Advanced Chemical Thermodynamics & Kinetics
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Lecture - 08
Molecular Interactions 03

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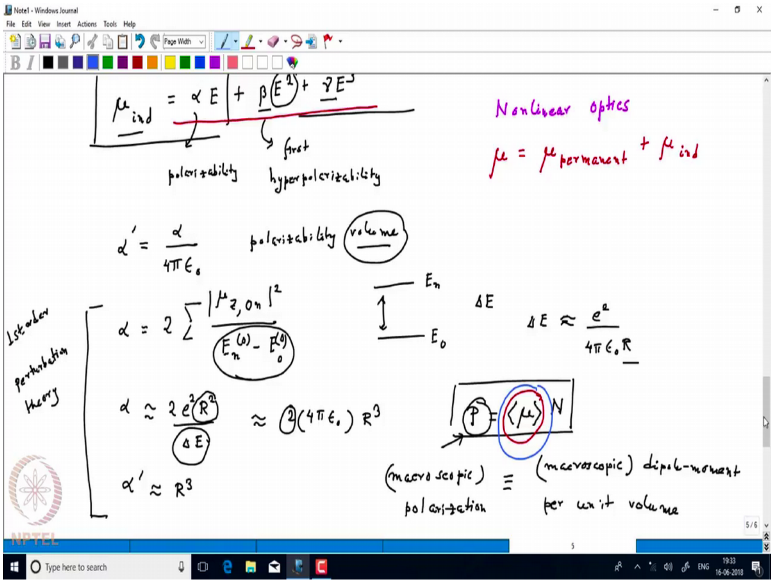

$$\mu_{ind} = \alpha E + \beta E^2 + \gamma E^3$$

polarizability

first hyperpolarizability

Nonlinear optics

$$\mu = \mu_{permanent} + \mu_{ind}$$

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0}$$ polarizability volume

1st order perturbation theory

$$\alpha = 2\sum \frac{|\mu_{z,0n}|^2}{E_n^{(0)} - E_0^{(0)}}$$

E_n, E_0, ΔE

$$\Delta E \approx \frac{e^2}{4\pi\epsilon_0 R}$$

$$\alpha \approx \frac{2e^2R^2}{\Delta E} \approx 2(4\pi\epsilon_0)R^3$$

$$\alpha' \approx R^3$$

$$\boxed{P = \langle\mu\rangle N}$$

(macroscopic) polarization $\equiv$ (macroscopic) dipole-moment per unit volume

Now, let us go back one step and let us try to understand, what is the value how one can calculate this average value of the induced dipole moment to calculate the macroscopic polarization because, if you can calculate that, we can calculate everything. Now, as I said that if we think about the permanent dipole moment and the absence of any electric external electric field, you can think of it is all kinds of orientations are possible. So, mu will be basically 0.

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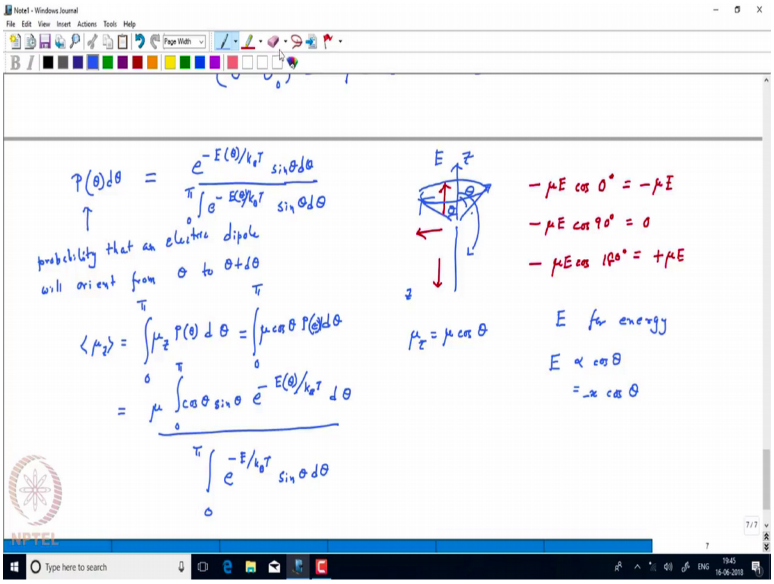

$$P(\theta)d\theta = \frac{e^{-E(\theta)/k_BT}\sin\theta d\theta}{\int_0^{\pi} e^{-E(\theta)/k_BT}\sin\theta d\theta}$$

↑ probability that an electric dipole will orient from θ to $\theta + d\theta$

$$\langle\mu_z\rangle = \int_0^{\pi}\mu_z P(\theta)\, d\theta = \int_0^{\pi}\mu\cos\theta\, P(\theta)d\theta$$

$$= \mu\frac{\int_0^{\pi}\cos\theta\sin\theta\, e^{-E(\theta)/k_BT}d\theta}{\int_0^{\pi} e^{-E/k_BT}\sin\theta d\theta}$$

$\mu_z = \mu\cos\theta$

$-\mu E\cos 0^\circ = -\mu E$

$-\mu E\cos 90^\circ = 0$

$-\mu E\cos 180^\circ = +\mu E$

E for energy

$E \propto \cos\theta$

$= -x\cos\theta$

And then, in the case of induced dipole moment, you can think that I have a basically a probability that the dipole will be oriented from an angle theta to theta plus d theta. If I call that probability as P theta d theta, so this P theta is again probability that a dipole again it is an electric dipole, because we have we are not considering and this will be probability that an electric dipole will orient from theta to theta plus d theta.

