**Course Name- Nanophotonics, Plasmonics and Metamaterials**

**Professor Name- Dr. Debabrata Sikdar**

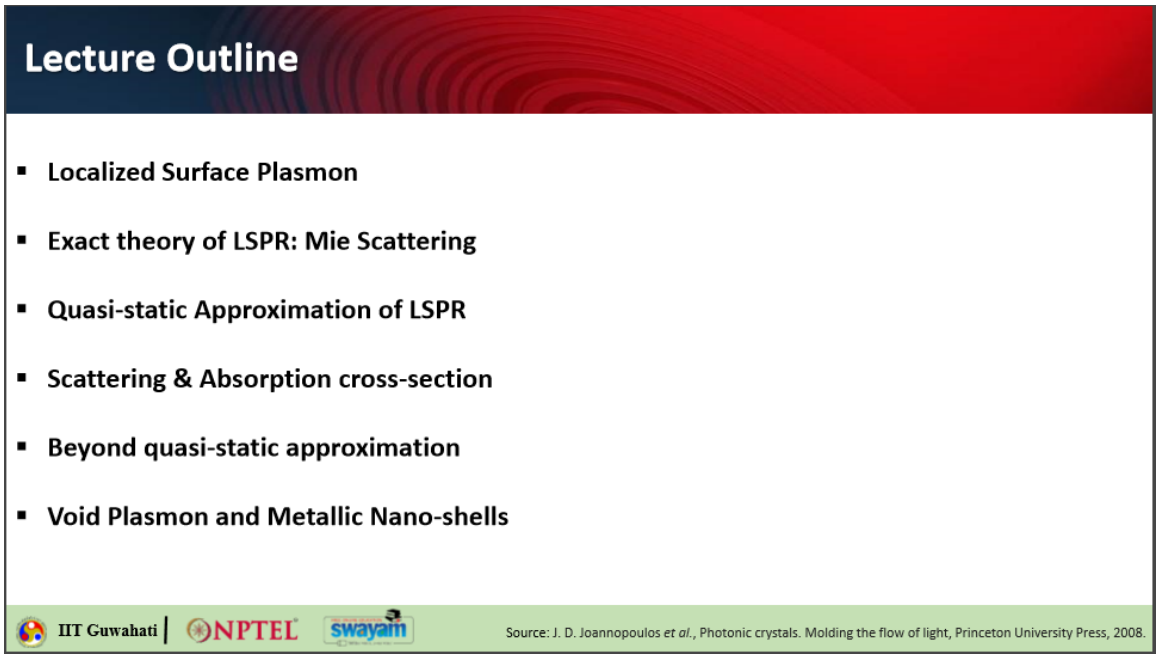
**Department Name- Electronics and Electrical Engineering**

**Institute Name- Indian Institute of Technology Guwahati**

**Week-07**

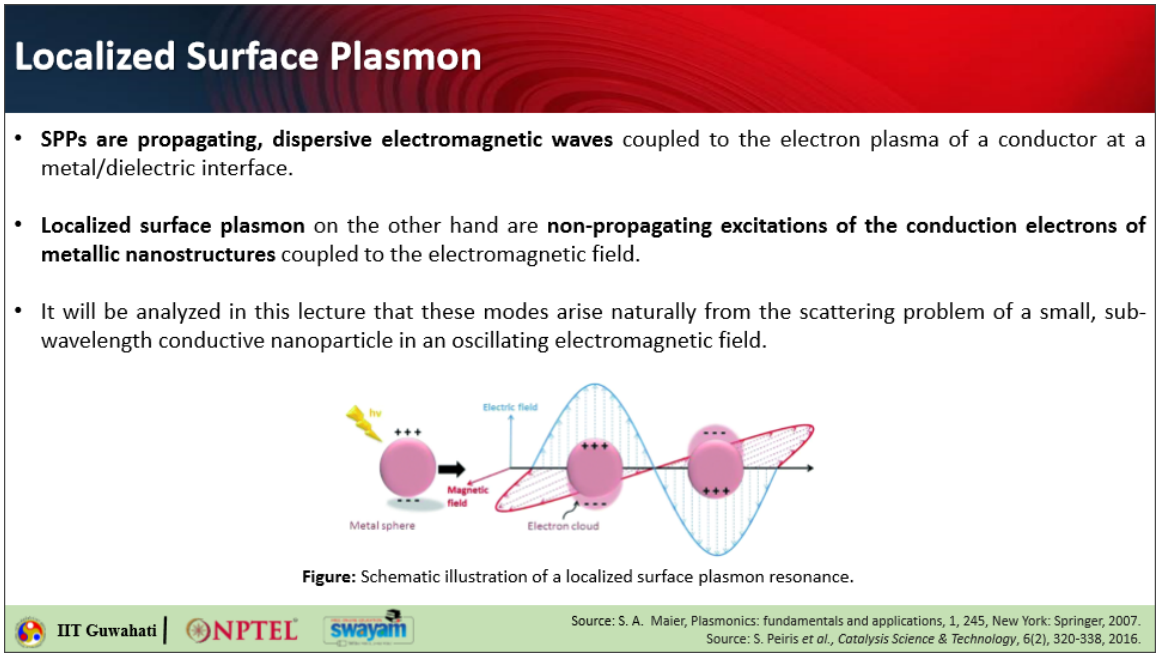
**Lecture -19**

Hello students, welcome to lecture 19 of the online course on Nanophotronics, Plasmonics and Metamaterials. Today's lecture will be on Localized Surface Plasmon Resonance or in short LSPR. So here is the lecture outline, we will first see what is localized surface plasmon and then we will see how to do the derivations of localized surface plasmon resonance conditions and we will treat using exact theory of LSPR that is Mie scattering theory or Mie theory. We will also look into the quasi-static approximation of LSPR. We will find out how to calculate the scattering and absorption cross section. We will also see how to handle the cases beyond quasi-static approximation and towards the end we will see the characteristics of void Plasmon and metallic Nano shells.




So, let us begin with localized surface plasmon. So, we have seen in the previous lecture the surface plasmon are basically the propagating waves which we call them as SPPs, surface plasmon polaritons. These are propagating dispersive electromagnetic waves

which are coupled to the electron plasma of a conductor and they are propagated metal dielectric interface. Now localized surface plasmon on the other hand are basically non-propagating that is why they are called localized and they are non-propagating excitations of the conduction electrons on metallic nanostructures which are coupled to the electromagnetic radiation.




Now you can look into this particular figure here. It shows the illustration of a localized surface plasmon resonance. So, this is a tiny metallic nanoparticle and with light falling on it with the electric field oscillating up and down the electron cloud is also getting so when the oscillate electric field is in this direction electron cloud is basically pushed downwards so that creates a kind of negative charge. All the electron clouds are pushed downwards so there is a kind of negative charge here you can say and there is lack of electrons on the top side so you can think of some positive charge formation there or there are some holes you can say. In that case you are able to see some charge separation that is positive and negative so this actually becomes like a dipole and as the electric field changes when the electric field is negative you will see the electron clouds are moved upwards in this case so you have the negative charges here and the absence of the electrons are felt here which are the positive charges and so the dipole also got reversed.

So that is how with the electric field this metallic nanoparticle gets a induced dipole that also oscillates. Now with that what happens you might know this fact that oscillating dipole radiates. Now in this particular case this metallic nanoparticles they also behave

like dipoles which are oscillating with incident electromagnetic field. Now you can analyze this problem using a scattering problem of a small sub wavelength size nanoparticle in an oscillating electromagnetic field. In this particular case it is important to remember that the curved surface of the nanoparticle exerts the restoring force on the driving or on the driven electrons so that they are pulled back and that is how this oscillation will start they kind of oval like a piece of jelly.

## Localized Surface Plasmon Resonance (LSPR)

- The curved surface of the nanoparticle exerts an effective restoring force on the driven electrons, so that a resonance can arise, leading to field amplification both inside and in the near-field zone outside the particle.
- This resonance is called the **Localized Surface Plasmon or Short Localized Plasmon Resonance**.
- Another consequence of the curved surface is that plasmon resonances can be excited by direct light illumination, in contrast to propagating SPPs, where the phase-matching techniques described in previous lectures have to be employed.

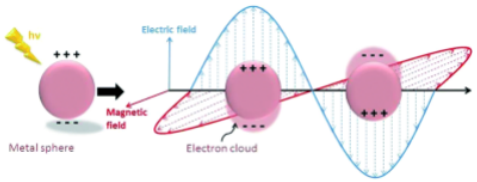



**Figure:** Schematic illustration of a localized surface plasmon resonance.

IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: S. Peiris *et al.*, *Catalysis Science & Technology*, 6(2), 320-338, 2016.

So, if you put a bulk of jelly on the table and try to poke it with a finger or a spoon you will see that the jelly is kind of wobbling. The similar kind of feature is also seen for surface electrons in this case. So, this lead to a field amplification both inside and in the near field zone of this particular particle. So inside and near field of the particles will get some kind of amplification of the electromagnetic fields and that is what will give rise to resonance. So, when this natural frequency of oscillation of the electrons matches the frequency of the incident field there is a resonance.

That means those metallic nanoparticles are able to strongly absorb or scatter light much larger than the geometrical cross section and that is the phenomena of resonance and we call that resonance as localized surface Plasmon resonance or you can say Plasmon resonance. So here what is the good thing as compared to the case of SPPs that here you do not need to worry about the phase matching condition. So, you can simply shine light and excite the Plasmons. So localized surface Plasmon can be excited by direct illumination. So, the physics of localized surface Plasmon will be explored in this particular lecture by considering the interaction of the metallic nanoparticles with

electromagnetic waves and we will see how do we get to the resonance condition.

We will also see the damping process because whenever there is a resonator there are some damping associated that decides basically the Q factor of the resonator. So, we will see how this damping process depends on the nanoparticle different sizes and shapes and how the interaction between the particles in an ensemble or in large assembly they actually affect this resonance. So along with that we will also see what are the other structures other than say solid nanoparticles that support this kind of resonance. So, we will see that the dielectric inclusion in metallic bodies or you can say that a void in a metallic surface that can also support this kind of localized surface Plasmon resonance and also nano shells they can also support. So, we will also look into this particular cases.

