Course Name- Nanophotonics, Plasmonics and Metamaterials

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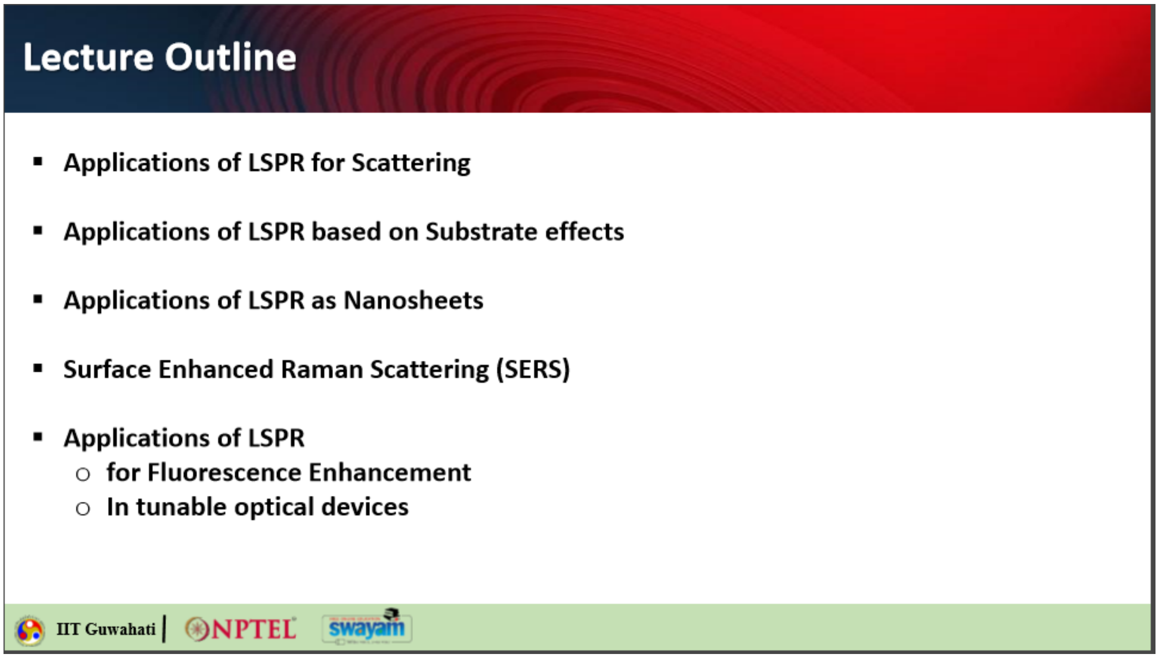
Week-07

Lecture -21

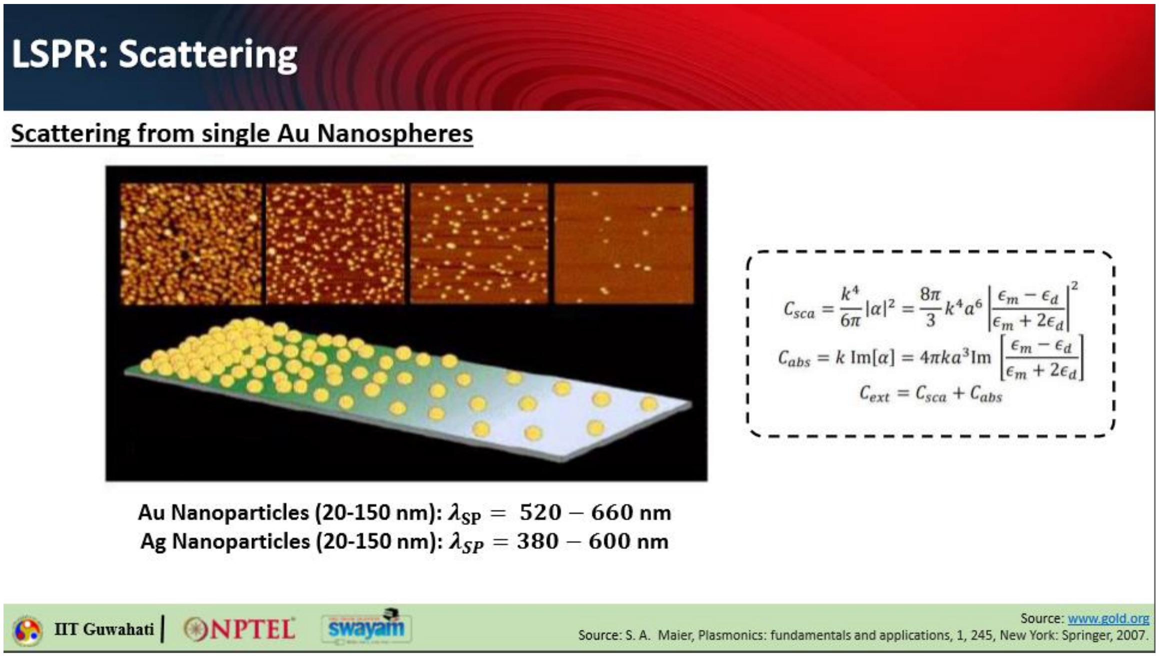
Hello everyone, welcome to lecture 21 of the online course on Nanophotonics, Plasmonics and Metamaterials. Today's lecture is on applications of LSPR. So here is the lecture outline, we will see how LSPR is used for scattering and we can use nano antennas for different or nanoparticles as nano antennas for different wavelengths. We will also see the effect of substrate on LSPR, we will see the application of LSPR in nanosheets, we will look into surface enhanced Raman scattering as well as we will also look into the applications of LSPR in fluorescence enhancement and in tunable optical devices. So, we have seen this diagram before that nanoparticles they scatter light very strongly when they are at resonance. So here the different colors of nanoparticles depending on their size.



Lecture Outline

- **Applications of LSPR for Scattering**
- **Applications of LSPR based on Substrate effects**
- **Applications of LSPR as Nanosheets**
- **Surface Enhanced Raman Scattering (SERS)**
- **Applications of LSPR**
  - **for Fluorescence Enhancement**
  - **In tunable optical devices**

Now if you see the gold nanoparticles when the size ranges from 20 to 150 nanometer that is the diameter, the resonance wavelength changes from 520 to 660 nanometer. For silver nanoparticles of similar size, the resonance starts from 380 nanometers to 600 nanometers. Now how you can calculate that at what size of the particle, what is the resonance wavelength, you can actually look into this formula that we obtained in the previous lectures. You can find out what is the scattering cross section, how you can calculate it from α which is the polarizability of this tiny particle.



LSPR: Scattering

Scattering from single Au Nanospheres

$$C_{sca} = \frac{k^4}{6\pi}|\alpha|^2 = \frac{8\pi}{3}k^4a^6\left|\frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}\right|^2$$

$$C_{abs} = k\,\mathrm{Im}[\alpha] = 4\pi k a^3\mathrm{Im}\left[\frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}\right]$$

$$C_{ext} = C_{sca} + C_{abs}$$

Au Nanoparticles (20-150 nm): $\lambda_{SP} = 520 - 660$ nm

Ag Nanoparticles (20-150 nm): $\lambda_{SP} = 380 - 600$ nm

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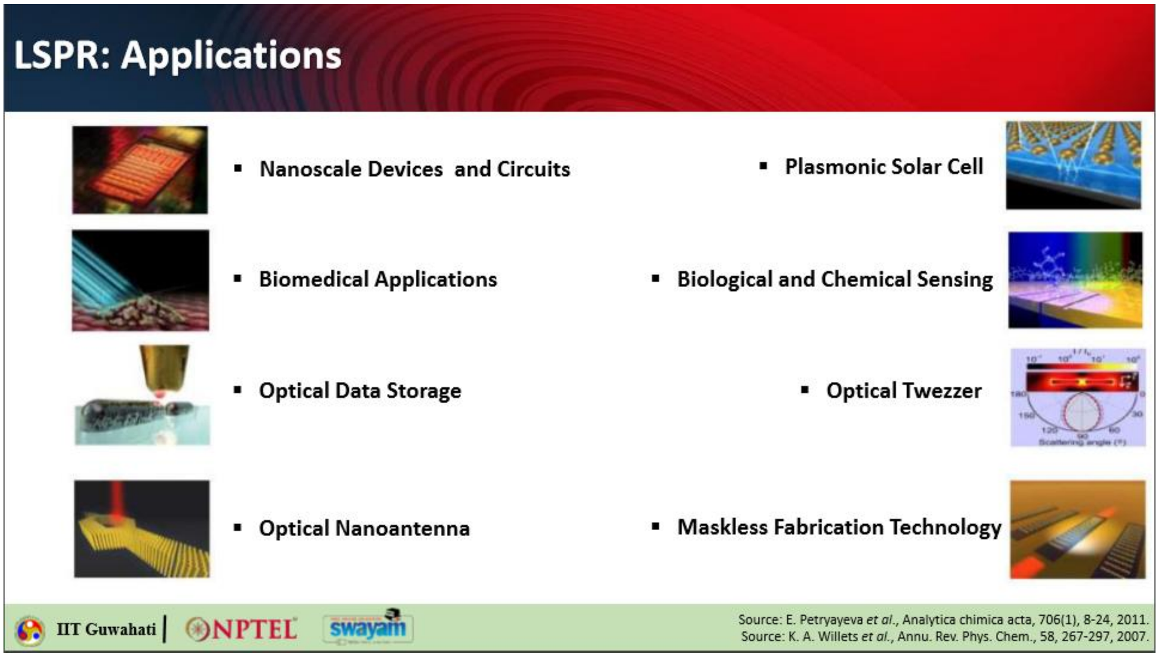
Source: www.gold.org

Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, this is the polarizability when you put it here this is the expression. Similarly, you can also find out what is absorption cross section which is calculated as $k\mathrm{Im}[\alpha]$ and this is what you can get. So overall extinction cross section will be given as scattering plus absorption cross section. Now the applications of nanoparticles and LSPR that ranges from nanoscale devices and circuits, these can be used for switching applications based on nanoparticles. They can be used as absorbers in plasmonic solar cells.

You can also use nanoparticles as absorbers as I mentioned previously you can inject gold nanoparticles with some you know biomarkers so that they can go and deposit on the tumor cell for a cancerous patient and when you shine infrared light through the human skin, infrared light can penetrate and go and get absorbed by those nanoparticles and there will be heat generated and that will allow the tumors to get killed by thermal ablation. You can also use them for biological and chemical sensing. So, in the presence of nanoparticles the near field gets enhanced so that also allows the you know enhancement in biological and chemical signatures or footprints of any molecules or biological species. They can also be used for optical data storage. Now nanoparticles gives you sub wavelength control of electromagnetic radiation so that can help you have much more denser optical data storage.



LSPR: Applications

- Nanoscale Devices and Circuits
- Biomedical Applications
- Optical Data Storage
- Optical Nanoantenna
- Plasmonic Solar Cell
- Biological and Chemical Sensing
- Optical Twezzer
- Maskless Fabrication Technology

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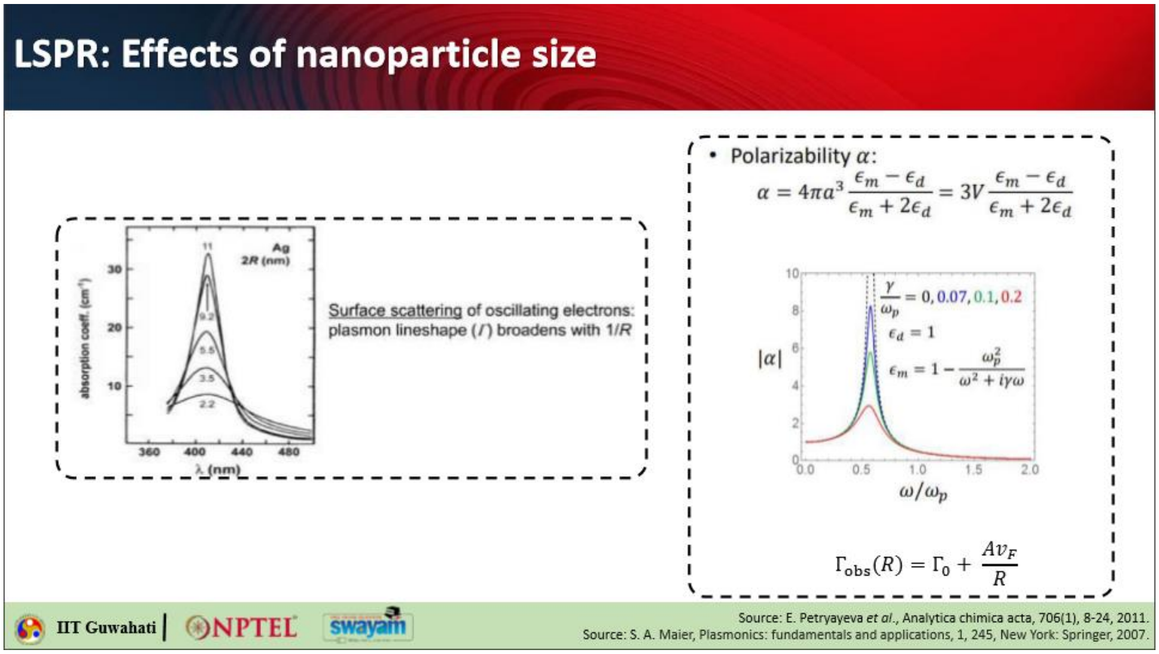
Source: E. Petryayeva *et al.*, Analytica chimica acta, 706(1), 8-24, 2011.
Source: K. A. Willets *et al.*, Annu. Rev. Phys. Chem., 58, 267-297, 2007.

You can use this force on single atoms to drag them somewhere in the near field. So, you can use them as optical tweezers. They can be used as directional nano antennas what we have seen in the previous lecture. You can also use them for maskless fabrication technology. Like if you have to make a metallic wire you instead of using mask you can line up nanoparticles and then you shine light and those nanoparticles at resonance will absorb that light get heated up and they will melt and that will give rise to a wire. So that is maskless fabrication technology.

Let us look into some details of LSPR right now. So, let us study the effect of nanoparticle size. In the previous lecture I told that you know surface scattering of oscillating electrons that actually changes the line shape of the Plasmon resonance. So, the Plasmon line shape gamma broadens with $\frac{1}{R}$.



LSPR: Effects of nanoparticle size

Surface scattering of oscillating electrons: plasmon lineshape (Γ) broadens with $1/R$

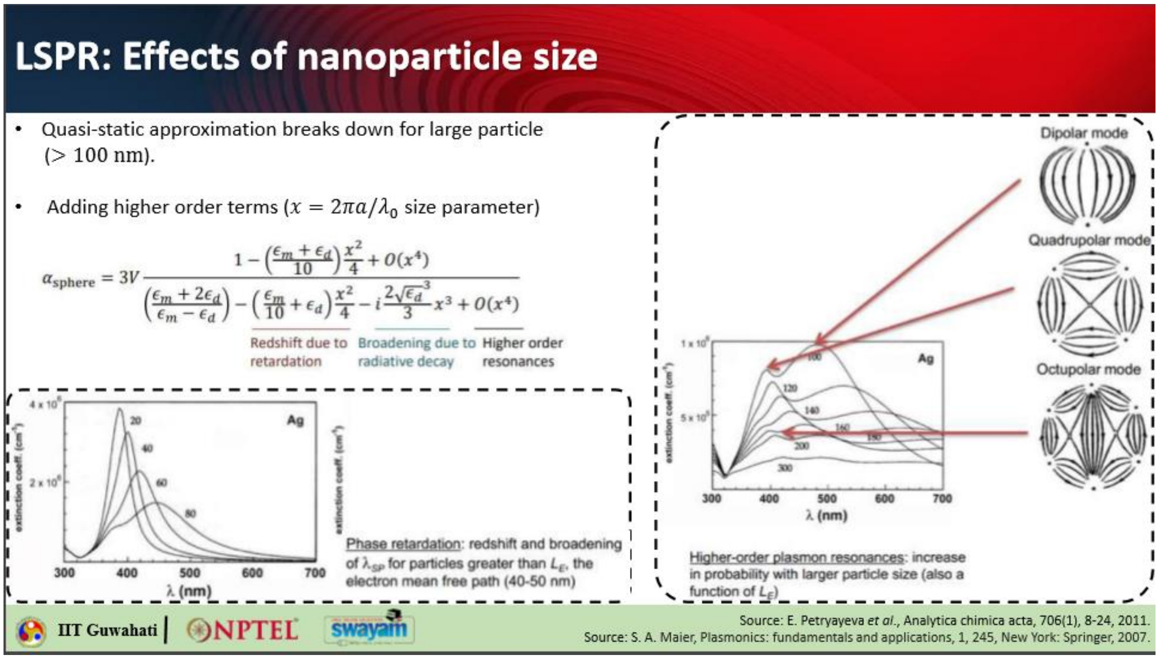
- Polarizability α:

$$\alpha = 4\pi a^3 \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} = 3V \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}$$

$$\Gamma_{\text{obs}}(R) = \Gamma_0 + \frac{Av_F}{R}$$

Source: E. Petryayeva *et al.*, Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, if you remember the expression of polarizability you can also see that how this polarizability depends on this gamma which is the damping constant of the metal nanoparticle. So, if you write down the permittivity of the metal like this $\epsilon_m = 1 - \frac{\omega_p^2}{\omega^2+i\gamma\omega}$. Gamma is the damping constant. Here it is shown that as γ increases you know the resonance get shorter means weaker and broader Okay and the broader is also associated with the damping directly. Now when the nanoparticle size is smaller than the mean free path of electron in that particular metal then there will be some additional scattering losses which is surface scattering. As it is shown here that γ is basically inversely proportional to R. So that is also seen here that this gamma will be now replaced by this new gamma which is the small gamma, small gamma is this capital gamma naught that same thing $\frac{Av_F}{R}$. A is a constant usually it is taken as 1. v_F is the Fermi velocity of electrons and R is the radius of that nanoparticle. Now on the other side this is when the particles are too small then the mean free path of the electrons you get additional scattering loss. There will be broadening in the spectra and the resonance becomes weaker. On the other side when quasi-static approximation breaks when the particle becomes too large greater than 100 nanometer. In such cases there are additional effects we have also seen that alpha gets now additional terms coming from redshift which is due to the retardation and also there are broadening due to radiative decay and you can see both of them here that this is for silver nanosphere as you keep on increasing the size of the silver nanosphere from 20 to 40 to 60 to 80 you see you are getting a redshift because the resonance is moving towards longer wavelength or red side and they are also getting broadened.



