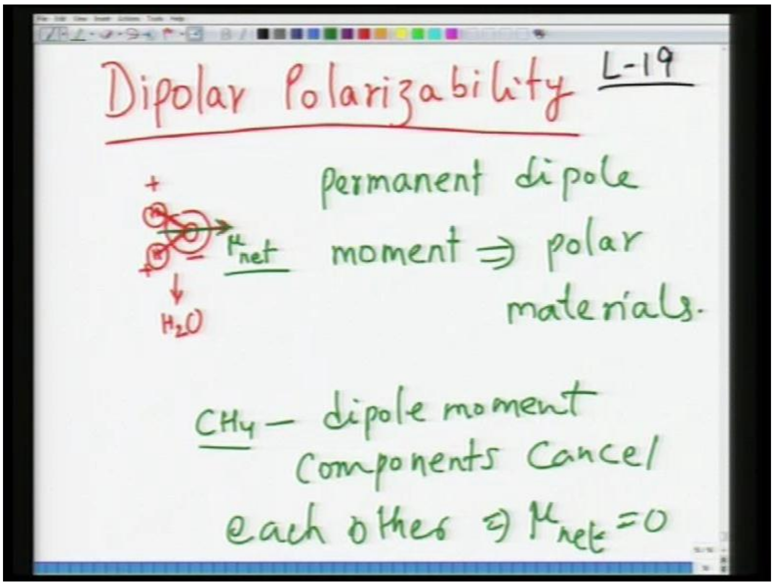

Dipolar Polarizability L-19

permanent dipole moment ⇒ polar materials.

CH_4 — dipole moment components cancel each other ⇒ $\mu_{net} = 0$

So, this is, let me just see, which lecture was last one. So, last one was 18th, so this would be 19th lecture. So, here what we will start is dipolar polarizability. Now, dipolar polarizability happens when there are dipoles, which are present and they are present independent of each other, which means, material has a permanent dipole moment. So, for instance, I can give you example of let us say, so this is hydrogen, hydrogen, oxygen, so this is naturally water molecule. So, you have a component.

So, you have basically two components and these two components will have a net dipole moment going in from this direction; this is positive, this is positive, this is negative. So, you have a component, this direction component, that direction vertical components cancel each other. So, as a result, you have a finite mu net for this molecule.

Now, each of these molecules, what it means is, that has a dipole moment. So, what we say, permanent dipole moment and these materials are called as polar materials. So, for instance, a water molecule has a permanent dipole moment and as a result, it will have, it will be called as polar material. On the on the other hand, if you take example like methane, methane is CH 4, so here in this case, all the dipole moments, dipole moment components cancel each other, that means, mu net is equal to 0. So, a symmetric molecule like methane will not have a dipole moment, but asymmetric molecule like water will have a dipole moment and that is why, materials having permanent dipole moment are called as polar materials and materials, which do not have a permanent dipole moment, they are called as non-, they are called as non-polar materials. So, this is just a definition, which you must remember.

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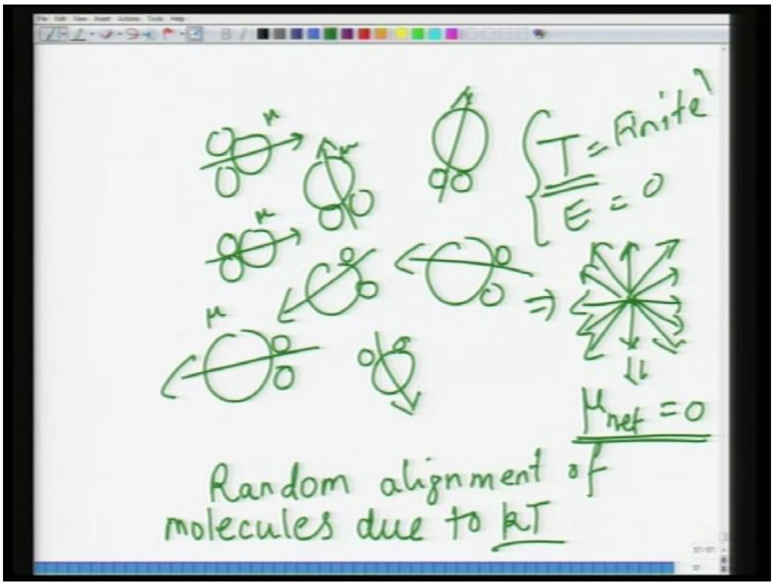

Now, what happens is, that in water, in case of water, for example, so you have many of these water molecules, now in case of water molecules each molecule's orientation is independent of each other because of high thermal energy at room temperature. So, this thermal energy prevents any kind of alignments. So, what you have here is, basically, what we have is random aligned molecules due to kT. So, so at a finite temperature T all these molecules have sufficient energy to randomize their orientation with respect to the each other.

So, when you have such a situation, so so given the fact, that each of these molecules will have mu, now since these, now what this will look like is, all the mu-s are in various different directions, so what the picture looks like is as if you have mu-s present in all the directions. If you have mu-s present in all the directions, then mu net for such a system will be equal to 0 and this happens when temperature is finite. Typically, room temperature and electric field is equal to 0. So, in the absence of any electric field and at a finite enough temperature, all these water molecules are randomly located with respect to each other and because of this randomisation assisted by the thermal energy, that is present leads to a picture in which all the dipole moments are randomly distributed. As a result, mu net is equal to 0.

So, so despite having permanent dipole moment a molecule like water does not give rise to any, any dipole moment, any appreciable dipole moment in the absence of electric field. When you apply electric field, then what happens? When you apply electric field, then the picture changes and what happens is, that schematically, all these molecules, which are present, they tend to align with the direction of, in the direction of applied field. So, the picture changes a little bit.

