Optical Sensors
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Lecture - 14
Plasmons - V
Localized Surface Plasmons, Sensing

Welcome to the 14th lecture of Optical Sensors course. Until now, we studied what are surface plasmons and we also studied optimized structures for producing surface plasmons at metal dielectric interface and we optimized the film thickness to be around 50 nanometers. And then we also studied different modalities - how to use it for sensing. Now, we will move to something called Localized Surface Plasmons which are basically plasmons in metallic nanoparticles, where the size of these nanoparticles is much smaller than the wavelength of light. And we will see how to use them for sensing applications.

What I am talking about is metallic nanoparticles, which are much smaller than the wavelength of light; like silver and gold nanoparticle of, say, 100 of nanometers, of 30, 40, 50 nanometer - something like that. But this is something very interesting; it has very beautiful optical properties; but it was in use very long back, actually.

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History

The Lycurgus Cup made by the Romans dates to the fourth century AD.

Reflected light, (in daylight) ➡ Green.

Transmitted Light ➡ Red.

The First Nanotechnologists

"Labors of the Months"
Norwich, England, ca.1480
(The ruby color is probably due to gold nanoparticles)

Ancient stained glass makers

For example, this Lycurgus Cup was made by Romans around 04th century AD, here you see. And it is so beautiful. You can see that in the reflected light, it appears to be green; but if you put a small source of light inside, say LED, and turn it on, in the transmitted light you will see it red.

Another example is these kinds of glasses; for example, the labors of the month one which is in Norwich, England; and it has ruby color which is actually because of nanoparticles - gold nanoparticles. So, ancient stained glassmakers were the first nano-technologists. They used to have small size particles dispersed in glass and then they could stain the glass using the optics of nanoparticles; it did not contain dyes, ok. That is the beauty.

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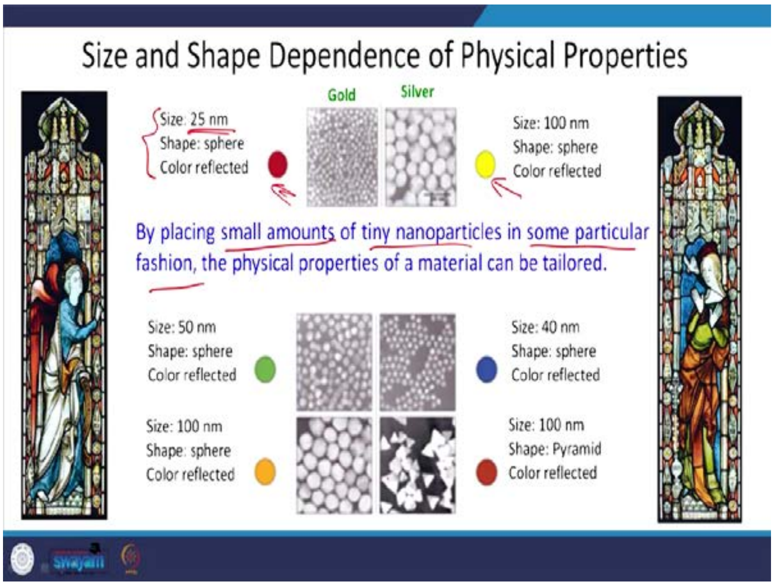

Size and Shape Dependence of Physical Properties

Gold

Silver

Size: 25 nm
Shape: sphere
Color reflected ●

Size: 100 nm
Shape: sphere
Color reflected ●

By placing small amounts of tiny nanoparticles in some particular fashion, the physical properties of a material can be tailored.

Size: 50 nm
Shape: sphere
Color reflected ●

Size: 40 nm
Shape: sphere
Color reflected ●

Size: 100 nm
Shape: sphere
Color reflected ●

Size: 100 nm
Shape: Pyramid
Color reflected ●

They also knew that by placing small amounts of tiny nanoparticles in some particular fashion; they can create various colors. For example, these stained glasses, they are not having any dyes - they do not have any dye. All the color which is appearing here is because of nanoparticles. While refluxing these glasses, they will add precursors of metal and that will turn into some nanoparticles in the molten stage and then they will cast it like that.

So, for example, here a 25 nanometers nanoparticle of gold appears red in reflected light; while 100 nanometers - it shows yellow. There are different colors because of different sizes and shapes, you can see that. Ancient glassmaker - they were not very, you know, accurate. They did not have this idea. What they knew that ok, if you change in this proportions you will see different colors; but they did not know that how to control the optical properties, not very precisely, ok. So, that is a matter of study nowadays. I mean, last 30 - 40 years people have been using it at large scale to study the optical properties when the size goes down and how to use it for different applications.

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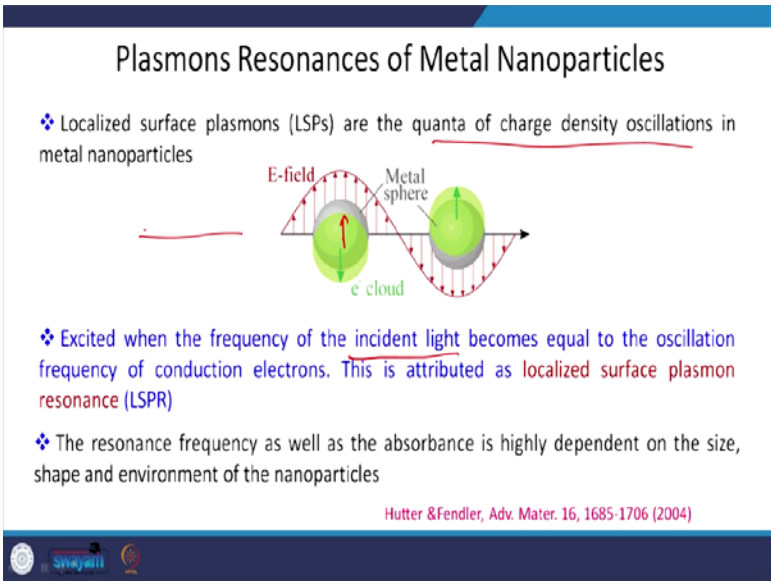

Plasmons Resonances of Metal Nanoparticles

- Localized surface plasmons (LSPs) are the quanta of charge density oscillations in metal nanoparticles

- Excited when the frequency of the incident light becomes equal to the oscillation frequency of conduction electrons. This is attributed as localized surface plasmon resonance (LSPR)
- The resonance frequency as well as the absorbance is highly dependent on the size, shape and environment of the nanoparticles

Hutter &Fendler, Adv. Mater. 16, 1685-1706 (2004)

Plasmon resonances of metal nanoparticles are basically quanta of charge density oscillations of metal nanoparticles. So, you can experience a metallic nanosphere as shown in the picture - when it is subjected to a time varying electric field; what happens actually that, if the electric field is pointing in upward direction, the electron cloud would slightly shift to the downward direction.

So, leaving behind a dipole here, you will solve for it analytically; dipole pointing in this direction, electrical field will be in the opposite direction. And if it is varying at a frequency of, say, omega, then this dipole will also be oscillating at a frequency of omega.

