Hello students. Welcome to this course, Mathematical Physics and Electromagnetic Theory – I. This is Section II, Electromagnetic Theory – I and unit 4, Microscopic Theory of Dielectrics. The name of the module is Polar molecules, Langevin- Debye formula. I am Yatin Desai, from Chowgule College, Margao, Goa.

Outline of this module is Polar molecules in a dielectric and Langevin- Debye formula. at the end of this module, you'll be able to comprehend the polarizability in polar molecules and derive an expression for Langevin-Debye formula.

Polar Molecules in a Dielectric: The expression for polarization is dipole moment per unit volume. Therefore, we write the polarization vector $\overrightarrow{P}$ as dipole moment $\overrightarrow{P_m}$; sum of the dipole moments, all the dipole moments which are contained in the volume ΔV.

So, polarization vector; $\overrightarrow{P}$ is given as $\frac{\sum \overrightarrow{P_m}}{\Delta V}$. If we have number of dipoles in a given volume of a dielectric, and in the absence of the electric field, if these dipoles are randomly oriented, then the total dipole moment is zero. That is, we can write $\overrightarrow{P} = 0$ when $\overrightarrow{E_{ext}} = 0$. That is, in absence of the external electric field. So, these dipoles cancel the effect of each other, which is shown in this diagram. But when the external (field) electric field is applied, all its molecular dipoles experience a torque, which is given by: $\overrightarrow{P_0} \times \overrightarrow{E_m}$, so, it is $P_0 E_m \cos\theta$; which try to rotate dipoles and make them parallel to the applied field. At sufficiently strong electric field we expect all the dipoles to be perfectly aligned and polarization $\overrightarrow{P}$ to attain the highest saturation value. But this is not observed in practice with sufficiently strong field. Polarization is far from saturation point. This lack of complete alignment is due to the thermal energy of molecules which tend to produce randomness in their orientation.

The average dipole moment per molecule is calculated using the principle of statistical mechanics, which states that at temperature T, the probability of finding a molecule with energy ω is proportional to $e^{-\frac{\omega}{KT}}$, where, K is the Boltzmann constant, T is absolute temperature and total molecular energy which is ω given as $\omega_K + \omega_P$; ω_K is the kinetic energy and ω_P is the potential energy.

The potential energy of permanent dipole $\overrightarrow{P_0}$ in the electric field $\overrightarrow{E_m}$ is; $\omega_P = -\overrightarrow{P_0}.\overrightarrow{E_m} = -P_0 E_m cos\theta$; where θ is an angle between $\overrightarrow{P_0}$ and electric field $\overrightarrow{E_m}$.

Effective dipole moment of a molecule is its component in the direction of $\overrightarrow{E_m}$ i.e., $P_0\cos\theta$ and it is different for different molecules. So, the average value of effective dipole moment is found as; $\langle P_0 cos\theta \rangle$ which is equal to integral of $P_0 cos\theta$ times that factor $e^{-\frac{\omega}{KT}}$ over all $d\omega's$ for the (full) all the energies (divide by) to normalise the result we write it as divided by; $\int e^{-\frac{\omega}{KT}} d\omega$. That $d\omega$ is the elementary solid angle which is given as; $\frac{ds}{r^2}$ and ds is (a) the width of that circular strip which is 2π times the radius of that circular strip which is $(rsin\theta)$; r is the radius of that circle and $rd\theta$ is the width of the strip. So, it is $\frac{2\pi(rsin\theta)rd\theta}{r^2}$ so this r^2 when we cancel with the numerator, we get it as $2\pi sin\theta d\theta$.