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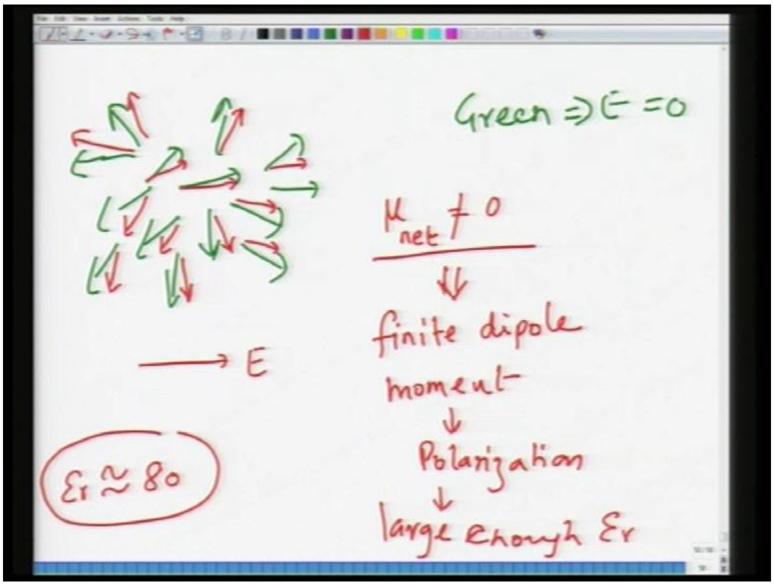

Now, the picture changes in such a manner, so I am not going to draw the molecule. So, let us say the previous picture was like this, so each molecule is represented by each of these, each of these arrows. So, this is the green, so green one is when E is equal to 0. Now, what I do is, that I apply electric field, let us say, electric field applied in, applied in this direction. So, what happens is, that this mu, so this application of electric field tends to rotate these dipole moments in that direction. Now, this rotation depends upon the strength of the field. Typically, it is not complete, but it is sufficient enough to give rise to, what is called as, a permanent finite dipole moment.

So, for instance, if the direction of field is this, will become like this, anyway. So, this will tend to become like that, this will tend to become like that. So, all of them will tend to orient themselves slightly along the applied field. So, if this has happened, which means, there is a natural, there is a, there is a net tendency of dipoles to align in the direction of applied field. As a result, what happens is, that this mu net is not equal to 0 and which means, which means, this gives rise to a finite dipole moment and then this gives rise to polarization and this results in large enough epsilon r.

Now, what you will see in many books is, many books show complete alignment in the direction, applied field, that is not necessarily true. Because if all the water molecules were completely aligned, the direction, applied field, the dipole moment or the dielectric constant, that you would observe will be huge. But what we see practically is epsilon r of the order of 80, which is large, but it is not huge. So, what it, what it basically suggests, that there is alignment, but that is not complete alignment in the direction of applied field. So, but whatever is given in the books is schematic diagram, it is just for the sake of illustrations, so do not take it literally as if all the molecules are going to align in the direction of applied field.

So, this essentially highlights, that orientation of all the dipoles is just a bit shifted towards the direction of applied field leading to, basically, an average non-zero dipole moment in the direction of applied field.

So, now thermodynamically speaking, what, what, what we need to do if such a situation is stable, then it must have a minimum free energy and for what you need, for to calculate free energy. To calculate the free energy you need something called as internal energy and then you need something called as entropy.

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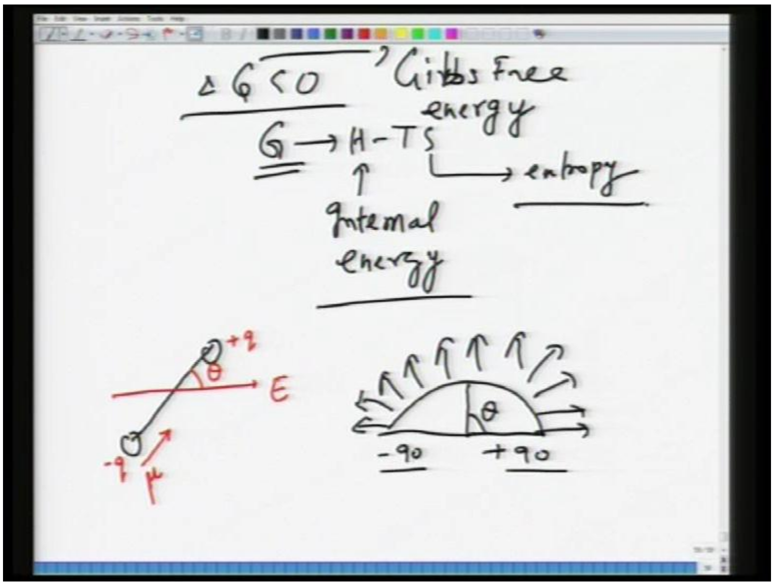

So, because you know, that for any for any stable system delta G must be negative and what is G meant, where delta G is nothing but your Gibbs free energy and G is composed of two terms, H minus T S, where H is enthalpy, which is a built up of a component of internal energy. So, H represents internal energy and S is entropy. So, these two factors have to be taken into account in order to calculate what is delta G. So, we must know what is delta S and we must know what is delta H.

So, for this, now as we, as we are saying, that all the dipoles are not completely aligned, some of them are aligned, some of them are slightly at certain angle, which means, we have a scenario. So, what we have is, basically we start with the picture like this, schematic. So, you take a charged dipole like this, apply an electric field E, which means, you will have, you have a mu and this angle, let us say, is theta. So, if this angle is, so this is a general picture.

So, theta will vary from minus, minus 90 to plus 90 because all these dipoles will be, so you can have. So, you can have dipoles going from, since you have dipoles going from, all the way from, so you have dipoles going all the way from, let us say, this is theta, so theta goes from plus 90 degree to minus 90 degree or plus pi 2 to minus pi by 2 or minus pi by 2 to plus pi by 2. But since you have net, slight tendency of dipoles to align in the direction of applied field, as a result, you have a net number of dipoles, which are finitely aligned, which are order, net number of dipoles aligning with the applied field giving rise to a net dipole moment and that we will calculate in while . So, this is the picture.

So, a schematic diagram is, you have a, you have a charged dipole, which is aligned at an angle theta with respect to the applied field with the dipole moment vector as mu.

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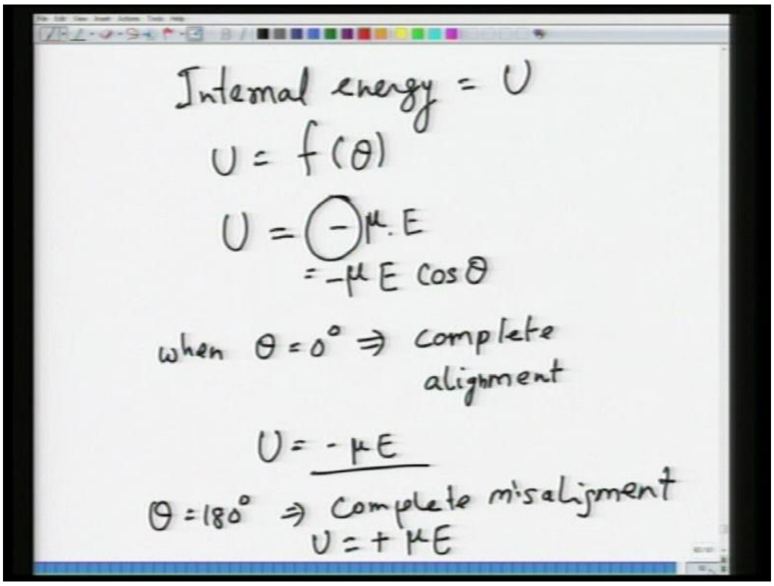