So, they get excited - this kind of oscillations, when the frequency of the incident light becomes equal to the oscillation frequency of conduction electrons. And this phenomenon is attributed as localized surface plasmon resonance. This resonance frequency, as well as the absorbance; because when there is resonance, light will get absorbed by this plasmons, ok. So, you see an absorbance. This absorbance as well as the resonance frequency is highly dependent on the size, shape and environment of the nanoparticles.

Suppose you have a sphere, now if you take triangle of the same material, it will have different resonance frequency and absorbance. Now, it was in air and then you put some water around, the resonance frequency will change, the absorbance will change. So, this is the property which we will use for sensing; because you know, when you change the environment basically it changes the resonance frequency. So, by measuring the change in the resonance frequency, you can say that how much change in the environment; environment means - when we are talking optics, it is change in refractive index, primarily.

We will arrive to that expression. But there are certain advantages. We studied propagating surface plasmons and now we are talking about something called localized surface plasmons. It has got certain advantages, that one has got certain different advantages. Every process has advantages and disadvantages!

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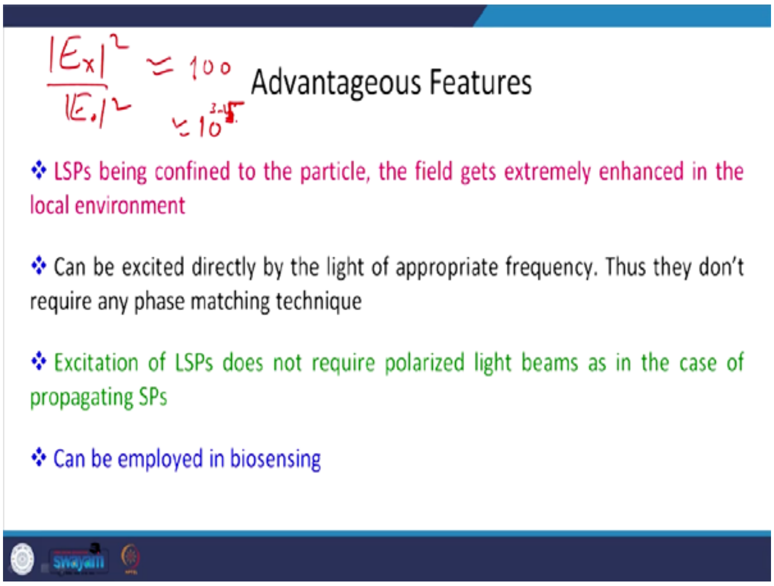

$$\frac{|E_x|^2}{|E_0|^2} \simeq 100$$

$$\simeq 10^{3-5}$$

Advantageous Features

- LSPs being confined to the particle, the field gets extremely enhanced in the local environment
- Can be excited directly by the light of appropriate frequency. Thus they don't require any phase matching technique
- Excitation of LSPs does not require polarized light beams as in the case of propagating SPs
- Can be employed in biosensing

First advantage here is that, since this LSPs are confined to the nanoparticle, the electromagnetic field gets extremely enhanced in the local environment of the nanoparticle.

That was happening in a propagating surface plasmons also. You are getting enhance electromagnetic field about 100 times; if you remember E x square is at the order of about 100 by E 0 square if we say; E 0 is incident electric field. So, but in this case, the particle is still much smaller. So, you get enhancements of the order of around 10 to power 4, 10 to 3 to 10 to power 4, may be more 10 to power 5, 10 to power 5, 3 to 10 to power 5 or even more - depending on the configuration; so it gets enhanced.

Most important thing is that, it can be excited directly by shining light of appropriate frequency; thus, there is no requirement of any phase matching technique. You remember that when we studied surface plasmons, we used to have a high index prism which was required to enhance the way vector of light incident at the interface.

But here it is not the case; you have a bottle of nanoparticles which is a colloidal solution, you simply shine light on it like this, and you can excite surface plasmons there. Also, it does not require any polarized light beam, if it is spherical basically. If it is, say, elongated you see that it changes a bit, but not much. And most important thing is that it can also be used for bio sensing; because it employs silver and gold and I told you that it can be used for sensing so, you will see. Let us consider LSPR in metal spheres and to solve it what we assume is that, the nanoparticle is much smaller than the wavelength of light.

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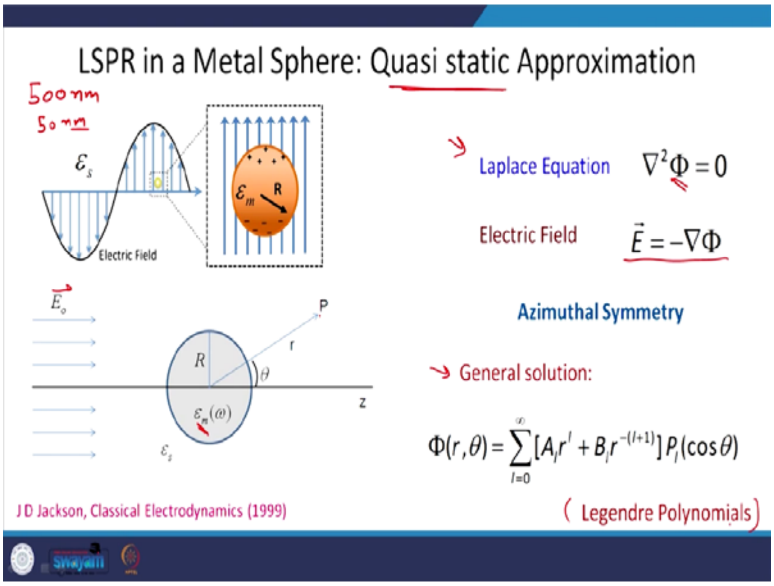

LSPR in a Metal Sphere: Quasi static Approximation

500nm
50nm

Laplace Equation $\nabla^2\Phi = 0$

Electric Field $\vec{E} = -\nabla\Phi$

Azimuthal Symmetry

General solution:

$$\Phi(r,\theta) = \sum_{l=0}^{\infty}[A_l r^l + B_l r^{-(l+1)}]P_l(\cos\theta)$$

(Legendre Polynomials)

J D Jackson, Classical Electrodynamics (1999)

So, you suppose our light is about 500 nanometers in wavelength and then this particle be considered around 50 nanometers, much smaller than the wavelength of light. We can approximate it as if the electric field which this metal nanoparticle is experiencing is almost constant; that is why we write it Quasi static approximation. This problem can be seen as a nanoparticle - nanosphere, for example, I am taking a sphere, because easy to solve for this and we consider that it is put in an electrostatic field of E 0.

The radius of the nanoparticles is R, the metal dielectric function is epsilon m - that is epsilon m 1 plus I epsilon m 2, we already know that. Epsilon s is the dielectric constant of the medium which is surrounding the nanoparticle. And let us say that at point P; I want to know, what is the electric field at distance r and angle theta.

So, if you want to solve this, then what we can do is that, once we solve it analytically for this electrostatic problem; then we can introduce the time varying part, omega part and we can see that how it behaves. So, we can solve it using Laplace equation, then we can evaluate what are the potentials, and then we can take a derivative of it to get the electric field. So, since it is azimuthal symmetric, the general solution can be given in terms of Legendre polynomials ok, where l is the order of polynomial.