## Localized Surface Plasmon Resonance (LSPR)

- The physics of localized surface plasmon will be explored in this lecture by first considering *the interaction of metal nanoparticles with an electromagnetic wave in order to arrive at the resonance condi*tion.
- The damping processes, **studies of plasmon resonances in particles of a variety of different shapes and sizes**, and the effects of interactions between particles in ensembles are analyzed.
- In addition, other important nanostructures apart from solid particles that support localized plasmons are **dielectric inclusions in metal bodies or surfaces, and nanoshells**.

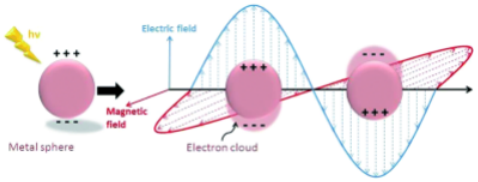



**Figure:** Schematic illustration of a localized surface plasmon resonance.

IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: S. Peiris *et al.*, *Catalysis Science & Technology*, 6(2), 320-338, 2016.

Now when you look for surface Plasmon resonance the Plasmonic materials which are considered are basically gold and silver nanoparticles because they are also particularly interesting because their resonance falls in the visible range of the electromagnetic spectrum. So that you can see directly that the particles are able to transmit and reflect bright colors and they are basically coming from absorption and scattering which are enhanced because of the resonance. And this effect has been found several years back maybe hundreds of years back you can see like the Gothic stained glass in Notre Dame De Paris. So there all these beautiful and bright colors are basically coming from gold or silver nanoparticles embedded into the glass. So, while making they used to make mix this metal to get this bright colors these are basically the colors coming out from the resonance of the nanoparticles.

## Localized Surface Plasmon Resonance (LSPR)

- For **gold and silver nanoparticles**, the resonance falls into the visible region of the electromagnetic spectrum.
- A striking consequence of this are **the bright colors exhibited by particles both in transmitted and reflected light**, due to resonantly enhanced absorption and scattering.
- This effect has found applications for many hundreds of years, for example **in the staining of glass for windows or ornamental cups.**

**Figure:** Gothic stained glass, Notre-Dame De Paris.

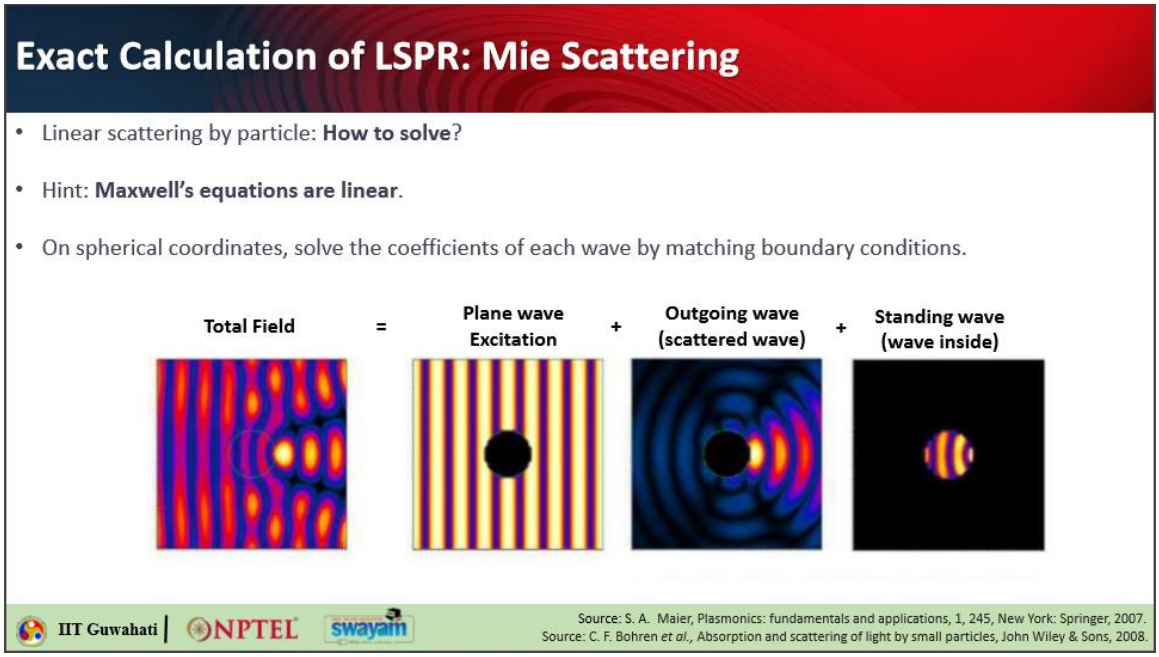
**Figure:** Lycurgus cup.

IIT Guwahati | NPTEL swayam

Source: https://www.friendsofnotredamedeparis.org/the-stained-glass-of-notre-dame-de-paris/
Source: https://www.sciencedirect.com/topics/engineering/lycurgus-cup.

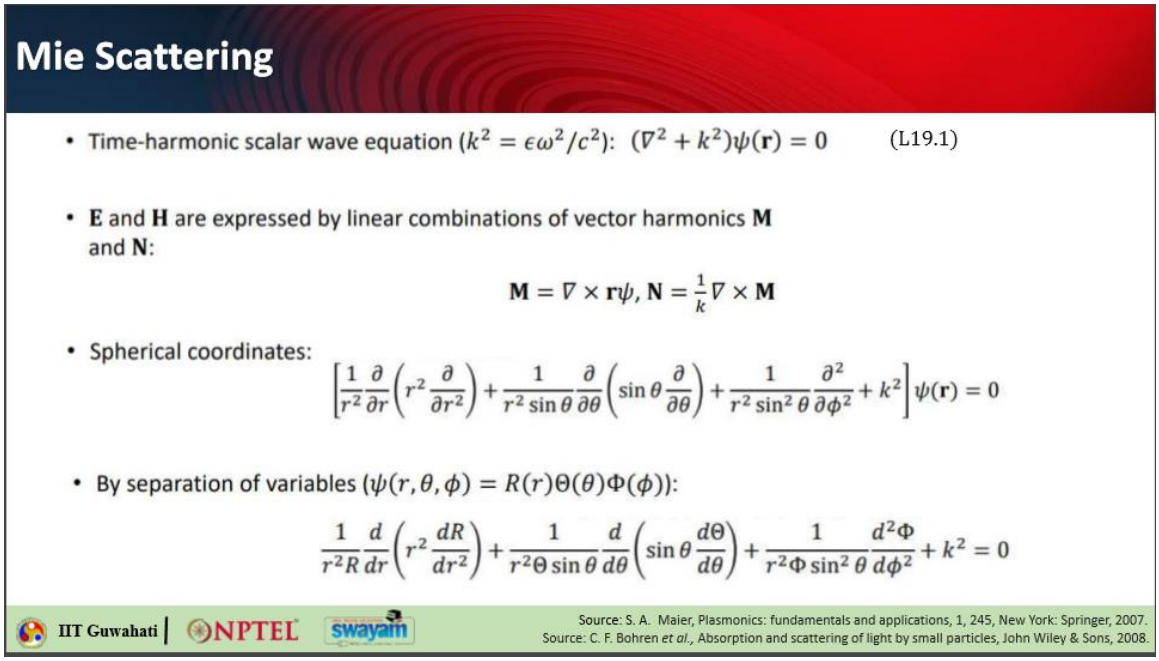
Basically, the Lycurgus cup this cup looks different in color when it is illuminated from outside it shows it looks like a green cup ok. But when the light source is inside ok that is the case when you actually see the light that is what is not absorbed is basically coming towards you. So, in that case from the white light source that is kept at the back of the cup if you remove the Plasmonic resonance that is at blue green you will see that the only red light is coming out towards you. So, you will be seeing the cup as a red cup when the light source is behind. But when the light source is in the front you just see the scattering and the scattering resonance is at the blue green or simply green so the cup appears green in color.

So it is the same cup but it looks different because of this Plasmonic properties. Now when we think of calculating a LSPR we need to first see is there any exact method of calculating the scattering and absorption from this particles nanoparticles. So, the solution comes from the Mie theory. So, in 1908 scientist ghost of Mie he was able to find an exact theory that can give explanation to the colors of different colloidal solutions of nanoparticles of different sizes. So, there was an experiment where people made colloids of different size of nano gold and silver nanoparticles and all of them look different in color.




So there has to be some relationship between the size of the particles with the wavelength and the color they strongly scatter or reflect. So that theory was known as Mie theory and how it works? This works from the concept that Maxwell's equations are linear. So, you can think of a total field that is a kind of summation of the plane of excitation plus the outgoing wave that is the scattered wave plus the standing wave that is the wave inside that particular particle or void. So, ghost of Mie actually did the solution for spherical particles. So, on spherical coordinate systems he was able to solve the coefficients for each of the wave by matching the boundary conditions and he was able to find out the exact calculation of the scattering and absorption cross section by these particles.