That probability we are saying that it will be of course, a dependent is you will be connected to the energy of the tribal, because we have already seen. If we have some orientation of the dipole in the electric field at a particular angle theta, then the energy stored is at the magnitude of the energy stored or the potential energy stored with respect to some baseline of energy potential energy, that we defined to be the 0 of potential, which is the 90 degree orientation, that is nothing but mu e cos theta or which is equivalent to saying mu dot e.

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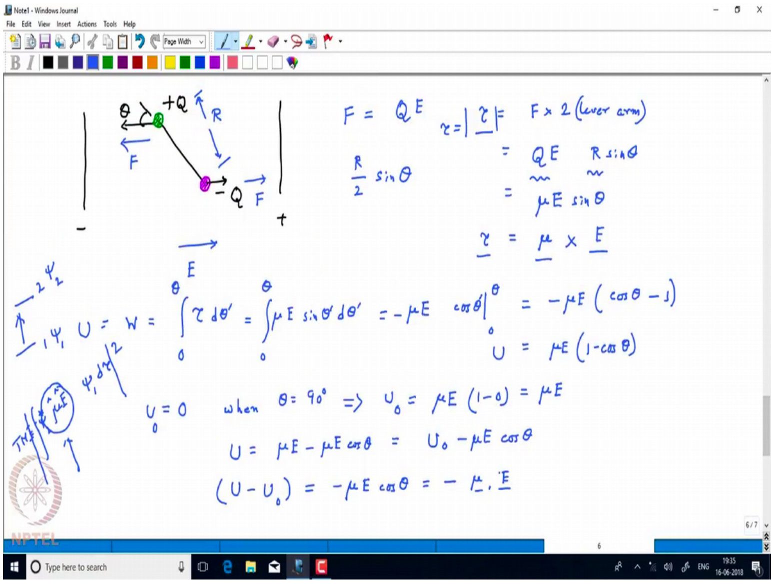

$F = QE$

$\frac{R}{2}\sin\theta$

$\tau = |\underline{\tau}| = F \times 2 \,(\text{lever arm})$

$= QE \quad R\sin\theta$

$= \mu E \sin\theta$

$\underline{\tau} = \underline{\mu} \times \underline{E}$

$U = W = \int_0^\theta \tau \, d\theta' = \int_0^\theta \mu E \sin\theta' \, d\theta' = -\mu E \cos\theta' \Big|_0^\theta = -\mu E(\cos\theta - 1)$

$U = \mu E(1 - \cos\theta)$

$U_0 = 0$ when $\theta = 90° \Rightarrow U_0 = \mu E(1 - 0) = \mu E$

$U = \mu E - \mu E\cos\theta = U_0 - \mu E \cos\theta$

$(U - U_0) = -\mu E \cos\theta = -\underline{\mu}\cdot\underline{E}$

And the negative sign, I did not tell that the negative sign implies that it is a stable energy. Meaning, when I have a dipole oriented in a particular fashion, it means that the energy of dipole is actually getting lowered from the energy, where actually it had a 90 degree. So, the dipole is basically trying to lower its energy. And as you can see that the maximum energy will be basically when the cos theta will be 90 degree to be 1 or the cos theta will be 0 degree or basically the dipole actually orients itself along the field.

Now, the same kind of discussion you also see in many ways like when you talk about nuclear magnetic resonance in a very very classic way, that I have permanent in a very classical way. That I have a tiny a permanent magnetic dipole moment not permanent, which are basically created by an external static field.

And then, you say that this can have two different extreme orientation; one is aligning along the field, and one is aligning opposing the field. So, in one case, the energy will be minus mu e, because it is with respect to the baseline, it is going down minus mu e cos theta is 0. And then, the other orientation will be cos theta will be basically 180 degree. So, cos 180 degree will be minus 1. So, the energy will be plus mu e, so that is a higher energy.

So, in reality, we will have all possible orientation of the dipole, but then since it is associated also with the energy will can think that there is a kind of Boltzmann distribution in the system. Because, I we know that for a finite temperature, I have basically many energy states, the minimum energy states corresponds to the basically parallel orientation with the electric field, and the maximum energy state corresponds to basically the opposite orientation of the energy, and the 90 degree is basically 0 of them.

So, we are saying that probability how do you calculate, that will be something like again any Boltzmann probability, the way you calculate it. So, it is basically the energy for that orientation theta K B T d theta divided by I have to since this is a normal distribution this is a probability distribution. So, I have to take into account of all possible distribution e to the power minus E theta K B T by d theta K B T into e by K B T into d theta, and theta can go from 0 to pi, because I said that it is basically 0 to 180 degree.

Now, we can think that in a three dimension, I will also have another angle phi, but right now actually the picture we are assuming here is basically this is only one direction in the electric field, and there is only one orientation that matters, which is basically the inclination in that thing. And if I actually think about the other orientation, meaning suppose this is the electric field direction, and this is the orientation of the dipole, so we are saying that this is theta; this is arbitrary; but this can happen this can take possible values like this.

And again, that two extreme values are like this. This is basically when the energies minus mu E cosine 0 degree cosine 0 degree, which is minus mu E. And similarly, the other extreme will be the dipole is oriented against the field. And energy will be minus mu E cosine 180 degree, which is plus mu E. And in between, I have a orientation which is something like this, where the dipole has energy of mu E cosine 90 degree, which is 0, so that was the reference energy or difference potential energy.

Now, we can think there will be many orientation, but then the dipole can be oriented at any angle on this other direction also. So, the dipole can be oriented like this also. But, the energy for this orientation, and this orientation, is the same, because it the theta is the same. So, we are not talking about that angle, which is basically the phi angle in the spherical polar coordinate. And you can think that there is a d theta d phi, but again that will get cancelled out, because all the phis are equivalent. And if we just integrate over 0 to 2 pi on d phi, I will have basically a 2 pi angle.