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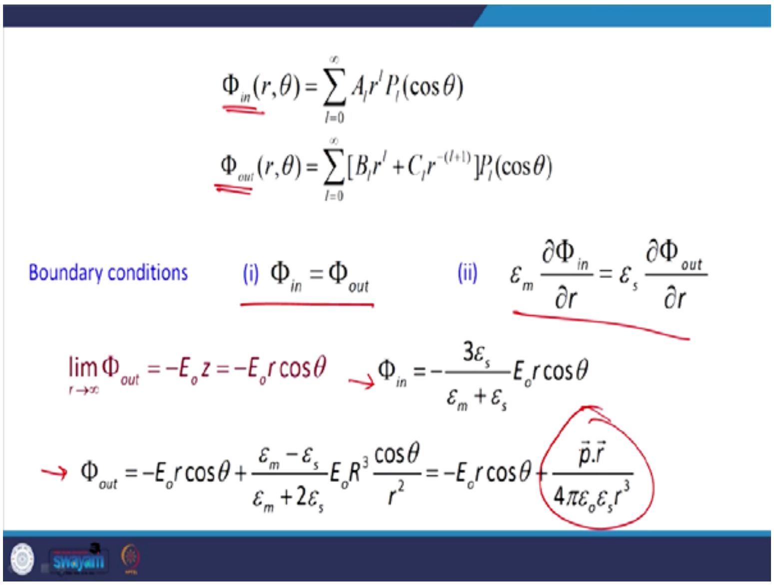

$$\underline{\Phi_{in}}(r,\theta)=\sum_{l=0}^{\infty}A_l r^l P_l(\cos\theta)$$

$$\underline{\Phi_{out}}(r,\theta)=\sum_{l=0}^{\infty}[B_l r^l + C_l r^{-(l+1)}]P_l(\cos\theta)$$

Boundary conditions (i) $\underline{\Phi_{in}=\Phi_{out}}$ (ii) $\underline{\varepsilon_m\frac{\partial\Phi_{in}}{\partial r}=\varepsilon_s\frac{\partial\Phi_{out}}{\partial r}}$

$$\lim_{r\to\infty}\Phi_{out}=-E_o z=-E_o r\cos\theta \rightarrow \Phi_{in}=-\frac{3\varepsilon_s}{\varepsilon_m+\varepsilon_s}E_o r\cos\theta$$

$$\rightarrow \Phi_{out}=-E_o r\cos\theta+\frac{\varepsilon_m-\varepsilon_s}{\varepsilon_m+2\varepsilon_s}E_o R^3\frac{\cos\theta}{r^2}=-E_o r\cos\theta+\boxed{\frac{\vec{p}.\vec{r}}{4\pi\varepsilon_o\varepsilon_s r^3}}$$

So, you can write the potentials inside and outside the sphere as a function of r and theta, and you apply these boundary conditions to arrive to these relations, right. These are the potential which you get after solving these equations.

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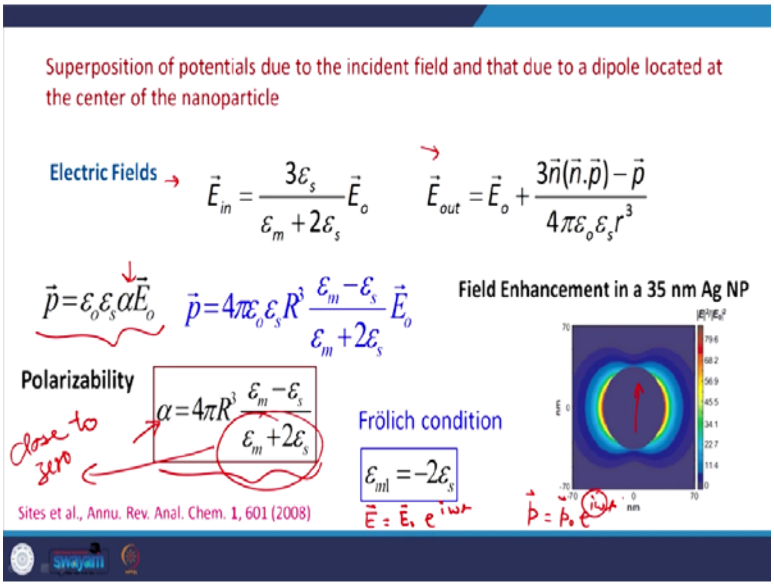

Superposition of potentials due to the incident field and that due to a dipole located at the center of the nanoparticle

Electric Fields →

$$\vec{E}_{in} = \frac{3\varepsilon_s}{\varepsilon_m + 2\varepsilon_s}\vec{E}_o \qquad \vec{E}_{out} = \vec{E}_o + \frac{3\vec{n}(\vec{n}.\vec{p}) - \vec{p}}{4\pi\varepsilon_o\varepsilon_s r^3}$$

$$\underbrace{\vec{p} = \varepsilon_o\varepsilon_s\alpha\vec{E}_o} \qquad \vec{p} = 4\pi\varepsilon_o\varepsilon_s R^3\frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + 2\varepsilon_s}\vec{E}_o$$

Polarizability

$$\boxed{\alpha = 4\pi R^3\frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + 2\varepsilon_s}}$$

close to zero

Frölich condition

$$\boxed{\varepsilon_{ml} = -2\varepsilon_s}$$

$\vec{E} = \vec{E}_0 e^{i\omega t}$

$\vec{p} = \vec{p}_0 e^{i\omega t}$

Field Enhancement in a 35 nm Ag NP

Sites et al., Annu. Rev. Anal. Chem. 1, 601 (2008)

Now, you take a derivative of it, you get the electric fields like this. There is something very important here; the outside on - you get this term, which is when we solve for a dipole term, you see p is the dipole movement of the dipole.

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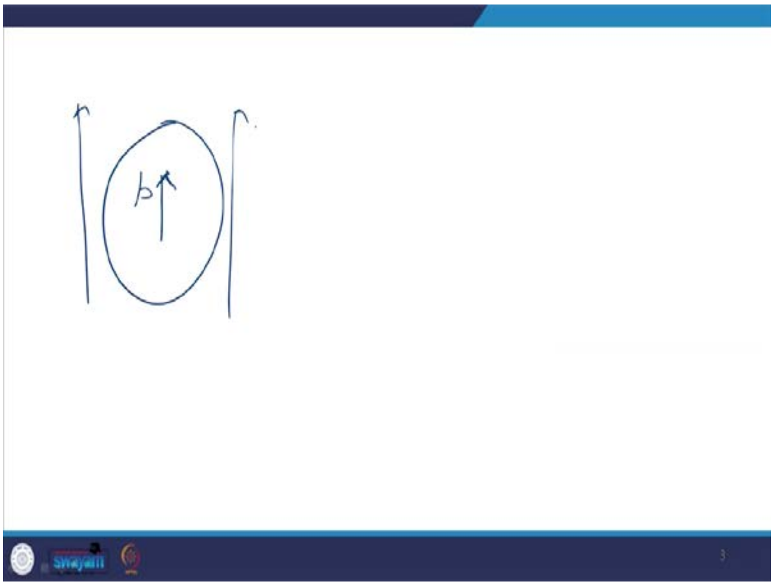

So, what happens actually is that, you have this sphere; it seems that there is a dipole sitting at the center - dipole p. This is electric field. And this dipole has certain role, we will come to that! In terms of polarizability alpha; the dipole movement can be written in terms of incident electric field, which is this thing. Alpha polarizability comes out to be this; and you see that this shoots up - it becomes very high, when this term is close to zero.