Therefore, $\langle P_0 cos\theta \rangle$ is $\int P_0 cos\theta e^{-\frac{\omega}{KT}} sin\theta d\theta$ divided by $\int e^{-\frac{\omega}{KT}} sin\theta d\theta$. In this equation (1), if you look at this factor, $e^{-\frac{\omega}{KT}}$; ω is the sum of $\omega_k + \omega_p$. So, in $e^{-\frac{\omega_k + \omega_p}{KT}}$; we can bring that part; $e^{-\frac{\omega_K}{KT}}$ out of this integral because the kinetic energy is not the function of θ. Therefore, it can be taken out of the integral both in the numerator as well as the denominator and we can cancel them out. So, what will remain is the $\langle P_0 cos\theta \rangle = \frac{\int P_0 cos\theta e^{-\frac{\omega_P}{KT}} 2\pi sin\theta d\theta}{\int e^{-\frac{\omega_P}{KT}} 2\pi sin\theta d\theta}$; because, $e^{-\frac{\omega_K}{KT}}$ part is cancelled. Since, the potential energy is $-P_0 E_m cos\theta$; once we replace in previous equation, we get $\langle P_0 cos\theta \rangle = \frac{P_0 \int e^{\frac{P_0 E_m cos\theta}{KT}} cos\theta sin\theta d\theta}{\int e^{\frac{P_0 E_m cos\theta}{KT}} sin\theta d\theta}$. Here, we had e raise to minus and we are writing ω_p also as minus. So, that minus of minus will become plus in both numerator as well as denominator. To solve this integral further, we replace $\frac{P_0 E_m}{KT}$ by y. Therefore, equation number (2) will look like $\langle P_0 cos\theta \rangle = \frac{P_0 \int e^{ycos\theta} cos\theta sin\theta d\theta}{\int e^{ycos\theta} sin\theta d\theta}$. This is equation # (3). Now, to solve this again we use the method of

substitution. We substitute, $cos\theta$ as x. Therefore, $-sin\theta d\theta = dx$. To take the average, we integrate this equation from θ = 0 to θ = π; though it is not shown in this particular equation. Therefore, when we change that $cos\theta$ to x; we have to substitute for θ = 0, the lower limit we have to substitute x = 1 and for the upper limit θ = π; we have to substitute x = -1. So, with these substitutions and the change in limit, we write that equation (3) in the next step as, average of $P_0 cos\theta$ equals $P_0 \int_{-1}^{1} e^{yx} x(-dx)$ because $sin\theta d\theta$ which is written as $-dx$, divided by $\int_{-1}^{1} e^{yx}(-dx)$. We can cancel this minus sign, both in numerator and denominator and we get this equation as equal to $P_0 \int_{-1}^{1} e^{yx} x dx$ divided by $\int_{-1}^{1} e^{yx}\, dx$. Limits of the integral are from minus 1 to plus 1. This is equation number (4). This equation is further solved by using integration by parts. So, once we solve this integration by parts where all steps are shown here, we get the average value of$P_0 cos\theta$ as $P_0 \left[\frac{\{e^y + e^{-y}\}}{\{e^y - e^{-y}\}} - \frac{1}{y}\right]$. Now, we have, the cosine hyperbolic of a function say θ, cos hyperbolic of θ as $\frac{e^{\theta}+e^{-\theta}}{2}$ and sin hyperbolic $\theta = \frac{e^{\theta}-e^{-\theta}}{2}$. Therefore, if you divide, say this cos hyperbolic θ, (divide) by sine hyperbolic θ; we will get, $\frac{e^{\theta}+e^{-\theta}}{e^{\theta}-e^{-\theta}}$, because that 2 will get cancelled. So, that cot hyperbolic θ is given as, $\frac{e^{\theta}+e^{-\theta}}{e^{\theta}-e^{-\theta}}$. So, if you look at this term here, which is similar to the first term inside this bracket, therefore, we write equation (5) as; $\langle P_0 cos\theta \rangle = P_0 \left[cothy - \frac{1}{y}\right]$. This equation (6) is also known as the Lagrangian formula.