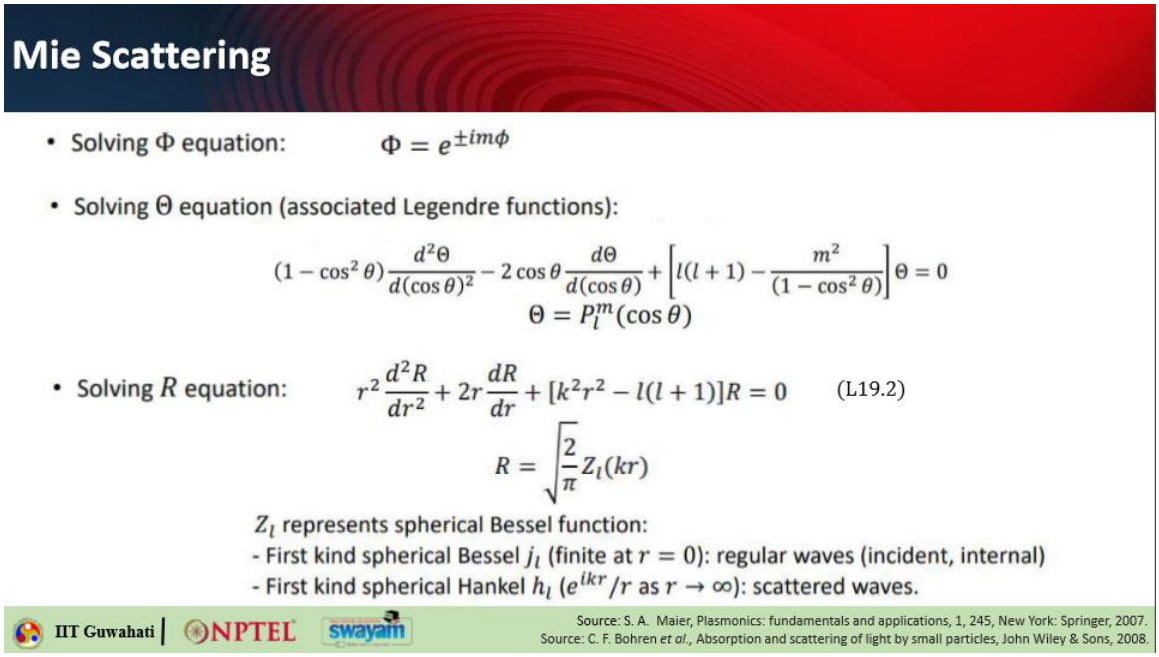
Now how it works? I will not go into the complete mathematical description of Mie theory. This can be found in this particular reference, the second reference as you see here, Bohren Hoffman book. So, in this particular book, Absorption and Scattering of Light by Small Particles, you can actually see the complete derivation of Mie theory. So, I am just showing the important formula here that will help you understand how this particular theory is derived and it is working. So, time harmonic scalar wave equation, we can write it.




So, what is $\psi$ ? $\psi$ is basically the electric potential, it is function of r here. So, this is the wave equation $(\nabla^2 + k^2)\psi(\mathbf{r}) = 0$. Now electric and magnetic field if you express them as linear combinations of the vector harmonics M and N, you can write $\mathbf{M} = \nabla \times \mathbf{r}\psi$, and $\mathbf{N} = \frac{1}{k}\nabla \times \mathrm{M}$. So, these are kind of some relations with electric and magnetic field. So then if you try to use this particular equation for a spherical coordinates or a particle with spherical symmetry like a sphere or nanosphere, you can actually write down this in terms of spherical coordinates.

So you have $r, \theta$ and $\phi$ coordinates. So now you are also able to write down your $\psi$ that is the electric potential in terms of r, theta, phi as three different variables. So, you can separate these variables and say that this is basically $R(r), \Theta(\theta),$ and $\Phi(\phi)$. So, these are the three variables and you can actually write down the equation now in this particular form. So, from here to here by assuming that $\psi(r, \theta, \phi)$ is basically this function.

Now if you solve it only for the $\Phi$ equation, you get $\Phi = e^{\pm im\phi}$. You can solve it for the $\theta$ equation, you will come up the $\theta$ is basically associated Legendre polynomial and when you solve it for the R function, that is the radius function, this is how it looks like and R turns out to be $\sqrt{\frac{2}{\pi}}Z_l(kr)$ where $Z_l$ represents spherical Bessel function. And in this particular equation you will see that you will require $j_l$ that is basically spherical Bessel function of the first kind which is finite at r = 0 and for rectangular waves you can use it for incident and internal cases. Also, for the scattered waves you can think of spherical Hankel function which is given as small $h_l$.




So, what is the specialty of this function? It can be written in the form of $e^{ikr}/r$ where r tends to as $r \to \infty$, okay. So, you can understand that this scattered wave at infinity will die down, will go to 0. So, with that you are able to express E and H of the incident field using the two vector harmonics M and N that you have seen here, okay. So, you are writing them as a linear combination of these two vector harmonics. So, H incident and E incident are the incident electric and magnetic fields.

Now then you apply the conditions like for a plane wave with incident angle $\theta = 0$, all the terms will vanish except for m = 1. So that gives you a simplified version. You can find out what is $A_{l,1}$ that term comes out to be like this and $B_{l,1}$ is basically $iA_{l,1}$. How does it help you? You can actually use this similar kind of expression for scattered and the internal field. So scattered field is also represented as combination of the vector harmonics, okay.

## Mie Scattering

- **E** and **H** of incident waves can be expressed as

$$\mathbf{H}_{\text{inc}} = -\frac{ik}{\omega\mu}\sum A_{lm}\mathbf{N}_{lm} + B_{lm}\mathbf{M}_{lm}$$

$$\mathbf{E}_{\text{inc}} = \frac{k}{\omega^2\epsilon\mu}\sum A_{lm}\mathbf{M}_{lm} + B_{lm}\mathbf{N}_{lm}$$

- For a plane wave with incident angle $\theta = 0$, all terms vanish except for $m = 1$

$$A_{l,1} = i^{(l-1)}E_0\frac{2l+1}{l(l+1)}, B_{l,1} = iA_{l,1}$$

- Similarly, the scattered and internal fields are given as

$$\mathbf{H}_{\text{scat}} = -\frac{ik}{\omega\mu}\sum a_l A_{l,1}\mathbf{N}_{l,1} + b_l B_{l,1}\mathbf{M}_{l,1}$$

$$\mathbf{E}_{\text{scat}} = \frac{k}{\omega^2\epsilon\mu}\sum a_l A_{l,1}\mathbf{M}_{l,1} + b_l B_{l,1}\mathbf{N}_{l,1}$$

$$\mathbf{H}_{\text{int}} = -\frac{ik}{\omega\mu}\sum c_l A_{l,1}\mathbf{N}_{l,1} + d_l B_{l,1}\mathbf{M}_{l,1}$$

$$\mathbf{E}_{\text{int}} = \frac{k}{\omega^2\epsilon\mu}\sum c_l A_{l,1}\mathbf{M}_{l,1} + d_l B_{l,1}\mathbf{N}_{l,1}$$

IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: C. F. Bohren *et al.*, Absorption and scattering of light by small particles, John Wiley & Sons, 2008.

Similarly internal fields are also written like this. I am not going into the description but what happens after you find out the incident field, the internal field and the scattered field you can apply the boundary conditions now. So, the boundary conditions say that the tangential component of the electric field and the magnetic field are continuous across the sphere boundary. So, if you consider the radius to be a you can write that E incident plus E scattered minus E internal cross r cap equals 0. Similarly, E incident plus e scattered minus E internal cross product with r cap so there is a curl, okay is also 0.

## Mie Scattering

- Boundary Condition: tangential components of **E** and **H** are continuous across the sphere boundary ($r = a$).

$$(\mathbf{E}_{\text{inc}} + \mathbf{E}_{\text{scat}} - \mathbf{E}_{\text{int}}) \times \hat{r} = 0$$

$$(\mathbf{H}_{\text{inc}} + \mathbf{H}_{\text{scat}} - \mathbf{H}_{\text{int}}) \times \hat{r} = 0$$

- Mie coefficients ($x = k_0 a$):

$$a_l = \frac{n^2 j_l(nx)[xj_l(x)]' - j_l(x)[nxj_l(nx)]'}{n^2 j_l(nx)[xh_l(x)]' - h_l(x)[nxj_l(nx)]'}$$

$$b_l = \frac{j_l(nx)[xj_l(x)]' - j_l(x)[nxj_l(nx)]'}{j_l(nx)[xh_l(x)]' - h_l(x)[nxj_l(nx)]'}$$

$$c_l = \frac{j_l(x)[xh_l(x)]' - h_l(x)[xj_l(x)]'}{j_l(nx)[xh_l(x)]' - h_l(x)[nxj_l(nx)]'}$$

$$d_l = \frac{nj_l(x)[xh_l(x)]' - nh_l(x)[xj_l(x)]'}{n^2 j_l(nx)[xh_l(x)]' - h_l(x)[nxj_l(nx)]'}$$

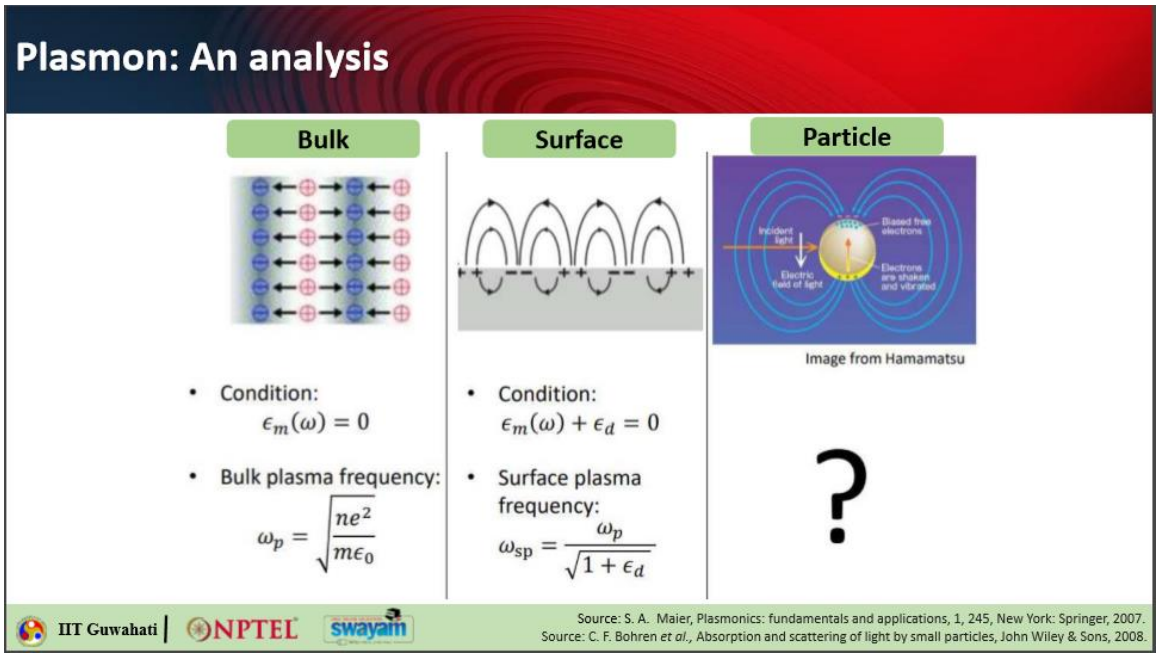
IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: C. F. Bohren *et al.*, Absorption and scattering of light by small particles, John Wiley & Sons, 2008.