Now, how do you calculate this probability. So, now I know that let us take this axis to be x-axis or z-axis, does not matter, let us say it is a z-axis. No, now so this average value of mu Z will be now, what is the average, value how do you calculate, so you take the mu Z, which is nothing but the Z component of the dipole moment. Now, if the dipole has an orientation theta with respect to the electric field, which is applied along this z-axis. So, then I should write it as mu Z cos theta, so that is the component of the dipole moment. Times the probability distribution P theta d theta, and then I have to integrate over all possible angles, which is 0 to pi to get the average value of the mu Z.

Now, then the mu Z is actually mu cosine theta. So, we just skipped one step here. So, let me write it as a mu, it is mu cosine theta. So, and it is basically the mu Z itself. So, it is mu Z, you take P d theta, and then integrate, which means actually take mu cosine theta, and then integrate.

And now, see that maybe we can write one more step, just for our understanding. So, what I am saying here is that you take mu Z, and then you take the probability distribution P theta d theta, and integrate between 0 and pi, which is saying equivalent to saying that we have mu Z is nothing but mu cosine theta P of theta d theta integrating over 0 and pi.

Now, mu is constant, because mu is basically the overall magnitude of the overall length of the vector, which is again dependent on the strength of the electric field, which is alpha times e, and that we can take out of the integration, because it is a length of the vector. And then, inside the parentheses, I have basically a cos theta, and then I have the integration. But, when I have the overall spherical polar coordinate integration, remember that if I want to integrate it, I missed one thing, so the spherical polar volume if I want to integrate, we should actually integrate there will be a sin theta d theta component both in the numerator as well as in the denominator.

And then, once we integrate it over all the orientation, I will have cos theta sin theta and then e to the power minus E, which is a function of theta K B T d theta integral 0 to pi divided by in the denominator, I will have e to the power minus E by K B T, so that is a normalization factor sin theta d theta, theta going from 0 to pi, so that will be the overall value. Now, you can actually integrate it, but will not do this integration right now, what we can show that we have basically the energy of the dipole, and we know that the energy of the dipole is also dependent on the angle, which is the mu times e times cos theta.

Now, here we are using the E for energy. And in earlier case, actually we are using E as the electric field, so there might be a confusion. And so just keep that in mind. So, we can write the energy as something like it is proportional to cos theta. Let me just write it as something like say x cos theta. So, x is basically the electric field, and a negative sign.

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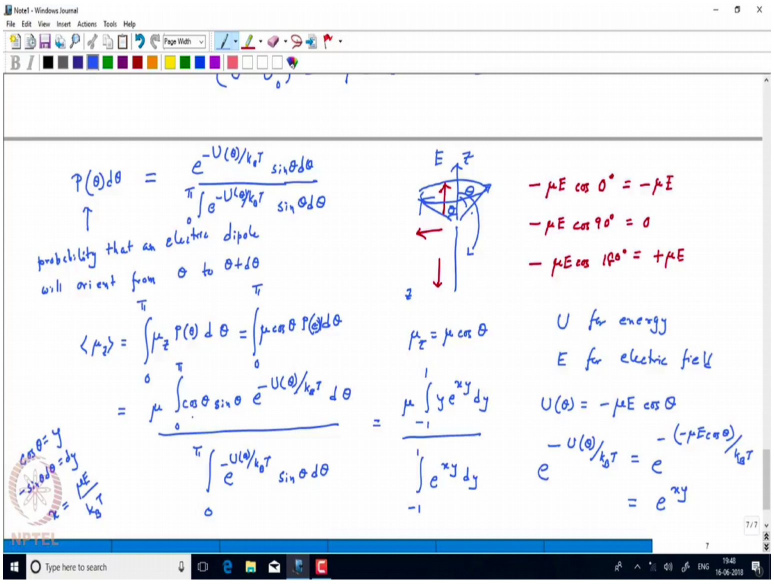

$$P(\theta)d\theta = \frac{e^{-U(\theta)/k_BT}\sin\theta d\theta}{\int_0^{\pi} e^{-U(\theta)/k_BT}\sin\theta d\theta}$$

probability that an electric dipole will orient from θ to $\theta + d\theta$

$-\mu E\cos 0^\circ = -\mu E$

$-\mu E\cos 90^\circ = 0$

$-\mu E\cos 180^\circ = +\mu E$

$$\langle\mu_z\rangle = \int_0^{\pi}\mu_z P(\theta)\,d\theta = \int_0^{\pi}\mu\cos\theta\, P(\theta)d\theta$$

$\mu_z = \mu\cos\theta$

U for energy

E for electric field

$$= \frac{\mu\int_0^{\pi}\cos\theta\sin\theta\, e^{-U(\theta)/k_BT}\,d\theta}{\int_0^{\pi} e^{-U(\theta)/k_BT}\sin\theta\, d\theta} = \frac{\mu\int_{-1}^{1} y e^{xy}dy}{\int_{-1}^{1} e^{xy}dy}$$

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

$$e^{-U(\theta)/k_BT} = e^{-(-\mu E\cos\theta)/k_BT} = e^{xy}$$

$\cos\theta = y$

$-\sin\theta d\theta = dy$

$x = \frac{\mu E}{k_BT}$

So, if we write it in this way, and the negative sign will let me just actually write the E as E Z, then probably it will be clear or we can use a slightly different notation, we can instead of writing the energy as U E, we can actually write it as U everywhere, so you can just replace it as the energy as U, which is the potential energy. And then, there will be no conflict confusion. So, just write E for the electric field, and U for the energy U for energy, and E for electric field, it will be basically U of theta e to the power divided by K B T. So, let me just rewrite it, it is U of theta divided by K B T, there is a minus sign.