Internal energy = U

$U = f(\theta)$

$U = \textcircled{$-$}\mu . E$

$= -\mu E \cos\theta$

when $\theta = 0^\circ \Rightarrow$ complete alignment

$\underline{U = -\mu E}$

$\theta = 180^\circ \Rightarrow$ complete misalignment

$U = +\mu E$

So, the internal energy, let us say, so the internal energy is, let us say, U and this U is nothing but U depends upon the orientation of this charged dipole with respect to the applied field. So, U is nothing but a function of this theta and this U can be written as, U can be written as minus of mu dot E or mu E cos theta. So, you can see, naturally when theta is equal to 0 what it means is, that complete alignment and this means, U is equal to minus mu E, which means, minimum energy and when you have theta is equal to 180 degree, then you have complete misalignment or both are out of phase and then U becomes plus mu E. So, you understand the sign of, the significance of this sign minus. This sign minus represents basically the, the reduction in the energy of the, internal energy of the dipole when it aligns completely with the applied electric field.

So, so U, mu U will vary from minus plus mu E to minus mu E as it goes from theta is equal to 180 degrees to 0 degrees. So, it depends how you take it. You can take minus pi by 2 to plus pi by 2 or you can take from, in the, in this case we are, we are, we are measuring, so let me just make a, make a correction there because I told you, so we are measuring theta from here. So, what basically it means is, that let me just make a correction here, this would mean 0 to 180. So, as a, so theta is increasing in this direction. So, closer to, so if this is E, then closer to E is equal to 0 and further away from E will be 180. So, it means the same, but just for the sake of clarity let us take 0 to 180 instead of minus pi by 2 to plus pi by 2.

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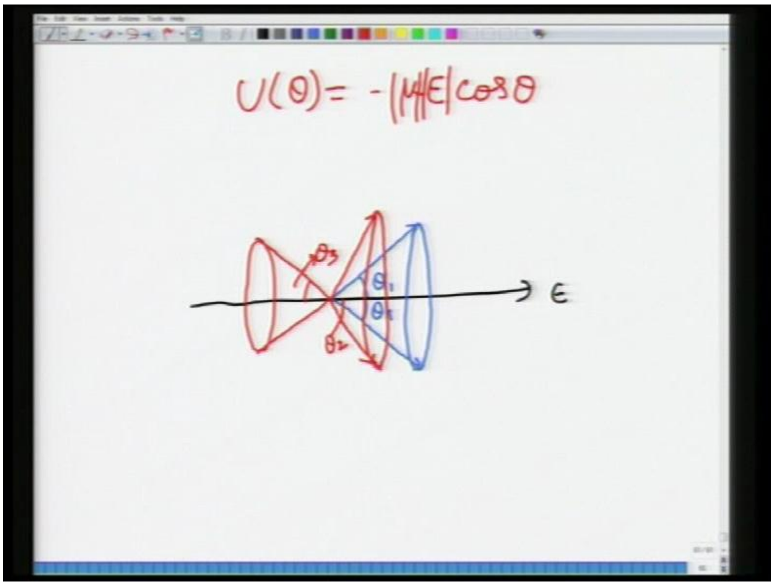

$$U(\theta) = -|\mu||E|\cos\theta$$

So, now, we can work out what internal energy is. So, this U theta, as we know, is equal to minus of mu E cos theta and we can take the mode of these in a, just to take the scaled values of these. So, what, what it means is, that you have, since you have many more thetas available, what you will have is, this is the applied field, right, and then you have one dipole like that at theta, another dipole like that at theta, and you might have several dipoles.

So, if you have, so you can have, you can have, this is the applied field and around the applied field you will have all these dipoles making an angle theta. So, what this makes is a kind of cone around. So, all the dipoles, which are oriented at an angle theta with respect to applied field E, will make a cone, which is, which has an apex angle of theta or apex angle of 2 theta. Similarly, you will have some other dipole moments. So, this is, let us say, theta 1. You will have some other dipole, which are making an angle theta 2. So, they will make another, this will be theta 2. You might have something in this direction as well, so theta 3.

So, what basically I am coming to is, now in order to calculate the net dipole moment along E you will have to integrate this overall energy with respect to theta in order to find out total dipole moment. But before we do that we need to find out, what is the net number of dipoles, which are aligned in the direction of E, then only we would be able to find what is the net dipole moment?

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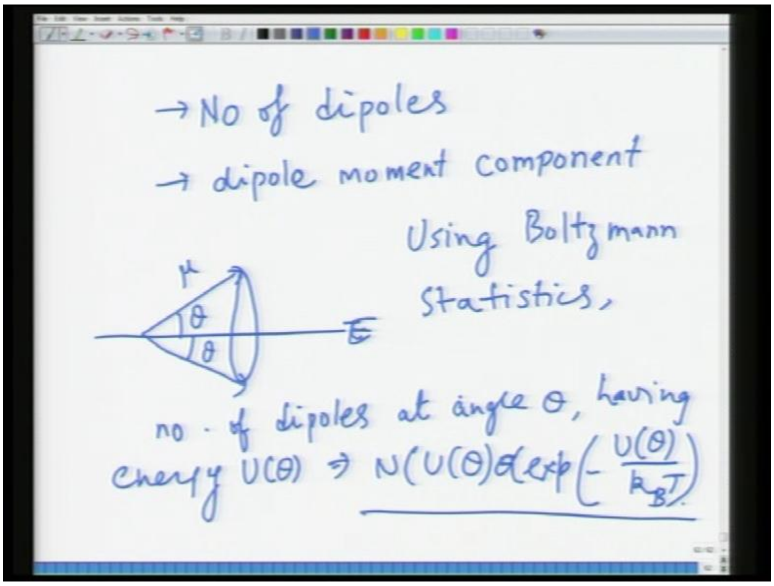

→ No of dipoles

→ dipole moment component

Using Boltzmann statistics,

no. of dipoles at angle θ, having energy $U(\theta) \Rightarrow \underline{N(U(\theta)) \propto \exp\left(-\frac{U(\theta)}{k_B T}\right)}$

So, in order to do that we need to first calculate, so first, so we need two quantities, one is number of dipoles and then we need the dipole moment component and then we need to multiply these two in order to get a complete picture. So, now, in order to get, first of all minimise the free energy. We said we need entropy; we need internal energy. We know what internal energy is, but we do not know what entropy is and to calculate the entropy of the system is mathematically not very easy.