LSPR: Effects of nanoparticle size

- Quasi-static approximation breaks down for large particle (> 100 nm).
- Adding higher order terms ($x = 2\pi a/\lambda_0$ size parameter)

$$\alpha_{\text{sphere}} = 3V \frac{1 - \left(\frac{\epsilon_m + \epsilon_d}{10}\right)\frac{x^2}{4} + O(x^4)}{\left(\frac{\epsilon_m + 2\epsilon_d}{\epsilon_m - \epsilon_d}\right) - \underbrace{\left(\frac{\epsilon_m}{10} + \epsilon_d\right)\frac{x^2}{4}}_{\text{Redshift due to retardation}} - \underbrace{i\frac{2\sqrt{\epsilon_d}^3}{3}x^3}_{\text{Broadening due to radiative decay}} + \underbrace{O(x^4)}_{\text{Higher order resonances}}}$$

Phase retardation: redshift and broadening of λ_{SP} for particles greater than L_E, the electron mean free path (40-50 nm)

Higher-order plasmon resonances: increase in probability with larger particle size (also a function of L_E)

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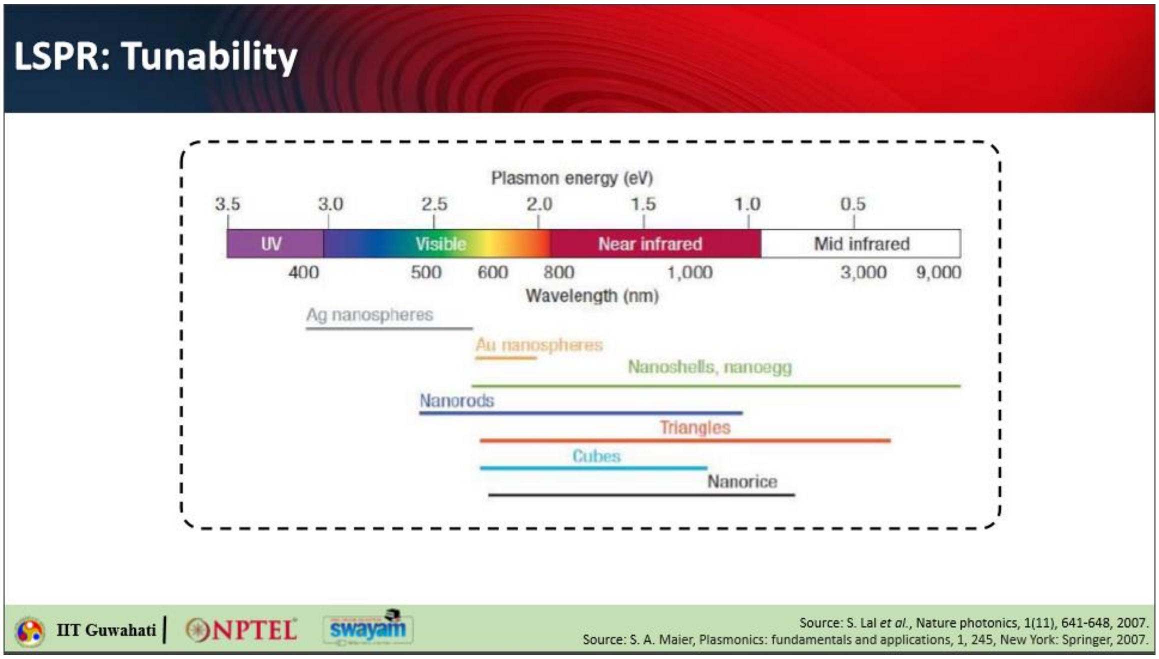
Source: E. Petryayeva *et al.*, Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, the broadening is because of this radiative decay and redshift in the larger particle is because of the retardation. Now what is this retardation? In quasi-static theory if you remember we assume that the phase on top of a particle does not change because the tiny particle is very tiny as compared to the wavelength of light but when the particle size increases and it becomes comparable or it becomes pretty large comparable in the sense like it is like $\lambda/4$, $\lambda/5$ something like that okay in that case you will see that you know over the surface of the particle there are some phase changes and that will not allow all the electrons to oscillate in sync or phase so that will cause the broadening and the redshift. So, these are the reason behind these two effects. So higher order resonances will come into picture like if you see if you further increase the size of the silver nanosphere from 100, 120, 140, 160, 180, 200 and 300 you see that the dipolar peak is getting weaker and weaker it is getting red shifted no doubt but it is getting weaker because new new resonances are coming up because here you see for 80 there was a small shoulder so this was a higher energy peak shorter wavelength means higher energy. So here also you can see that particular case that you are able to see that this is the dipolar peak and at higher energy you are getting another peak and with larger particles both higher energy and the dipolar peak are actually getting red shifted so this one got shifted here this one got shifted here further increase this got shifted here so they are all red shifting and at 140 you see another shoulder is coming up and 160 you got another peak.

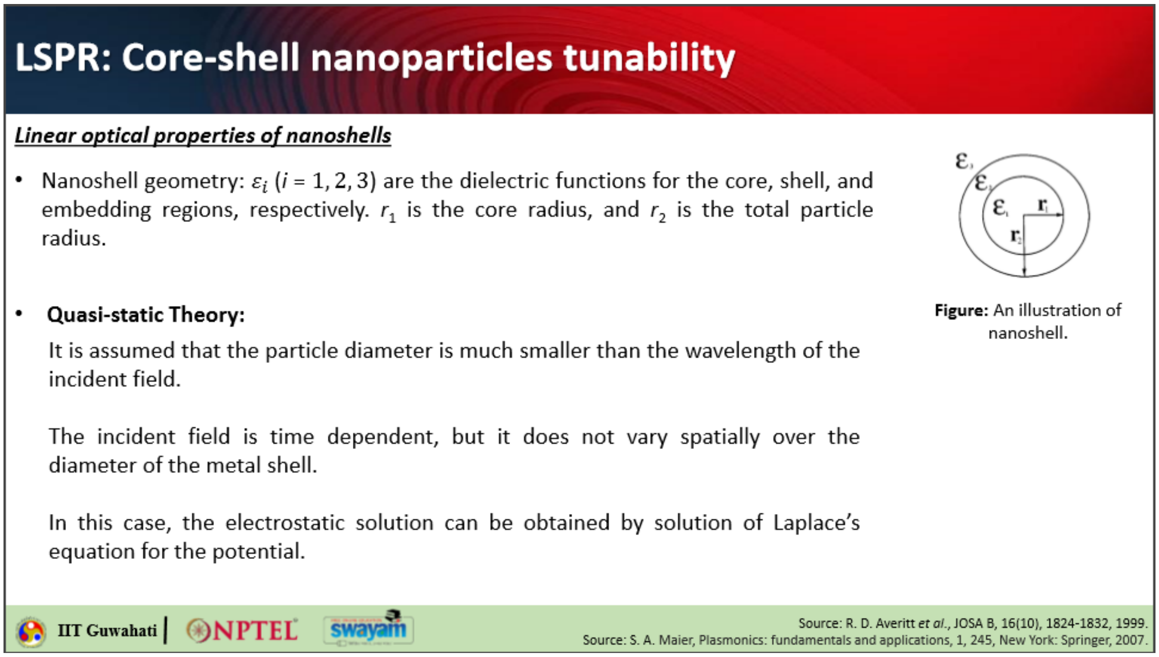
So dipolar then the next mode comes into picture is octopolar then the next mode comes into picture is sorry dipolar, quadrupolar and octopolar 2, 4 and 8 okay and so on. So, with that you understood that it is possible to you know have different plasmon resonance with a single particle sphere say or single material sphere like gold nanosphere or silver nanosphere but the resonance strength weakens and it also becomes too much broad so that is not a very very strong resonance. So, you can look into this particular chart and that will help you about the tunability of localized surface plasmon resonance. So silver nanospheres scatter from 380 to around 600 as we discussed so gold nanospheres starting from say 520 to 660 as we discussed before but look at this nano shells or nano eggs they have very wide range of tunability starting from visible range to mid infrared you can tune with them. Similarly, nanorods, triangles, cubes, nanowires these are different different shapes of the plasmonic nano antenna which allows you to achieve Plasmon resonance at different wavelength and this is the tuning range means just by changing the size of the particle you can go from this wavelength to this wavelength or this to this for nanorods.



LSPR: Tunability

Source: S. Lal *et al.*, Nature photonics, 1(11), 641-648, 2007.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So that is a huge kind of tunability. Now let us look into the mathematical derivation of how nano shell or core shell nanoparticles they give this tunability. So, if you consider a core shell nanoparticle so this is how it looks like this is a core and this is the shell so the core radius is r_1, the overall radius is r_2 . So, what is the shell thickness r_2-r_1. So, this material the core material is ε_1, shell material is ε_2 and the outside surrounding media is ε_3.



LSPR: Core-shell nanoparticles tunability

Linear optical properties of nanoshells

- Nanoshell geometry: ε_i ($i = 1, 2, 3$) are the dielectric functions for the core, shell, and embedding regions, respectively. r_1 is the core radius, and r_2 is the total particle radius.
- **Quasi-static Theory:**

  It is assumed that the particle diameter is much smaller than the wavelength of the incident field.

  The incident field is time dependent, but it does not vary spatially over the diameter of the metal shell.

  In this case, the electrostatic solution can be obtained by solution of Laplace's equation for the potential.

Figure: An illustration of nanoshell.

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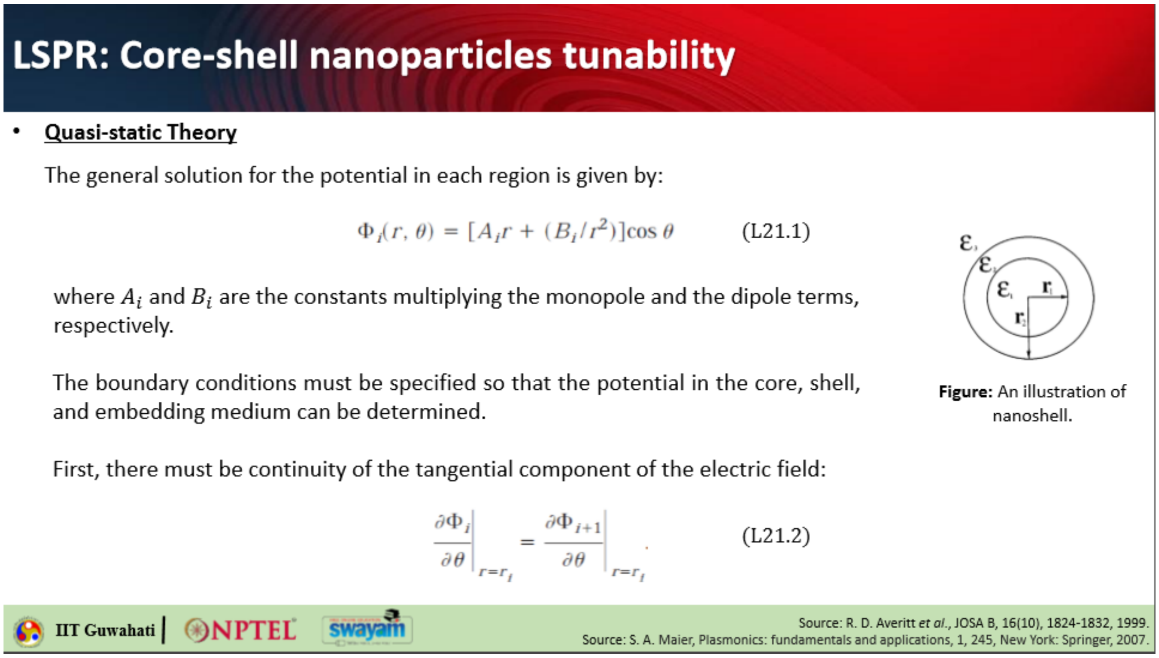
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Now in quasi-static theory we have to remember certain things that the particle diameter so r_2 or diameter so it is $2r_2$ should be much smaller than the wavelength of light. Then the incident field is time dependent but it does not vary spatially on the particle. So that is what quasi-static. And in that case you can actually use electrostatic solution by you know solving the Laplace equation for potential. So, this is how you can define the potential phi so Ai and Bi are the two constants which correspond to monopole and dipole terms.

So, this is the general formula I means you can put $i = 1, 2, 3$ so that will be the generic equation of potential in the three region. Now what next you have to apply the boundary conditions at the core shell and the embedding medium boundary to see and to find out what are these constants A_1, A_2, B_1, B_2 or now A_3, B_3 and so on. Now what are the boundary conditions always remember it has to be the continuity of the tangential component of the electric field. So, if you write that this is how you write it. So, at different layers this is how the tangential component should be continuous.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

The general solution for the potential in each region is given by:

$$\Phi_i(r,\theta) = [A_i r + (B_i/r^2)]\cos\theta \qquad \text{(L21.1)}$$

where A_i and B_i are the constants multiplying the monopole and the dipole terms, respectively.

The boundary conditions must be specified so that the potential in the core, shell, and embedding medium can be determined.

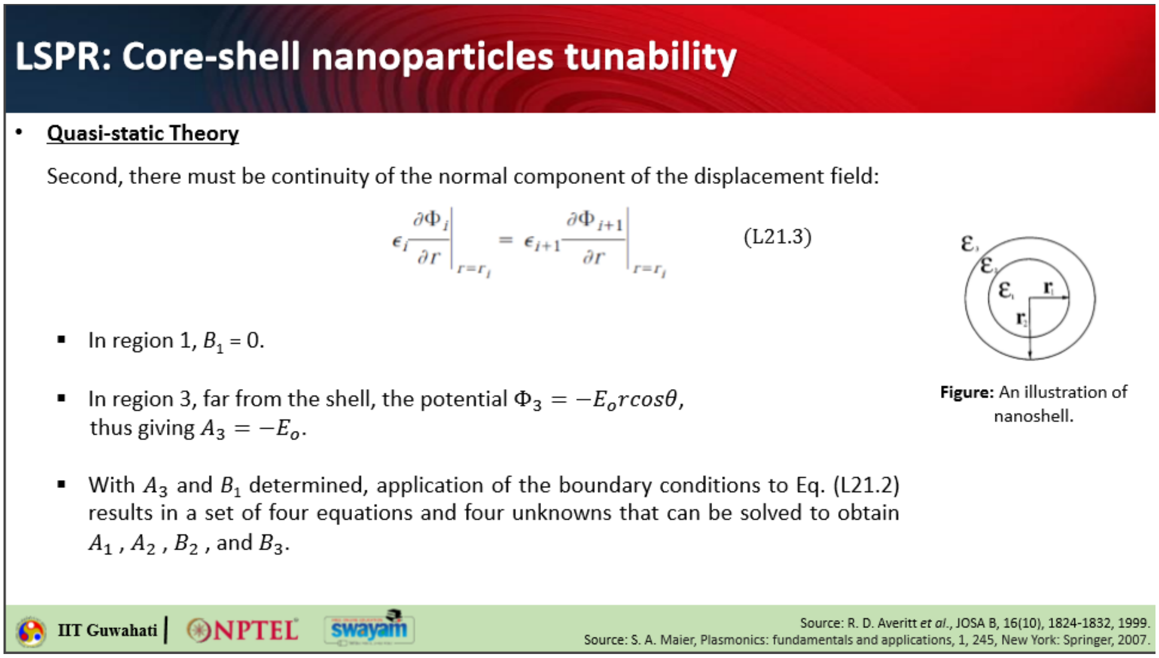
First, there must be continuity of the tangential component of the electric field:

$$\left.\frac{\partial \Phi_i}{\partial \theta}\right|_{r=r_i} = \left.\frac{\partial \Phi_{i+1}}{\partial \theta}\right|_{r=r_i} \qquad \text{(L21.2)}$$

Figure: An illustration of nanoshell.

Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Now with that if you put the second condition which is the normal component of the displacement field. So normal component is so $\frac{\partial \Phi_i}{\partial r}$ is basically electric field and when you multiply with ε that is the permittivity this gives you D that is the displacement field. So, the displacement fields are also continuous the normal components. So normal components you can find out by taking the derivative with respect to r what is normal and the tangential one you can find with respect to theta that is shown here. So, once you do that you can put there is no monopole here so the term A_1 goes to 0 only dipole will be formed.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

  Second, there must be continuity of the normal component of the displacement field:

$$\epsilon_i \frac{\partial \Phi_i}{\partial r}\bigg|_{r=r_i} = \epsilon_{i+1} \frac{\partial \Phi_{i+1}}{\partial r}\bigg|_{r=r_i} \qquad \text{(L21.3)}$$

  - In region 1, $B_1 = 0$.
  - In region 3, far from the shell, the potential $\Phi_3 = -E_o r cos\theta$, thus giving $A_3 = -E_o$.
  - With A_3 and B_1 determined, application of the boundary conditions to Eq. (L21.2) results in a set of four equations and four unknowns that can be solved to obtain A_1 , A_2 , B_2 , and B_3.

Figure: An illustration of nanoshell.