Now when we try to plot this average value of $\frac{\langle P_0 cos\theta \rangle}{P_0}$ and y on this side, where y is given as; $\frac{P_0 E_m}{KT}$. So, it will increase linearly. Then it will increase gradually and then it will saturate. So, this is the nature of the plot (when we get) when we plot $\frac{\langle P_0 cos\theta \rangle}{P_0}$ against y. For most dielectric, P_0 is such that, y is much smaller than 1, that is y much much smaller 1. Therefore, Cot hyperbolic of y which is given as $\frac{e^y + e^{-y}}{e^y - e^{-y}}$ when we expand this e^y in the form of the series and e^{-y} in the form of the series as (given) shown here. Then, we notice that + y, – y is getting cancelled. $\frac{y^3}{3!}$ and $-\frac{y^3}{3!}$ is getting cancelled. Similarly, in the denominator, because there is a minus sign here, plus one and minus one is getting cancelled. Then, $+\frac{y^2}{2!}$ and this $\frac{y^2}{2!}$ will get cancelled, and we have retained only the terms up to the third power of y, because y is much much less than one, because the higher orders will be very small number can be ignored in comparison with the other quantities. Therefore, cot hyperbolic of y is 1 + 1 two and $\frac{y^2}{2!}$ + $\frac{y^2}{2!}$ which is y^2. Similarly, (y + y) in the denominator, we have y minus of minus, + y; 2y. Minus $\frac{y^3}{3!}$, so, $\frac{y^3}{6} + \frac{y^3}{6}$ which will be $\frac{y^3}{3}$. Now from here, if you take 2 common, it will be $\left(1 + \frac{y^2}{2}\right)$ and $2y$ common will have $\left(1 + \frac{y^2}{6}\right)$. So, if you cancel two and two, you will have, $\frac{1}{y}\left(1 + \frac{y^2}{2}\right)\left(1 + \frac{y^2}{6}\right)^{-1}$. So, if we expand it by using the binomial theorem, we'll get it as $\frac{1}{y}\left(1 + \frac{y^2}{2}\right) and \left(1 - \frac{y^2}{6}\right)$. If you multiply this, we'll get that Cot hyperbolic of y as $\frac{1}{y}\left(1 + \frac{y^2}{3}\right)$. So, if you multiply this inside, we will get it as $\frac{1}{y} + \frac{y}{3}$. This is equation #7. So, we write that Cot hyperbolic of y as $\frac{1}{y} + \frac{y}{3}$ in our previous equation, #6. Therefore, that equation #6 can now be written as average of $P_0 cos\theta$ as, $P_0 \left[\frac{1}{y} + \frac{y}{3} and - \frac{1}{y}\right.$ which was already there$\left.\right]$. So, this $-\frac{1}{y}$ will now get cancelled with plus $+\frac{1}{y}$ and we'll get $P_0 \frac{y}{3}$, as average of $P_0 cos\theta$. Let us substitute back y which was given as; $\frac{P_0 E_m}{KT}$. Therefore, average value of $P_0 cos\theta$ will be ${P_0}^2 \frac{E_m}{3KT}$. We call this as equation #8. Let N be number of molecules per unit volume. Therefore, the polarization magnitude of the polarization vector will be N times that $P_0 cos\theta$, average dipole moment. So, $\frac{P}{N}$ is average of $P_0 cos\theta$, which is $\frac{{P_0}^2 E_m}{3KT}$. $\frac{P}{N}$ is nothing but P_m, the dipole moment which is $\propto E_m$.

Therefore, $\propto E_m$ becomes $\frac{{P_0}^2 E_m}{3KT}$. If you cancel that E_m on both the sides, you'll get $\propto$ as $\frac{{P_0}^2}{3KT}$, which is equation #9 and we call it the orientational polarizability.
Considering non-polar molecules only; which we have done in the previous module, $\propto_0$ is $4\pi\varepsilon_0 {R_0}^3$, which we also call it as deformation polarizability. Therefore, the total molecular polarizability of a dielectric is; $\propto$ which is $\propto_0 + \frac{{P_0}^2}{3KT}$. which is the sum of actually the deformation polarizability and the orientational polarizability. This formula is also called as Langevin-Debye equation.

These are the references for this module.

Thank you.