PH 673
Nano

Lecture #6

Plasmon resonances in small metallic objects

Consider wave equation $\Rightarrow$

$$\left(\vec{\nabla}^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{E}(\vec{r},t) = 0 \Rightarrow \vec{E}(\vec{r},t) = \vec{E}(\vec{r})T(t)$$

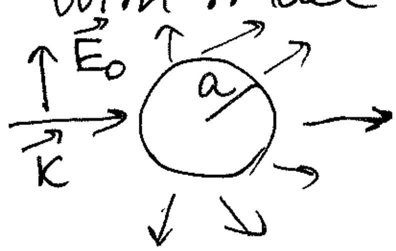
$$\underbrace{\frac{\vec{\nabla}^2\vec{E}(\vec{r})}{\vec{E}(\vec{r})}}_{\parallel \atop -k^2} = \underbrace{\frac{1}{c^2}\frac{\ddot{T}(t)}{T(t)}}_{=} \Rightarrow \vec{\nabla}^2\vec{E} + k^2\vec{E} = 0$$

Helmholtz equation

$$\ddot{T} + \omega^2 T = 0$$

$$k = \frac{\omega}{c}$$

Consider interaction with small particles $\Rightarrow$ if $a \ll \lambda \Rightarrow$ use quasi-static approximation



electric dipole approximation $\Rightarrow \vec{k}\cdot\vec{r} \ll 1$

neglect retardation effects

instead of Helmholtz equation can solve Laplace equation $\vec{\nabla}^2 V = 0$

For spherical particles $\Rightarrow$

$$\nabla^2 = \frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \right.$$

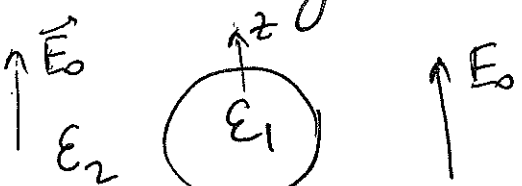
$$\left. + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

General solution $\Rightarrow$

$$V(r,\theta) = \sum_{l=0}^{\infty}\left(A_l r^l + \frac{B_l}{r^{l+1}}\right)P_l(\cos\theta)$$

azimuthal symmetry

Boundary conditions:



$V_{in} = V_{out}$ at $r=a$

$$\varepsilon_1 \frac{\partial V_{in}}{\partial r} = \varepsilon_2 \frac{\partial V_{out}}{\partial r} \text{ at } r=a$$

asymptotics: $V_{out} \to -E_0 \underbrace{z}_{r\cos\theta}$ at $r\to\infty$

(note: $V_{out} = \underbrace{V_0}_{\text{due to forward-propagating wave}} + \underbrace{V_{scatt}}_{\text{due to scattering}}$)

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

$$V_{out} = -E_0 r\cos\theta + \sum_{l=0}^{\infty}\frac{B_l}{r^{l+1}}P_l(\cos\theta)$$

$r=a$: $\displaystyle\sum_{l=0}^{\infty} A_l a^l P_l(\cos\theta) = -E_0 a\cos\theta + \sum_{l=0}^{\infty}\frac{B_l}{a^{l+1}}P_l(\cos\theta)$

recall: $P_1(\cos\theta) = \cos\theta \Rightarrow$

$$\left.\begin{aligned} l=1 &\Rightarrow A_1 a = -E_0 a + \frac{B_1}{a^2} \\ l\neq 1 &\Rightarrow A_l a^l = \frac{B_l}{a^{l+1}} \end{aligned}\right\} \quad (1)$$

$$\Rightarrow B_l = A_l a^{2l+1}$$

Also: (at $r=a$) $\Rightarrow$

$$\varepsilon_1 \sum A_\ell \, \ell \, a^{\ell-1} P_\ell(\cos\theta) = \left[-E_0\cos\theta - \sum \frac{B_\ell}{a^{\ell+2}} \cdot (\ell+1) P_\ell(\cos\theta)\right]\varepsilon_2 \Rightarrow$$

$$\left.\begin{aligned} &\ell = 1 \Rightarrow \varepsilon_1 A_1 = -\varepsilon_2\left[E_0 + \frac{B_1}{a^3}\cdot 2\right] \\ &\ell \neq 1 \Rightarrow \varepsilon_1 A_\ell \, \ell \, a^{\ell-1} = -\frac{B_\ell}{a^{\ell+2}}(\ell+1)\,\varepsilon_2 \end{aligned}\right] \quad 2$$

Look at 1 & 2 $\Rightarrow$

$$\ell \neq 1 \Rightarrow \varepsilon_1 A_\ell \, \ell \, a^{\ell-1} = -\frac{A_\ell a^{2\ell+1}}{a^{\ell+2}}(\ell+1)\varepsilon_2 =$$