Now, U of theta already you know that it is a minus mu E cos theta. So, then we can actually integrate it, it will be e to the power minus cos theta times something divided by K B T. And the minus sign will become plus eventually. And then, will have the integrand of the form, something like that after we make some substitution, and how do we make the substitution, suppose like I have sin theta d theta, so I can actually make a substitution like let us say cos theta equal to let say y. And then, I know that minus sin theta d theta is basically dy.

So, in that way, I can make a substitution and I can rewrite this expression as, it is mu times integral minus 1 to plus 1 y e to the power xy dy. But again, x is nothing but this quantity, mu E minus not with the minus sign, just the mu E. Because, we are writing it as you can see e to the power I had cosine mu E minus mu E cosine theta, so that I am writing it as basically if I write it e to the power minus U of theta divided by K B T, which is nothing but e to the power minus mu E cos theta divided by K B T. And then, cos theta we are taking to be 1. So, we are writing it as e to the power xy. So, x is nothing but mu E divided by K B T; x is nothing but mu E divided by K B T, where K B is the Boltzmann constant.

Now, we can actually make this substitution very easily. And you will figure out that the denominator will be e to the power minus e to the power xy dy and in the numerator, I will have y times e to the power xy, because I have a sin theta d theta will be basically dy with a minus sign. And those two minus sign in the numerator and the denominator will cancel out, but I also have a cos theta, and that is why I have a y here in the numerator.

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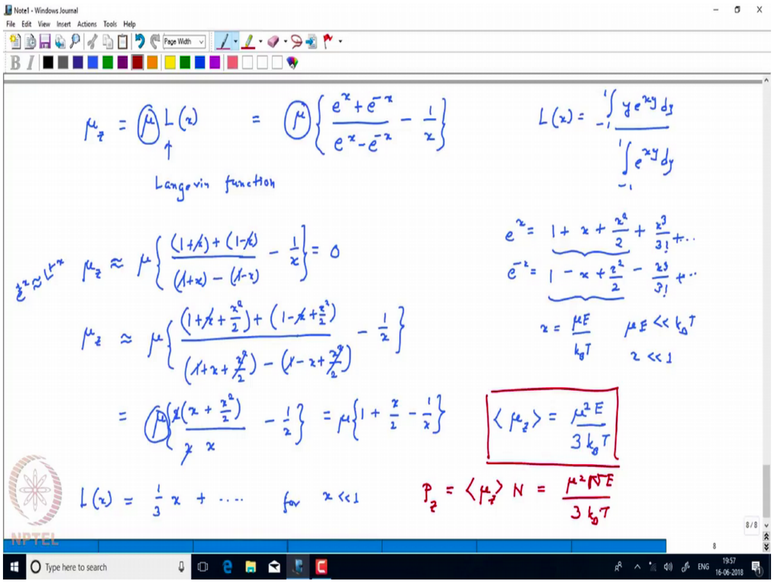

$$\mu_z = \mu \underset{\uparrow}{L(x)} = \mu\left\{\frac{e^x+e^{-x}}{e^x-e^{-x}} - \frac{1}{x}\right\} \qquad L(x) = \frac{\int_{-1}^{1} y e^{xy}\,dy}{\int_{-1}^{1} e^{xy}\,dy}$$

Langevin function

$$e^x = \underbrace{1 + x + \frac{x^2}{2}} + \frac{x^3}{3!} + \cdots$$

$$e^{-x} = \underbrace{1 - x + \frac{x^2}{2}} - \frac{x^3}{3!} + \cdots$$

$$e^x \approx 1+x \qquad \mu_z \approx \mu\left\{\frac{(1+\cancel{x})+(1-\cancel{x})}{(\cancel{1}+x)-(\cancel{1}-x)} - \frac{1}{x}\right\} = 0$$

$$x = \frac{\mu E}{k_B T} \qquad \mu E << k_B T \qquad x << 1$$

$$\mu_z \approx \mu\left\{\frac{(1+\cancel{x}+\frac{x^2}{2})+(1-\cancel{x}+\frac{x^2}{2})}{(\cancel{1}+x+\cancel{\frac{x^2}{2}})-(\cancel{1}-x+\cancel{\frac{x^2}{2}})} - \frac{1}{x}\right\}$$

$$= \mu\left\{\frac{\cancel{2}(x+\frac{x^2}{2})}{\cancel{2}\,x} - \frac{1}{2}\right\} = \mu\left\{1 + \frac{x}{2} - \frac{1}{x}\right\}$$

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

$$L(x) = \frac{1}{3}x + \cdots \quad \text{for } x << 1 \qquad P_z = \langle \mu_z \rangle N = \frac{\mu^2 N E}{3 k_B T}$$

And then, this function we can integrate it, but we will not integrate it as such we just write it as a mu Z, which we have already got the formula is nothing but mu into something which is known as the Langevin function. So, Langevin function is defined as L of x is nothing but integral y e to the power xy dy divided by e to the power xy dy with a limits minus 1 to 1 minus 1 to 1. So, this is the Langevin function.

And I am giving you the answer, and the answer is mu times will have e to the power x plus e to the power minus x divided by e to the power x minus e to the power minus x minus I will have 1 by x. So, this will be the final form of mu Z. But again, x we have to substitute, because x is as we said it is nothing but mu E divided by K B T.

Now, what will be the form of that? Now we have to expand e to the power x and e to the power minus x. Now, you know that e to the power x is nothing but 1 plus x plus x square by

2 factorial plus x cube by 3 factorial and so on. And similarly, e to the power of minus x will have all these terms, so all the whenever we have x or x cube, will have basically minus sign minus x cube by 3 factorial and so on.