So, when this term is close to zero, you arrive at a resonance condition - that is called Frolich condition, and at that point you have enhanced electromagnetic fields. For example, in this silver nanoparticle, you can see that, if the dipole is oscillating in this direction, the electric field enhancement is in this direction. That we already solved for and I already showed you that if you have a dipole oscillating at an angle; then along it is axis you do not have any radiation coming out, while at 90 degrees it will have maximum radiation coming out.

So, this is the polarizability and electric field for static field - when the sphere is put in a static field. Now, you add the term. So, if you add like E is equal to E 0 E to power i omega t term; then P is equal to - again, it will be P 0 e to power i omega t. So, there will come a frequency term, ok. So, it will become an oscillating dipole; an oscillating dipole will radiate 90 degrees to its axis.

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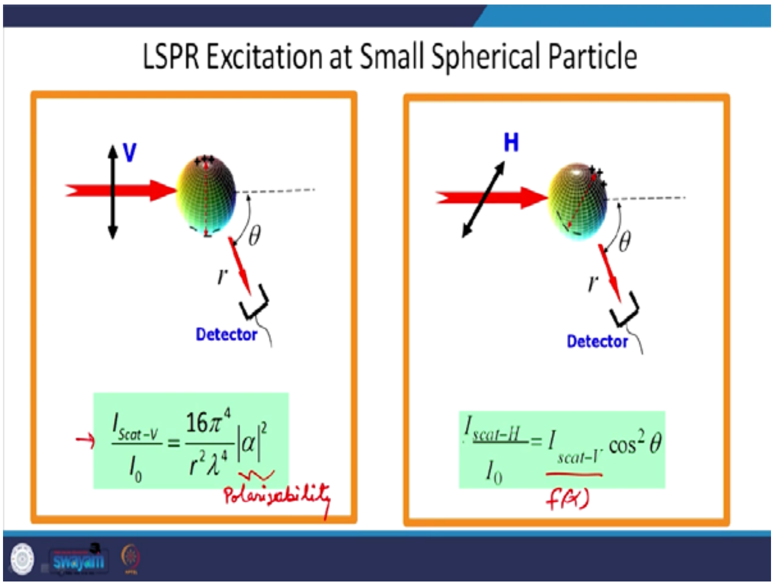
LSPR Excitation at Small Spherical Particle

$$\rightarrow \frac{I_{Scat-V}}{I_0} = \frac{16\pi^4}{r^2\lambda^4}|\underbrace{\alpha}_{\text{Polarizability}}|^2$$

$$\frac{I_{scat-H}}{I_0} = \underbrace{I_{scat-V}}_{f(\alpha)}\cdot\cos^2\theta$$

So, if you consider now polarized light, suppose the incident light is polarized vertically and we are using a detector at an angle theta; then the ratio of scattered and incident intensities is given by this relation, where alpha is the polarizability which you derived already. For horizontal one, it is a function of cos square theta to the vertical one. So, this is also a function of polarizability, you see - they both are a function of polarizability.

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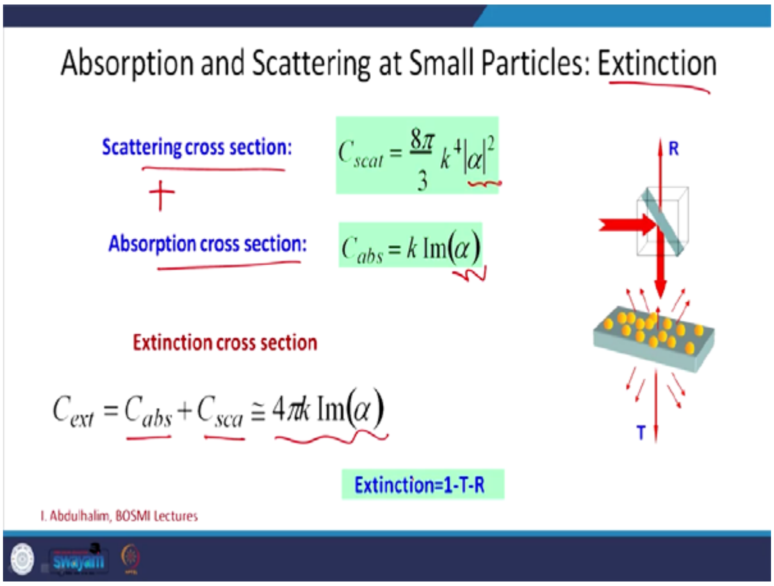

Absorption and Scattering at Small Particles: Extinction

Scattering cross section: $C_{scat} = \frac{8\pi}{3} k^4 |\alpha|^2$

+

Absorption cross section: $C_{abs} = k \,\mathrm{Im}(\alpha)$

Extinction cross section

$$C_{ext} = C_{abs} + C_{sca} \cong 4\pi k \,\mathrm{Im}(\alpha)$$

Extinction=1-T-R

I. Abdulhalim, BOSMI Lectures

So, if we want to see what absorption and scattering are, then we need to know the absorption cross section and scattering cross section, both. And this was the function of alpha, this is also function of alpha and they added together are called extinction.

So, extinction cross section is given by absorption cross section plus scattering cross section which is almost this term. Experimentally it is very easy to determine. Suppose, you have a vial of colloidal nanoparticles and then you shine light on it and then you get the transmitted light and you get reflected one. From that one there will be some light lost; because of absorption and scattering, so that you, always, can calculate.

If there is no reflection coming out, then it is 1 minus transmission; and if there is reflection also, then it is 1 minus reflection minus transmission. You can always calculate extinction – that is - what light got extinct, because of these nanoparticles and that is a characteristic,c which people see while doing experiments also. So, they both depend on a size and shape, I will come to that.