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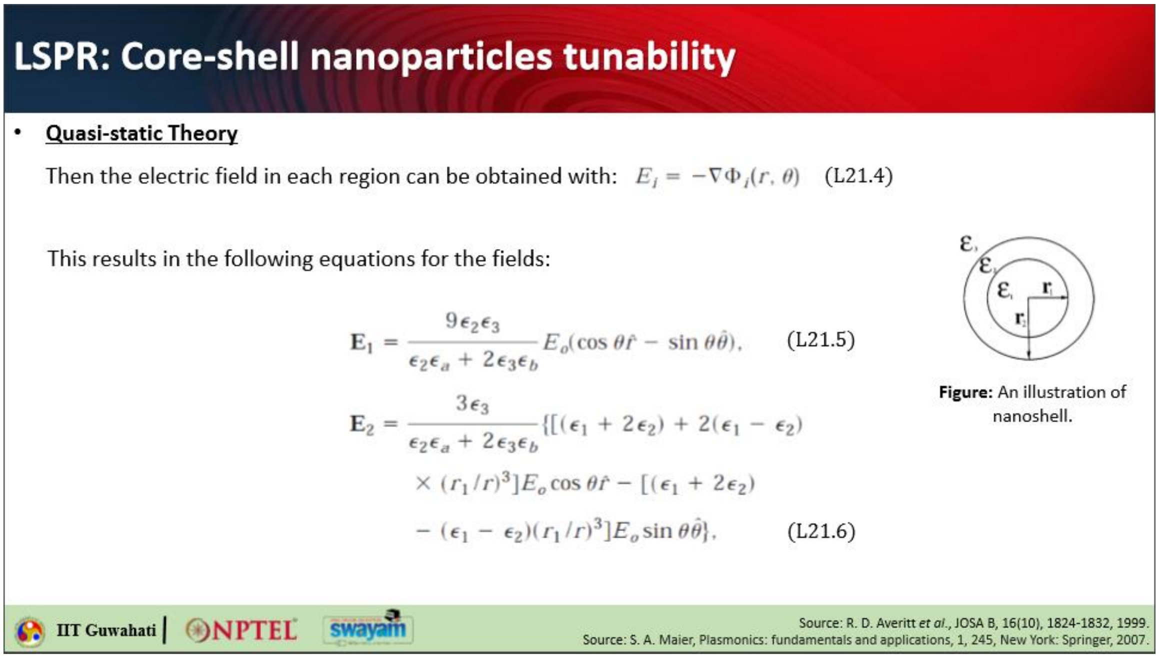
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, you can also find out what is there is no electric charge at the center so you can put B_1 also equals to 0. In the outer region in the space far away from the particle the potential $\Phi_3 = -E_o r\cos\theta$. E_o is the incident electric field. So that also tells you that A_3 is nothing but $-E_o$. So A_3 and B_1 you have determined and you can put it back into the previous equations and solve it to find out what is A_1, A_2, B_1, B_2.

So once you do that you can obtain the potential phi I am not going into the derivation that that is easy but a bit lengthy. So once that you can always find out what is E_1, E_2 and E_3 that are the three different electric fields. So, these are the expressions. Do the calculation or you can plot it using some kind of programming software like MATLAB or Python you will be able to get these equations and then finally you will find out the electric field in the third region that is E_3.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

Then the electric field in each region can be obtained with: $E_i = -\nabla \Phi_i(r, \theta)$ (L21.4)

This results in the following equations for the fields:

$$\mathbf{E}_1 = \frac{9\epsilon_2\epsilon_3}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b} E_o(\cos\theta\hat{r} - \sin\theta\hat{\theta}), \qquad \text{(L21.5)}$$

$$\begin{aligned}\mathbf{E}_2 = \frac{3\epsilon_3}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\{[(\epsilon_1 + 2\epsilon_2) + 2(\epsilon_1 - \epsilon_2)\\ \times (r_1/r)^3]E_o\cos\theta\hat{r} - [(\epsilon_1 + 2\epsilon_2)\\ - (\epsilon_1 - \epsilon_2)(r_1/r)^3]E_o\sin\theta\hat{\theta}\}, \qquad \text{(L21.6)}\end{aligned}$$

Figure: An illustration of nanoshell.

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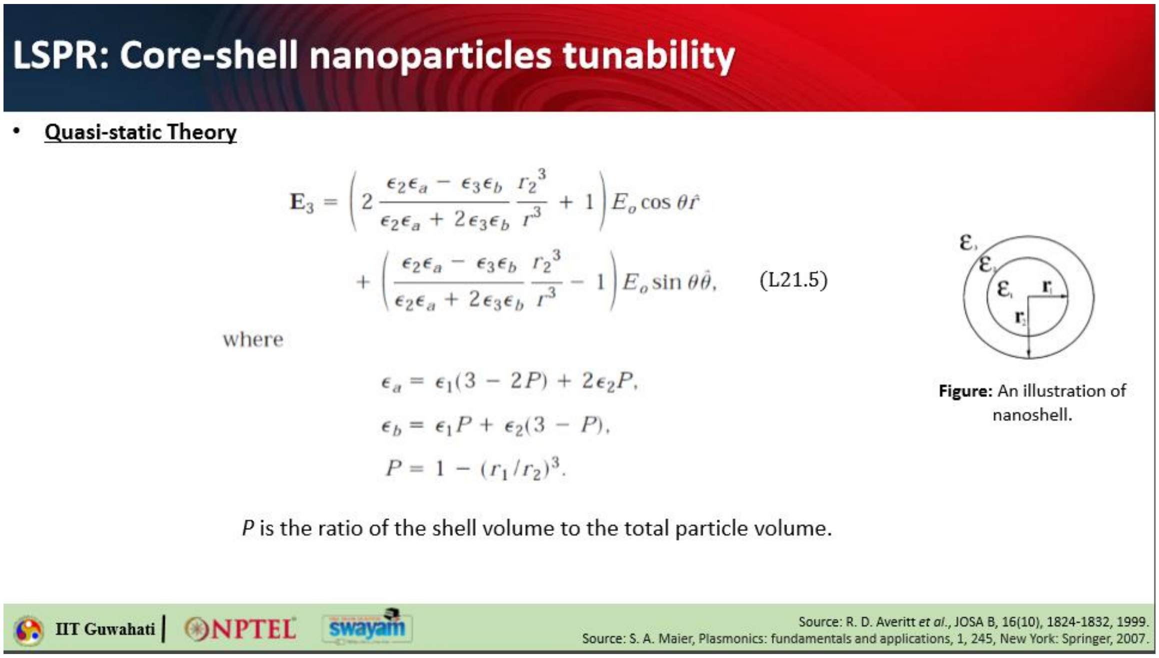
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, there you can see that you are actually having some components like ϵ_a that is dependent on ϵ_1 and ϵ_2 and also P. P is nothing but the volume fraction. So, it is the ratio of the shell volume to the overall partial volume. So, this is the parameter that brings into the ratio of shell and overall particle volume into the picture. So ϵ_a, ϵ_b are the two new terms which are nothing but this.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

$$\begin{aligned}\mathbf{E}_3 = \left(2\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\frac{{r_2}^3}{r^3} + 1\right)E_o\cos\theta\hat{r}\\ + \left(\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\frac{{r_2}^3}{r^3} - 1\right)E_o\sin\theta\hat{\theta}, \qquad \text{(L21.5)}\end{aligned}$$

where

$$\epsilon_a = \epsilon_1(3 - 2P) + 2\epsilon_2 P,$$

$$\epsilon_b = \epsilon_1 P + \epsilon_2(3 - P),$$

$$P = 1 - (r_1/r_2)^3.$$

P is the ratio of the shell volume to the total particle volume.

Figure: An illustration of nanoshell.

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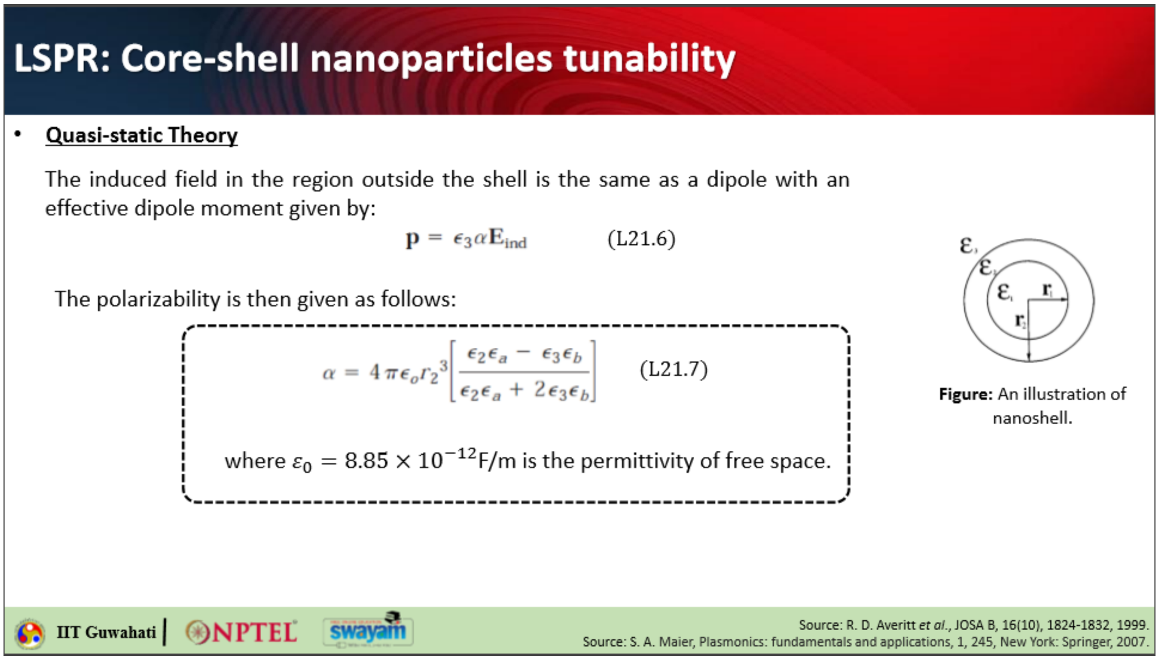
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, these are basically some kind of simplification in the formula. Overall how we do that the polarizability P of an equivalent dipole of this cochlear nanoparticle will be given as $\epsilon_3\alpha\mathbf{E}_{\text{ind}}$. So, you can from that you can find out what is the α that is the overall polarizability that is induced by this particle and this is the form. So $4\pi\epsilon_o r_2{}^3$ and this is the equation. I am not going through details but you can compare this with the nanosphere and you will be able to see the difference and here ϵ_2, ϵ_3 and ϵ_1 . Where is ϵ_1 in this? That is actually inside ϵ_a and ϵ_b. So, with this you can find out what is α. Once α it is very straightforward you can obtain the scattering cross section.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

The induced field in the region outside the shell is the same as a dipole with an effective dipole moment given by:

$$\mathbf{p} = \epsilon_3\alpha\mathbf{E}_{\text{ind}} \qquad \text{(L21.6)}$$

The polarizability is then given as follows:

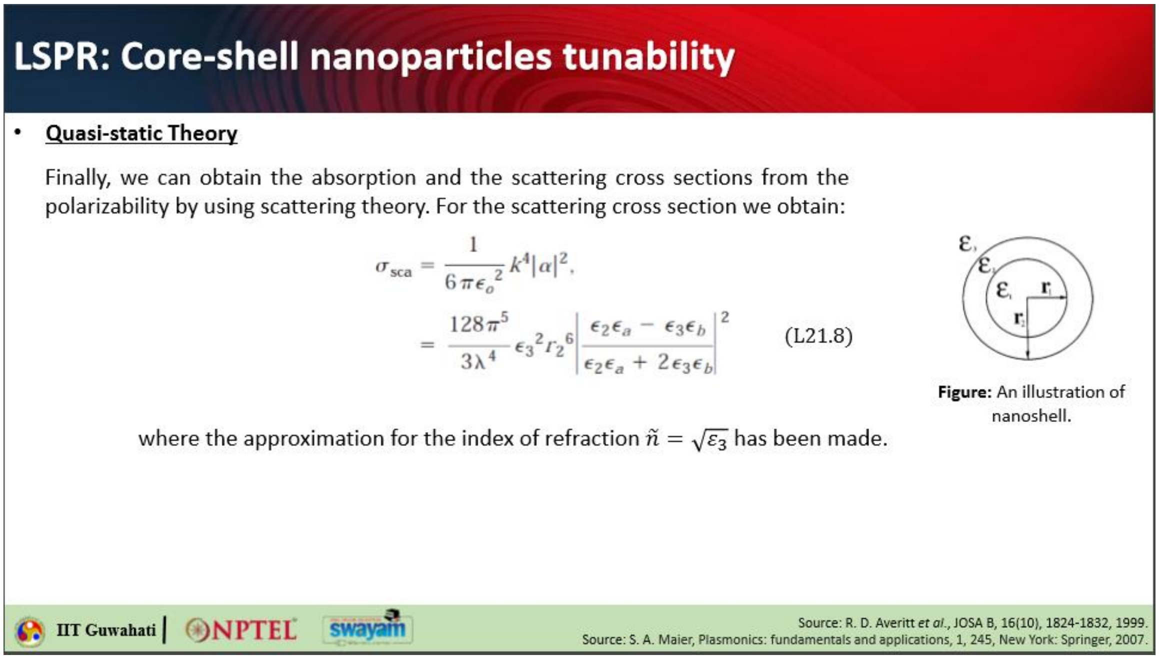
$$\alpha = 4\pi\epsilon_o r_2{}^3\left[\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\right] \qquad \text{(L21.7)}$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$F/m is the permittivity of free space.

Figure: An illustration of nanoshell.

Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, sigma is a cross section. So, sigma scattering is $\frac{1}{6\pi\epsilon_o^2}k^4|\alpha|^2$, you put this you get this particular formula. So here one thing you can remember that and that is a refractive index outside can be taken as $\sqrt{\varepsilon_3}$ because this surrounding media is a dielectric so you can simply take this one not a problem.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

Finally, we can obtain the absorption and the scattering cross sections from the polarizability by using scattering theory. For the scattering cross section we obtain:

$$\begin{aligned}\sigma_{\text{sca}} &= \frac{1}{6\pi\epsilon_o{}^2}k^4|\alpha|^2, \\ &= \frac{128\pi^5}{3\lambda^4}\epsilon_3{}^2 r_2{}^6\left|\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\right|^2 \qquad \text{(L21.8)}\end{aligned}$$

where the approximation for the index of refraction $\tilde{n} = \sqrt{\varepsilon_3}$ has been made.

Figure: An illustration of nanoshell.

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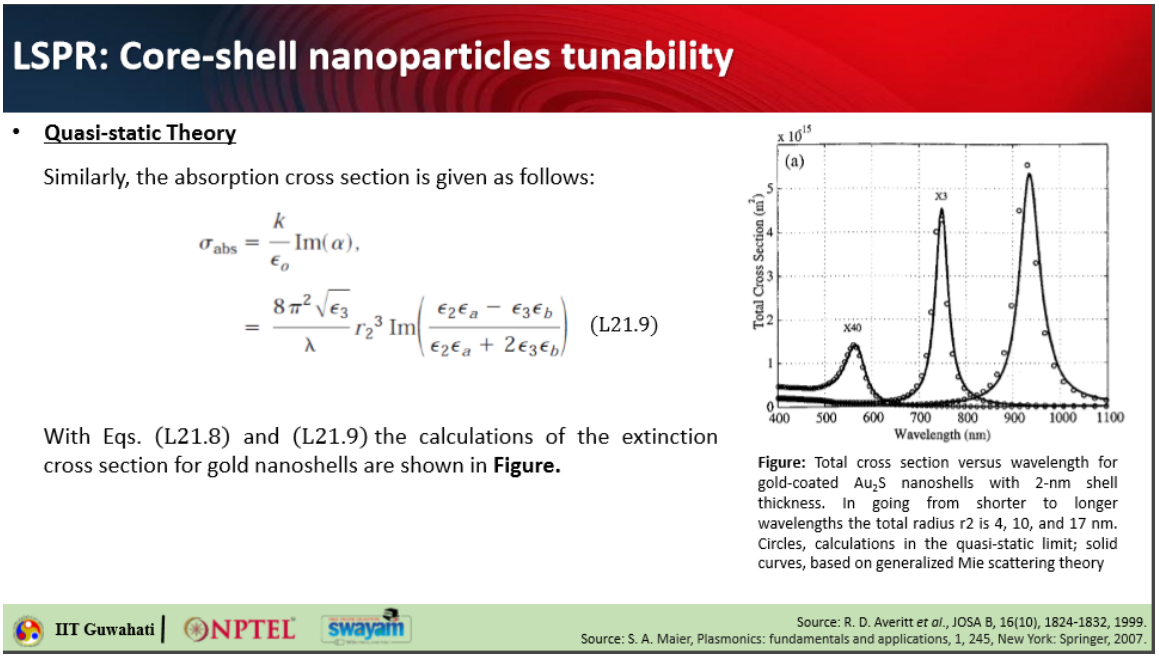
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Similarly you can obtain what is the absorption cross section that is basically $\frac{k}{\epsilon_o}\text{Im}(\alpha)$ this gives you the once you put α you get expression $\frac{8\pi^2\sqrt{\epsilon_3}}{\lambda}r_2{}^3\ \text{Im}\left(\frac{\epsilon_2\epsilon_a-\epsilon_3\epsilon_b}{\epsilon_2\epsilon_a+2\epsilon_3\epsilon_b}\right)$. So overall you will be able to find out the case. Now the using this you can find out the total cross section.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

Similarly, the absorption cross section is given as follows:

$$\begin{aligned}\sigma_{\text{abs}} &= \frac{k}{\epsilon_o}\text{Im}(\alpha), \\ &= \frac{8\pi^2\sqrt{\epsilon_3}}{\lambda}r_2{}^3\ \text{Im}\left(\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\right) \qquad \text{(L21.9)}\end{aligned}$$

With Eqs. (L21.8) and (L21.9) the calculations of the extinction cross section for gold nanoshells are shown in **Figure.**

Figure: Total cross section versus wavelength for gold-coated Au_2S nanoshells with 2-nm shell thickness. In going from shorter to longer wavelengths the total radius r2 is 4, 10, and 17 nm. Circles, calculations in the quasi-static limit; solid curves, based on generalized Mie scattering theory

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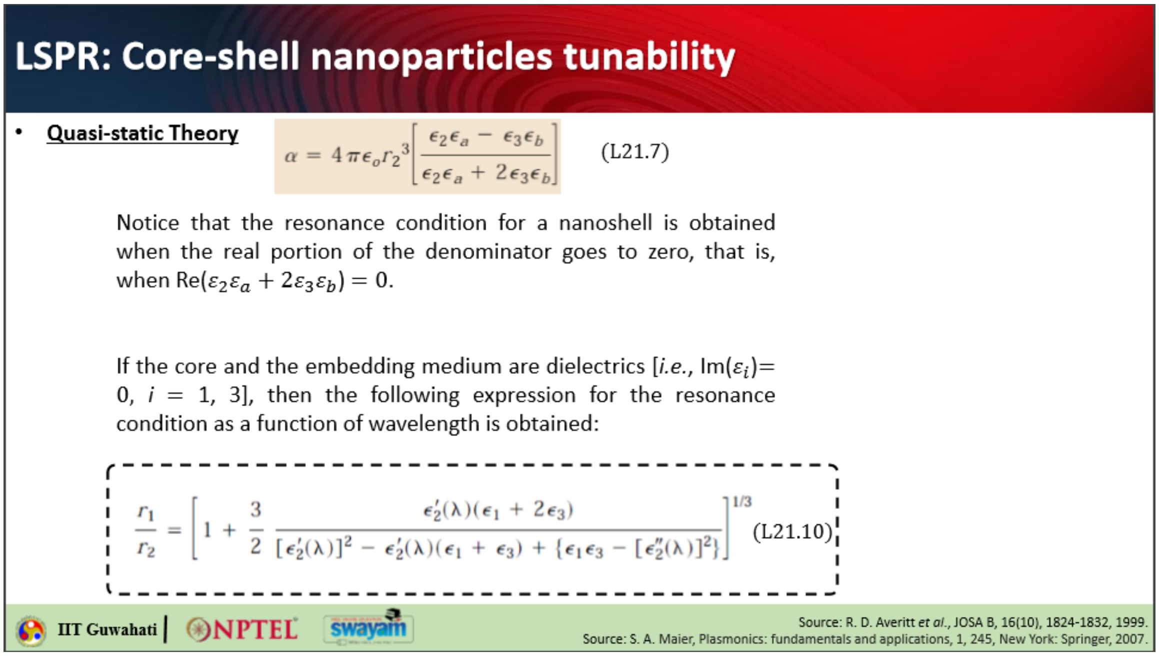
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

If now let us take one example of gold coated gold sulphide nanoshell it means the core is basically gold sulphide and it is coated by gold. So, if you take that kind of a particle with 2 nanometer shell thickness. Look at this figure this figure shows the calculation of the total cross section. So, it is basically summation of scattering cross section and absorption cross section and this is a gold coated Au_2S nanoshell. So, gold is the core and you have gold sulphide on the outer shell and the shell thickness is 2 nanometer and in these three cases r_2 has been changed from 4, 10 and 17.