So, now you can think that how many terms we will include. Now, I will show you suppose I just include the first two terms, 1 and x, but then I will have a problem, what is the problem. So, then if I want to calculate mu Z, I will not get an x dependence let us show it. So, if I just truncate x up to the second term, now when we are truncating it. So, x is what, x is mu E, which is the energy and the magnitude of the potential energy divided by K B T. What we are saying if a mu E is much less than K B T or the thermal energy, then we can say that x is much less than 1, and then we can make this approximation, otherwise you cannot make this approximation.

And then, the mu Z will have the form of mu. And then, this first term e to the power x minus e to the power minus x if we just approximate it to be say 1 plus x plus 1 minus x for e to the power minus x, in the denominator we will have a minus sign and minus 1 minus x. Now, what we see here is that it is basically mu times the entire thing. Then I see the in the numerator I have the x cancels out, in the denominator the 1 cancels out, and what I will have is 2 divided by I will have x minus x, which is 2 x, so I will have 1 by x minus 1 by x which will be 0. So, I cannot approximate. So, I have to take at least up to the second order term, otherwise I cannot write it in terms of x.

So, let us so it is basically taking if I take e to the power x to be 1 plus x or minus x as 1 minus x, something like that. But now, I am making the approximation I am truncating up to the third term, and let us see what will be the value. Again, this is an approximate expression for a mu Z, so I will have mu times 1 plus x plus x square by 2 plus I will have 1 minus x plus x square by 2 divided by I will have 1 plus x plus x square by 2 minus 1 minus x minus x square by 2, this will be plus. And as before the x term gets cancelled here, and the denominator both one gets canceled as well as x square by 2 term gets cancelled. And I also have minus 1 over x here, so let us see the value, so this mu.

Now, what I have in the numerator is two times 1 plus x square by 2, and then a numerator so all you have a 2, so you can omit the 2 right away. So, I will have x plus x square by 2 divided by in the denominator as you can see, I will have basically 2 x, so I will have like this minus 1 over x. So, then I can actually divide the numerator denominator by x. So, what I will have is 1 plus I will have x square by 2 in the denominator, and then I will have x square by x by 2 minus 1 minus x. And then, you can show that you can actually work it out, we have to probably take another function, so that way you can actually work out the overall value of the Langevin function.

So, you can show that we can actually get a leading order term for the Langevin function, and that value will be nothing but one third of x. Again, this will be a series, but I am not showing you how it appears. So, I just showed you that if I truncate the series up to 1 plus x, what will be the value up to the second term. If I truncate it up to 3rd term, what will be the value. And then, in that way you can show that finally under this approximation that x is a much much less than 1, you can think the Langevin function to be one third of x.

So, since mu is nothing but mu Z is nothing but mu times the Langevin function. What we just got is mu Z or the average value of the Z component is nothing but what we had is let us look back, so I have one mu here, which is here this mu, and then I have basically the Langevin function, and the Langevin function is telling me it is one third of x, so it is mu times one third of x. And x itself is mu E by K B T, so it is nothing but mu square E by 3 K B T. So, thus we see that the average value of the dipole moment or the component of the dipole moment the Z component of the dipole moment is a mu square E by 3 K B T.

And then, you can actually readily understand what will be the value of this macroscopic polarization. Because, the macroscopic polarization along say z-axis will be nothing but this average value times the number density, which will be nothing but mu square N E divided by 3 K B T, so that is how we can show that what will be the value of the microscopic dipole moment.

So, as we see that the macroscopic dipole moment is related to the molecular or dipole moment, which is the mu which is the basically length of the vector, and then which are further connected to the strength of the applied electric field divided by K B T. So, it will be always dependent on the temperature taking. So, basically if we have a higher temperature, then we have a lower the macroscopic dipole moment or macroscopic polarization.

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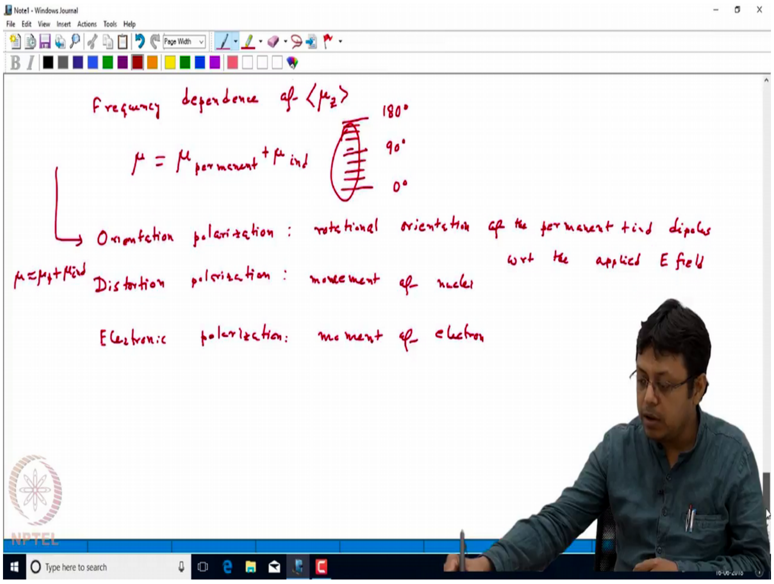

Frequency dependence of $\langle \mu_z \rangle$

$\mu = \mu_{permanent} + \mu_{ind}$

180°

90°

0°

Orientation polarization : rotational orientation of the permanent + ind dipoles wrt the applied E field

$\mu = \mu_p + \mu_{ind}$

Distortion polarization : movement of nuclei

Electronic polarization: moment of electron

Now, the question is this electric field when you apply we can actually have a frequency dependence of the electric field. So, let us now talk about little bit about the frequency dependence of mu Z or the average value of mu Z. Now, think about it how the dipole moment is created. Now, you can think that I have a permanent dipole moment, I have a collection of permanent dipole moment, and when I am applying the field, if the electric field is now and the polarizability is low, and the or the electric field is not too high.