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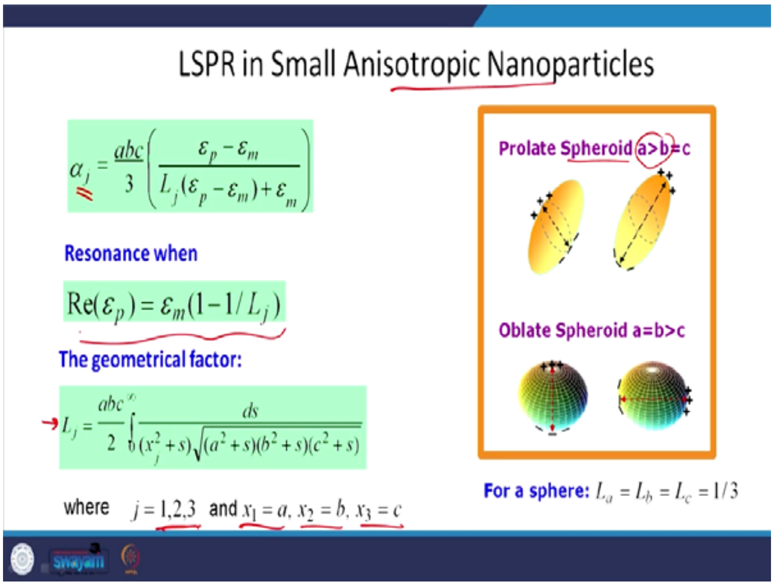

LSPR in Small Anisotropic Nanoparticles

$$\alpha_j = \frac{abc}{3}\left(\frac{\varepsilon_p - \varepsilon_m}{L_j(\varepsilon_p - \varepsilon_m) + \varepsilon_m}\right)$$

Resonance when

$$\mathrm{Re}(\varepsilon_p) = \varepsilon_m(1 - 1/L_j)$$

The geometrical factor:

$$L_j = \frac{abc}{2}\int_0^{\infty}\frac{ds}{(x_j^2 + s)\sqrt{(a^2+s)(b^2+s)(c^2+s)}}$$

where $j = 1,2,3$ and $x_1 = a,\ x_2 = b,\ x_3 = c$

For a sphere: $L_a = L_b = L_c = 1/3$

But what happens if you take an anisotropic nanoparticle. Anisotropic means, all the dimensions are not the same; say for example, if you take a spheroid; be it prolate or oblate, you see that one of the dimensions is greater. So, a is, for example, greater than b and c. So, it becomes kind of spheroid; an ellipsoid, when a is not equal to b not equal to c. So, this becomes like an egg, ok.

And what do you see is that, alpha is now a function of j indices and they can vary. So, if m is the medium surrounding this; actually, it should be s - later on we will see. And if you have different dimensions x 1, x 2, x 3; then you have to have a geometrical factor which also plays a key role in determining the resonance. So, for the spheres, it was very simple - that you put x 1 is equal to x 2 is equal to x 3; but here you have to have geometrical factor, which will also play a key role in determining the resonance and extinction.

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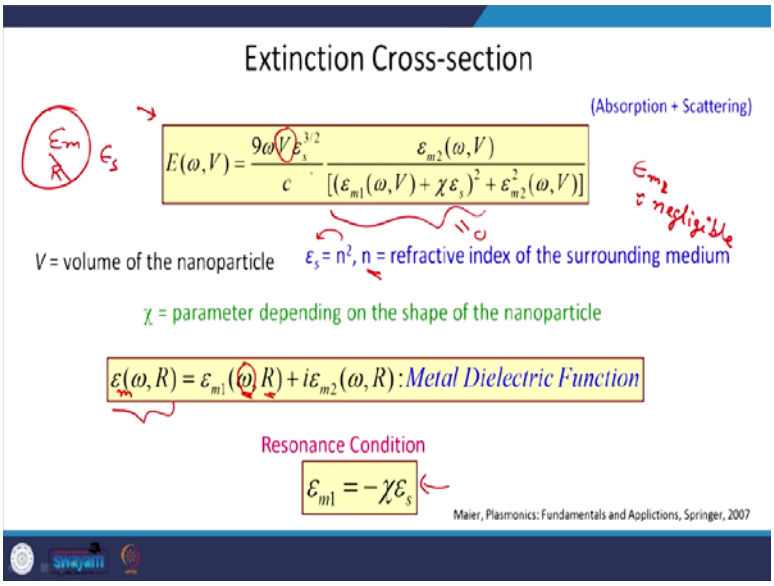

Extinction Cross-section

(Absorption + Scattering)

ε_m R ε_s

$$\boxed{E(\omega,V)=\frac{9\omega V\varepsilon_s^{3/2}}{c}\frac{\varepsilon_{m2}(\omega,V)}{[(\varepsilon_{m1}(\omega,V)+\chi\varepsilon_s)^2+\varepsilon_{m2}^2(\omega,V)]}}$$

$= 0$

ε_{m2} ≈ negligible

V = volume of the nanoparticle

$\varepsilon_s = n^2$, n = refractive index of the surrounding medium

χ = parameter depending on the shape of the nanoparticle

$$\boxed{\varepsilon(\omega,R)=\varepsilon_{m1}(\omega,R)+i\varepsilon_{m2}(\omega,R):\textit{Metal Dielectric Function}}$$

Resonance Condition

$$\boxed{\varepsilon_{m1}=-\chi\varepsilon_s}$$

Maier, Plasmonics: Fundamentals and Applictions, Springer, 2007

So, for example, to summarize it, we can write extinction with this equation - 9 omega by c into V; V is the volume of the nanoparticle, epsilon s is the dielectric function of the mediums surrounding the nanoparticle. Suppose this is a nanoparticle which has epsilon m and radius R, and this is the dielectric function of the medium, which is surrounding the nanoparticle. Suppose your nanoparticle is dispersed in water, then n will be the refractive index of water and epsilon s is equal to n square - that will be the dielectric function of the medium surrounding it, ok, and this term which is multiplied to this one.

You see here that this epsilon m, which is the metal dielectric function - it is a function of omega and R; that means, if you change the size of the nanoparticle the metal dielectric function itself changes. That is something size dependence of the metal dielectric function - it has to be considered here.

Second thing is that it is a function of omega also; omega means it is a function of wavelength, so its dispersive character is also something which will determine the sensing part, we will come to that. So, absorption plus scattering can be written as this equation and the resonance condition is given by this. Here, when this term becomes close to zero; let us say that epsilon m 1 - epsilon m 2 is kind of negligible. So if we consider it to be negligible; then this one is playing the major part and when this comes close to zero, you have a resonance.

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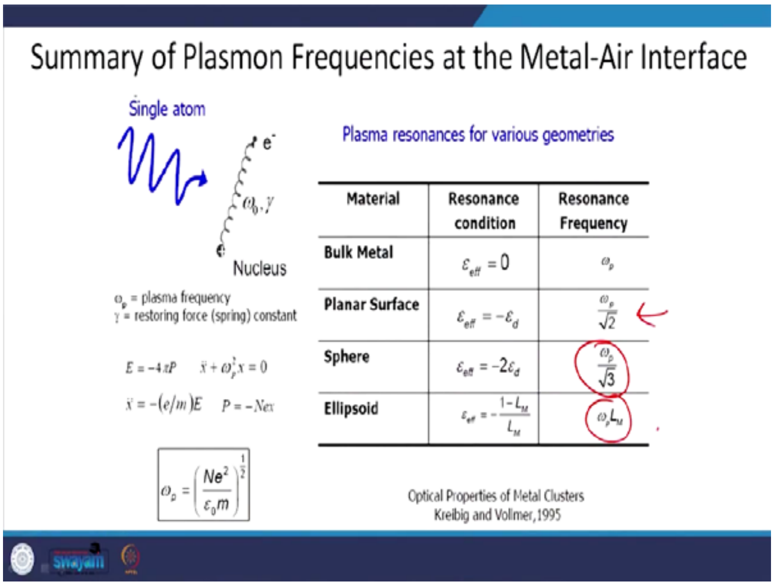