So you can see as the overall size of the particle becomes larger you get a red shift and the resonance also gets stronger. And these circles that you see they are basically from the quasi-static theory calculation and the solid line is from the generalized Mie scattering theory. So, we have seen the Mie scattering theory possible for nanospheres. They are also possible for core shell nanoparticles and you see that the quasi-static theory is very close to the Mie scattering theory. It means for this size of particles quasi-static theory is a very very good approximation.



LSPR: Core-shell nanoparticles tunability

- **Quasi-static Theory**

$$\alpha = 4\pi\epsilon_o r_2^3 \left[\frac{\epsilon_2\epsilon_a - \epsilon_3\epsilon_b}{\epsilon_2\epsilon_a + 2\epsilon_3\epsilon_b}\right] \quad \text{(L21.7)}$$

Notice that the resonance condition for a nanoshell is obtained when the real portion of the denominator goes to zero, that is, when $\mathrm{Re}(\varepsilon_2\varepsilon_a + 2\varepsilon_3\varepsilon_b) = 0$.

If the core and the embedding medium are dielectrics [*i.e.*, $\mathrm{Im}(\varepsilon_i) = 0$, $i = 1, 3$], then the following expression for the resonance condition as a function of wavelength is obtained:

$$\frac{r_1}{r_2} = \left[1 + \frac{3}{2}\frac{\epsilon_2'(\lambda)(\epsilon_1 + 2\epsilon_3)}{[\epsilon_2'(\lambda)]^2 - \epsilon_2'(\lambda)(\epsilon_1 + \epsilon_3) + \{\epsilon_1\epsilon_3 - [\epsilon_2''(\lambda)]^2\}}\right]^{1/3} \quad \text{(L21.10)}$$

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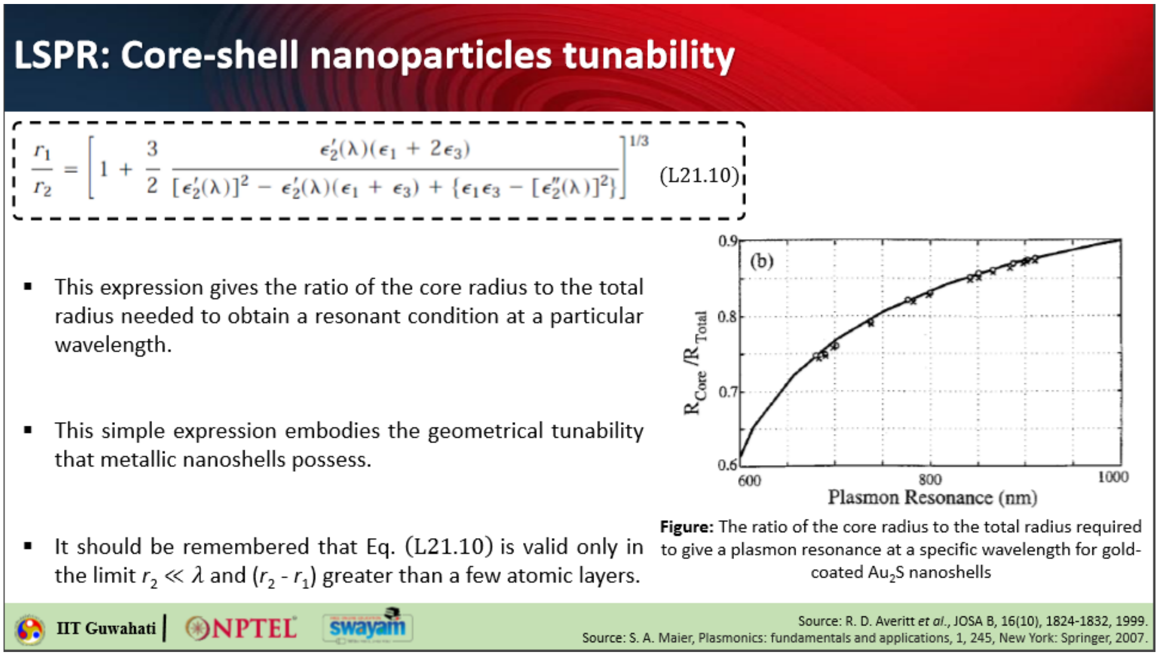
Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, if someone tells you okay this is the polarizability alpha what is the condition for resonance? The condition for resonance is that when the denominator the real part of the denominator goes to 0. So, you can write real of this going to 0. So, you can actually find out what is that so you put ϵ_a and ϵ_b into this equation you can find out the condition r_1/r_2 equals this. So, this is the condition for resonance. So, you again take that example of gold coated Au_2S nanoshells okay and in that case you can see R core which is basically r_1 divided by r total that is basically r_2 is this one.



LSPR: Core-shell nanoparticles tunability

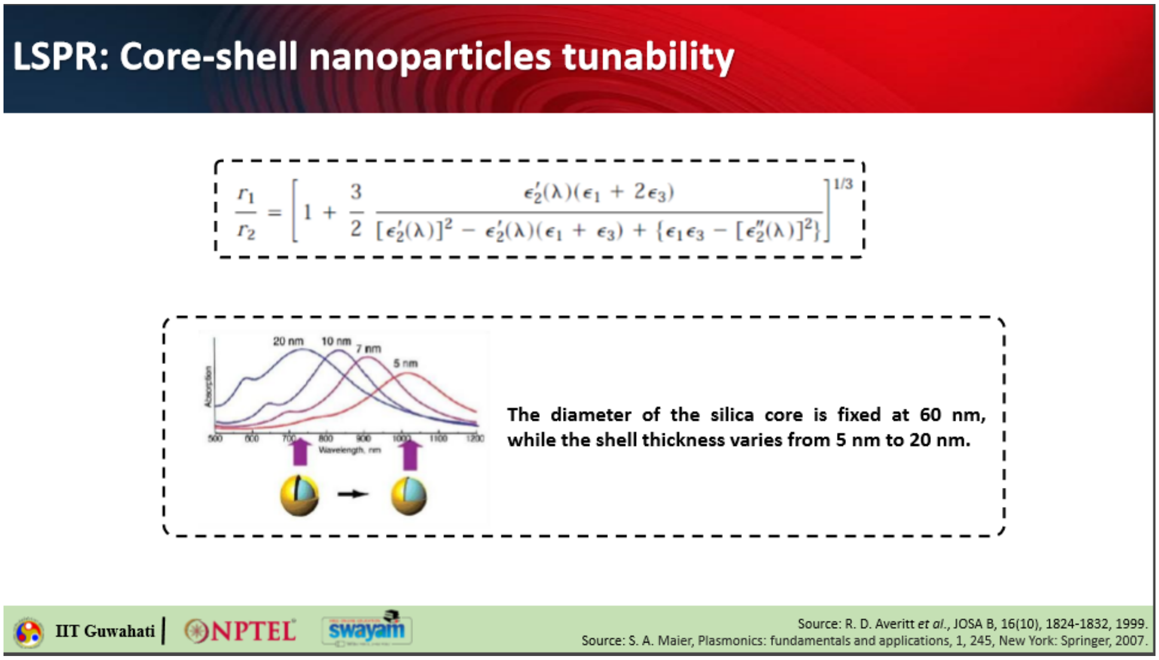
$$\frac{r_1}{r_2} = \left[1 + \frac{3}{2}\,\frac{\epsilon_2'(\lambda)(\epsilon_1 + 2\epsilon_3)}{[\epsilon_2'(\lambda)]^2 - \epsilon_2'(\lambda)(\epsilon_1 + \epsilon_3) + \{\epsilon_1\epsilon_3 - [\epsilon_2''(\lambda)]^2\}}\right]^{1/3} \quad \text{(L21.10)}$$

- This expression gives the ratio of the core radius to the total radius needed to obtain a resonant condition at a particular wavelength.
- This simple expression embodies the geometrical tunability that metallic nanoshells possess.
- It should be remembered that Eq. (L21.10) is valid only in the limit $r_2 \ll \lambda$ and (r_2 - r_1) greater than a few atomic layers.

Figure: The ratio of the core radius to the total radius required to give a plasmon resonance at a specific wavelength for gold-coated Au_2S nanoshells

Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, you can change this ratio from 0.62 or something or 61 to 0.9 only this much variation you are able to change the resonance wavelength from 600 to 1000. Now you can correlate with that kind of large span of nanoshell that I have shown previously that it is possible to get a huge tunability by going to this kind of core shell nanoparticles where a metallic core is coated with a nanoshell okay and this also can be done so in this case this particular graph is for Au_2S nanoshell coated with gold. So here the core is Au_2S that is a dielectric which is gold sulfide and it is coated by gold.



LSPR: Core-shell nanoparticles tunability

$$\frac{r_1}{r_2} = \left[1 + \frac{3}{2}\,\frac{\epsilon_2'(\lambda)(\epsilon_1 + 2\epsilon_3)}{[\epsilon_2'(\lambda)]^2 - \epsilon_2'(\lambda)(\epsilon_1 + \epsilon_3) + \{\epsilon_1\epsilon_3 - [\epsilon_2''(\lambda)]^2\}}\right]^{1/3}$$

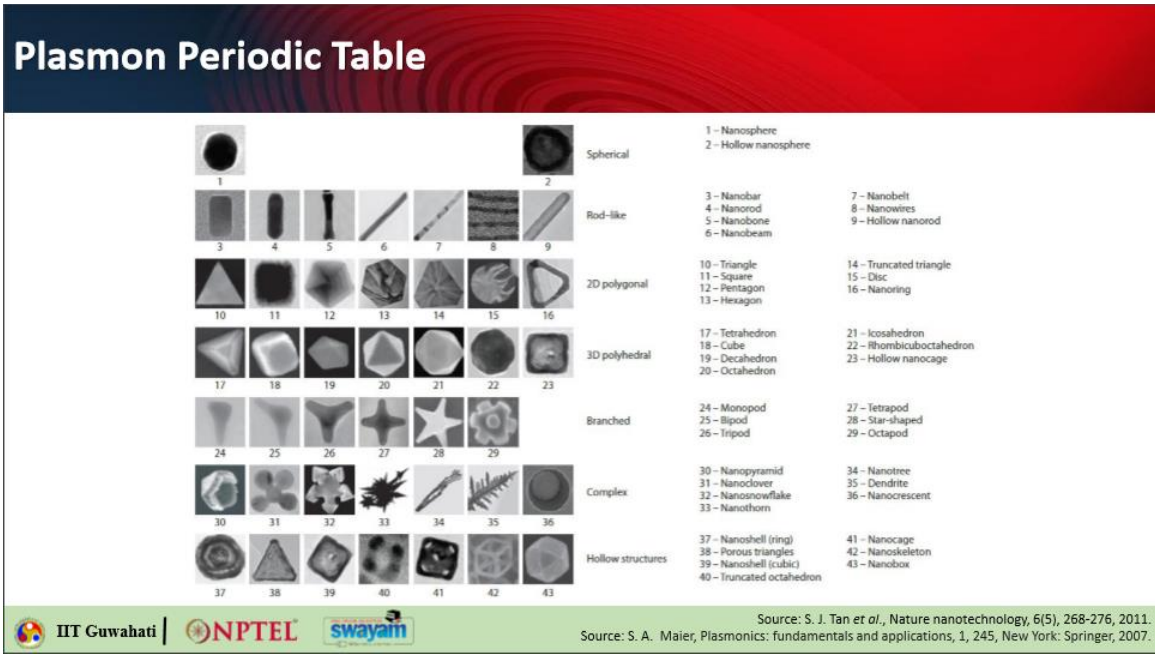
The diameter of the silica core is fixed at 60 nm, while the shell thickness varies from 5 nm to 20 nm.

Source: R. D. Averitt *et al.*, JOSA B, 16(10), 1824-1832, 1999.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So here is another example of a silica core which is kept fixed at 60 nanometers and then the gold thickness or the shell thickness has been varied from 5 nanometers to 20 nanometers. So here it is 5 nanometers, here it is 20 nanometers. You can see for 5 it is here, for 20 it is blue shifted. So thicker the gold shell the resonance goes back towards the actual gold nanosphere resonance. So more thicker you will make it will go towards 520 okay.

This is how you can remember that what happens with this thing okay. So always remember it is very simple formula. So ϵ_1 is the core permittivity, the core can be gold or it can be or any metal or it can be even dielectric and ϵ_2 in this case we are considering that the core is basically dielectric and the shell that is ϵ_2 is having real and imaginary part that means it is a metal okay. So, this formula is particularly for one case that is dielectric core metallic shell nanoparticle. So once again to avoid confusion let me reiterate gold coated Au_2S nanoshell means the core is Au_2S that is gold sulphide which is basically a dielectric material and it is coated with gold that is why it is called gold coated Au_2S nanoshells.

Now there are different other particles also possible. So, you can see all different shapes and sizes are possible. These are spherical, these are all rod type different types of rods, these are like 2D polygonal type, these are 3D polyhedral type, there can be branched, there can be complex nanoparticles, then you can also have particles with hollow structures. So, all these different plasmonic structures are possible which shows different kind of LSPR properties and also they will have it will be difficult for anyone to calculate the resonance condition for this complex shape particles but for sphere and rods you will be able to approximate them using quasi-static theory and all. Remaining you have to go for different other methods.



Plasmon Periodic Table

Spherical
1 – Nanosphere
2 – Hollow nanosphere

Rod-like
3 – Nanobar
4 – Nanorod
5 – Nanobone
6 – Nanobeam
7 – Nanobelt
8 – Nanowires
9 – Hollow nanorod

2D polygonal
10 – Triangle
11 – Square
12 – Pentagon
13 – Hexagon
14 – Truncated triangle
15 – Disc
16 – Nanoring

3D polyhedral
17 – Tetrahedron
18 – Cube
19 – Decahedron
20 – Octahedron
21 – Icosahedron
22 – Rhombicuboctahedron
23 – Hollow nanocage

Branched
24 – Monopod
25 – Bipod
26 – Tripod
27 – Tetrapod
28 – Star-shaped
29 – Octapod

Complex
30 – Nanopyramid
31 – Nanoclover
32 – Nanosnowflake
33 – Nanothorn
34 – Nanotree
35 – Dendrite
36 – Nanocrescent

Hollow structures
37 – Nanoshell (ring)
38 – Porous triangles
39 – Nanoshell (cubic)
40 – Truncated octahedron
41 – Nanocage
42 – Nanoskeleton
43 – Nanobox

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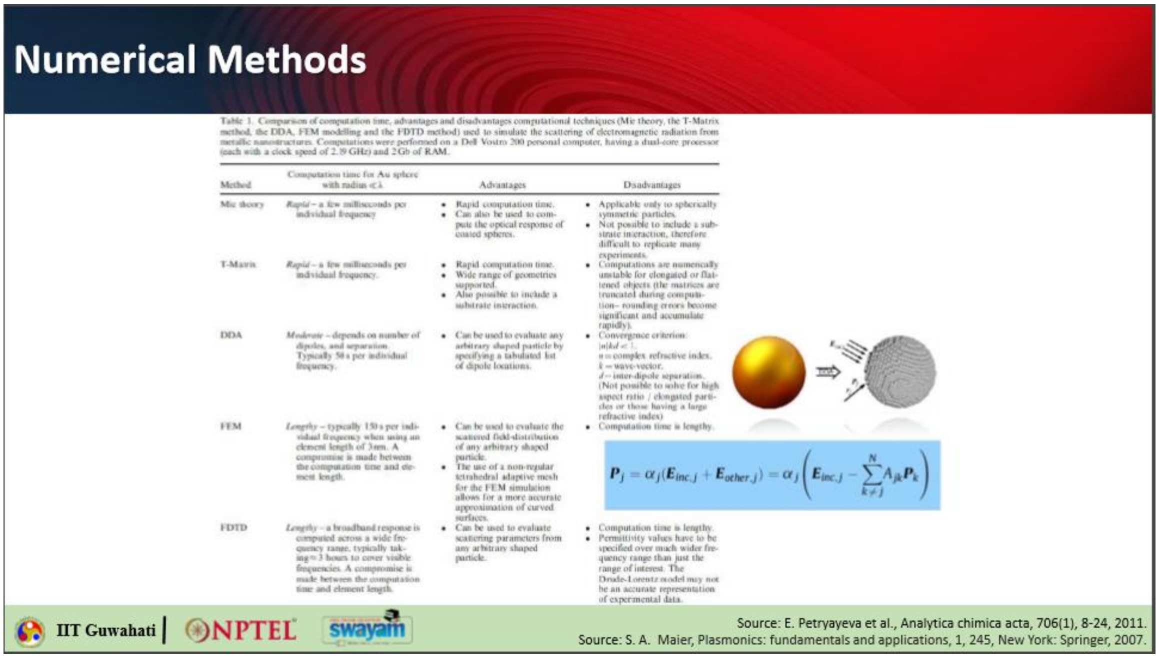
Source: S. J. Tan *et al.*, Nature nanotechnology, 6(5), 268-276, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Here are some of the numerical methods that you can use. So, as I mentioned Mie theory can be used for spherical particles or infinite cylinders. You can go for transfer matrix method where you have multiple layers and you can multiply them these are like different types of. If transfer matrix method is also kind of a computational method. Discrete DDA, Discrete Dipole Approximation is what is shown here.