Then actually the induced dipole moment we can ignore, so basically the all the mu is basically the mu permanent. And then, these small little dipoles are trying to orient themselves, and then they are basically populating many energy states between which corresponds to the orientation, which is basically the lowest energy state will be which is a 0 degree orientation, then a 90 degree orientation, and 180 degree orientation, and there will be many many such orientation in between.

And they are basically populating all these states according to the Boltzmann distribution, which is defined for a particular temperature that we had calculated. And then, we can actually calculate, because since different states will have different Z component of the dipole moment, we can actually calculate the overall macroscopic dipole moment, which is a macroscopic average of all these tiny little electric dipoles, which are oriented at different angle.

And then if it is permanent dipole moment that will according to the applied electric field, they are trying to orient. But, if I actually switch the field to fast faster than the orientation time scale of the molecule is syllable determining time scale of the molecule itself, then the molecule will not actually feel any effect of the field. Because it will see as if the electric field is actually changing sign very rapidly, so it will see on a time average basis the electric field is basically 0. So, it will not be able to follow the electric field.

So, what I am saying here is that, the orientation contribution of the dipole moment or basically the orientation polarization, which actually comes from the permanent dipole moment. So, that if I just increase the electric field more than something that the rotational time scale, which means actually if the electric field frequency is something on the order of in the in the microwave or it is more, then actually the rotational time scales are not since they are much slower than the electric field frequency, I will not see an orientational dipole.

So, basically if I switch the electric field frequency, let us say from very low frequency to approaching microwave origin, where actually we are having faster frequency or the very fast switching of the electric field. Then actually the contribution of the electrical orientation polarization will a to the total observed macroscopic polarization will be 0, as I am going to the higher electric field frequency. Remember that, I am talking about the electric field frequency, not the electric field strength. Now, we can actually keep on thinking what are the other contributions, how basically the macroscopic polarization is contributed is there any other contribution.

Now, there is a second term, which is the mu induced term. And the mu induced taken has a linear and non-linear component, let us say it has a linear component for the time being. And now, the linear component comes from, which is the induced dipole moment. How basically the electron cloud get redistributed. So, basically that will also have two parts; initially will have something like known as distortion polarization, so that basically happens, because the molecule has many bonds.

And then, the one due to the effect of the electric field, the bond is one bond is stretched or one bond is compressed. And from again the bond lengths are not permanent, there are doing all these vibrations. But, what I am saying that in the presence of this external perturbation, the equilibrium bond length will increase or decrease and that will give rise to a induced polarization. So, this is the permanent part.

And now, from now onward I have mu is equal to mu permanent plus mu induced, but the permanent thing will vanish, if I increase the frequency above micro averaging. And then, I will have a distortion polarization, where basically these nuclei are moving. So, the orientation polarization is basically coming from the rotational orientation of the permanent as well as induced dipole moment, I should always write it as a permanent plus induced, then it is basically orientation of the permanent plus induced dipoles with respect to the applied electric field.

Then the next thing comes is basically the movement of nuclei. So, it is directly connected to a bond vibrations. But again, if I actually increase the frequency too much, then these the bond vibrations also has a typical time scales of picoseconds or sub picoseconds a few hundreds of femtoseconds. Then actually if I increase it too much that it is oscillating more than 10 to the power 12 per second, it is a tera more than actually terahertz frequency. Then the vibrations also will not sense, it will see that as if the electric field is switching too fast, that it is a kind of 0 effect on it.

So, then I am also not see the distortion polarization, so the only polarization that will survive is because of the movement of electron, because the movement of electrons are very fast. So, will see basically electronic polarization, which is due to the movement of electron. So, if my oscillating field strength if it is a dis field or if it is doing its slow motion, which is much slower than the orientation on dipole, then I will see contribution from all the effects, all the motions. Like it will have an orientation polarization, the bonds will be stretched from the or compressed from the equilibrium position, so that will give me the distortion polarization component, as well as there will be an electronic polarization.

But, moment I sweep my frequency to a higher side, then I will first see the orientation polarization first vanishes, because it is too fast for the molecule to basically rotationally aligned with the field. And then, I will see if I keep on increasing the field frequency at above some particular frequency, I will see the distortion polarization also gets vanished. And then, eventually I will see the electronic polarization also gets vanished, but that will happen at a very very higher frequency.

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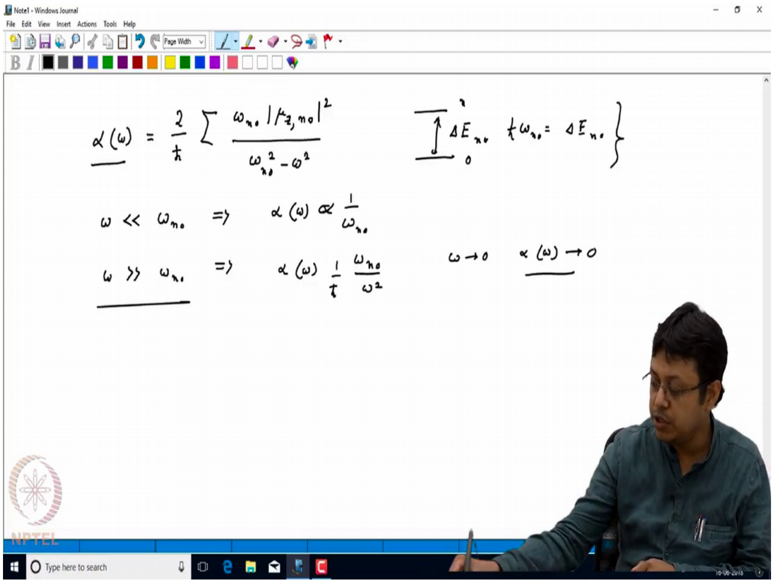