So, what, what gives us respite is what is called as Boltzmann approximation. So, what we are saying is, using the Boltzmann approximation, Boltzmann approximation gives us a number N, let us say, N number of dipoles having energy U of dipoles making angle theta, and that is given by, as, that is proportional to exponential of minus U by kTs, that simplifies our life. So, basically if you have scenario like this, so this is E and this is the dipole moment mu, this is angle, angle theta for this cone. What I am saying is, that using Boltzmann statistics I can calculate number of dipoles at angle theta having energy U theta, this can be given as N U theta is equal to exponential of minus of U theta divided by or proportional to exponential divided by k B T. So, this makes sense, this is nothing but Boltzmann statistics.

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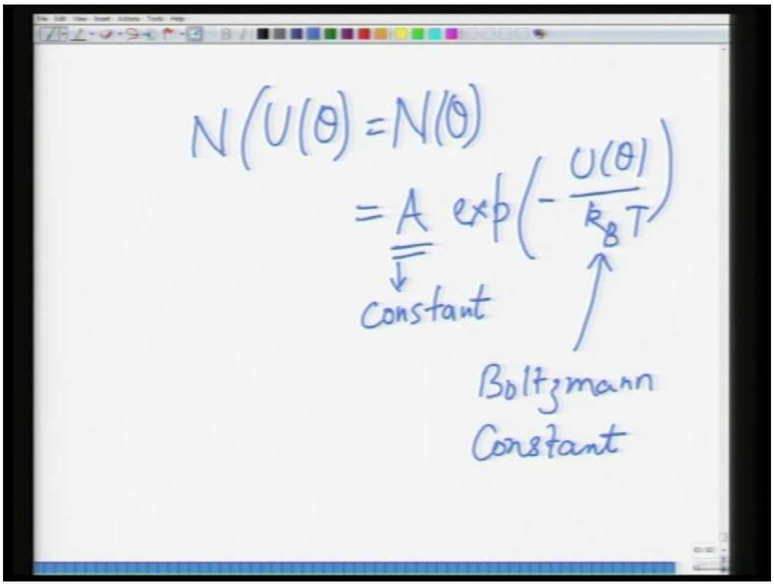

$$N(U(\theta) = N(\theta)$$

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

Boltzmann Constant

So, what N U theta would be, or you can say this just as N and this N theta would be equal to A constant exponential minus of U theta divided by k B T, where kT is nothing but Boltzmann constant and you can find the value of this constant in any book. So, now what we can do is that we can calculate the component to dipole moment parallel to the applied field.

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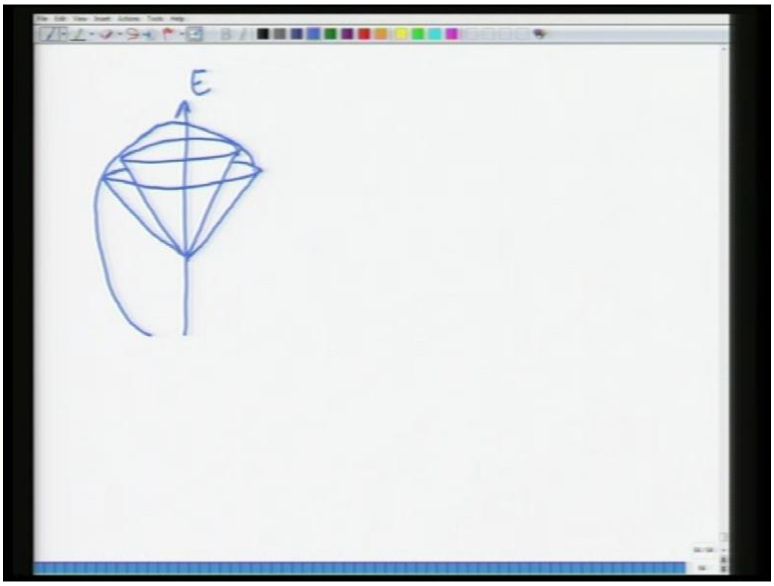

The component of, so so what we can, we can, we can remake this picture now as, so so this is the direction of applied field, so I will just turn it 90 degrees on the counter clockwise. So, this is your, this is E, this is one cone, we, we might have another cone and these allowing on the, so so this basically looks like as if it is a sphere; hang on.

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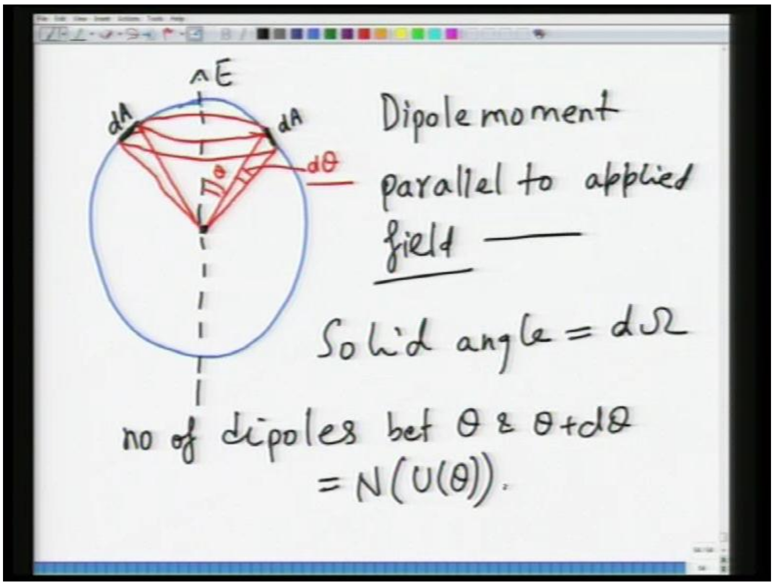

Dipole moment parallel to applied field ——

Solid angle = $d\Omega$

no of dipoles bet θ & $\theta + d\theta$ $= N(U(\theta))$.

So, what, basically we draw it as a sphere. Let us say, this is the direction of applied field E. So, the first cone, let us say, is this; another cone can be this, alright. And so what we are interested in basically, so let us say this angle is theta and this angle is d theta. So, this is the picture, that, so this is the spherical representation of dipoles.

So, what, so what we want to basically calculate is the dipole moment, so parallel to applied field. For that we need, first we need the solid angle d omega, which is, so this is the segment; so this is the segment. Let us say d A prime or dA, just dA, let us say, so so first we need the quantity and this dA will subtend a solid angle on this part. So, solid angle d omega and within the segment theta to d theta. So, solid angles subtended by dA within the segment theta to theta plus d theta. So, this is up to theta and then you have d theta, sorry, you have a segment of, so what we are interested in number of dipoles lying between this segment theta to d theta.