Numerical Methods

Table 1. Comparison of computation time, advantages and disadvantages computational techniques (Mie theory, the T-Matrix method, the DDA, FEM modelling and the FDTD method) used to simulate the scattering of electromagnetic radiation from metallic nanostructures. Computations were performed on a Dell Vostro 200 personal computer, having a dual-core processor (each with a clock speed of 2.19 GHz) and 2 Gb of RAM.

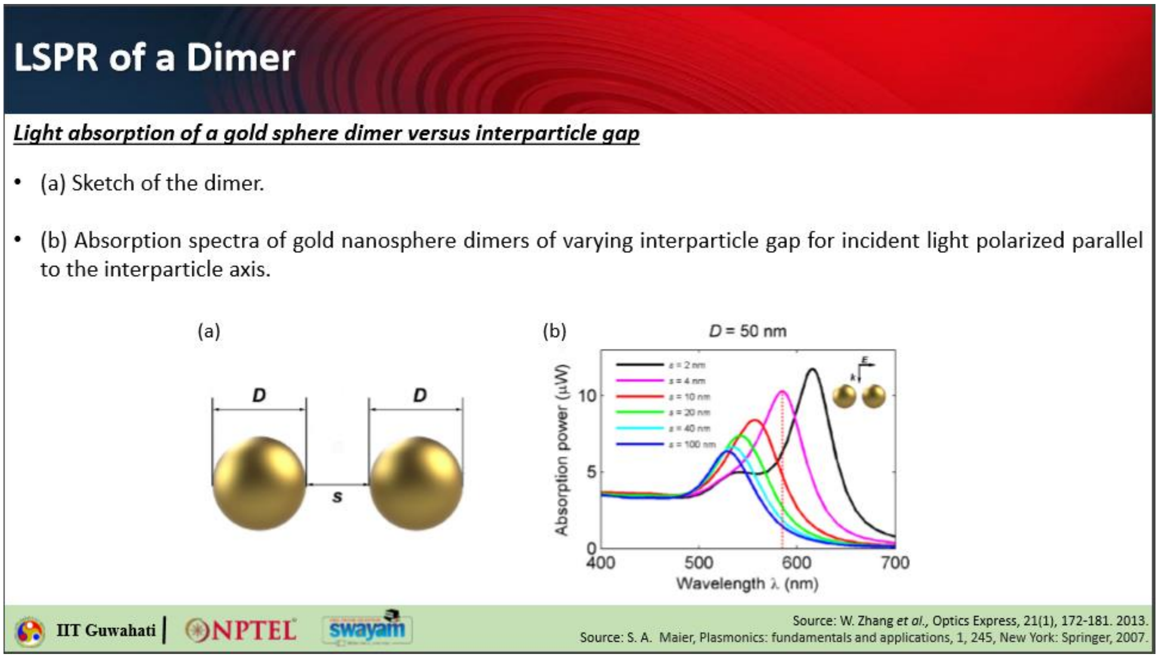
Method	Computation time for Au sphere with radius $\ll\lambda$	Advantages	Disadvantages
Mie theory	*Rapid* – a few milliseconds per individual frequency	• Rapid computation time. • Can also be used to compute the optical response of coated spheres.	• Applicable only to spherically symmetric particles. • Not possible to include a substrate interaction, therefore difficult to replicate many experiments.
T-Matrix	*Rapid* – a few milliseconds per individual frequency.	• Rapid computation time. • Wide range of geometries supported. • Also possible to include a substrate interaction.	• Computations are numerically unstable for elongated or flattened objects (the matrices are truncated during computation– rounding errors become significant and accumulate rapidly).
DDA	*Moderate* – depends on number of dipoles, and separation. Typically 50 s per individual frequency.	• Can be used to evaluate any arbitrary shaped particle by specifying a tabulated list of dipole locations.	• Convergence criterion: $\|n\|kd < 1$. n = complex refractive index. k = wave-vector. d = inter-dipole separation. (Not possible to solve for high aspect ratio / elongated particles or those having a large refractive index)
FEM	*Lengthy* – typically 150 s per individual frequency when using an element length of 3 nm. A compromise is made between the computation time and element length.	• Can be used to evaluate the scattered field-distribution of any arbitrary shaped particle. • The use of a non-regular tetrahedral adaptive mesh for the FEM simulation allows for a more accurate approximation of curved surfaces.	• Computation time is lengthy.
FDTD	*Lengthy* – a broadband response is computed across a wide frequency range, typically taking ≈ 3 hours to cover visible frequencies. A compromise is made between the computation time and element length.	• Can be used to evaluate scattering parameters from any arbitrary shaped particle.	• Computation time is lengthy. • Permittivity values have to be specified over much wider frequency range than just the range of interest. The Drude-Lorentz model may not be an accurate representation of experimental data.

$$\boldsymbol{P}_j = \alpha_j(\boldsymbol{E}_{inc,j} + \boldsymbol{E}_{other,j}) = \alpha_j\left(\boldsymbol{E}_{inc,j} - \sum_{k \neq j}^{N} A_{jk}\boldsymbol{P}_k\right)$$

Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, a sphere or any other shape can be approximated with tiny-tiny dipoles and then the response of each dipole is calculated in the presence of the incident electric field plus the electric field of the neighboring dipoles and in this case you will be able to do approximation for any complicated shape. So DDA method is a numerical method that allows you to do for any complicated shape but there is a convergence criterion that mod NkD, D is the inter dipole separation that should be less than 1 for this calculation to converge. Then you have finite element method or you can use FDTD this is finite difference time domain method. So, there are two different approaches for calculating the scattering and absorption cross-section. Always remember that FEM is a frequency domain method where you are doing it solving it for every frequency whereas in time domain method you can actually do it for one time pulse that covers a broadband of frequency and you can get the entire spectrum in one go.

So these are different methods that does the same objective. Now we studied all the single nanoparticles till now. Now we can also look at what happens when the two particles come together. In that case the separation between the particles also plays a very important role. So here you can see the absorption spectrum of the dimer two particles is called dimer.



LSPR of a Dimer

Light absorption of a gold sphere dimer versus interparticle gap

- (a) Sketch of the dimer.
- (b) Absorption spectra of gold nanosphere dimers of varying interparticle gap for incident light polarized parallel to the interparticle axis.

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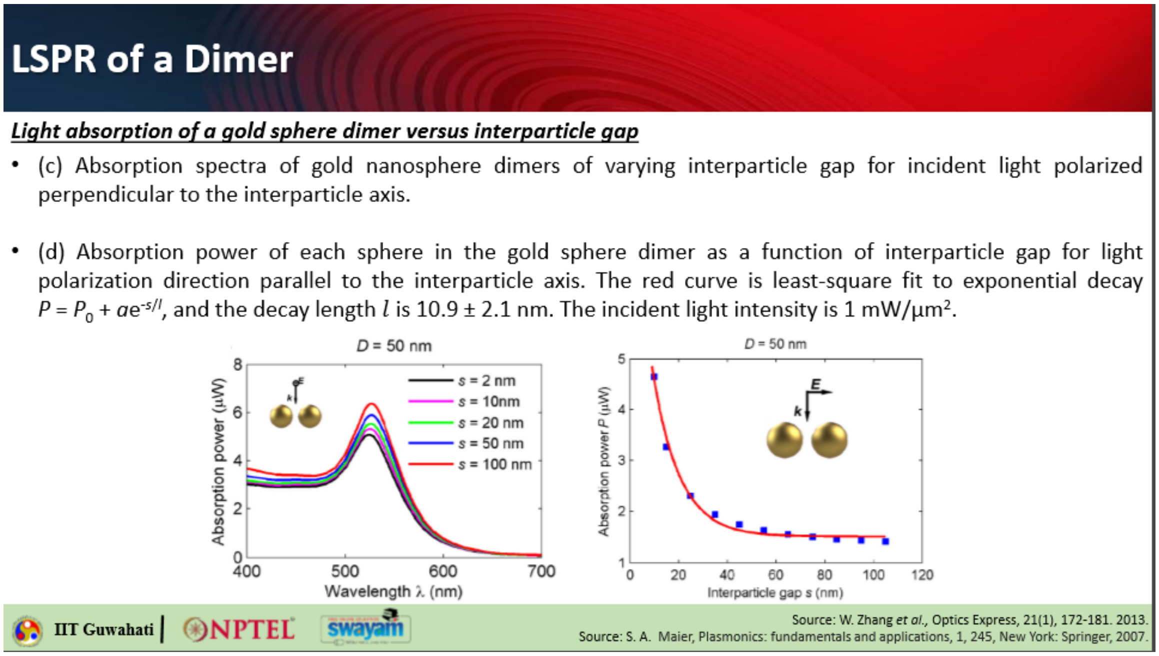
Source: W. Zhang *et al.*, Optics Express, 21(1), 172-181. 2013.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, when the electric field is polarized along the length of this nanoparticle axis you see depending on the separation. So, separation this is 100, 40, 20, 10, 4 and 2. So it is kind of a non-linear interaction and it gets very stronger and you get significant amount of redshift when the particles are very close to each other. So, what happens when the particles are very close to each other they interact the near field of the particles they interact very strongly with each other and that changes the overall plus 1 resonance of this coupled system. But the same particle dimer you take but you change the electric field direction perpendicular to the dimer axis you will see that the change is not that significant.

It only increases or to some extent for s equal to the it even gets weaker because you can see here the electric field is in and out of the plane and that is how each particle is more or less behaving like single particles. The coupling between them is along this axis but there is no electric field along this axis. So, there is no essentially any effect of coupling. So, absorption power if you calculate the absorption power for a 50 nanometer diameter particle so you can actually plot that with function of this gap. So, you can see the absorption power significantly increases when the separation reduces for the electric field polarized along the dimer axis.



LSPR of a Dimer

Light absorption of a gold sphere dimer versus interparticle gap

- (c) Absorption spectra of gold nanosphere dimers of varying interparticle gap for incident light polarized perpendicular to the interparticle axis.
- (d) Absorption power of each sphere in the gold sphere dimer as a function of interparticle gap for light polarization direction parallel to the interparticle axis. The red curve is least-square fit to exponential decay $P = P_0 + ae^{-s/l}$, and the decay length l is 10.9 ± 2.1 nm. The incident light intensity is 1 mW/μm^2.

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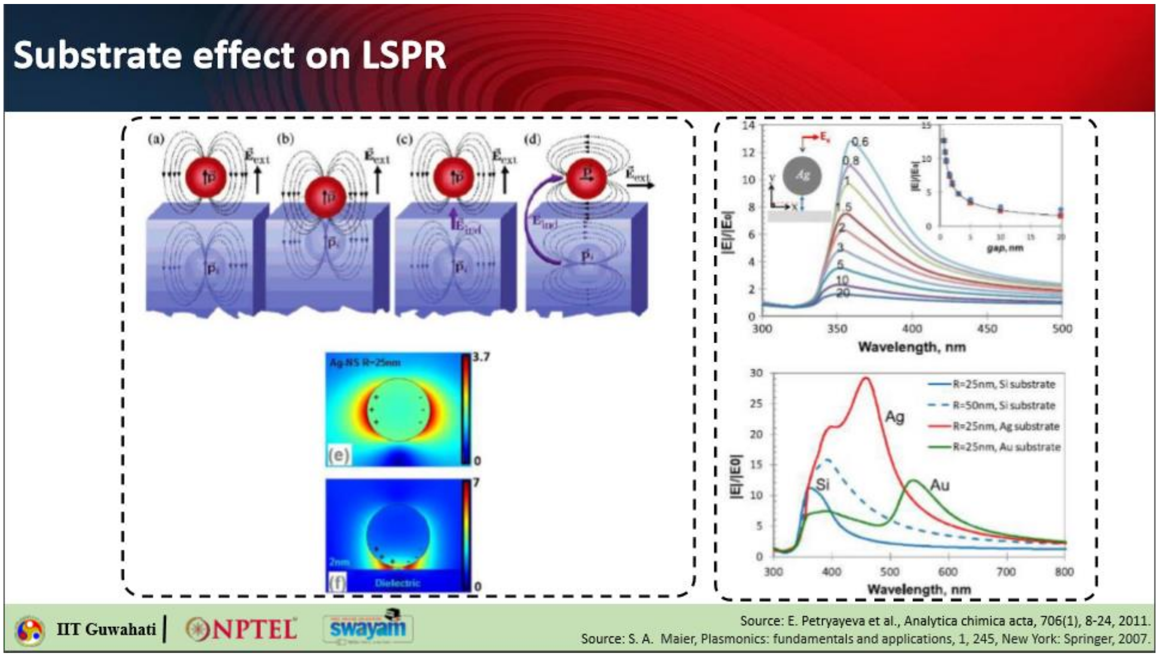
Source: W. Zhang *et al.*, Optics Express, 21(1), 172-181. 2013.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, this is an exponential fit that you can see $P = P_0 + ae^{-s/l}$ and the decay length is also found out that is where the initial resonance decay up to 1/ e^{th} value and this is the incident in light intensity used here. So, with this kind of scale you will be able to measure what is that diamond like separation between the particles because you have a kind of power law. This is an exponential decay so you can follow this decay pattern and you will be able to guess what is the nanoscale separation between the particles. So, these particles were assumed to be all in air but in reality that is not the case.

In reality your particles will be placed on a substrate. Now when a particle is placed on a substrate there is some effect from the dielectric substrate or the metallic substrate. Let's assume that here that substrate is a dielectric substrate. I will tell you briefly what happens in metallic substrate as well. But here in dielectric substrate when you put a particle close to each other each charge will form an image charge. So, a positive charge will induce a negative charge and negative charge will induce a positive charge.



Substrate effect on LSPR

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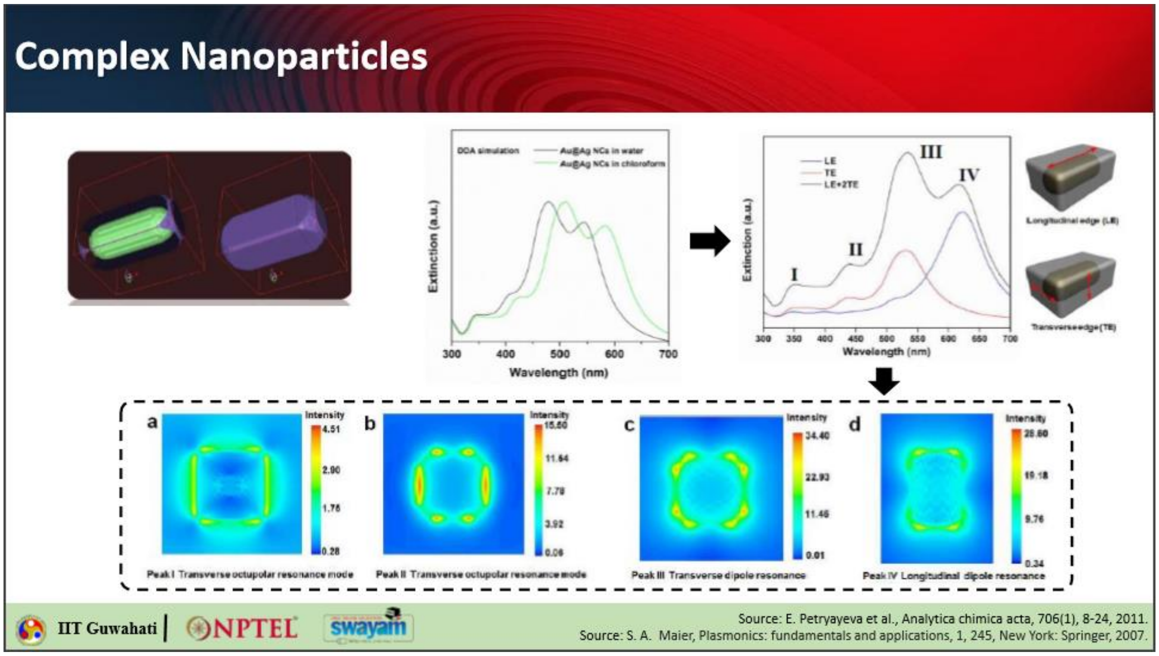
Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So that way there will be a particle and there will be image created inside the substrate. Now if this part is if the particle and its image are very close to each other that will only happen when the particle is placed directly on the substrate or it is placed very close to the substrate you will see that they also start interacting with each other. Now that also depends on the polarization direction of the incident electric field. If electric field is polarized along this direction the coupling will be strong that you have seen right now because this now becomes a dimer again. But if it is along this one that is orthogonal to the dimer axis then the interaction will be weak.

Here also you can see that when it is in air you have more or less uniform electric field on both sides but when you have a dielectric substrate the field is basically confined in this near field zone. So here also you can see that with reduction in size or gap sorry not size gap of the silver nanosphere to a dielectric substrate you are getting much stronger resonance and there is a redshift. And this is a comparison for different size and silica substrate and gold and silver substrate what happens. So, depending on whether it is a dielectric substrate or a metallic substrate the charge image charge formation will be different. Now there can be other complex size nanoparticles possible so something like you know we say gold nanorod coated with silver nanocuboid.