$$\underline{\alpha(\omega)} = \frac{2}{\hbar}\sum\frac{\omega_{n0}|\mu_{z,n0}|^2}{\omega_{n0}^2-\omega^2}$$

$$\left.\begin{matrix} n \\ \updownarrow \Delta E_{n0} \\ 0 \end{matrix}\quad \hbar\omega_{n0} = \Delta E_{n0}\right\}$$

$$\omega \ll \omega_{n0} \Rightarrow \alpha(\omega) \propto \frac{1}{\omega_{n0}}$$

$$\underline{\omega \gg \omega_{n0}} \Rightarrow \alpha(\omega)\ \frac{1}{\hbar}\frac{\omega_{n0}}{\omega^2} \qquad \omega \to 0 \quad \underline{\alpha(\omega)} \to 0$$

Now, we can move on and then ask this question that at what will be basically how we can actually understand this frequency dependence. Again, for that we can actually get an expression for the alpha, and again now this is using the second order perturbation theory, which you cannot discuss here. So, I am just writing the expression and which tells us that if there is a frequency omega n 0, then the mu Z component, which is basically corresponding to a transition of omega n 0 again is basically the frequency of transition.

If this is delta e between say 0 and n some if we think about some transition, as you said that any spectroscopic transition can be actually connected to basically a creating an induced dipole moment. So, then you can say that this omega n 0 is nothing but or h bar omega n 0 is nothing but delta E n 0. Some picture we also draw for understanding, when we talked about the origin of the name that why you call alpha prime as polarizability volume.

Now, we can again make an approximation that we can think that this omega if it is a like too fast or if omega is too slow, then actually will have if omega is actually small or omega is much smaller than omega n 0, then that will give me alpha of omega, which is a frequency dependence. So, than now you see the basically the polarizability is actually frequency dependent. And that will be basically omega n 0 square, so that will go as overall 1 over omega n 0. So, if I have a very very high frequency, I will not get any response.

However, if I have the other limit that omega is much much higher than omega n 0, then what I will have this alpha will be dependent on you can write it as something like omega n 0 divided by omega square. And then, again there is a h bar 1 over h bar. So, as you can see that if the omega tends to 0, basically the alpha omega will also tends to 0.

So, now will have a if we at a we are saying that if the external frequency is very high compared to the natural frequency, so we can actually think this is a actually a natural frequency of which are present already in the molecule, which actually corresponds to some energy level or some associated frequency of or from frequency associated with some energy levels in the molecule.

So, if that external frequency is too fast, and it is very high compared to the natural frequencies, then I will not see the effect of polarization, then actually I will see this thing actually will also tends to the alpha will tends to 0. So, these are basically different manifestations of what we can think about the polarization or the induced dipole moment.

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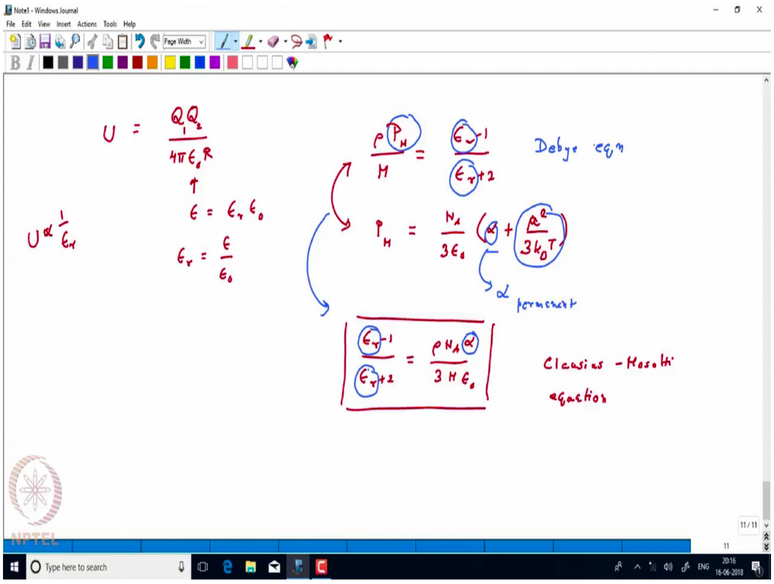

$$U = \frac{Q_1 Q_2}{4\pi\epsilon_0 R}$$

$$\uparrow$$

$$\epsilon = \epsilon_r \epsilon_0$$

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

$$U \propto \frac{1}{\epsilon_r}$$

$$\frac{\rho P_M}{M} = \frac{\epsilon_r - 1}{\epsilon_r + 2}$$

Debye eqn

$$P_M = \frac{N_A}{3\epsilon_0}\left(\alpha + \frac{\mu^2}{3k_B T}\right)$$

α permanent

$$\boxed{\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho N_A \alpha}{3 M \epsilon_0}}$$

Clausius - Mosotti equation

Now, moving on you can actually think about this interaction part that I have basically many interactions between distributed charges. And then, you can ask this question, what is the overall potential. Now, you know that the potential energy, which we wrote as a U or which is commonly written as V, but we can write it as U. And that is basically between two charges is Q 1 Q 2 by 4 pi epsilon 0 R, but that will be in the basically the energy in vacuum.