So, what is this number of dipole, number of dipoles? So, number of dipoles between theta and theta plus d theta will be equal to, you have N U theta, which we calculated using Boltzmann statistics at any given theta multiplied by d omega and d omega is the solid angle.

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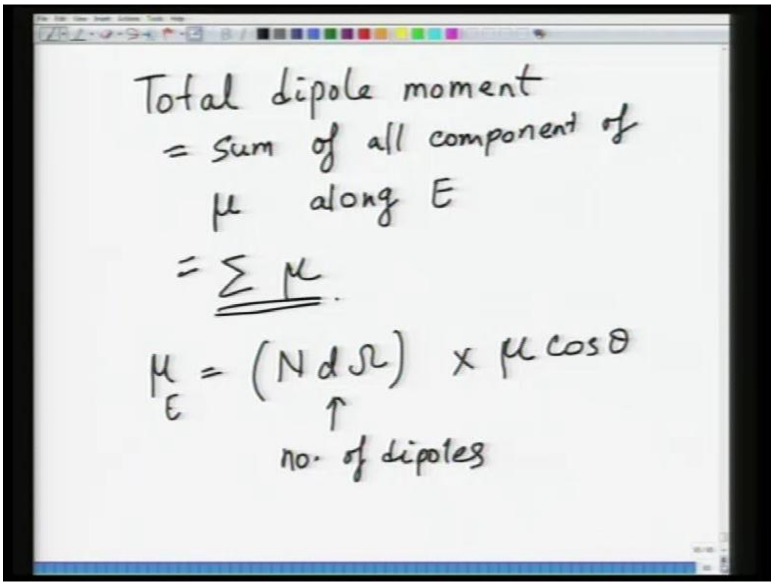

Total dipole moment

= sum of all component of μ along E

$= \underline{\underline{\sum \mu}}$.

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

↑

no. of dipoles

And the total dipole moment, the total dipole moment will be nothing but sum of all components of mu E, excuse me, mu, mu, all components of mu along E, basically sigma mu. So, this mu E, which is in the direction of applied field, will be equal to number of, number of dipoles within that segment multiplied by what is... So, if you go by, if we go back to previous picture, if, let us say each of these has value mu, then this will be mu cos theta, right.

So, now what we need to do is that we need, so this is within, for that segment now we need to, now what we can see is, that we can vary the theta from 0 to 180 degree. And if we vary the theta from 0 to 180 degree, if you want to calculate for all the dipoles, which are in this region, then we need to integrate it from 0 to 180 degrees or 180 degrees to 0. So, what we need to do is that.

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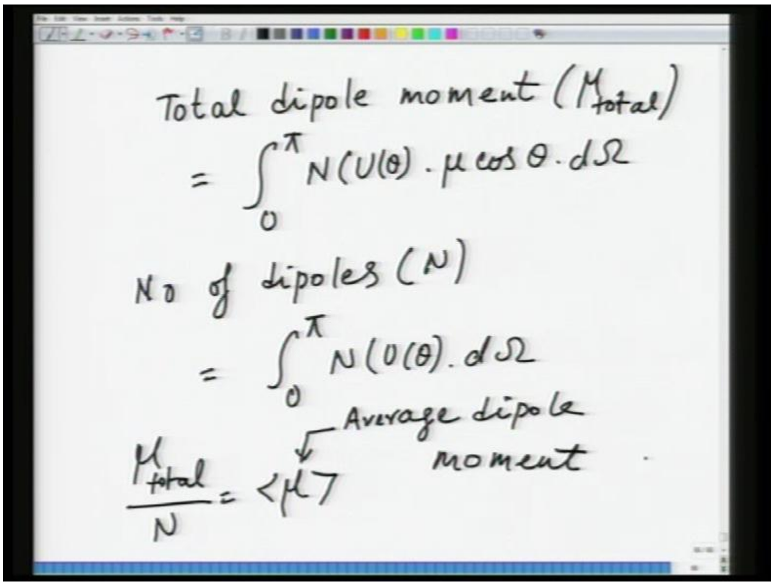

Total dipole moment (μ_{total})

$$= \int_0^\pi N(U(\theta) \cdot \mu \cos\theta \cdot d\Omega$$

No of dipoles (N)

$$= \int_0^\pi N(0(\theta) \cdot d\Omega$$

Average dipole moment

$$\frac{\mu_{total}}{N} = \langle \mu \rangle$$

So, the total, so the total, the total dipole moment would be from 0 to pi N U theta mu cos theta. So, this would be 2 into, because we are taking on the both sides, so 2 into N U theta mu cos theta into d omega and number of number of dipoles would be 0 to pi N, sorry, we do not need to take 2, because this 2 is already included in the number of dipoles because we are taking all the dipoles, which are forming that cone. So, this is N U theta into d omega.

So, if I now, so this is mu total, so if I divide mu total by number of dipoles, which is N, this gives me mu total divided by N, gives me average dipole moment.

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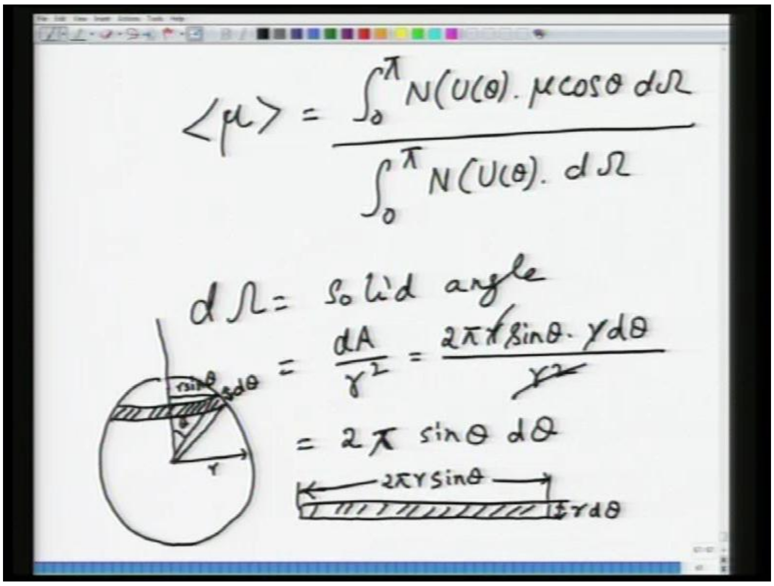

$$\langle \mu \rangle = \frac{\int_0^{\pi} N(U(\theta).\ \mu \cos\theta\ d\Omega}{\int_0^{\pi} N(U(\theta).\ d\Omega}$$

$d\Omega =$ solid angle

$$= \frac{dA}{r^2} = \frac{2\pi \cancel{r} \sin\theta .\ r d\theta}{\cancel{r^2}}$$

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

So, this mu average is 0 to pi N U theta into mu cos theta d omega divided by 0 to pi N U theta into d omega. Now, we need find out what is d omega? d omega is solid angle and by definition, solid angle for this unit area dA would be equal to dA divided by r square. And as you can see, so in this sphere, you have sphere, so you basically are interested in this strip of thickness d theta and this is the radius of sphere. So, if this is, so basically this is theta. If this is r, then the area of this strip, which is this shaded strip, so if you, this could be equal to r sine theta into, so this would be basically r sine theta into 2 pi r d theta divided by r square. So, r r will cancel each other, what you will have is 2 pi sine theta d theta.