So, this kind of complex rods complex shapes are also possible you can write discrete dipole approximation codes to simulate the extinction property of this one. So here is the property in water and chloroform so there is a distinct shift in the resonance property when there is change in the refractive index. So that is what you can expect that this nanoparticles resonance is very much dependent on the surrounding permittivity. So, they all can actually act as a refractive index sensor. One more other thing is that you can also now do a thorough analysis of these different peak positions you see there are four different peaks.



Complex Nanoparticles

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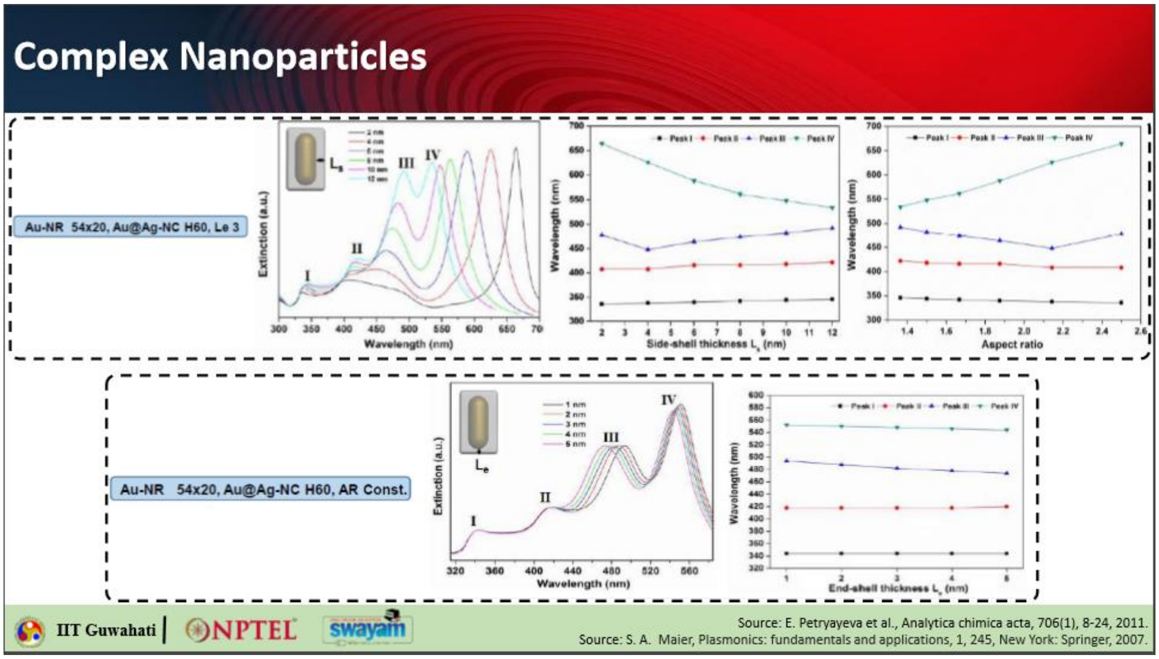
Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, when you see this peak positions you can see that what is basically creating these peaks. So, simulation helps you to understand this because in real life when these nanoparticles are dispersed in solution they some of them may be in this way some of them may be in this way. So, there is a possibility of you to excite the longitudinal mode or the transverse mode. So transverse mode can be in two ways it can be in this direction or this direction but the longitudinal mode is along the length. Now simulation allows you to see that this particular mode is basically coming from the longitudinal elements longitudinal edge excitation and other three modes are basically coming from the transverse excitation and when you add them up they will you will get this one.

So unpolarized light can be assumed to be a combination of this polarization plus this polarization or you can take a weighted average of it because there are two cases of transverse polarization. So, you can make it like LE +2TE by 3 then you can get this kind of a graph. So, this graph reproduces this one that is perfectly fine and if you look into the electric field distribution at 4 this is the case. So, this is the longitudinal dipole this one this is for the 3 peak number 3 this is a transverse dipole.



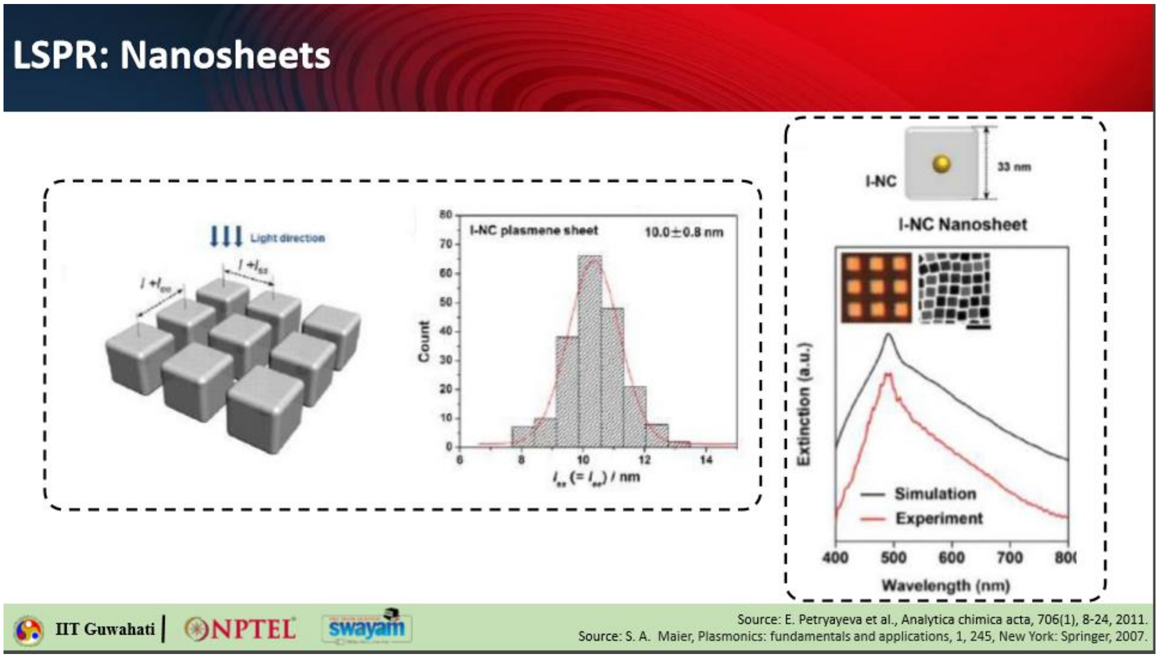
Complex Nanoparticles

Au-NR 54x20, Au@Ag-NC H60, Le 3

Au-NR 54x20, Au@Ag-NC H60, AR Const.

Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Then you are also able to see these are octopolar modes type 1 and type 2. Now quadrupolar mode you will not be able to see because that is basically a dark mode that can only be seen in the absorption spectrum not in the scattering spectrum. Now so this nanoparticles plasmon resonance are also highly tunable depending on differential. So here there are two types of shell thickness one is side shell thickness L_S. So, when you change L_S this is how you can change the resonance peak positions and you can also change Le that is the edge shell thickness. So, you see the overall L_S has got much stronger effect than Le because this actually changes the aspect ratio of the overall structure much significantly than this one because it is already a longitudinal structure.



LSPR: Nanosheets

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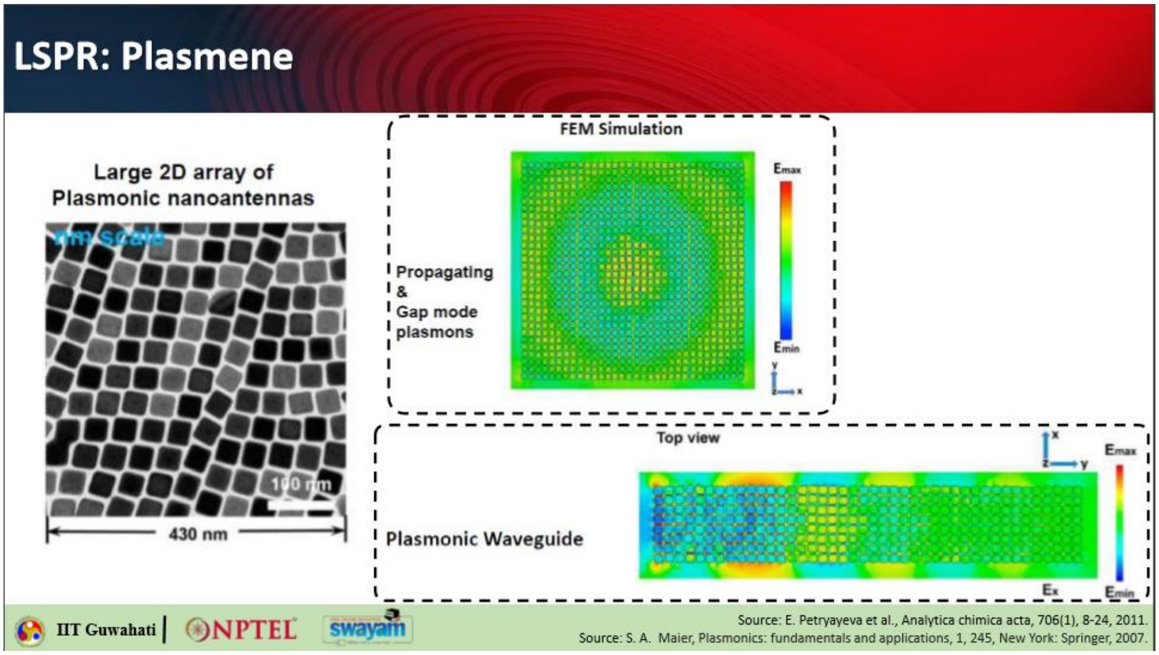
Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Now what to do with this kind of nanoparticles and why do we learn this because if you make a 2D array of nanosheets that we have seen in the previous lecture also in this case let us assume that we are taking a silver nanocuboid and it is basically fabricated using a gold seed at the center. So, you start with a gold nanoparticle seed and then you start depositing silver on top of that and with time more and more silver gets deposited and you get a cubic shape. So, in this case the Lss side to side separation and edge to edge separation are same and when you measure it in an experimental spectrum so these are the actual distribution. So here you see the main gap is around 10 nanometers. So, you can also use a Gaussian kind of distribution to it and you can simulate this kind of nanosheets extinction spectrum through simulation and you will get a very similar kind of a resonance characteristics.

This simulation can be done using DDSCAT or you can use COMSOL or CST any other software numerical simulation tool. Now why it is important because this kind of large 2D array of plasmonic nano antennas can give rise to free surface propagating modes just like graphene has got abundance of surface plus bond propagating on top of it when you can excite it. This also gives you this kind of surface plus bond propagation on the top of the surface of this closely packed you can say plasmonic nano antenna array. So, it's like a sheet. So, this is a sheet of this nice packing of nano antennas and you can get this propagating plus one modes.



LSPR: Plasmene

Large 2D array of Plasmonic nanoantennas

FEM Simulation

Propagating & Gap mode plasmons

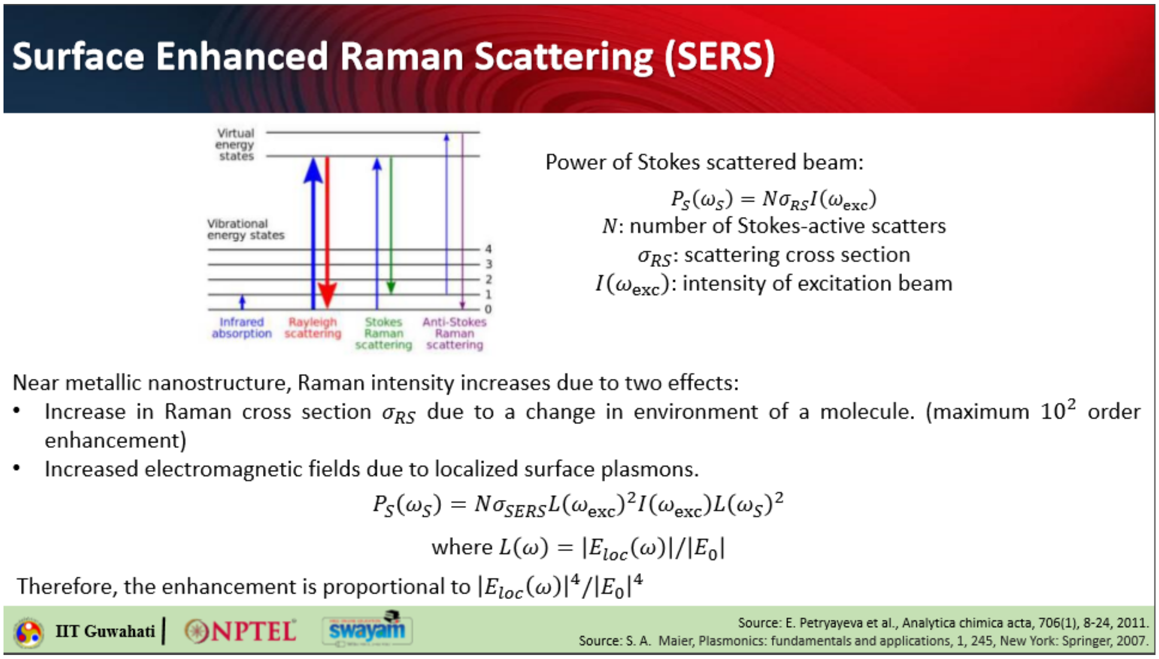
Top view

Plasmonic Waveguide

Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

You can also cut this sheets in form of wave guides and you can find surface plus bond propagation along the edges and along the center of the nano ribbon. So, these are plus mean nano ribbon and plus mean nanosheet. Now why these are important because this plasmonic nanosheets as you can see they have so many so much of region around these nanoparticles which are having very strong local field concentration. So, if you use that for surface enhanced Raman scattering you should be able to sense very tiny amount of molecule. Now coming back to what is surface enhanced Raman scattering you remember the power of Stokes scattered beam.

So this is Rayleigh scattering the same energy comes back. This is Stokes scattering so you jump from here 0th state to the virtual high state and when you come back you don't come back to the 0 state you come back to a higher energy state. So, there is a difference in the energy. So, this is called Stokes Raman scattering. The other case was also possible that you actually jump to the higher state from not 0th state of the ground level or you can you can actually start from first state but when you come back you come back to the 0.



Surface Enhanced Raman Scattering (SERS)

Power of Stokes scattered beam:

$$P_S(\omega_S) = N\sigma_{RS} I(\omega_{\text{exc}})$$

N: number of Stokes-active scatters

σ_{RS}: scattering cross section

$I(\omega_{\text{exc}})$: intensity of excitation beam

Near metallic nanostructure, Raman intensity increases due to two effects:

- Increase in Raman cross section σ_{RS} due to a change in environment of a molecule. (maximum 10^2 order enhancement)
- Increased electromagnetic fields due to localized surface plasmons.

$$P_S(\omega_S) = N\sigma_{SERS} L(\omega_{\text{exc}})^2 I(\omega_{\text{exc}}) L(\omega_S)^2$$

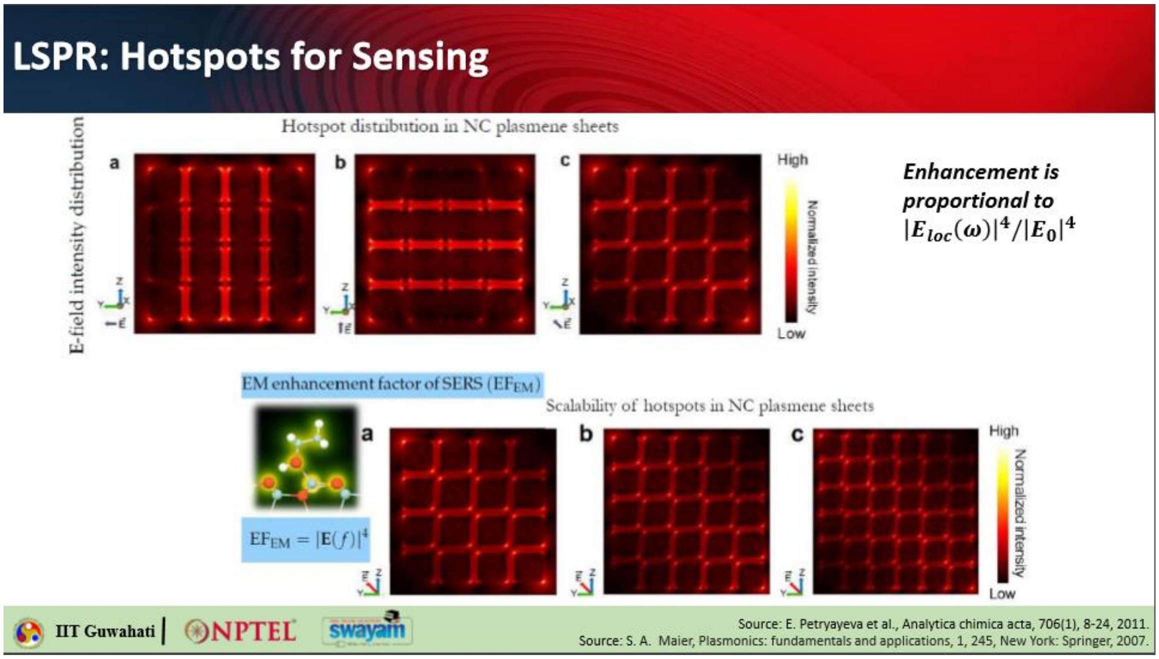
$$\text{where } L(\omega) = |E_{loc}(\omega)|/|E_0|$$

Therefore, the enhancement is proportional to $|E_{loc}(\omega)|^4/|E_0|^4$

Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, you are you are releasing more energy while coming. So, these are different vibrational energy state and this particular case is called Anti-Stokes Raman scattering. So, the power of the Stokes so if you look into the Stokes scattering that is the most common one. So, in that case $P_S(\omega_S)$ is proportional to or you can say $P_S(\omega_S) = N\sigma_{RS} I(\omega_{\text{exc}})$, N is the number of Stokes active scatterers, σ_{RS} is the scattering cross section of that atoms or molecules and $I(\omega_{\text{exc}})$ is the intensity of the excitation beam. Now when you do this experiment or you do this probing of the molecule in the presence of a metallic nanostructure near the nanostructures the Raman intensity this scattering Raman scattering intensity increases dramatically and that happens in because of two things one is the increase in Raman cross section due to change in environment of the molecule that is you can get up to like 10^2 order of enhancement because the particles that scatterers surrounding media now has a metallic particle okay. So, the surrounding environment has changed and the second thing is coming from the increased electromagnetic field due to localized surface plasmon resonance.