So, this is how you can actually this curl is actually giving you what? It is giving you the tangential components, okay. So, they become 0. Now you can write down Mie coefficients as a size independent. So $x = k_0 a$ , okay.

So $a$ is the radius. So, $x$ is actually containing the information of the radius as well as the wavelength of the incident light and you can find out all this coefficient $a_l$, $b_l$, $c_l$, $d_l$ and that helps you to actually compute all this particular fields. So, what are the fields? External field and external field or scattered field you can find out from this calculations. So, from this you are also able to find out the amount of scattered light, amount of what is not scattered is basically absorbed. So those kind of things you can find out exactly for a spherical symmetry, okay. So, for spherical particles Mie theory provides exact solution.

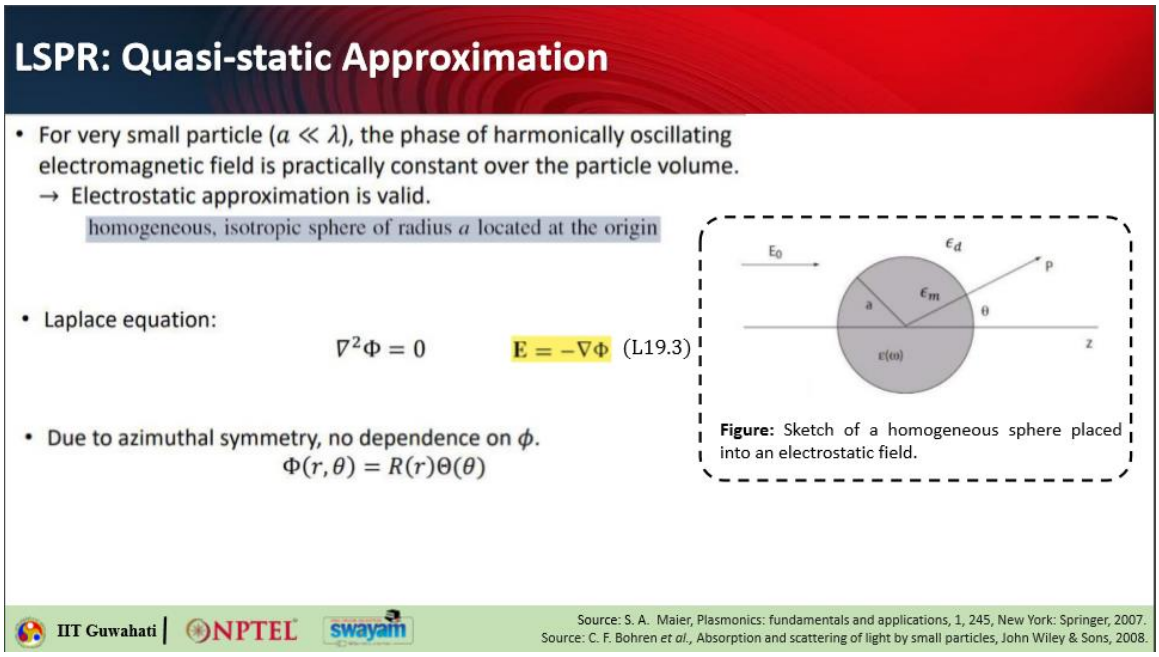
Now this is what we have been looking so far. So, if you think of plasmon as an overall picture we have seen bulk plasmon, surface plasmon and then particle plasmon. We have seen that for the bulk plasmon the condition was that $\epsilon_m(\omega)$ should be equal to 0. So that is where the permittivity of that metal becomes 0. So, this is the boundary and that happens at plasma frequency $\omega_p$ , okay.




And the value is $\sqrt{\frac{ne^2}{m\epsilon_0}}$. So here you can see all this n is the electron concentration, e is the electronic charge, m is the mass of electron and $\epsilon_0$ is the permittivity of vacuum, okay. So, all these parameters are basically fixed. So, plasma frequency, bulk plasma frequency is also not tunable. Whereas you can go to surface plasmon and this is the condition.

We have seen that $\epsilon_m(\omega) + \epsilon_d = 0$. So, the condition is basically $\epsilon_m(\omega) = -\epsilon_d$ . So, where they are matching you are able to excite surface plasmon resonance. And here the surface plasma frequency actually becomes $\omega_{sp}$, so that is $\omega_{sp} = \frac{\omega_p}{\sqrt{1+\epsilon_d}}$. So, you can reduce the frequency when you go to surface plasmon.

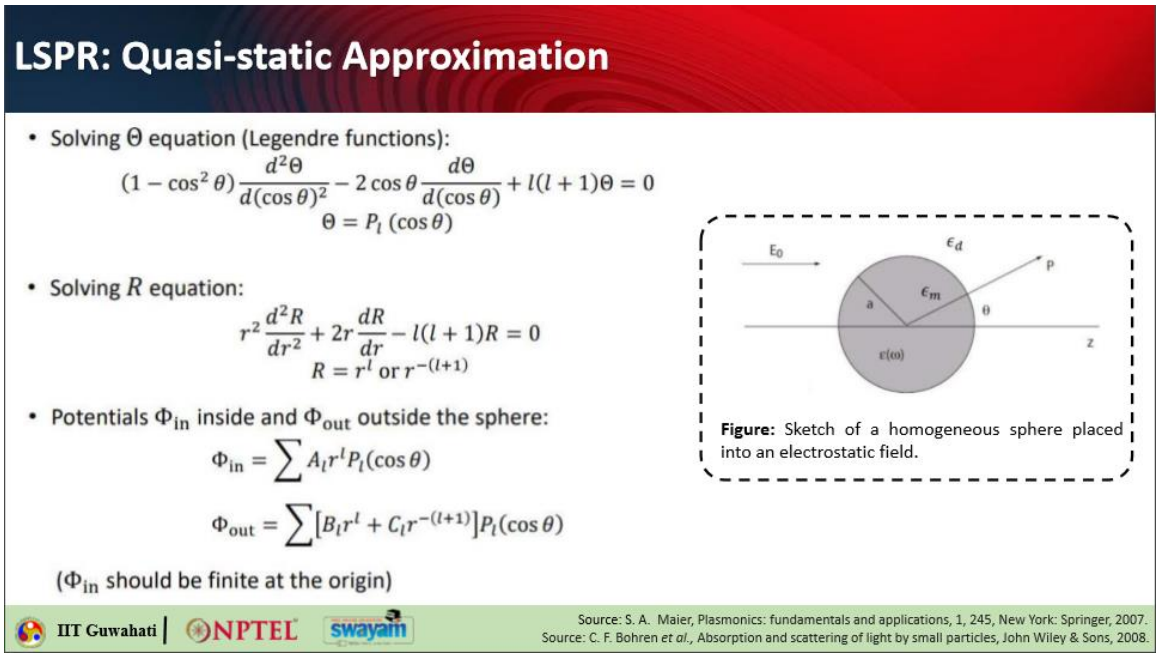
So our aim would be here to find out what is the resonance condition for particle plasmon or localized surface plasmon and then what will be the surface plasma frequency in this case. So, let us look into a much more simplified approximation to Mie theory that is basically quasi-static approximation. Now what is quasi-static approximation? The name itself suggests it is quasi-static. So, for very small particles when I say very small, the radius of the particle is much much smaller than the wavelength, okay. We can say that the phase of the harmonically oscillating electromagnetic field is practically constant over the particle volume because the particle is very small, okay.




So, in that case instead of electrodynamics you are able to use the electrostatics, okay. So, you can actually think of this particular situation that you have a homogeneous isotropic sphere of radius $a$ that is located at origin here, okay. So, this is the permittivity of the metal, this is the permittivity of the surrounding dielectric, there is the incident electric field $E_0$, radius is $a$, P is the particular point and this is angle $\theta$, okay. So, in this case you can think of Laplace equation. So $\nabla^2\Phi = 0$ and E is nothing but $-\nabla\Phi$ .

So you can solve Laplace equation to find out the potential in and outside the particle. So

here also due to azimuthal symmetry you can ignore the $\Phi$ dependency and you can simply take the dependency of $r$ and $\theta$. So again, the potential can be split into variables like $R(r), \theta(\theta)$and then you solve the $\theta$ equation it gives you again the Legendre polynomial, so $\theta = P_l(\cos\theta)$and when you solve the R equation you get $R = r^l$ or $r^{-(l+1)}$. So, in that way you are also able to write down what is the potential inside that is $\Phi_{in}$ that is inside the sphere and also $\Phi_{out}$ that is outside the sphere. So, these are the two expressions from this equation that tells you what is the potential inside and outside the sphere.




So, these are the new coefficients that you have introduced. Now there are certain things like $\Phi_{in}$ should be finite at the origin also when you look at $\Phi_{out}$, so $\Phi_{out}$ when it is too far it should be same as the incident electric fields potential assuming that the particles effect is no longer present at a far distance. So $\Phi_{out}$ is $-E_0 z$ which is nothing but $-E_0 z$ you can write it as $-E_0 r\cos\theta$ as $r \to \infty$. So, if you apply these two conditions you will be able to find out the coefficients, so you will be able to find out what is $B_1$. So $B_l = -E_0$ and $B_l = 0$ for all other cases when $l \neq 1$.

So in that case you are able to find out one coefficient that is $B_l$. How about $A_l$ and $C_l$? So here also you can say that the tangential components of the electric fields are continuous that means $C_l = A_l = 0$ for all the cases $l \neq 1$. So, let us take the tangential components, so $-\frac{1}{a}\left(\frac{\partial\Phi_{in}}{\partial\theta}\right)$ at $r = a$ that is at this point for inside potential and outside potential they should be same. So that gives you this kind of a equation. What is the other case that the normal component of the electric field is also continuous.