So, basically what I am going do is that you have a, you are just taking a segment of the sphere. So, if you just open it up, this will open up like this, so this will be the segment. Now, this distance is r r sine theta. So, what you will have is, so if this is r sine theta, you have a circle of radius r sine theta. So, the length would be 2 pi r sine theta. So, this would be equal to 2 pi r sine theta, whereas this would be r d theta. So, if you multiply these two together what you get is r sine... I should have taken 2 pi r sine theta into r d theta. So, I will modify this for the sake of clarity, this would be 2 pi r sine theta into r d theta divided by r square. So, these cancel each other, so what you have is 2 pi sine theta d theta.

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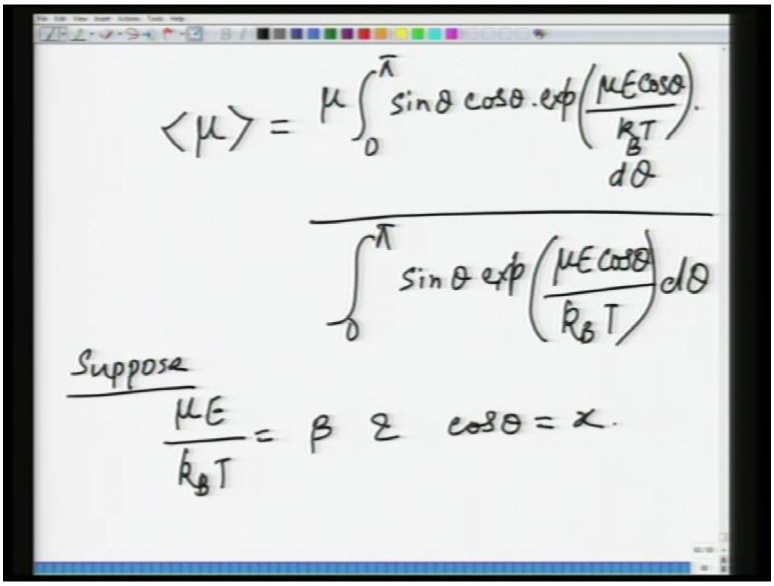

$$\langle \mu \rangle = \frac{\mu \int_0^{\pi} \sin\theta \cos\theta . \exp\left(\frac{\mu E \cos\theta}{k_B T}\right) . d\theta}{\int_0^{\pi} \sin\theta \exp\left(\frac{\mu E \cos\theta}{k_B T}\right) d\theta}$$

Suppose

$$\frac{\mu E}{k_B T} = \beta \ \& \ \cos\theta = x.$$

So, now, you have got a magnitude of d omega. So, if you now put the value of d omega what you get is, so mu, average mu is equal to mu coming out of it, this 0 to pi sine theta cos theta, you just have to replace d omega into exponential of mu E cos theta by kT or k B T into d theta divided by 0 to pi sine theta exponential of mu E cos theta divided by k B T d theta.

So, we have, we have, we have 0 down to this expression for average dipole moment, which is due to all these dipole moments, which are, which are at some angle theta around the applied electric field, and since they have a natural tendency to incline in the direction of applied field, so there are always some, so there is net finite dipole moment and this is average. So, we what we have done is, we have calculated total finite dipole moment divided by the number of dipoles and this gives rise to average thing.

Now, in order to solve this equation we take this mu E, mu E divided by k T is equal to what is beta, so suppose, and cos theta as equal to x.

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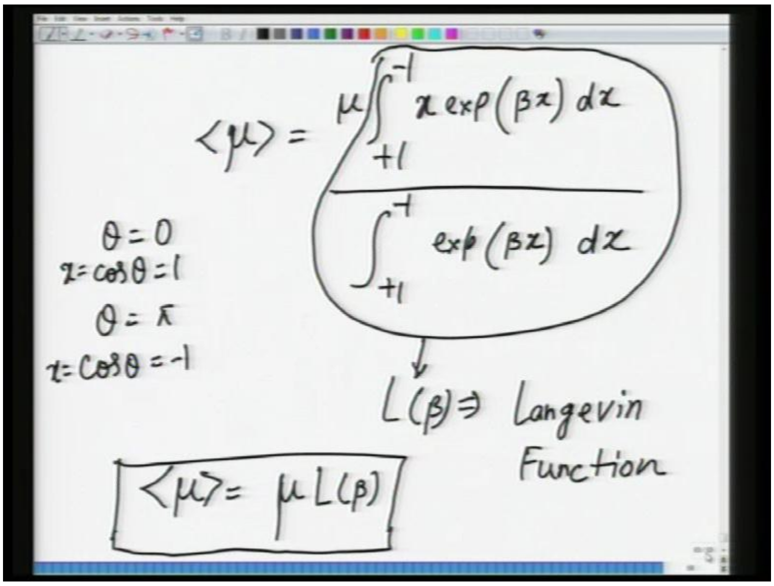

$$\langle\mu\rangle = \mu\frac{\int_{+1}^{-1} x\exp(\beta x)\,dx}{\int_{+1}^{-1}\exp(\beta x)\,dx}$$

$\theta = 0$

$x = \cos\theta = 1$

$\theta = \pi$

$x = \cos\theta = -1$

$L(\beta) \Rightarrow$ Langevin Function

$$\boxed{\langle\mu\rangle = \mu L(\beta)}$$

So, when you substitute in this equation, so supposing mu E by k T is equal to beta and cos theta is equal to x and if you substitute in the previous equation, you get the expression for average mu, which is mu. So, if you, if you change cos, if you change cos theta from 0 to pi theta, from 0 to pi, then naturally x will vary from plus 1 to minus 1. Because because if, if theta was equal to 0 degree, cos theta will be equal to 1, theta would be equal to pi cos theta or x is equal to cos theta, would be equal to minus 1.