Now that plays a very very important role. So now this is the normal case when no nanoparticle is there but this is the case when nanoparticle is present. You can see that two new terms got added up what is $L(\omega)$ this one $L(\omega)$ excitation square okay and $L(\omega_S)^2$, what is this L? L is basically the enhancement factor which is $|E_{loc}(\omega)|/|E_0|$, what is $E_{loc}(\omega)$? There is a localized electric field over the incident electric field. So, you are able to get very strong enhancement and because of this two cases that Raman scattering is maximum when the excitation also matches with the scatterer frequency. So, these two terms can be combined and you will get it to the power of 4. So, the enhancement that happens because of LSPR to the SERS is basically $|E_{\text{loc}}(\omega)|^4/|E_0|^4$.



LSPR: Hotspots for Sensing

Hotspot distribution in NC plasmene sheets

E-field intensity distribution

Enhancement is proportional to $|E_{loc}(\omega)|^4/|E_0|^4$

EM enhancement factor of SERS (EF_{EM})

Scalability of hotspots in NC plasmene sheets

$EF_{EM} = |\mathbf{E}(f)|^4$

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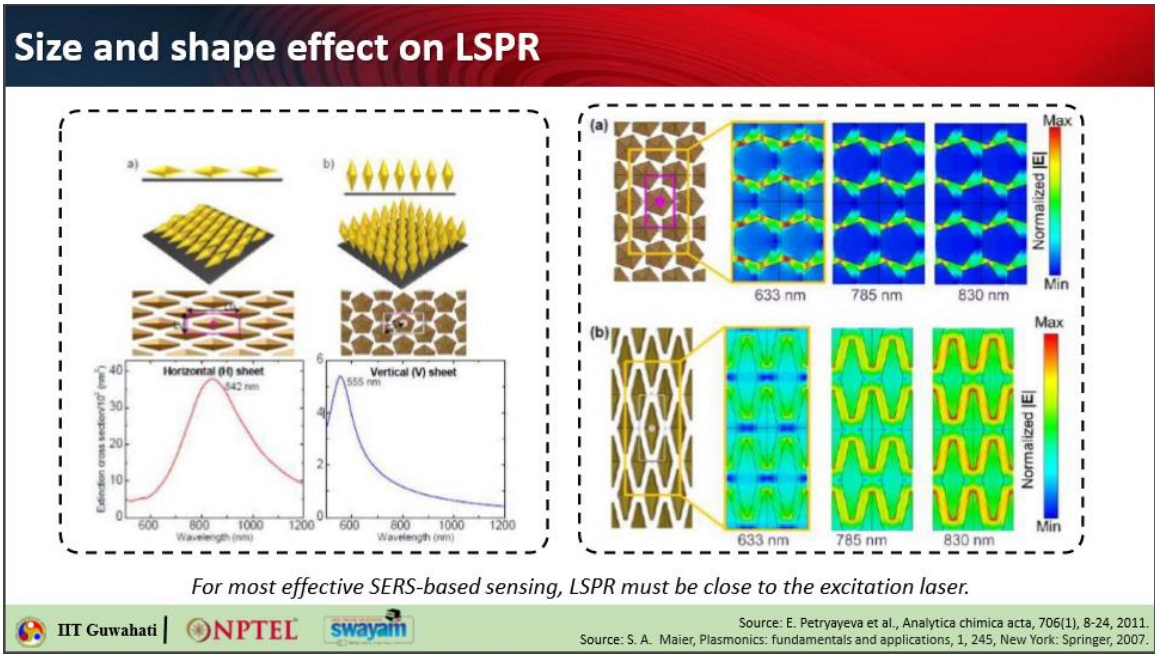
Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So that is how it affects. So now you can see the importance of this plasmon sheet that if you take this plasmon sheet and have electric field polarized along this axis you will feel this all these hotspots. So, you can do sensing very very tiny even femtomolar amount of molecules or you know atoms can be sensed. Similarly, when you have the electric field along this direction vertical direction you actually form the hotspots in the vertical direction and in a case of unpolarized light you can actually have electric field mainly concentrated at the corners of the nanosheet okay. So, they all can be used for sensing. So, enhancement factor is basically dependent on the enhancement of electric field to the power 4.

So that is how this nanosheets are important. These are also scalable. So, you can work with the small area or large area you will get similar effect. There are different effects of size and shape of the nanoparticles participating in this LSPR. So, you can think of this kind of a structure okay. So, these are analog to say liquid crystals when they are forming a horizontal sheet they have a resonance around 842 but when these nanoparticles are all standing up they form a vertical sheet.



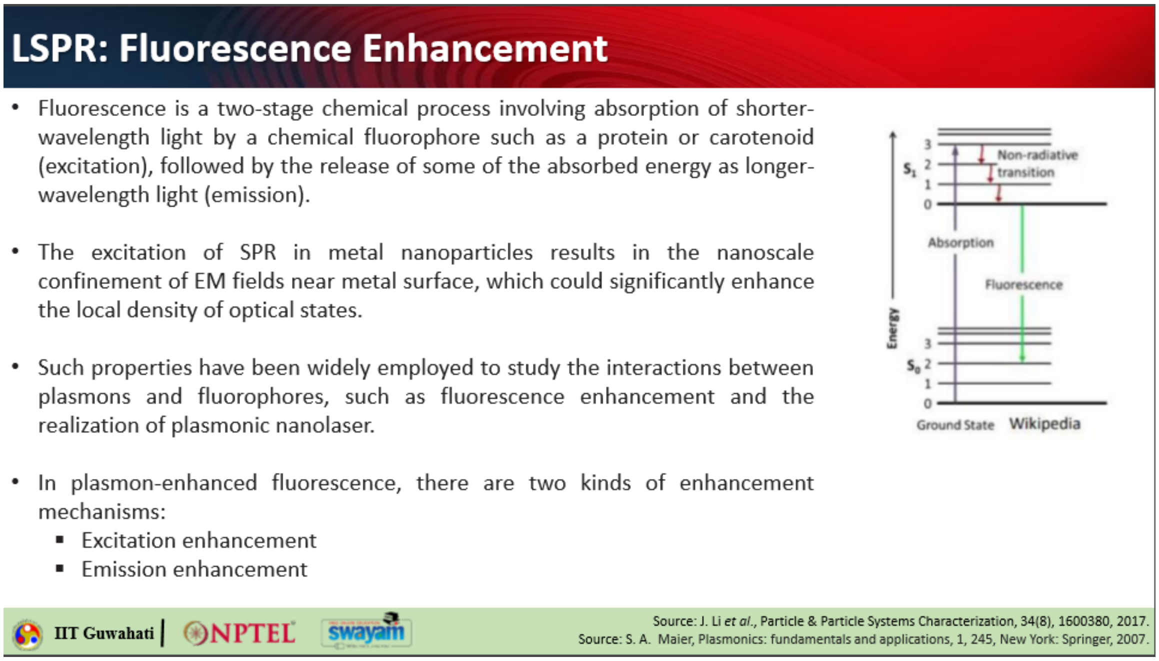
Size and shape effect on LSPR

For most effective SERS-based sensing, LSPR must be close to the excitation laser.

Source: E. Petryayeva et al., Analytica chimica acta, 706(1), 8-24, 2011.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So, you will get a 555 nanometer wavelength. So, what you see here is that for this kind of vertical sheet only at laser wavelength which is close to its resonance you get the strongest electric field. For other cases the electric field in the near vicinity of the particle is not that strong. Similarly, for the horizontal sheet the resonance is at 842 nanometers. So only when the probing laser is close to that resonance wavelength you get the strongest hotspots in between the particles.

Other cases these are not that strong. So always remember for most effective SCRS based sensing the LSPR of the nanoparticle must be close as close as possible to the excitation laser wavelength. Next important application for LSPR is the enhancement in fluorescence. Now what is fluorescence? If you look into Wikipedia for the definition of fluorescence it is basically a two-stage chemical process that involves absorption of a shorter wavelength or higher energy light by a chemical fluorophore which is basically a protein or a carotenoid and followed by the release of some of the absorbed energy as longer wavelength.



LSPR: Fluorescence Enhancement

- Fluorescence is a two-stage chemical process involving absorption of shorter-wavelength light by a chemical fluorophore such as a protein or carotenoid (excitation), followed by the release of some of the absorbed energy as longer-wavelength light (emission).
- The excitation of SPR in metal nanoparticles results in the nanoscale confinement of EM fields near metal surface, which could significantly enhance the local density of optical states.
- Such properties have been widely employed to study the interactions between plasmons and fluorophores, such as fluorescence enhancement and the realization of plasmonic nanolaser.
- In plasmon-enhanced fluorescence, there are two kinds of enhancement mechanisms:
  - Excitation enhancement
  - Emission enhancement

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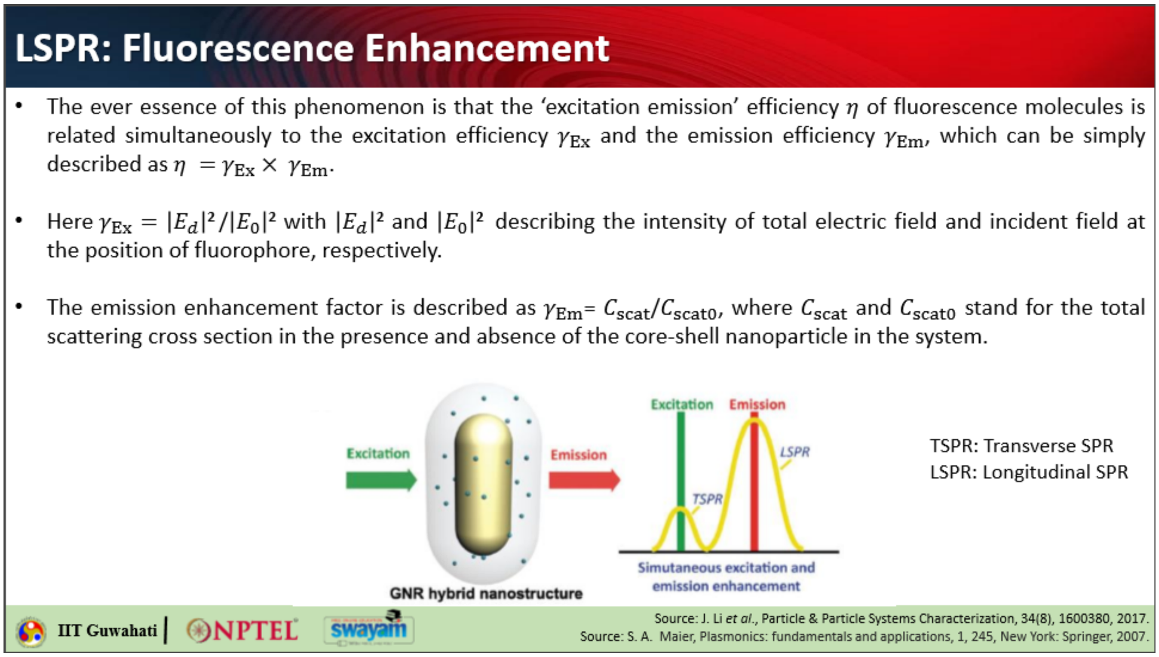
Source: J. Li *et al.*, Particle & Particle Systems Characterization, 34(8), 1600380, 2017.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

Longer wavelength means shorter energy. So, this is where it is giving down shorter energy. So, this is called fluorescence. Now again the excitation of surface plus bond resonance in nanoparticles result in nanoscale confinement of electromagnetic field near the metallic surface and that could significantly enhance the density or local density of optical states. So that will also allow you to improve the fluorescence effect. So, such properties are widely employed to study the interaction between plasmons and fluorophores such as fluorescence enhancement and the realization of plasmonic nanolaser. So, in plasmon enhanced fluorescence there are two kinds of important mechanism or you can say enhancement mechanism one is excitation enhancement and other is emission enhancement.

So how it works you can see here that the ever essence of this phenomena is that the excitation emission efficiency η of the fluorescence molecule is related simultaneously to the excitation efficiency which is γ_{Ex} and the emission efficiency which is γ_{Em} . So η can be written as $\gamma_{\mathrm{Ex}} \times \gamma_{\mathrm{Em}}$. Now what is γ_{Ex} ? γ_{Ex} basically is the ratio of the electric field intensity in the of the total field over the incident field in the position of the fluorophore and what is γ_{Em} ? That is basically the scattering cross section ratio of scattering cross section in the presence and absence of the metallic nanoparticle.



LSPR: Fluorescence Enhancement

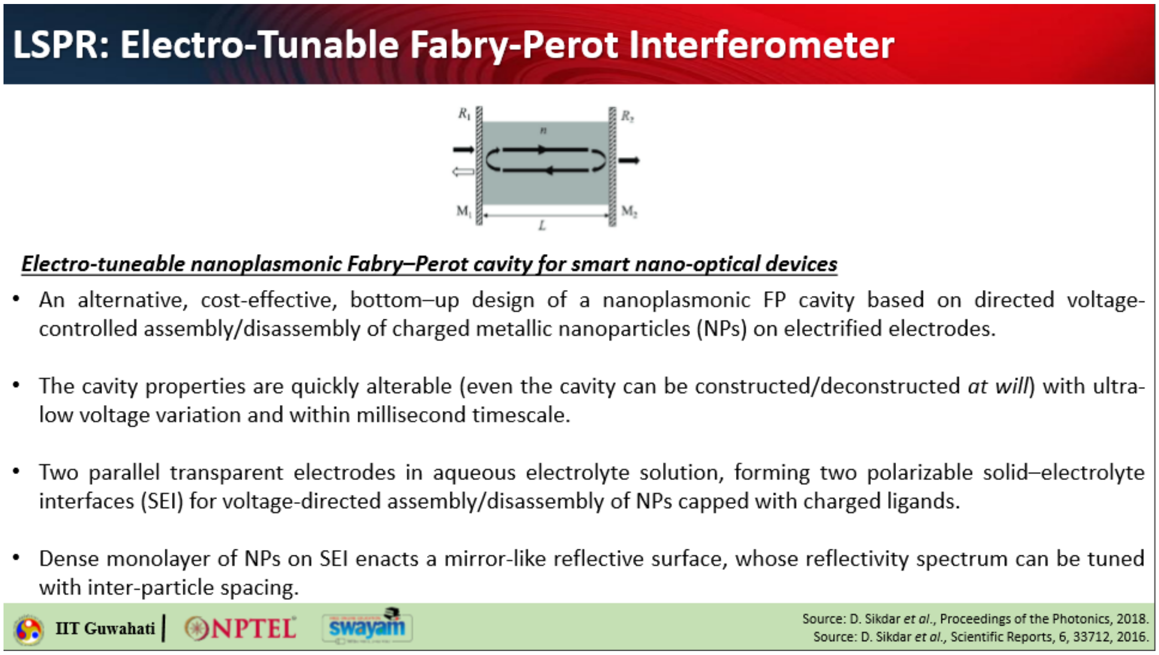
- The ever essence of this phenomenon is that the 'excitation emission' efficiency η of fluorescence molecules is related simultaneously to the excitation efficiency γ_{Ex} and the emission efficiency γ_{Em}, which can be simply described as $\eta = \gamma_{\mathrm{Ex}} \times \gamma_{\mathrm{Em}}$.
- Here $\gamma_{\mathrm{Ex}} = |E_d|^2/|E_0|^2$ with $|E_d|^2$ and $|E_0|^2$ describing the intensity of total electric field and incident field at the position of fluorophore, respectively.
- The emission enhancement factor is described as $\gamma_{\mathrm{Em}} = C_{\mathrm{scat}}/C_{\mathrm{scat0}}$, where C_{scat} and C_{scat0} stand for the total scattering cross section in the presence and absence of the core-shell nanoparticle in the system.

TSPR: Transverse SPR
LSPR: Longitudinal SPR

Source: J. Li *et al.*, Particle & Particle Systems Characterization, 34(8), 1600380, 2017.
Source: S. A. Maier, Plasmonics: fundamentals and applications, 1, 245, New York: Springer, 2007.

So that way you are able to boost up this particular η by boosting both these two. So, there is one particular example in this paper where they have used a gold nanorod and they have used the excitation the transverse excitation to match with the excitation wavelength so that is where they got one resonance and they have also got the longitudinal surface plus bond resonance to match the emission wavelength. So, this is how they were able to boost up both and that has dramatically boosted the efficiency of you know fluorescence. So that is eta was boosted by double impact on excitation efficiency as well as emission efficiency. Prior to this paper what people used to do? People used to either boost up this one using one nanoparticle LSPR or either this one or this one or worst case to get a compromised not worst case I should say to get a compromised optimum they used to choose a LSPR which is in the middle of these two wavelengths. But in this particular paper they found a way to excite both from the same particle because they were able to excite when you put unpolarized light on this particle both this and this will be excited right because transverse and longitudinal both plus bonds will be excited so you will get boost in both these two efficiencies.

So that was one very good example of using nanoparticles for fluorescence enhancement. Next we move on to some examples of using nanoparticles or LSPR in electro tunable Fabry-Perot interferometer. Now what is the Fabry-Perot interferometer? You must have known this. This is basically cavity from between two mirrors there is a dielectric media in between which is having a permittivity of n and this is the length L of the cavity. So once some light enters this cavity it goes through multiple like reflections and only those light which only those wavelength which satisfies the constructive interference condition that is a round trip phase should be indicated multiple of 2π they are able to come out of this others other wavelengths will get cancelled.