$= -A_\ell a^{\ell-1}(\ell+1)\varepsilon_2 \rightarrow$ can't be satisfied unless $A_\ell = 0$ $(\ell \neq 1)$

$$A_\ell = 0 \Downarrow B_\ell = 0$$

For $\ell = 1 \Rightarrow$

$$\begin{array}{cc} A_1 & B_1 \end{array}$$

$$\begin{bmatrix} a & -\frac{1}{a^2} \\ \varepsilon_1 & +\frac{2\varepsilon_2}{a^3} \end{bmatrix} \begin{bmatrix} A_1 \\ B_1 \end{bmatrix} = \begin{bmatrix} -E_0 a \\ -\varepsilon_2 E_0 \end{bmatrix} \Rightarrow$$

$$\Delta = +\frac{2\varepsilon_2}{a^2} + \frac{\varepsilon_1}{a^2}; \quad \Delta_{A_1} = \begin{vmatrix} -E_0 a & -\frac{1}{a^2} \\ -\varepsilon_2 E_0 & +\frac{2\varepsilon_2}{a^3} \end{vmatrix} = -\frac{2\varepsilon_2 E_0}{a^2} - \frac{\varepsilon_2 E_0}{a^2} = \frac{\varepsilon_2 E_0}{a^2}(-3)$$

$$A_1 = -\frac{3\varepsilon_2 E_0}{\cancel{a^2}} \frac{\cancel{a^2}}{\varepsilon_1 + 2\varepsilon_2} = -\frac{3\varepsilon_2 E_0}{\varepsilon_1 + 2\varepsilon_2}$$

$$B_1 = E_0 a(\varepsilon_1 - \varepsilon_2) \cdot \frac{a^2}{\varepsilon_1 + 2\varepsilon_2} = E_0 a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$$

$$\Delta_{B_1} = \begin{bmatrix} a & -E_0 a \\ \varepsilon_1 & -\varepsilon_2 E_0 \end{bmatrix} = (\varepsilon_1 - \varepsilon_2) \cdot E_0 a$$

So, $V_{in} = A_1 r\cos\theta = -\frac{3\varepsilon_2 E_0}{\varepsilon_1 + 2\varepsilon_2} \underbrace{r\cos\theta}_{= z}$ (4)

$$V_{out} = -E_0 r\cos\theta + \underbrace{E_0 a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{\cos\theta}{r^2}}$$

$\Downarrow$ $\vec{E} = -\vec{\nabla} V$

due to scattering; $\vec{V}_{dipole} = \frac{1}{4\pi\varepsilon_2} \frac{\vec{\mu}\cdot\hat{r}}{r^2}$

$$\vec{E}_{in} = \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}\vec{E}_0 \; ; \quad \vec{E}_{out} = \vec{E}_0 + \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{a^3}{r^3}\right) E_0 \cdot (2\vec{n}_r \cos\theta + \vec{n}_\theta \sin\theta)$$

show!

$$\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 = \frac{\alpha(\omega)}{4\pi\varepsilon_0}$$

polarizability

Note: • $\mathrm{Re}\,\varepsilon_1 = -2\varepsilon_2 \Rightarrow$ resonance!

• $\frac{1}{r^3}$ dependence in the scattering

• $E_{scatt} \Rightarrow$ as if due to induced dipole $\vec{\mu} = \varepsilon_2 \alpha(\omega) \vec{E}_0$

Also: $a < d = \frac{\lambda}{4\pi\sqrt{\varepsilon_1}}$ ← skin depth

What do we measure? $\Rightarrow$

scattering cross-section $\Rightarrow \sigma_{scatt} = \left(\frac{\omega}{c}\right)^4 \left(\frac{1}{6\pi\varepsilon_0^2}\right) n^4 |\alpha(\omega)|^2 \sim a^6$

refr. index of the surrounding; $n^4 = \varepsilon_2^2$

dominates in larger particles

absorption cross-section

$$\Rightarrow \sigma_{abs} = \frac{\omega}{c\varepsilon_0} n\, \mathrm{Im}\,\alpha(\omega) \sim a^3$$

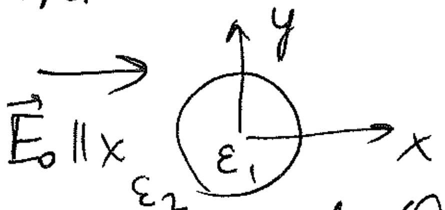
extinction = absorption + scattering $\Longrightarrow$ dominates in smaller particles

· Transition between two regimes (scattering vs absorption dominating) $\Rightarrow$ distinct color charge $\Leftarrow$ Lycurgus cup! 5

Au: small particles absorb green & blue $\Rightarrow$ render red color
large particles scatter green $\Rightarrow$ render green color

What if we charge geometry? $\Rightarrow$

e.g. thin metal wire (long $\parallel z$)



$\Rightarrow$ use polar coordinates

$$\vec{\nabla}^2 V = 0 \Rightarrow \frac{1}{\rho}\left(\frac{\partial}{\partial \rho}\left(\rho \frac{\partial V}{\partial \rho}\right)\right) + \frac{1}{\rho^2}\frac{\partial^2 V}{\partial \varphi^2} = 0;$$

$$V(\rho,\varphi) = R(\rho)\Phi(\varphi) \Rightarrow \frac{1}{R}\left(\rho \frac{\partial}{\partial \rho}\left(\rho \frac{dR}{d\rho}\right)\right) =$$

$$= -\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = m^2$$

work through and show

$$\vec{E}_{in} = \frac{2\varepsilon_2}{\varepsilon_1+\varepsilon_2}\vec{E}_0 \; ; \; \vec{E}_{out} = \vec{E}_0 + E_0 \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{a^2}{\rho^2} \cdot$$

$$\cdot (1-2\sin^2\varphi)\vec{n}_x + 2E_0\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\frac{a^2}{\rho^2}\sin\varphi\cos\varphi\,\vec{n}_y \Rightarrow$$

fields diverge when $\boxed{\mathrm{Re}\,\varepsilon_1(\omega) = -\varepsilon_2}$

(also note $\frac{1}{\rho^2}$ dependence vs $\frac{1}{r^3}$ in spherical case)