PH 673
Nano

Lecture #5

Optical properties of metals and metallic nanoparticles & nano-structures

First bulk metal

- optical properties can be described by a complex dielectric function $\mathcal{E}(\omega)$ ← frequency of light

$$\mathcal{E}(\omega) = 1 + \chi_e(\omega), \quad \vec{D}(\omega) = \varepsilon_0 \mathcal{E}(\omega) \vec{E}(\omega) = \varepsilon_0 E(\omega) + \underbrace{\vec{P}(\omega)}_{= \varepsilon_0 \chi_e(\omega) \vec{E}(\omega)}$$

$\vec{P} = ne\vec{r}$, n ← # electrons per unit volume

- conduction electrons move freely in the bulk
- interband excitations can happen at $E_{photon} > E_g$

Drude - Sommerfeld theory ⇒ free-electron gas ⇒

$$m_e \ddot{\vec{r}} + m_e \underbrace{\Gamma}_{= \frac{v_F}{l}} \dot{\vec{r}} = e\vec{E}_0 e^{-i\omega t} \Rightarrow \vec{r}(t) = \vec{r}_0 e^{-i\omega t} \text{ (ansatz)}$$

$\vec{E}_0$ ← light field

v_F ← Fermi velocity

l ← mean free path between scattering events

⇓ find $\vec{r}$ ⇒ find $\mathcal{E}_{Drude}$ ⇒

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} = \text{, where}$$

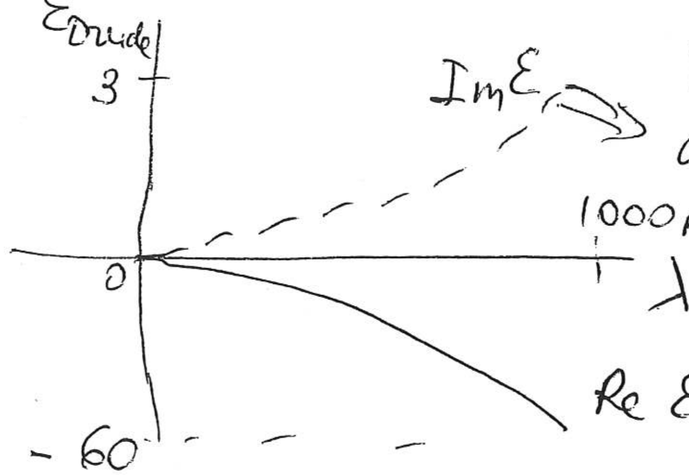
$$= 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i\frac{\Gamma\omega_p^2}{\omega(\omega^2+\Gamma^2)}$$

$$\omega_p = \sqrt{\frac{n e^2}{m_e \varepsilon_0}}$$

↑ volume plasma frequency

For example, for Au: $\omega_p = 13{,}8 \cdot 10^{15}\, s^{-1}$ ← 136,5 nm

$\Rightarrow \Gamma = 1{,}075 \cdot 10^{14}\, s^{-1}$



⇒ dissipation of energy due to motion of electrons in the metal

Re ε ← negative ⇒ light can penetrate only to a very small extent since

$n = \sqrt{\varepsilon}$

Drude - Sommerfeld

⇒ good for IR, but

for shorter λ's ⇒ need to account for bound electrons

< 550 nm in Au ↖ measured Im ε ↑ much more sharply than predicted by Drude - Sommerfeld

Bound electrons in metals exist e.g. in lower-lying shells of metal atoms ⇒

$$m\ddot{\vec{r}} + m\gamma\dot{\vec{r}} + \underline{\alpha\vec{r}} = e\vec{E}_0 e^{-i\omega t} \Rightarrow \vec{r}(t) \Rightarrow \varepsilon(\omega)_{interband}$$

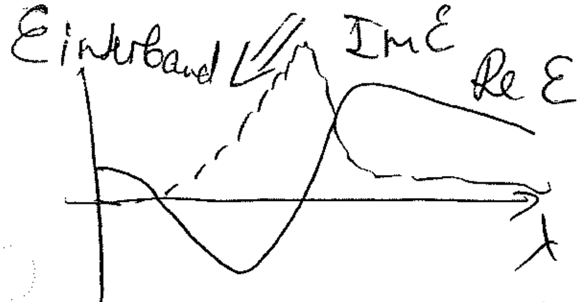
↑ radiative damping for bound electrons ↖ restoring force

$$\varepsilon_{\text{interband}}(\omega) = 1 + \frac{\widetilde{\omega}_p^2}{(\omega_0^2-\omega^2) - i\gamma\omega} = ,$$

where $\widetilde{\omega}_p = \sqrt{\frac{\tilde{n}e^2}{m\varepsilon_0}}$, $\tilde{n}$ - density of bound electrons