Summary of Plasmon Frequencies at the Metal-Air Interface

Single atom

ω_p = plasma frequency
γ = restoring force (spring) constant

$E = -4\pi P \qquad \ddot{x} + \omega_p^2 x = 0$

$\ddot{x} = -(e/m)E \qquad P = -Nex$

$$\boxed{\omega_p = \left(\frac{Ne^2}{\varepsilon_0 m}\right)^{\frac{1}{2}}}$$

Plasma resonances for various geometries

Material	Resonance condition	Resonance Frequency
Bulk Metal	$\varepsilon_{eff} = 0$	ω_p
Planar Surface	$\varepsilon_{eff} = -\varepsilon_d$	$\frac{\omega_p}{\sqrt{2}}$
Sphere	$\varepsilon_{eff} = -2\varepsilon_d$	$\frac{\omega_p}{\sqrt{3}}$
Ellipsoid	$\varepsilon_{eff} = -\frac{1-L_M}{L_M}$	$\omega_p L_M$

Optical Properties of Metal Clusters
Kreibig and Vollmer,1995

So, if you summarize these omega p terms for plasmons; we can see that for sphere, it comes to be like this and ellipsoid it is like this. So, we arrived here, we calculated the asymptotic values there.

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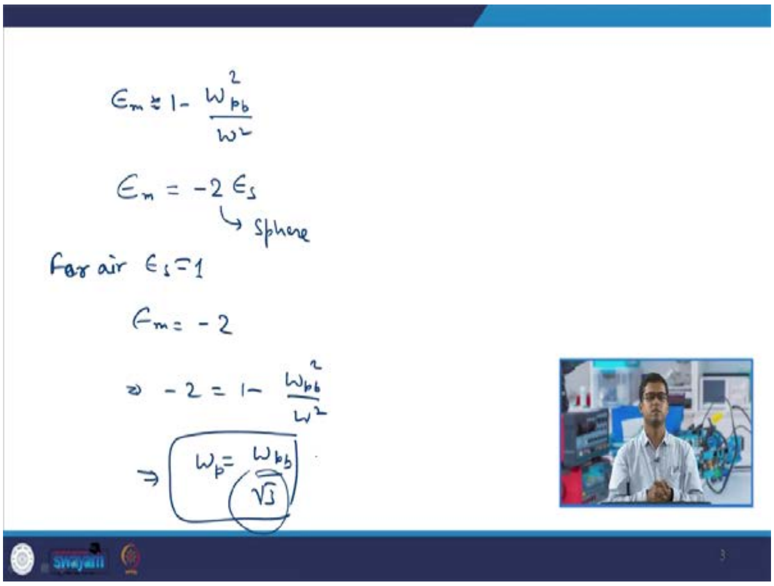

$$\epsilon_m \simeq 1 - \frac{\omega_{pb}^2}{\omega^2}$$

$$\epsilon_m = -2\,\epsilon_s$$

↳ Sphere

For air $\epsilon_s = 1$

$$\epsilon_m = -2$$

$$\Rightarrow -2 = 1 - \frac{\omega_{pb}^2}{\omega^2}$$

$$\Rightarrow \boxed{\omega_p = \frac{\omega_{pb}}{\sqrt{3}}}$$

And if you want to solve for it, say for metal; we know that epsilon metal is equal to roughly 1 minus omega p square upon omega square.

Let us say it is omega p b; omega p square minus omega square. And the resonance occurs when epsilon m is equal to 2 epsilon s. This is 2 for sphere; for other shapes it will be different. For air, epsilon s equals to 1. So, epsilon m is equal to minus 2. So, let us put here minus 2 is equal to 1 minus omega p square by omega square. So, actually it was omega p. So, if you write it like this - arrange it, then it will be omega is equal to omega p by root 3.

So, what happens actually is that - let us say that it is omega p b, omega p will be omega p b; that means, that for metallic nanospheres, the plasma frequency becomes 1 by root 3 of bulk plasma frequency. Suppose you have a bulk piece of metal, the bulk plasma frequency it will have around 10 to power 16 or so; but when you form a nanoparticle from this bulk piece, its plasma frequency itself changes to 1 by root 3 of this value. So, that is why you are getting something like this here. If you have other shapes, then it will be a function of that shape.

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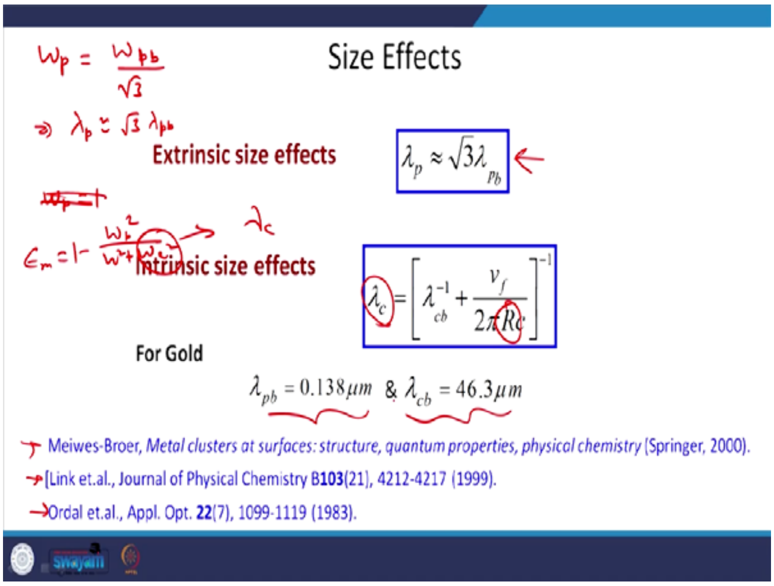

Size Effects

$\omega_p = \frac{\omega_{pb}}{\sqrt{3}}$

$\Rightarrow \lambda_p \simeq \sqrt{3}\lambda_{pb}$

Extrinsic size effects

$$\boxed{\lambda_p \approx \sqrt{3}\lambda_{pb}} \leftarrow$$

$\epsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + \omega_c^2} \rightarrow \lambda_c$

Intrinsic size effects

$$\boxed{\lambda_c = \left[\lambda_{cb}^{-1} + \frac{v_f}{2\pi R c}\right]^{-1}}$$

For Gold

$\lambda_{pb} = 0.138\mu m$ & $\lambda_{cb} = 46.3\mu m$

Meiwes-Broer, *Metal clusters at surfaces: structure, quantum properties, physical chemistry* (Springer, 2000).

[Link et.al., Journal of Physical Chemistry **B103**(21), 4212-4217 (1999).

Ordal et.al., Appl. Opt. **22**(7), 1099-1119 (1983).

If you write it in terms of - omega p was omega p b by root 3; this implies that lambda p will be under root 3 lambda p b - that is what we have written here. This is called extrinsic size effects. It is not dependent on the size of the nanoparticle. It says that you had a bulk piece of metal, it has a plasma frequency of omega p b, now made a nanoparticle out of it, it became omega p which is one by root 3 of that, or in terms of plasma wavelength, it will be like under root 3 times; but it does not tell you if the nanoparticles is 10 nanometers or 20 nanometers. It does not change with that; that is why we call it extrinsic size effect.