## LSPR: Quasi-static Approximation

- $\Phi_{out} = -E_0 z = -E_0 r\cos\theta$ $(\mathbf{E} = -\nabla\Phi_{out} = E_0\hat{z})$ as $r \to \infty$:

$$B_1 = -E_0 \text{ and } B_l = 0 \text{ for } l \neq 1$$

- Tangential components of **E** are continuous($C_l = A_l = 0$ for $l \neq 1$):

$$-\frac{1}{a}\left(\frac{\partial\Phi_{in}}{\partial\theta}\right)_{r=a} = -\frac{1}{a}\left(\frac{\partial\Phi_{out}}{\partial\theta}\right)_{r=a}$$

$$A_1 a\sin\theta = \left(-E_0 a + \frac{C_1}{a^2}\right)\sin\theta$$

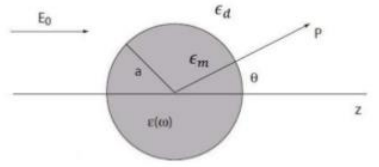



**Figure:** Sketch of a homogeneous sphere placed into an electrostatic field.

- Normal components of **D** are continuous:

$$-\epsilon_0\epsilon_m\left(\frac{\partial\Phi_{in}}{\partial r}\right)_{r=a} = -\epsilon_0\epsilon_d\left(\frac{\partial\Phi_{out}}{\partial r}\right)_{r=a}$$

$$\epsilon_m A_1\cos\theta = \epsilon_d\left(-E_0 - \frac{2C_1}{a^3}\right)\cos\theta$$

- Coefficients are

$$A_1 = -\frac{3\epsilon_d}{\epsilon_m + 2\epsilon_d}E_0 \text{ and } C_1 = \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}E_0$$

IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: C. F. Bohren *et al.*, Absorption and scattering of light by small particles, John Wiley & Sons, 2008.

Here in quasi-static approximation the electric field magnetic field does not come into the picture. So, we will be considering about the flux, so the normal component of the flux will also be continuous. So, you can find out what is the flux here $-\epsilon_0\epsilon_m$ and then you have this one which is basically $\frac{\partial\Phi_{in}}{\partial r}$ and you are calculating at this boundary so that is $r = a$. Similarly, you can put it for this one outside region this one.

So this gives you this particular expression. So, you have two variables $A_1$ and $C_1$ and you have got two equations now. You solve for it and you can get what are the coefficients $A_1$ and $C_1$. So mathematics is looking bit messy but it is not that complicated if you are interested you can always try this on your own else you can simply take this coefficients from this slide that $B_1$ is $-E_0$, $A_1$ is $-\frac{3\epsilon_d}{\epsilon_m+2\epsilon_d}E_0$ and $C_1$ is basically $\frac{\epsilon_m-\epsilon_d}{\epsilon_m+2\epsilon_d}E_0$. So, you have got all three coefficients $A_1$, $B_1$ and $C_1$. So now you are in a position to write down what is the electric potential inside and outside the particle.

## LSPR: Quasi-static Approximation

- Electric potential:

$$\Phi_{in} = -\frac{3\epsilon_d}{\epsilon_m + 2\epsilon_d} E_0 r\cos\theta$$

$$\Phi_{out} = -E_0 r\cos\theta + \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}\frac{E_0 a^3\cos\theta}{r^2}$$

$$= -E_0 r\cos\theta + \frac{\mathbf{p}\cdot\mathbf{r}}{4\pi\epsilon_0\epsilon_d r^3}$$

where $\mathbf{p} = 4\pi\epsilon_0\epsilon_d a^3 \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}\mathbf{E}_0 = \epsilon\epsilon_d\alpha\mathbf{E_0}$.

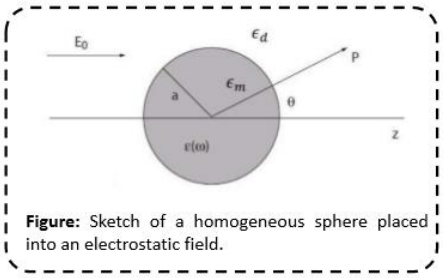



**Figure:** Sketch of a homogeneous sphere placed into an electrostatic field.

- Polarizability $\alpha$:

$$\alpha = 4\pi a^3 \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} = 3V\frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \qquad \text{(L19.4)}$$

IIT Guwahati | NPTEL swayam

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.
Source: C. F. Bohren *et al.*, Absorption and scattering of light by small particles, John Wiley & Sons, 2008.

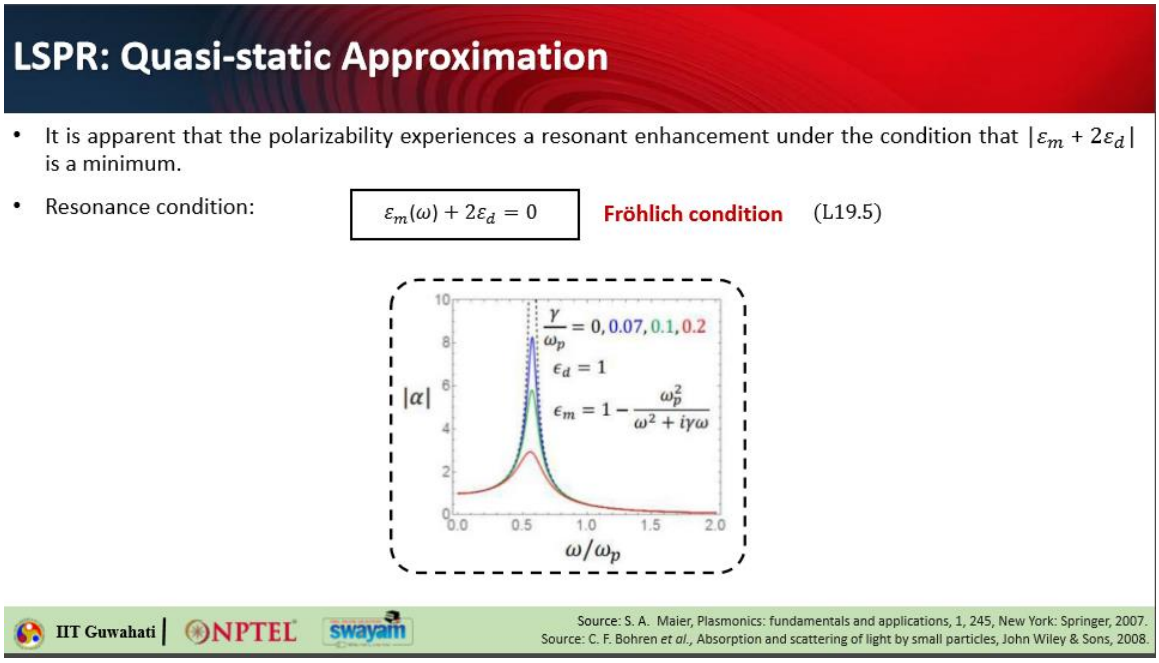
So $\Phi_{in}$ is having $A_1$ coefficient, $\Phi_{out}$ has got $B_1$ and $C_1$ coefficient. So, you can put those here and this is how it looks like. So, this is the potential inside the particle and this is the potential that is outside the particle. Now there is something interesting in this particular expression of potential outside the particle. So, if you see there is a distinct contribution coming from the electric field which is the incident electric field that is fine and then there is an extra component that is coming into the picture from the particles point of view.

So if you look here so this looks like there is a dipole and there is a potential because of this dipole. So, you can actually think of a dipole with a polarizability p which is given by this expression. So, this term you can take as $\frac{\mathbf{p}\cdot\mathbf{r}}{4\pi\epsilon_0\epsilon_d r^3}$. So, when you equate these two you will get that p equals this is the expression and this can be written as and this polarization is proportional to the electric field.

So that constant you can take as polarizability $\alpha$. So $\alpha$ is the term $4\pi a^3\frac{\epsilon_m-\epsilon_d}{\epsilon_m+2\epsilon_d}$. So, this can be written as 3V that is the volume of the particle. So, what is the volume V of this particle $\frac{4}{3}\pi a^3$. So $4\pi a^3$can be written as 3V so this is basically the polarizability $\alpha$ of the particle. Now with this particular expression you can find out what is the resonance condition.

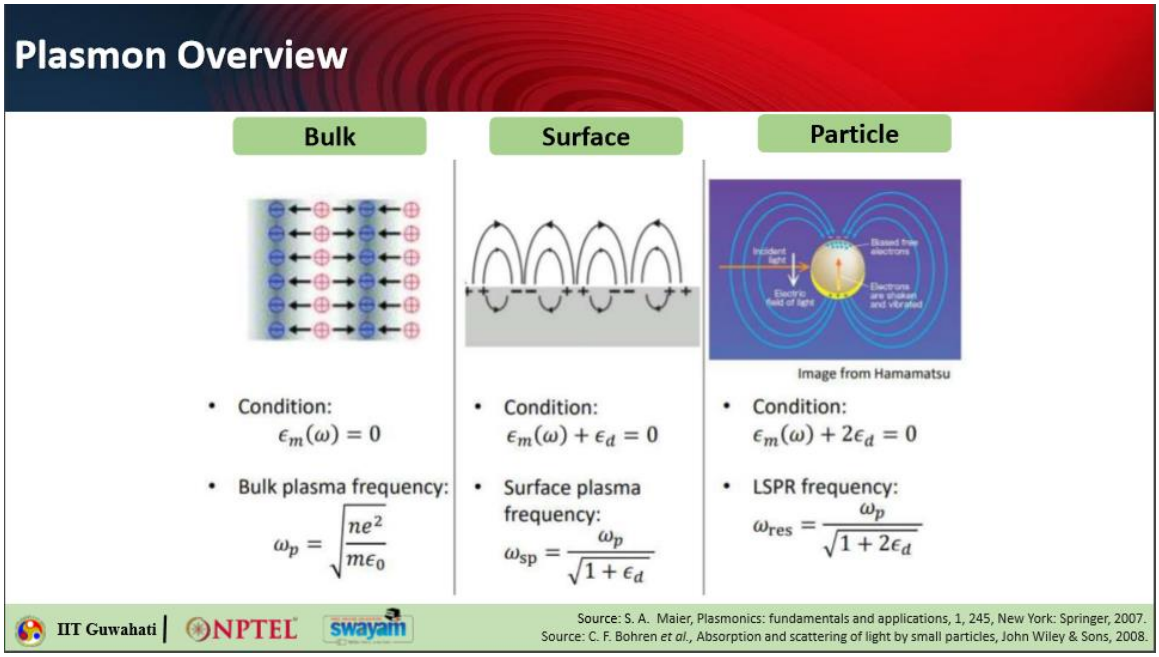
So you can see that the polarizability will experience a resonant enhancement when the condition that the denominator of this is very small. That means when $|\varepsilon_m + 2\varepsilon_d|$ is very small. So, you can now $\epsilon_m$ is basically a complex right because it is a metal. So, metal in

visible wavelength typically they have complex permittivity. So, in this condition and what is $\epsilon_d$ that is basically the dielectric one which is a real number.