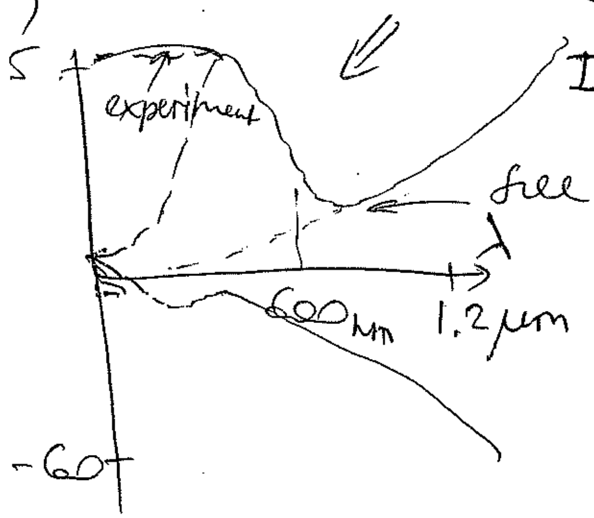
$$\omega_0 = \sqrt{\frac{\alpha}{m}}$$

$$= 1 + \frac{\widetilde{\omega}_p^2(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} + i\frac{\gamma\widetilde{\omega}_p^2\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}$$



$\widetilde{\omega}_p = 4.5\cdot 10^{15}\,s^{-1}$
$\gamma = 9\cdot 10^{14}\,s^{-1}$
$\omega_0 = \frac{2\pi c}{\lambda}$, $\lambda = 450\,nm$

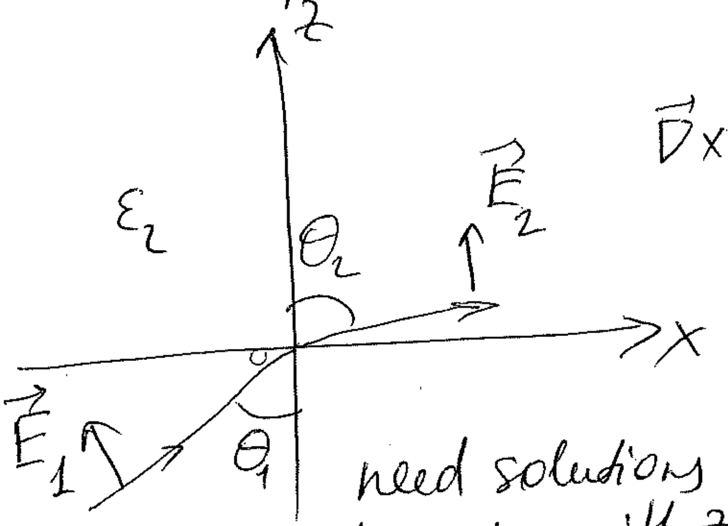
So, need to add ε_{free} and ε_{bound} contributions



Note: for Au, single interband transition is not enough to reproduce experiment at < 500 nm

Surface plasmon polaritons (SPPs)

Surface plasmons ← quanta of surface charge density oscillations



need solutions decaying with z

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E} - \left(\frac{\omega}{c}\right)^2 \varepsilon \vec{E} = 0$$

$$\vec{E}_{1,2} = \begin{pmatrix} E_{1,2x} \\ 0 \\ E_{1,2z} \end{pmatrix} e^{i(k_x x - \omega t)} \cdot e^{i k_{1,2} z}$$

Boundary conditions: at $z=0$ $\quad E_{1x} = E_{2x}$

$$\varepsilon_1 E_{1z} = \varepsilon_2 E_{2z}$$

$$\Downarrow$$

$$k_{1x} = k_{2x} = k_x$$

$$k_x^2 + k_{\substack{\cancel{z}\\1,2}}^2 = \underbrace{k^2}_{=\left(\frac{\omega}{c}\right)^2} \varepsilon_{1,2}$$