Also, this lambda c; if you remember this term - epsilon m, epsilon m was 1 minus omega p squared upon omega squared plus omega c square. If you write omega c in terms of lambda c that, the decaying function was there that is lambda c; lambda c is dependent on the radius of the nanoparticle. You can see about these things in these kinds of publications. The bulk one is like this; and if you apply the size corrections, you can still go beyond that for different sizes.

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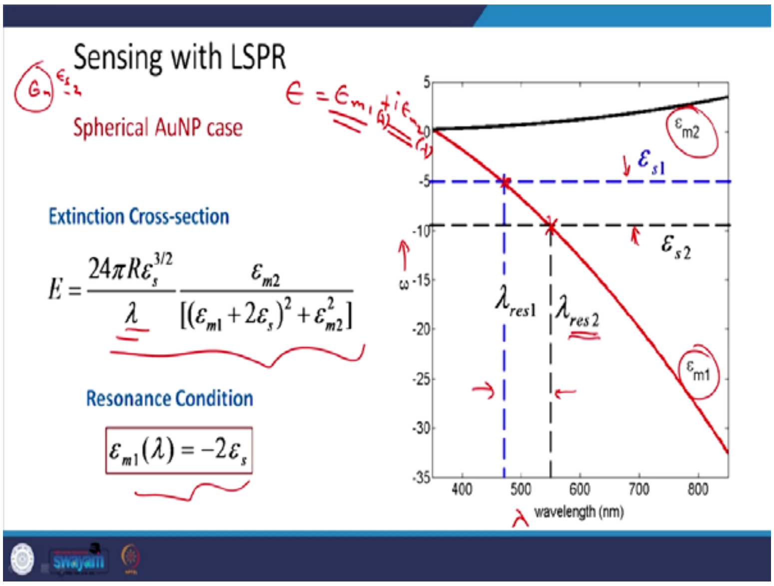

Sensing with LSPR

Spherical AuNP case

Extinction Cross-section

$$E = \frac{24\pi R\varepsilon_s^{3/2}}{\lambda}\frac{\varepsilon_{m2}}{[(\varepsilon_{m1}+2\varepsilon_s)^2+\varepsilon_{m2}^2]}$$

Resonance Condition

$$\boxed{\varepsilon_{m1}(\lambda) = -2\varepsilon_s}$$

If you want to use it for sensing applications, say, for example. I have written this - the same expression now in terms of lambda, rather than writing in terms of omega; because now we are going to measure the wavelength here. And if you plot the metal dielectric functions as a function of wavelength - I am just plotting epsilon is equal to epsilon m 1 plus i epsilon m 2, I am plotting this and this as a function of lambda.

Here is epsilon; the red curve is the real part; the black curve is the imaginary part. Now we take a medium which has dielectric function epsilon s, which is surrounding the nanoparticle. What you see is that, for epsilon s 1 this will be intersecting here. This is the condition where you have resonance. So, this is the resonance condition and at some value of lambda 1, it will be resonating at epsilon s 1.

Now, you change the dielectric function, say, suppose it was water, then you added sugar to it. So, it becomes epsilon 1 s 1 to epsilon s 2. Now, we have to satisfy it at lambda resonance 2; only there it will be intersecting with this curve. So, when you change the dielectric function in terms of the reflective index, say epsilon s 1 to epsilon s 2; basically, there was a shift in the resonance wavelength from lambda resonance 1 to lambda resonance 2. So, by measuring the change in lambda, you can say that how much change the surrounding dielectric function occurred - this is how you use it for sensing.

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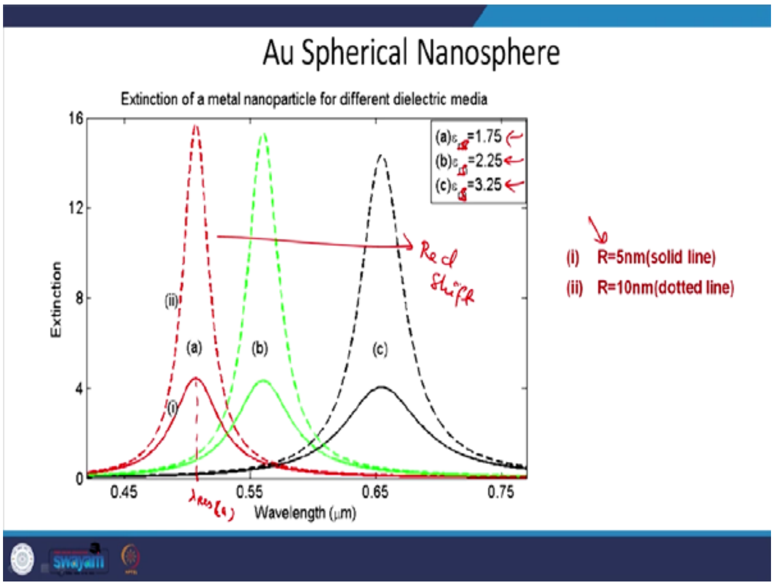

Au Spherical Nanosphere

We have plotted here the extinction cross section as a function of wavelength for different nanoparticles of different sizes. Also, we are changing now the dielectric constant of the medium which is surrounding it - it is actually epsilon s. And you can see that, for any nanoparticle, let us say that nanoparticle of radius of 5 nanometer and dielectric function 1.7 nanometers, you can see a peak in the extinction - that is how it is characterized. And the resonance is here; the maximum value of the peak that gives the resonance wavelength, so this is lambda resonance, resonance for 1 or (a).

Now, you change the diameter here from 5 nanometer to 10 nanometers, you do not see much difference in the resonance wavelength; because lambda p b is not a function of radius. It was lambda c. So, the extinction cross section - means the power will change, but it is not affecting the resonance wavelength essentially. However, if we change the dielectric constant of the medium which is surrounding the nanoparticle, so if you change refractor index around; basically, you see that once you increase the refractive index, it shows the red shift. It shows red shift with an increase, ok. So, that is how you use it for sensing.

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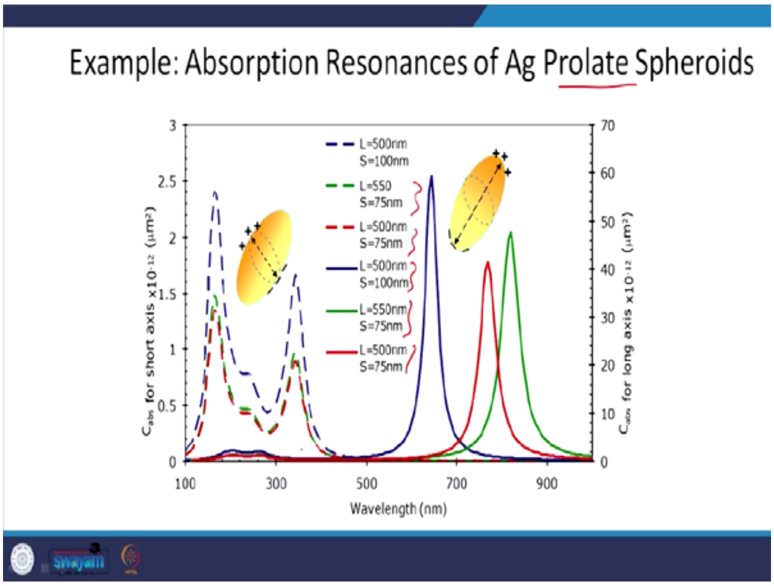

Example: Absorption Resonances of Ag Prolate Spheroids

If you take prolate spheroids of silver, which has L and S at different values, you can see that you have two resonances; one is here, another one is here. So, you can tune the resonance - where it resonates by changing the polarizations. So, you can know that which is long axis, which is short axis and then you can tune the resonance according to the spectral range you want to work on - that is the beauty here.