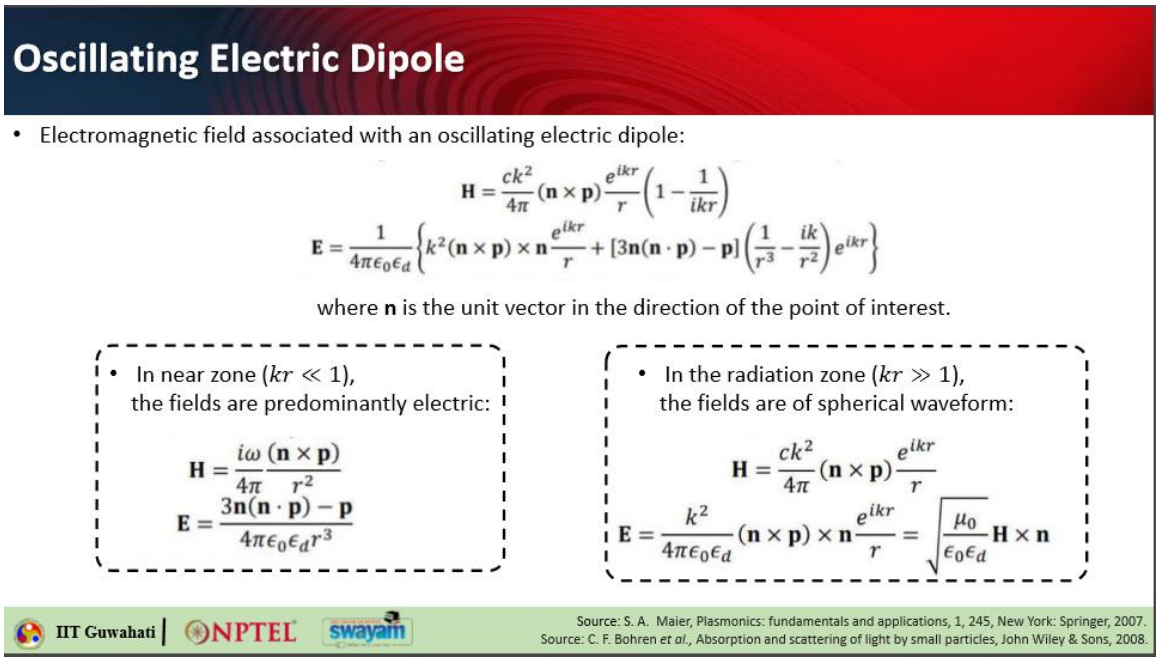



So, you can think of this as real of $\epsilon_m(\omega) + 2\epsilon_d$ will be equal to 0. So, this is a condition for the resonance and it is also known as Frohlich condition So you can understand that this is the resonance condition. Now if you consider the metal to be a Drude kind of metal. So $\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$, where $\gamma$ is the damping constant and if you try to plot the modulus of this polarizability over a normalized frequency the frequency is $\omega/\omega_p$ here. In that case if you take $\gamma$ = 0 that you will give you a infinite because then this term becomes 0 completely.

So you will get a asymptote it is going up infinitely but if you consider some finite value of $\gamma$ then you will get this 0 for $\gamma$ equals $0.07\omega_p$ you will get this blue curve $0.1\omega_p$ you will get this curve and $0.2\omega_p$ you will get this curve. So, what you can see is that as $\gamma$ that is a damping getting increased the Q -factor of the resonance decreases the resonance position more or less remains same but the width of the peaks are getting broader.

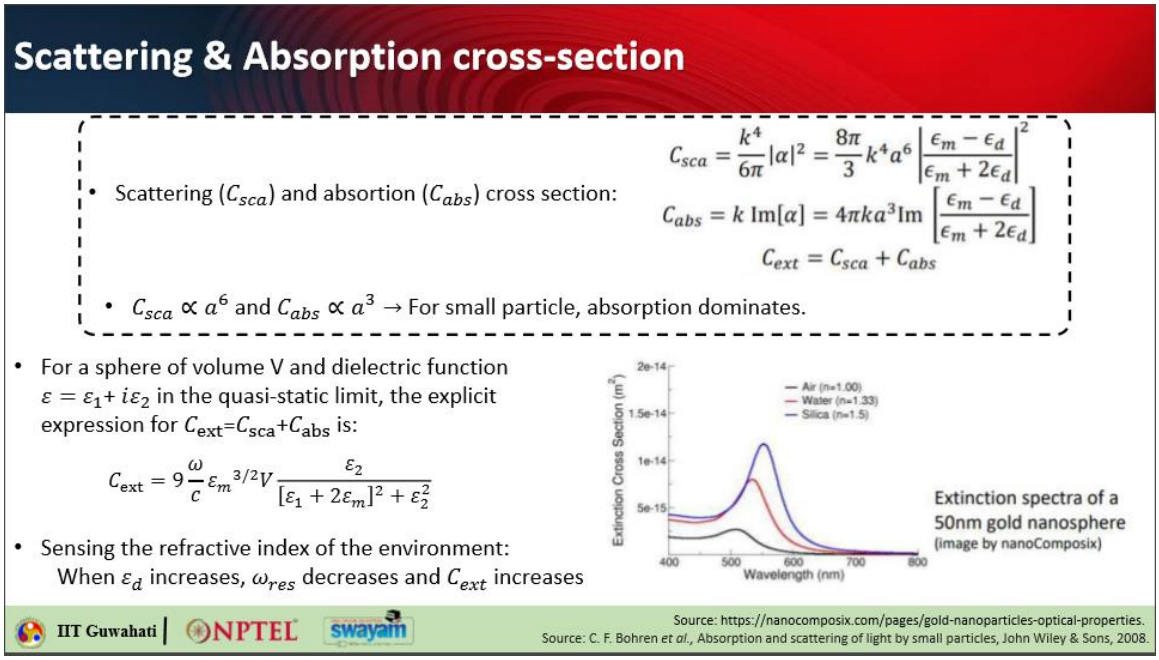



So that is what is more damped. So now coming back to this slide to fill this vacant spot so the condition now we have derived that $\epsilon_m(\omega)$ should be equal to $-2\epsilon_d$ for resonance or you can say $\epsilon_m(\omega) + 2\epsilon_d = 0$ and LSPR frequency is nothing but $\frac{\omega_p}{\sqrt{1+2\epsilon_d}}$ ok. So, this is how the resonance frequencies have shifted from bulk to surface to particle plus bonds. Now coming back to the point that oscillating dipoles radiate so you can actually find out the electromagnetic field which is associated with an oscillating electric dipole ok. So, this is the exact calculation this is not within quasi-static approximation this is a exact theory so you can see that H is nothing but this is the expression for H what is n? n is the unit vector in the direction of the point of interest and p is the dipole moment of that particular dipole.




So, this two gives you the expression for E and H ok. So, from this you can see that in the near field the fields are you can say predominantly electric because in the near field regime you will get mainly electric fields and in the radiation zone that is when *kr* is much much greater than 1 ok the fields are of the spherical waveform. So, this from these particular ones if you put this two conditions so in the near zone *kr* is much much lesser than 1, in radiation zone *kr* is much much greater than 1 you can find out that the field in near field is mainly electric whereas in the radiation zone or the far field zone they are of the spherical waveform ok. Now coming back to the quasi-static we have seen that we are able to obtain alpha that is the polarizability of a particle. Now what do we do with that we are able to find out the scattering and absorption cross section using these two simple formulas. So, scattering cross section will be $C_{sca} = \frac{k^4}{6\pi}|\alpha|^2$ and c abs that is the cross section of absorption will be $C_{abs} = k\mathrm{Im}[\alpha]$ .

Now if you see the values here scattering is proportional to $a^6$ and absorption is proportional to $a^3$. So, you can understand that for small particles absorption dominate over scattering but as the particle size increases scattering quickly gains and then it becomes the major contributing factor ok. And extinction cross section is nothing but the summation of the scattering and absorption. So, extinction means whatever is the amount of light getting lost or extinct.