Now, in a medium, I have to replace this epsilon 0 by epsilon, where actually I can write this epsilon as epsilon r times epsilon 0, where basically this epsilon r is the relative permittivity.

So, it is basically an unit less quantity, that basically tells me what is the permittivity of the medium with respect to the vacuum, and that already you know. And basically the meaning of the permittivity is that, how if the permittivity value is higher, as you can see that this interaction potential will basically go as 1 over epsilon r in a medium.

So, if the relative permittivity is high, which means the interaction potential will be lowered. Something like I have say two charges, and then I have suppose sodium chloride crystal, so in a crystal, there will be some attractive potential between the sodium and the chloride ions, the moment we actually dissolve it in water.

So, what happens is that the water molecules actually sulfate sodium ions and the chloride ions, so as a effect the screen out, the electronic the columbic interactions between the sodium and the chloride ions. So, as an effect, the interaction potential is reduced or the interaction energy is reduced, and that is the meaning of the dielectric constant, which is connected to the permittivity. And then, we can actually get an equation of this macroscopic dipole moment with the dielectric constant, because whatever we derived so far in the macroscopic dipole moment equation is from actually the molecular dipole moment.

But, now the question is a how if the interaction actually goes as 1 over epsilon r, how the macroscopic polarization will go and then, there is a equation will not try to derive it, which basically tells if I take the density times, this macroscopic polarization divided by molar mass that will be equal to epsilon r minus 1 divided by epsilon r plus 2, and that equation is known as a Debye equation.

And then, we can where actually P M is this P is not only the macroscopic polarization, it is the molar polarization. So, we can actually use a small m for that. So, it basically tells me the polarization for one mole. So, this P M here is the macroscopic polarization. So, it is basically the dipole moment per unit volume for one mole. And then, we have an equation, which is which basically connects these macroscopic polarization with the relative permittivity. And this is known as the Debye equation.

And again, we can actually connect it to the molar polarization, meaning actually from the epsilon r, we can actually get back to the equation of the alpha. And then, the equation looks like something like this, the microscopic polarization is already we know this thing that N A divided by 3 epsilon, it basically comes from the expression of alpha.

And what is the average value of mu Z, which you already saw that P Z is basically mu Z into N, which is mu square N E by 3 K B T. And then, we can have a permanent dipole moment contribution also. So, we can have N A by 3 epsilon 0 into alpha plus mu square by 3 K B T. And then, we can combine these two equation, this equation we can easily get from the this so this alpha is the basically in our notation, this is the alpha permanent. And this part is coming from the mu square by 3 K B T, which we actually already derived, which is coming from the orientation and all other effect, which is basically coming from the induced dipole moment.

And then, if we combine these two, we can get an equation, which is something like epsilon r minus 1 divided by epsilon r plus 2 is rho times N A times alpha divided by 3 M into epsilon 0. Now, this equation is known as Clausius Mossotti equation, which basically connects the macroscopic dipole moment P M. We have actually eliminated P M in this equation, which basically connects the polarizability alpha with the permittivity epsilon or the relative permittivity epsilon r.

So, let us now summarize whatever we have discussed so far is that, we first talked about the electric multiples, how what are the interactions between them. We focused mostly on the permanent dipole moments, and then we said that the dipole moment can be permanent or the dipole moment can actually be induced with an external electric field. Then we talked about how one can actually think about the orientation of the dipole, in an external electric field. And then, we talked about little bit about spectroscopic transition, how one can think about spectroscopic transition in a very classical way.

And then, we talked about these all this energy dependence how the how the energy actual of a dipole depends on the angle of the orientation, and we showed you the derivation. And then, we showed the average averaging of it, where you did not show you the exact derivation, but we talked about the Langevin function, how basically you can get an average of all these things, and then get the leading term of the Langevin function. And under the approximation, that your thermal energy K B T is much higher than the interaction potential, which is a mu E on the so, then you can actually approximate it to be something like this that the average value of the Z component of the macroscopic polarization, will be mu square E by 3 K B T.

And then, we moved on so, this equation will be using eventually in later on. And then, we moved on and we talked about many different contributions of the or the different response of the macroscopic polarization two different time scales, and we know that this polarization comes from orientation factor, were actually both the permanent and as well as the induced part can induce dipole moment can orient with the external field.

Then the induced dipole moment also has a distortion polarization, which comes from stretching of the compression of the bonds, and then it has an electronic polarization. But, these all these contributions are a very very characteristic frequency dependence and if we can actually sweep the frequency of the external field, we will see that this polarization effects actually gradually vanishes.

And finally, we talked about the screening effect in a solvent in a medium, where actually the medium basically reduces the interaction potential between the charges. And there we talked about what is the relationship between the permittivity or the relative permittivity, which is the epsilon r to the polarizability. And we talked about the Clausius Mossotti equation as well as the Debye equation. So, the Debye equation time and permanent dipole moment equation, which is already derived basically gives rise to the Clausius Mossotti equation, but we do not derive here the Debye equation.

So, in the next section, will be discussing on the on using this concept will be discussing what is the interaction between two molecules or many molecules, and what is the average interaction between these molecules that actually gives rise to an overall attractive force that actually gives rise to liquid and a solid phases, which are known as condensed phases. And that was the motivation behind this discussion, that we will try to understand why basically the condensed phase emerges as a, what is the very much molecular mechanism behind this condensed phase.

And again, the fundamental idea behind this is basically dipole or induced dipoles exist. And then, these dipoles and induced dipoles basically interact with each other. And we will basically talk about the attractive and the repulsive interactions. And then, we will see how basically we can write the interaction potential or the macroscopic interaction potential in terms of all these tiny dipolar interactions.

Thank you.