LSPR: Electro-Tunable Fabry-Perot Interferometer

Electro-tuneable nanoplasmonic Fabry–Perot cavity for smart nano-optical devices

- An alternative, cost-effective, bottom–up design of a nanoplasmonic FP cavity based on directed voltage-controlled assembly/disassembly of charged metallic nanoparticles (NPs) on electrified electrodes.
- The cavity properties are quickly alterable (even the cavity can be constructed/deconstructed *at will*) with ultra-low voltage variation and within millisecond timescale.
- Two parallel transparent electrodes in aqueous electrolyte solution, forming two polarizable solid–electrolyte interfaces (SEI) for voltage-directed assembly/disassembly of NPs capped with charged ligands.
- Dense monolayer of NPs on SEI enacts a mirror-like reflective surface, whose reflectivity spectrum can be tuned with inter-particle spacing.

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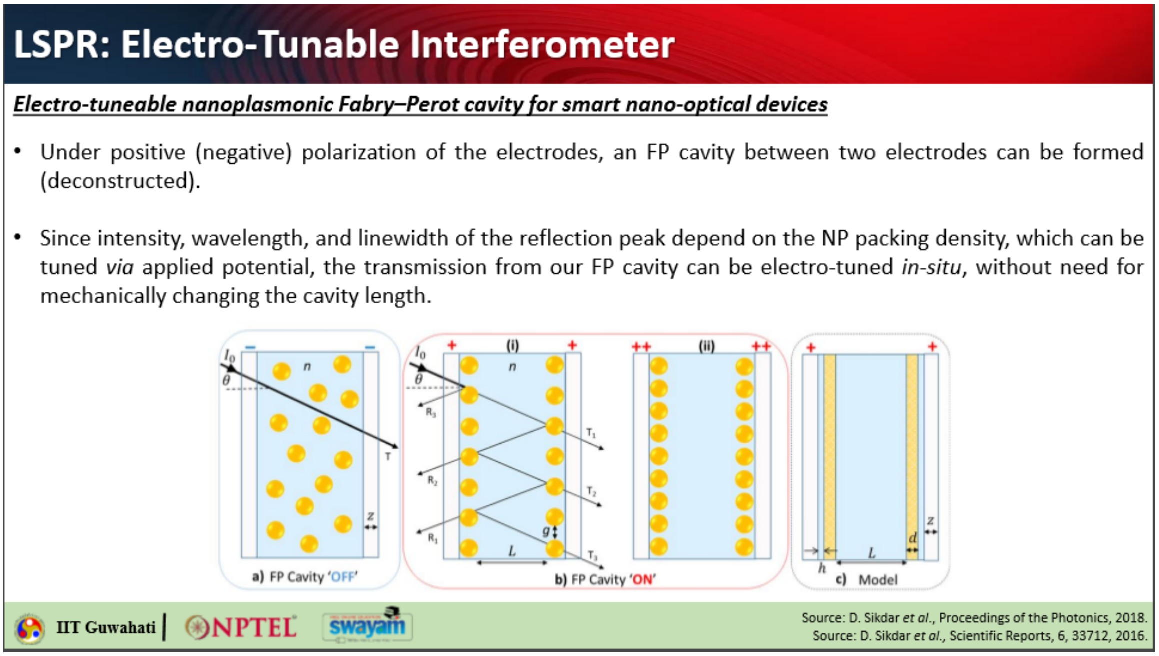
Source: D. Sikdar *et al.*, Proceedings of the Photonics, 2018.
Source: D. Sikdar *et al.*, Scientific Reports, 6, 33712, 2016.

So, you actually send a broadband light you will get a single narrow transmission peak. So, this is how Fabry-Perot interferometer can be used as a selective transmission filter. Now how do you change the transmission wavelength? Either you have to mechanically adjust the length of this cavity or you have to physically change the cavity medium n then this particular transmission wavelength will change. Now nanoparticle based solutions or plasmonic nanoparticle solutions allow you to achieve an electro tunable Fabry-Perot interferometer cavity. So, what you can do I will quickly go to the structure. So, you can use two metallic electrodes transparent metallic electrodes like ITO and you can use an aqueous solution or water solution filled with gold nanoparticles which are having negatively charged they are having some kind of ligands associated which keep them negatively charged.



LSPR: Electro-Tunable Interferometer

Electro-tuneable nanoplasmonic Fabry–Perot cavity for smart nano-optical devices

- Under positive (negative) polarization of the electrodes, an FP cavity between two electrodes can be formed (deconstructed).
- Since intensity, wavelength, and linewidth of the reflection peak depend on the NP packing density, which can be tuned *via* applied potential, the transmission from our FP cavity can be electro-tuned *in-situ*, without need for mechanically changing the cavity length.

a) FP Cavity 'OFF'

b) FP Cavity 'ON'

c) Model

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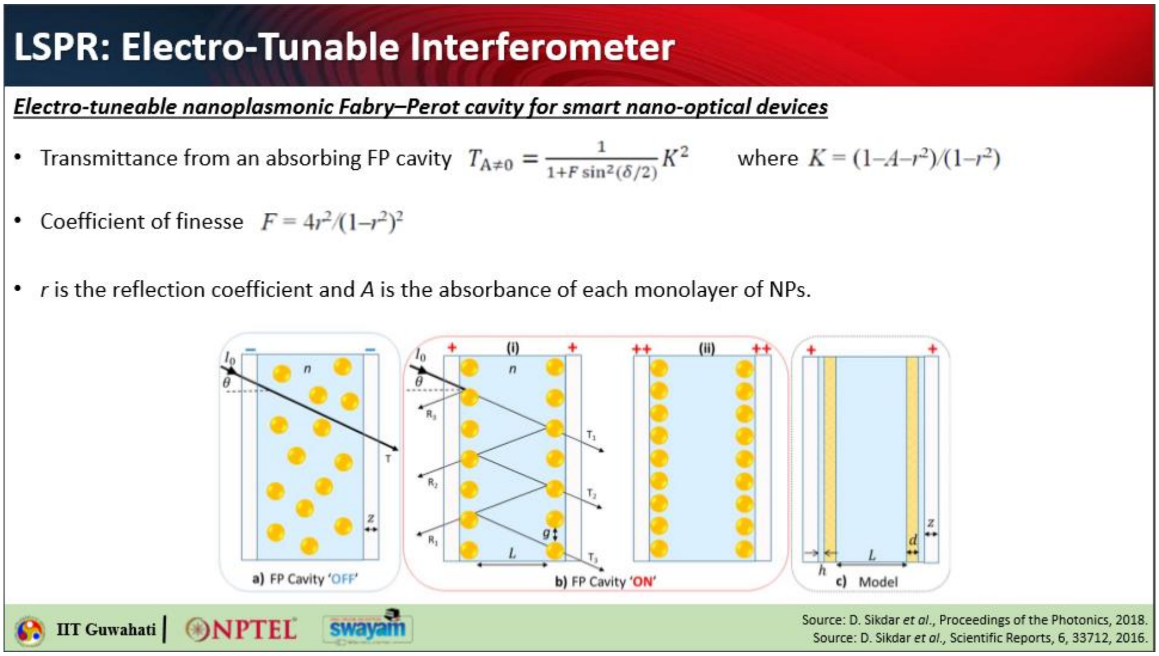
Source: D. Sikdar *et al.*, Proceedings of the Photonics, 2018.
Source: D. Sikdar *et al.*, Scientific Reports, 6, 33712, 2016.

Now when your electrodes are negatively charged nanoparticles are also negatively charged they repel each other so nanoparticles will be in the solution in the cavity itself but light can simply enter and reflect some part will get absorbed. But as soon as you make the electrodes positively charged what will happen this negative nanoparticle negatively charged nanoparticles will come and assemble on top of this electrodes and they will start forming an array 2D array and as they keep on getting denser and denser the reflectivity of the 2D array will get stronger and that is the reason why I have shown those kind of 2D assembly. So here also you are able to pack a very dense assembly of particles 2D sheet of particles and they form like mirrors. So, these are basically electrically tunable mirrors and using this you can change what should be the transmission wavelength. So, one thing I forgot to mention here is that other than this one and this one the third method is to change the reflectivity R_1 and R_2 of the Fabry-Perot interferometer.



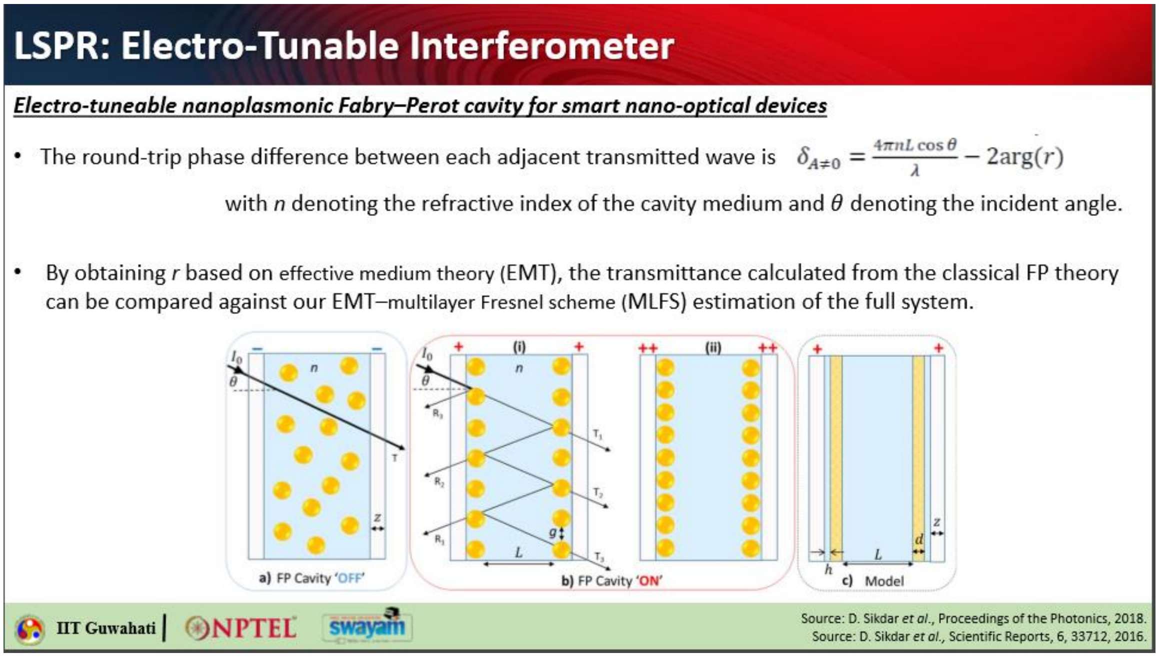
LSPR: Electro-Tunable Interferometer

Electro-tuneable nanoplasmonic Fabry–Perot cavity for smart nano-optical devices

- Transmittance from an absorbing FP cavity $T_{A\neq 0} = \frac{1}{1+F\sin^2(\delta/2)}K^2$ where $K = (1–A–r^2)/(1–r^2)$
- Coefficient of finesse $F = 4r^2/(1–r^2)^2$
- r is the reflection coefficient and A is the absorbance of each monolayer of NPs.

Source: D. Sikdar *et al.*, Proceedings of the Photonics, 2018.
Source: D. Sikdar *et al.*, Scientific Reports, 6, 33712, 2016.

So, in this particular case we are using nanoparticles to change R_1 and R_2 of the mirrors that also allows you to change the reflectivity. So, this is the transmittance formula T when absorption in the cavity is non-zero so you have $\frac{1}{1+F\sin^2(\delta/2)}K^2$, Now what is K? $K = (1 - A - r^2)/(1 - r^2)$, where A is the absorption and r is basically the reflection coefficient of this mirrors we are taking identical mirrors. And capital F is the coefficient of fineness that can be calculated like this. So, what is important here to see that by changing the voltage you are able to bring more nanoparticles and that will allow you to build a mirror with tunable reflectivity. So, this is one of my research work which has been published long back and with that I will show you some of the results.



LSPR: Electro-Tunable Interferometer

Electro-tuneable nanoplasmonic Fabry–Perot cavity for smart nano-optical devices

- The round-trip phase difference between each adjacent transmitted wave is $\delta_{A\neq0} = \frac{4\pi nL\cos\theta}{\lambda} - 2\arg(r)$ with n denoting the refractive index of the cavity medium and θ denoting the incident angle.
- By obtaining r based on effective medium theory (EMT), the transmittance calculated from the classical FP theory can be compared against our EMT–multilayer Fresnel scheme (MLFS) estimation of the full system.

a) FP Cavity 'OFF'

b) FP Cavity 'ON'

c) Model

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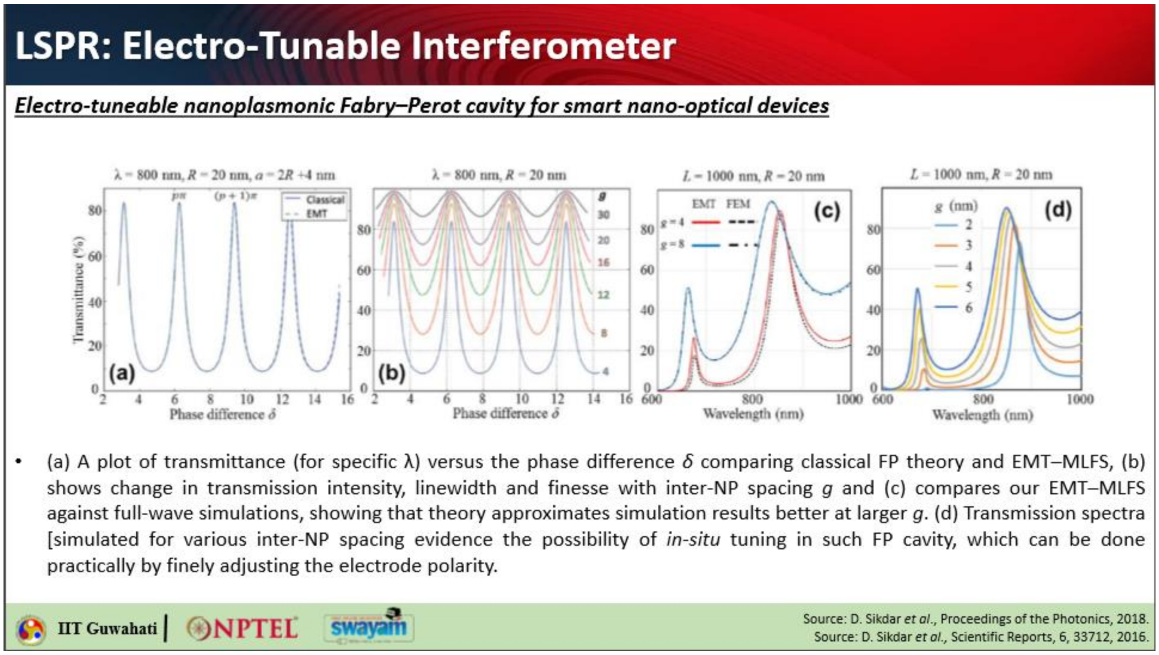
Source: D. Sikdar *et al.*, Proceedings of the Photonics, 2018.
Source: D. Sikdar *et al.*, Scientific Reports, 6, 33712, 2016.

So here the δ which is the round trip phase difference that also can be seen is basically a function of r. So, by changing r you are able to change this one as well. So, when you compare this with here you see this is the plot of the transmittance for a specific lambda so I am taking 800 nanometers. Nanoparticle size is chosen to be 20 nanometer these are gold nanoparticles and a is the lattice spacing which is $2r$ +a that is the gap, $2r$ is the diameter plus a $4r$, 4 is the gap between this particle surface to surface gap. So, when you do this you are able to match the effective medium theory calculations with classical Fabry-Pérot interferometer cavity and you are able to see that you are getting peaks, peak transmittance at integral multiple of π.

So, at $p\pi$, $(p+1)\pi$, $(p+2)\pi$ or $(p-1)\pi$, you are able to get the transmittance. So, these are the cases where your phase round trip phase is getting integral multiple of 2π. So, these are look at b so here what is the difference here lambda is same the particle radius is same but the gap between the particles are changing. So, gap between the particles changing means what the coupling between the particles will change so the overall reflectivity of that surface that is created by this array of particles will also change. So here you can see this is for g equals 30 means the gap between the particles is 30 then 20, 16, 12, 8 and 4. So as you can see when it is 4 means the particles are very close to each other you can see very strong effect of this resonance Fabry-Pérot interferometer cavity resonance and that is how you get a very high quality factor.

But as you keep on increasing the gap between the particles the mirrors are becoming weaker mirror reflectivity is getting down so your cavity quality factor is also coming down. But this does not actually show you the wavelength tunability yet. Let me show you that as well. So here you get g = 4, g = 8 so this is the wavelength tunability here you can see.



LSPR: Electro-Tunable Interferometer

Electro-tuneable nanoplasmonic Fabry–Perot cavity for smart nano-optical devices

- (a) A plot of transmittance (for specific λ) versus the phase difference *δ* comparing classical FP theory and EMT–MLFS, (b) shows change in transmission intensity, linewidth and finesse with inter-NP spacing *g* and (c) compares our EMT–MLFS against full-wave simulations, showing that theory approximates simulation results better at larger *g*. (d) Transmission spectra [simulated for various inter-NP spacing evidence the possibility of *in-situ* tuning in such FP cavity, which can be done practically by finely adjusting the electrode polarity.

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Source: D. Sikdar *et al.*, Proceedings of the Photonics, 2018.
Source: D. Sikdar *et al.*, Scientific Reports, 6, 33712, 2016.

The cavity length is fixed nanoparticle size is fixed cavity length is 1000 nanometer that is 1 micron. So, you can change the nanoparticle sizes from 4 gap between the nanoparticles from 4 nanometers to 8 nanometers you can see you are able to move from here to here. You can also see a linear scaling like 2, 3, 4, 5, 6 this is the way you change the gap so you are also able to continuously tune the transmittance peak. Though the peak transmittance value also reduces because that is a kind of price you will pay with this particular cavity because when the mirror quality comes down so the quality factor also gets affected as we have seen here. That the wavelength selectivity or wavelength tunability is continuous with this particular different gaps. So how you can change? You can change the potential on the electrodes and that will give you electrically tunable Fabry-Perot interferometer cavity.

So these are just examples of one or two tunable optical devices that we can make using this. So, if you are interested in much more of this kind of electrically tunable LSPR based devices or their applications you want to know more you can always discuss with me by dropping an email to this particular email address. So here we will stop. Thank you.