So, plus 1 to minus 1 x exponential of beta x d x divided by plus 1 to minus 1 exponential of beta x d x and this is called as, and this whole thing, which is there in this body, this is called as L beta or Langevin function. So, this mu becomes, average mu becomes equal to mu L beta. So, now this gives rise to, what is called as, a finite value of average mu.

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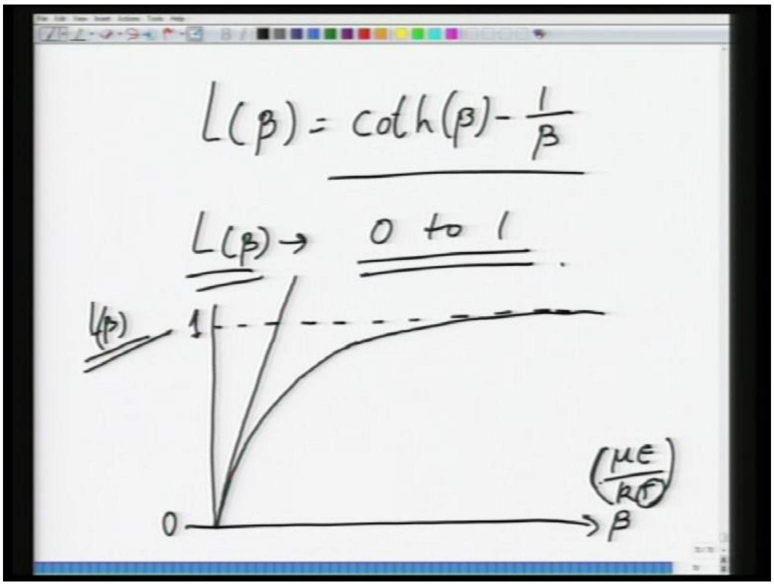

$L(\beta) = \coth(\beta) - \frac{1}{\beta}$

$L(\beta) \rightarrow$ 0 to 1

So, this Langevin function L beta is defined as, cot of hyperbolic beta minus 1 by beta. So, we are not going into theory of Langevin function, but basically this function is, you know, cot of hyperbolic x, which is nothing but cos of hyperbolic x divided by sine of hyperbolic x, so which you can represent in exponential functions of x. So, we are not going into details of this, but the values of L x vary between, so this L beta will vary between 0 to 1.

So, when you plot this L versus beta, so if this is L, this is 0, then it varies something like, like that and this slope at lower values of beta, which is, which gives rise to, what is called as, a asymptotic value, this is 1 by 3. This L beta will give rise to, what you can say, is nothing but it will in the end signifies what is the dipole moment.

So, and what is beta? Beta is nothing but mu E by kT. So, what it tells you is the effect of temperature, right. So, higher values, higher values of beta would mean lower temperatures. And lower values of beta, on the contrary, would mean higher temperatures. So, this gives rise to as an effect of temperature.

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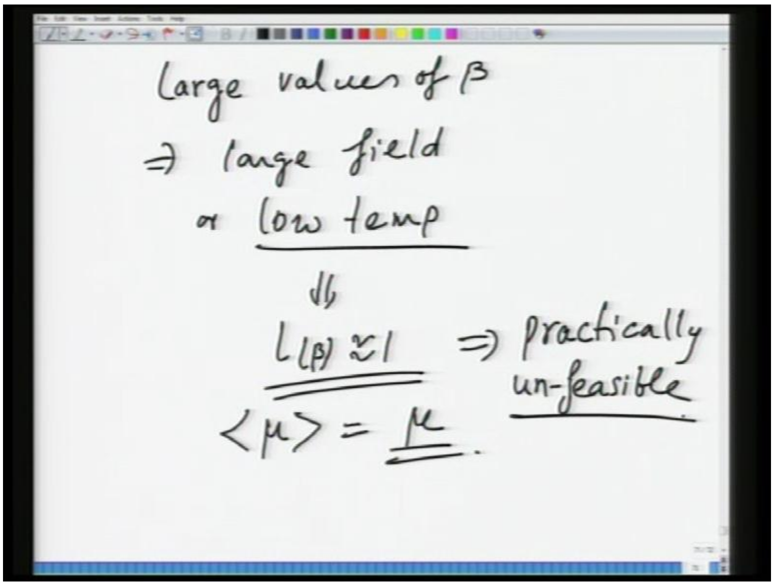

Large values of β

$\Rightarrow$ large field

or low temp

$\Downarrow$

$L(\beta) \simeq 1 \Rightarrow$ practically un-feasible

$\langle \mu \rangle = \mu$.

So, for large values of beta what this would imply? This would imply large field, as you can see, that mu E by kT. So, larger the E is larger than beta is or low temperature and what that would basically mean is, that larger the temperature is, lower the, sorry, larger the field is, lower the temperature is. This situation would tend to align all the dipoles in the direction of applied field because lower temperature would mean lower thermal vibrations, as a result, lower thermal randomisation.

So, tendency to align in the direction of applied field will increase and if you have large enough field to apply, to align all the dipoles, that would mean, all the dipoles would align. So, intuitively, if that means, that is true, then L beta will become equal to 1. So, average mu in such a case situation would be equal to mu. So, which means what? It means is, that, that all the dipoles are aligned. So, averaged dipole moment for each dipole would be equal to mu. So, that is fantastic. So, this is theoretically correct and for small values of beta. But this situation is something, which is not practically feasible. So, L beta is not 1, is equal to 1, is not practically achievable because large enough field, we are talking about very high fields, and low temperature means, temperature closer to 0 k, so so practically un-feasible.