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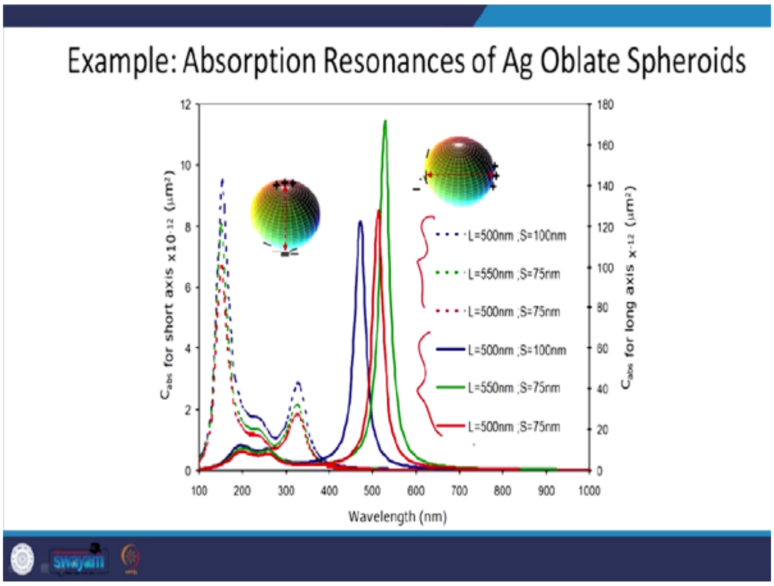

Example: Absorption Resonances of Ag Oblate Spheroids

If you want to study for oblate spheroids, you can see that for the short axis, you have these ones; and the long axis, you have longer resonance wavelengths. So, this is absorption for the long axis. For the same sphere, it will have two resonances; one along the long axis, one along the short axis. And by measuring these both you can say that, you can use it for sensing again by choosing different polarizations.

So, if you have this nanoparticle and you want to excite only this LSPR, you shine it with this kind of polarization; so, it will not have these short axis resonances. But, if you choose any random one, it can always be resolved in two components; horizontal and vertical and then you can have both the resonances.

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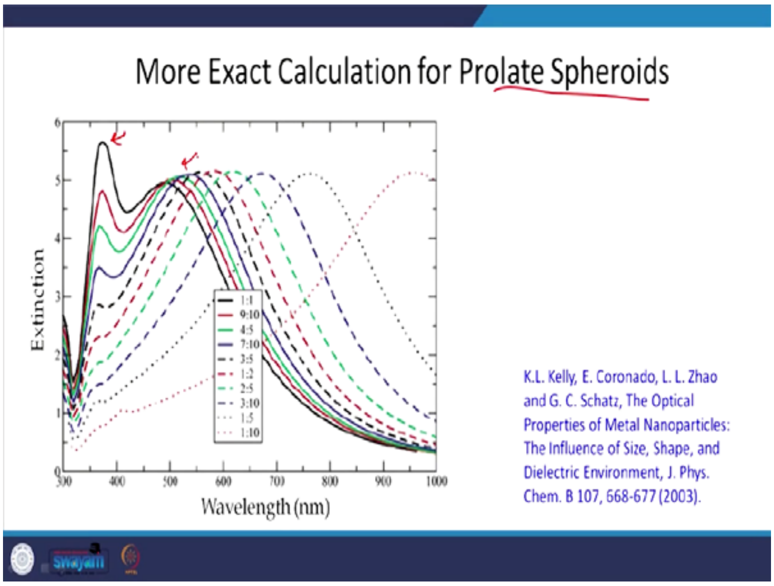

More Exact Calculation for Prolate Spheroids

K.L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, J. Phys. Chem. B 107, 668-677 (2003).

If we want to have for prolate spheroids more exact calculations, you see that, for each value of these ratios, you have two resonances; the black curve, then these curves, and the other one is quite broad in nature. So, by choosing wisely, you can use either of this or this for sensing applications, ok.

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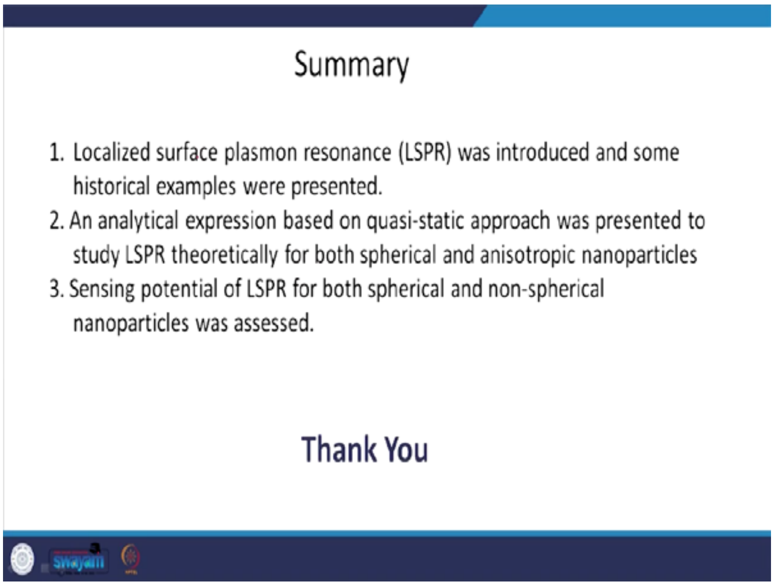

Summary

1. Localized surface plasmon resonance (LSPR) was introduced and some historical examples were presented.
2. An analytical expression based on quasi-static approach was presented to study LSPR theoretically for both spherical and anisotropic nanoparticles
3. Sensing potential of LSPR for both spherical and non-spherical nanoparticles was assessed.

Thank You

So, let us summarize it up. Today we discussed what localized surface plasmons are and showed some historical examples; like the Lycurgus Cup and stained glasses. And then we derived an analytical expression based on Quasi static approach to solve LSPR theoretically and we studied it for both spherical and anisotropic nanoparticles. And then we studied also that how to use it for sensing.

So, you have extinction cross section for the nanoparticle. And from there you deduce this resonance condition which depends on the size, shape and the environment. Environment means the reflective index of the medium surrounding the nanoparticle. And then we saw that for different ratios and different reflective index of the medium surrounding the nanoparticle, it had different resonance wavelength. So, by using the change in the resonance wavelength; one can say that, how much change in the refractive index occurred. So, that is how you use it for sensing applications.

In the next talk we will study the field enhancement due to these nanoparticles and we will try to see if we can use it for any further applications.

Thank you.