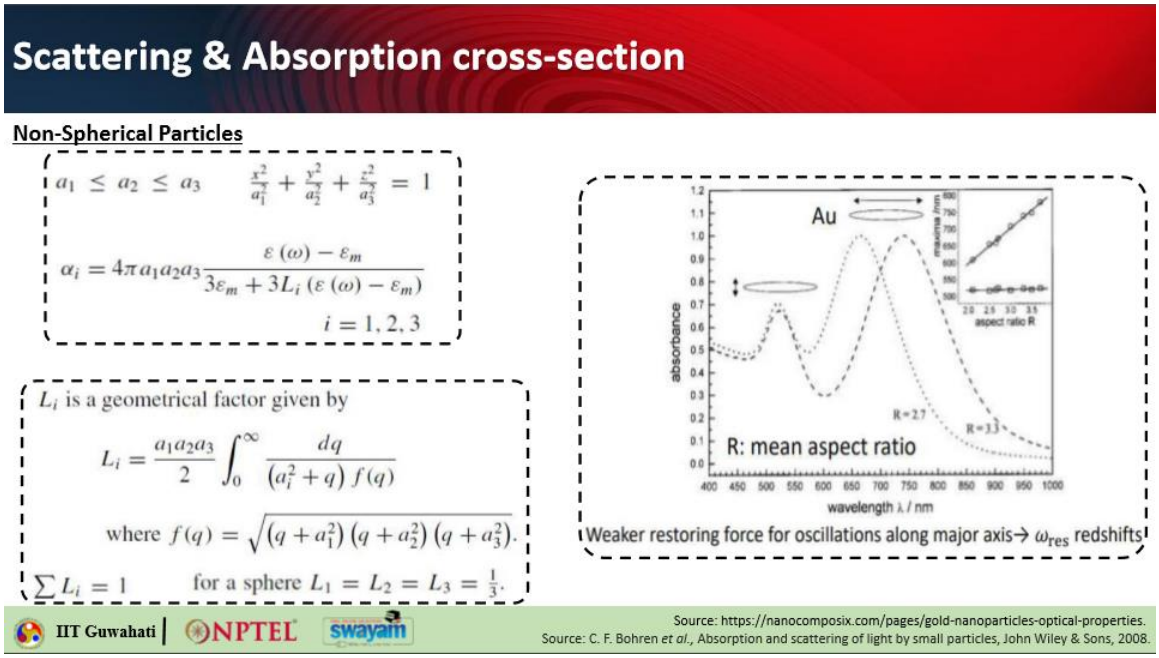

So, these are the two observations from this particular formula fine. So you can also write down like this like if you take a sphere of volume V which has got a metal permittivity epsilon given as epsilon 1 plus i epsilon 2 within the quasi-static limit you can write a simplified formula for scattering cross section as $C_{\text{ext}} = 9\frac{\omega}{c}\varepsilon_m{}^{3/2}V\frac{\varepsilon_2}{[\varepsilon_1+2\varepsilon_m]^2+\varepsilon_2^2}$. So $\varepsilon_2$ is basically the imaginary part of the metal permittivity and $\varepsilon_1$ is the real part of the metal permittivity. So, you can also find out what is the resonance here. So again, if you look into the plot so this is basically extinction spectra of a 50 nanometer gold nanosphere. So, what is the difference here? So, the black curve is when the surrounding media is air.

In this case $\varepsilon_m$ is the surrounding media. So, it is not metal it is here it is surrounding media is $\varepsilon_m$. So, if you put $\varepsilon_m$ = 1 you will get this particular graph from this equation and then red one is water and n is the refractive index that is 1.33. So $\varepsilon_m$ will be square of 1.33 that is 1.69 I believe and then the last one is for silica that is n equals 1.5. So $\varepsilon_m$ in this case will be 2.25. So, this is what we can see that you are able to do the refractive index sensing using this kind of gold nanosphere because the resonance peak position is getting changed.

So as the dielectric okay so there is a bit of yeah this should be d okay or you can say this is medium I will correct this later on. So, this is basically $\varepsilon_d$ okay. You can say it is a dielectric or you can also say this is the medium okay. So, when $\varepsilon_d$ increases the resonance frequency is also from here to here the resonance frequency actually increased yeah no sorry the wavelength actually increased it means the resonance frequency actually decreased and your cross section of extinction actually increases.

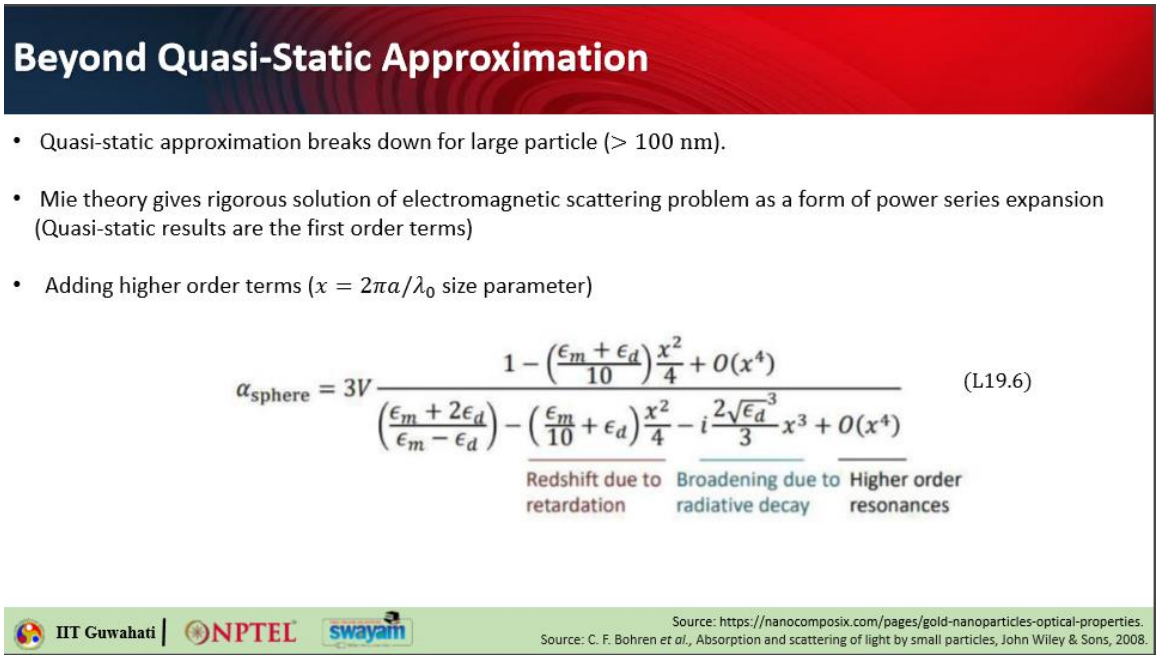
So once again this is in terms of wavelength. So, wavelength is increasing means it is getting red shifted that means the energy is getting reduced. You can also apply quasi-static approximation for non-spherical particles something like nano rod or nano ellipsoid. So, in that case you can have 3 particular axes so you can consider this particular case is in ellipsoid so it will have 3 axis $a_1$, $a_2$ and $a_3$ these are basically the semi-axis. So, this is how the equations are correlated.

So you can find out polarizability in different directions okay for the 3 cases. So, if you consider the cross section to be same and only the length to be different so there will be 2 different cases so which are shown here. So, you can also have longitudinal excitation or transverse excitation of the electrons on the surface of such nanoparticles depending on their incident electric field polarization. So, the light is falling from the top it has got a horizontal electric field like this so the electrons will also oscillate along the length of the nano rod. So, this is the nano rod or nano ellipsoid and you will get one particular kind of polarizability. But when the electric field is coming from this direction sorry the light is coming from this direction with this electric field oscillating in this direction up and down like this then the polarizability will be different.



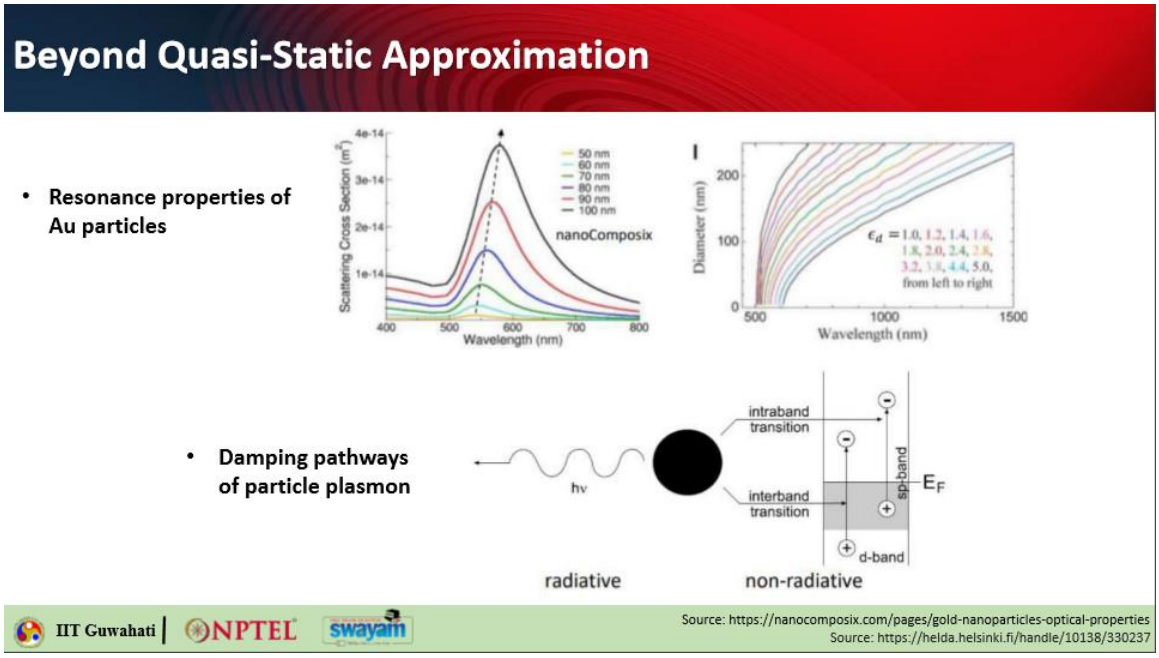

So alpha i gives you the polarizability along the 3 direction which has got a geometrical factor $L_i$ in this particular equation and $L_i$ can be obtained from here. So, as you can see this is a generic case for a sphere $L_1$, $L_2$ and $L_3$ are same one third because summation of $L_i$ should be equal to 1. So, with this you are able to find out the polarizability of an

ellipsoid and if you plot the absorbance versus wavelength you will see that for the 2 cases okay so if you change the aspect ratio that is the ratio of the height over the diameter of this okay so as you change the aspect ratio there is a large shift of the resonance. First observable thing is that in such a particle there are basically 2 resonance peak so one resonance this particular resonance peak corresponds to the surface plus 1 resonance along the length of the nanorod whereas this one is along the transverse direction so this is called transverse dipolar resonance this is called longitudinal dipolar resonance and when you increase the aspect ratio of the particle you see that the transverse peak does not shift that significantly whereas the peak of the longitudinal plus 1 undergoes much more red shift red shift means shift towards longer wavelength what happens to the energy? Energy reduces okay.