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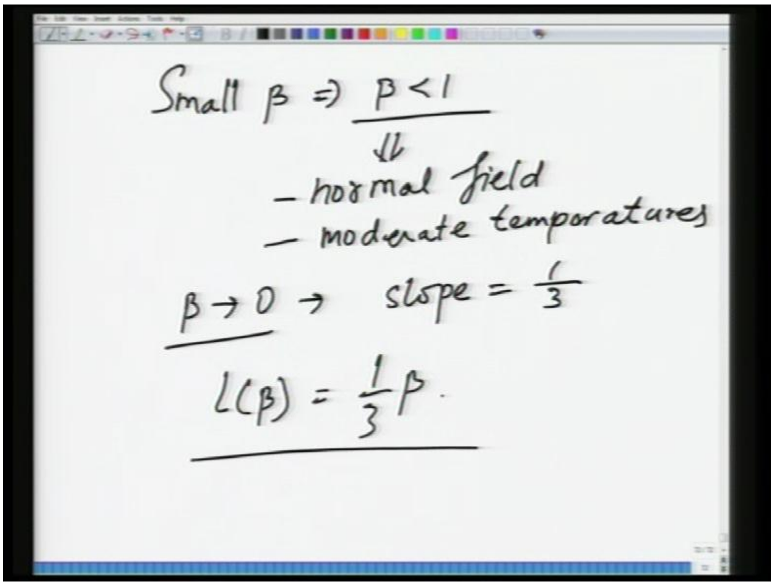

Small $\beta \Rightarrow \beta < 1$

$\Downarrow$

- normal field
- moderate temperatures

$\beta \to 0 \to$ slope $= \frac{1}{3}$

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

So, on the contrary, small values of beta, which means, beta is smaller than 1, what that would mean is normal field. So, normal magnitude of field that we have encountered in devices and moderate temperatures, moderate or high temperatures closer to room temperature, etcetera and so for beta closer to 0 this slope becomes, as I said, is equal to 1 by 3. And as a result, this L beta for a smaller (( )) values is given as 1 by 3 beta and this is what we use for the calculation of average mu.

And this is generally true, because in practical situations for normal fields and moderate temperatures, beta tends to be much smaller than 1, much more closer to 0. As a result, this L beta is equal to be 1 by 3 beta, is a, is a, is a, is a correct kind of an approximation.

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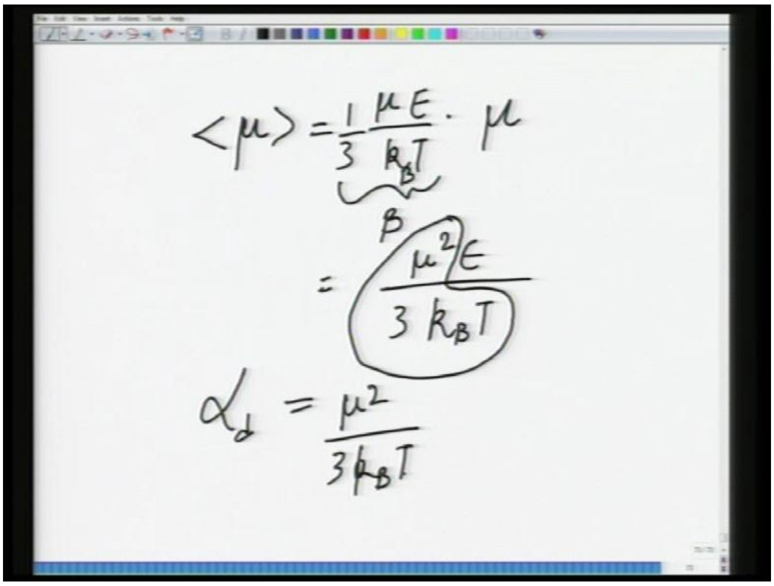

$$\langle\mu\rangle = \underbrace{\frac{1}{3}\frac{\mu E}{k_B T}}_{\beta} \cdot \mu$$

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

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

So, if you now substitute this what you get is average mu becomes equal to mu E by kT 1 by 3. This is the beta into mu, so what it gives you is, that mu square E divided by 3 k B T; let us include k B. So, what is alpha from here? So, alpha d, which is dipolar, is nothing but this because mu is equal to alpha E. So, alpha becomes mu square divided by 3 k B T. So, this is a fantastic expression because now for the first time you see that the polarizability of a material is dependent on temperature. In the previous cases we did not see that. So, electronic and ionic polarizabilities were independent of temperature.

But what we see here is the, as the temperature increases the polarizability goes down and which is true because as temperature increases, the randomisation would increase and material would. So, the, so the net polarization would tend to go down and so basic question holds pretty well for large enough temperatures or moderate temperatures and moderate nominal, nominal values of, sorry, what did I do, I rubbed it, nominal values of field, this alpha. So, this is the expression for dipolar polarizability.

So, so what essentially now we have established is, we have established a mechanism to look at the polarizability of polar materials, which give rise to fundamental phenomena, very important phenomena, called as dipolar polarization. And the polarizability, this we have worked out, is worked out at a condition when fields are nominal and temperature reasonably high. When the temperatures are very close to 0 Kelvin or the fields are very high, so that all the dipoles can be aligned. In that case, the average dipole moment will be equal to nothing but dipole moment of each of the dipole or theoretical dipole moment. So, so basically this establishes this.

So far we have established mathematical or sought of analytical treatment of three polarizabilities. We looked at electronic polarizability, which is dependent upon the size of the atom and which is present for all the materials because all the materials will have atoms. Then you have ionic polarizability; ionic polarizability is true for ionic solids, symmetric ionic solids. And then of course, symmetric, non-symmetric both, as long as you have ions of different case types.

And then of course, you have dipolar polarizability, which is there for dipole, which is there for materials, which have dipole moment and these dipole moments tend to be randomly distributed with respect to each other in the absence of, in the, in the, and in the absence of applied field. But when you applied, apply a finite amount of field, these dipole moments tends to align in the direction of applied field and this gives rise to, what is called as, a finite magnetic dipole moment. I keep on saying magnetic, it is electric dipole moment.

And then we looked at the formalism, we said, that if all the dipoles, if the dipoles in various places of the crystal, making different angles. So, let us say this angle was theta. So, you will have cones of different angles, different thetas with respect to applied field. And then what you are interested in calculating the number of dipoles at any angle theta and the energy, with having energy U theta, which is coming from Maxwell Boltzmann statistics and then we integrate these in order to find out the total number of dipoles. You need to integrate from 0 to pi and in order to find out the total dipole moment, you need to multiply the component of dipole moment parallel to an electric field multiplied by the total number of dipole. So, when you take the ratio of these two, what gives rise to the average dipole moment?

And then we looked into Langevin function and looked at how it gives rise to, what we have arrived to, the expression of alpha d, which is the dipoles polarizability, which is a very important expression because it, for the first time we have encountered the temperature dependence. So, this is a very important outcome, which whose repercussions will be much more clear as we go on discussing more about polar materials.

So, we will, we will finish here today. In the next class what we will take is the... So, far we have, we have not looked in the effect of frequency in quantitative way, so we will, we will look at the effect of frequency or alternating electric field on the behaviour of dielectrics. So, which is very important from the point of view of applications and there we come, again come in contact with some the fundamental quantities. And we will see that at this dielectric constant, which we are saying epsilon r at the moment, it will have a real part, it will have an imaginary part. And then we will also learn about quantities such as loss factor, etcetera. So, we will finish here, in the next class we will take up these topics.

Thank you.