Now quasi-static approximation is it good throughout? No. For very very tiny particles or very very large particles it is a problem so let us look into the case of first very large particles where the particle size is more than 100 nanometer. So in those cases you should go for Mie theory because they provide you an exact solution in form of power series expansion and quasi-static are basically the only the first order terms from that expression okay however for quasi-static to little larger particles you can actually add some extra terms like you can add some effects coming from redshift due to retardation okay then broadening due to radiative decay and some higher order resonance you can add those terms to make your quasi-static approximation little bit more accurate. But always remember for spherical particles Mie theory provides you the exact solution. So, this is what we have seen that if you start from 50 nanometer where this is the size of the particle

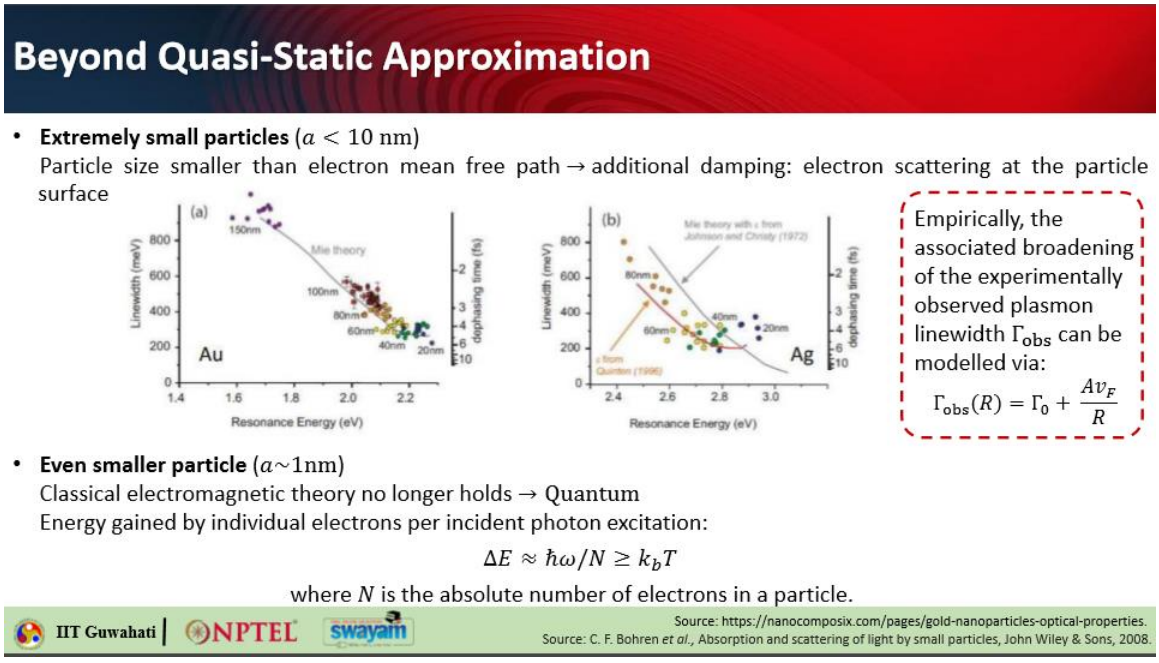
your quasi-static approximation is pretty good but slowly as you move towards larger particle up to here 100 nanometer okay we will see that there is a redshift there is a spectral broadening so these are the effects that comes into picture. So there will be radiative decay that gives you spectral broadening there is also redshift due to retardation because when the particle becomes large the initial approximation that the electric field over the particle volume does not change significantly that does not hold good so there will be a phase lag between the electron movement from one end on the others end of the particle because the particle size is large so all these effects will be considered and they will try to make your quasi-static theory more inaccurate when you try to go to larger particles.




Here is an figure that shows you that with the size of the particle and change in the permittivity how the resonance wavelength is going to change and here is the damping pathways for particle plus 1 means there are two types of decay one is by the radiative decay the name itself tells you a radiation through which the decay takes place so you will get a photon out of it the other damping may be because of the non radiative factors that is it is getting absorbed okay and this is this can be of two types like it can be inter-band from one band from the d band to sp band if you go and or it can be also intra-band so within the same band you are moving from a lower to higher energy level okay so that kind of transition also can give you damping in this particular particles so overall you will be able to get broadening because of this.

Now if you come to the other end like if you go to extremely small particles which are less than 10 nanometers in size then also there is a problem like usually for particles which are

smaller than the electron mean free path in a metal say in gold the mean free path is 42 nanometers so one it means an electron can travel up to 40 or 42 nanometer without colliding with another electron. Now if the particle itself is smaller than 42 nanometer what will happen before the electrons get collided with another electrons they will actually hit the boundary of the particle and that will actually give you additional damping okay so these are called additional damping coming from reduced mean free path and that can be also empirically associated with some broadening which and there is some simple formula that can correlate the damping constant gamma with the actual damping constant plus a is a constant which is usually taken as one for isotropic cases $v_F$ is the Fermi velocity and R is the radius or the reduced distance of the collision. If you are thinking of a thin film or a thin shell you can take that shell dimension or thin film dimension as this R and that will give you some additional damping and that you can put it back into the Drude formula to get what will happen to this particular resonance. So here is a calculation of such line width and defacing time versus resonance energy and this has been done for gold as well as silver and is as you can see that this line is basically Mie theory and for the particles which are smaller like 40 nanometers, 60 nanometers they are very much lying on the Mie theory.




Similarly, you can also see from here okay for extremely small particles that is where the radius becomes one nanometer or so that is where you have to remember that the classic electromagnetic theory will no longer hold good so you have to go for quantum mechanics to solve it. So there the energy gained by individual electrons per incident photon excitation can be written as $\Delta E$ which is $\hbar\omega/N$ and that should be greater than equal to $k_bT$ and N is what N is the absolute number of electrons in that particular particle. So, with

that we understood that there are particle plus bonds which are tunable and what are the different damping mechanisms for this and there is another sort of plus bond that is also possible which is called void plus bond. So void means if you take a sheet of metal and make a whole out of it there also you will see that when there is light incident on this they will if the whole is sub wavelength you are able to excite electron clouds to move on one side so you will get positive on the other side so this behaves like a source of plus bond. So in this case you swap $\varepsilon_m$ and $\varepsilon_d$ so this is the metal this is the dielectric permittivity if you swap this in the metal sphere dipole moment what you got in the previous one you get this.

So in this case the Frohlich condition of the resonance also will get changed so it becomes $\varepsilon_d + 2\varepsilon_m = 0$ or you can write $\varepsilon_m(\omega) = -\varepsilon_d/2$ that means you can also find out what is the resonance frequency ($\omega_{\text{res}}$) that comes out to be $\sqrt{2/3}\omega_p$ that is the resonance frequency for void plus bonds are also different. Also, there are two cases like this the sphere plus bond that you have seen where it is omega B that is the bulk or you can say omega p that is the plasma frequency of the bulk metal over square root of 3 here it is different okay there is an additional factor of square root of 2 coming into the picture. Now there are two possible hybridized modes for these two things to come together and create a shell so this is called a nano shell. So, in nano shell there are possibilities that they are in the anti-bonding kind of orientation so where the outside dipole and the inner dipole are in the opposite direction or you can also have this case where the outside dipole so you can see the outside layer plus plus charges then out this side also there are negative charges they create one dipole towards the inner side you will also have another dipole plus and minus. So here both the dipoles are in the same orientation so the overall energy is lowered okay and this is called bonding type of interaction and this is called anti-bonding type of interaction.

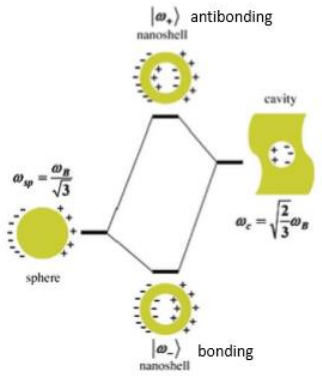
## Void Plasmon and Metallic Nano-shells

- Dipole moment of spherical nanovoids can be obtained by simply substituting $\varepsilon_m \leftrightarrow \varepsilon_d$ in metal sphere dipole moment:

$$\alpha = 4\pi a^3 \frac{\varepsilon_d - \varepsilon_m}{\varepsilon_d + 2\varepsilon_m} = 3V \frac{\varepsilon_d - \varepsilon_m}{\varepsilon_d + 2\varepsilon_m} \qquad \text{(L19.7)}$$

- Fröhlich condition becomes: $\varepsilon_m(\omega) = -\varepsilon_d/2$.
- For Drude metal particles in free space, $\omega_{res} = \sqrt{2/3}\ \omega_p$
- Metal nanoshells:
  Sphere (b) + void (a) → two hybridized modes $\omega_{\pm}$

$$\omega_{l,\pm}^2 = \frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1 + 4l(l+1)\left(\frac{a}{b}\right)^{2l+1}}\right] \qquad \text{(L19.8)}$$




IIT Guwahati | NPTEL swayam

Source: D. Radziuk and H. Moehwald, *Physical Chemistry Chemical Physics*, 17(33), 21072-21093, 2015.
Source: C. F. Bohren *et al.*, Absorption and scattering of light by small particles, John Wiley & Sons, 2008.

So, in this case in this particular two cases you will have two hybridized modes the resonance frequency of these modes are given as $\omega_{l,\pm}^2$ okay so this is how it is obtained. So, you have $\frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1 + 4l(l+1)\left(\frac{a}{b}\right)^{2l+1}}\right]$ so you can take $l = 1$ and find out what is the first order okay anti-bonding mode and bonding mode for this particular cases. So, they are also tunable because you can change the metal you can change the shell thickness and you can also get a lot of tunability out of this void plasmons okay or you can say nano shells void plasmons are this one you can nano shells if you remember from the initial lectures they were the ones having the largest tunability. So, depending on the application you are able to design nano shells that can give you that particular resonance at that particular operating wavelength okay. So, with that we will stop here today and in the next lecture we will go into little bit of more details of this resonance effects and if you have got any queries regarding to this lecture you can always drop an email at this particular email address mentioning MOOC on the subject line. Thank you.