Both half-spaces are source-free

$\Downarrow$

$$\vec{\nabla}\cdot\vec{D} = 0 \Rightarrow \varepsilon_1 \frac{\partial E_{1x}}{\partial x} + \varepsilon_1 \frac{\partial E_{1z}}{\partial z} = 0 \quad \text{(same with } 1 \to 2\text{)}$$

$$\Downarrow$$

$$k_x E_{\substack{1x\\2}} + k_{\substack{1z\\2}} E_{\substack{1z\\2}} = 0$$

4 equations $\Rightarrow$ 4 unknowns $(E_{1x}, E_{2x}, E_{1z}, E_{2z}) \Rightarrow$

solve $\Rightarrow$ get another condition

show!

$$\omega = \alpha / k$$

$$\varepsilon_1 K_{2z} = \varepsilon_2 K_{1z}$$

$\Downarrow$

together with $K_x^2 + K_{1,2z}^2 = \left(\frac{\omega}{c}\right)^2 \varepsilon_{1,2}$

$\Downarrow$ show!

$$K_x^2 = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \underbrace{K^2}_{= \left(\frac{\omega}{c}\right)^2} \; ; \; K_{1,2z}^2 = \frac{\varepsilon_{1,2}^2}{\varepsilon_1 + \varepsilon_2} \left(\frac{\omega}{c}\right)^2$$

For the interface mode to exist, need imaginary $K_{1,2z}$ and real K_x $\Rightarrow$

$$\left.\begin{array}{l} \varepsilon_1 \varepsilon_2 < 0 \\ \varepsilon_1 + \varepsilon_2 < 0 \end{array}\right\} \Rightarrow \text{so: } \varepsilon_1 = \underbrace{\varepsilon_1'}_{<0} + i \varepsilon_1''$$

small

$< 0 \Rightarrow$ metal

$\varepsilon_2 \rightarrow$ real, $> 0 \Rightarrow$ dielectric

$\Downarrow$

show!

$$K_x = K_x' + i K_x'' \Rightarrow \quad K_x' \simeq \sqrt{\frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2}} \frac{\omega}{c} \; ;$$

$$|\varepsilon_1''| \ll |\varepsilon_1'|$$

$\Downarrow$

SPP wavelength $\rightarrow$ $\lambda_{SPP} = \frac{2\pi}{K_x'} \simeq \sqrt{\frac{\varepsilon_1' + \varepsilon_2}{\varepsilon_1' \varepsilon_2}} \lambda$

$$K_x'' \simeq \sqrt{\frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2}} \frac{\varepsilon_1'' \varepsilon_2}{2 \varepsilon_1' (\varepsilon_1' + \varepsilon_2)} \frac{\omega}{c}$$

excitation wavelength in vacuum

⑥

SPP propagation length $\Rightarrow \frac{1}{e}$ decay length of E-field $\left(\frac{1}{K_x''}\right)$ or intensity $\left(\frac{1}{2K_x''}\right)$

due to ohmic losses of the electrons participating in the SPP $\Rightarrow$ heating

decay length of SPP E-field away from the interface (mode confinement)

$$K_{1z} \approx \frac{\omega}{c}\sqrt{\frac{\varepsilon_1'^2}{\varepsilon_1'+\varepsilon_2}}\left[1+i\frac{\varepsilon_1''}{2\varepsilon_1'}\right];$$

$\uparrow$ to 1st order of $\frac{|\varepsilon_1''|}{|\varepsilon_1'|}$

$\Rightarrow \frac{1}{e}$ decay of E-field

$$K_{2z} \simeq \frac{\omega}{c}\sqrt{\frac{\varepsilon_2^2}{\varepsilon_1'+\varepsilon_2}}\left[1-i\frac{\varepsilon_1''}{2(\varepsilon_1'+\varepsilon_2)}\right] \quad \left(\frac{1}{K_z'}\right)$$

Example:

$\lambda = 633\,nm$ $\quad \varepsilon_1 = -18.2+0.5i$ (Ag)

$\varepsilon_2 = 1$ $\quad \varepsilon_1 = -11.6+1.2i$ (Au)

air

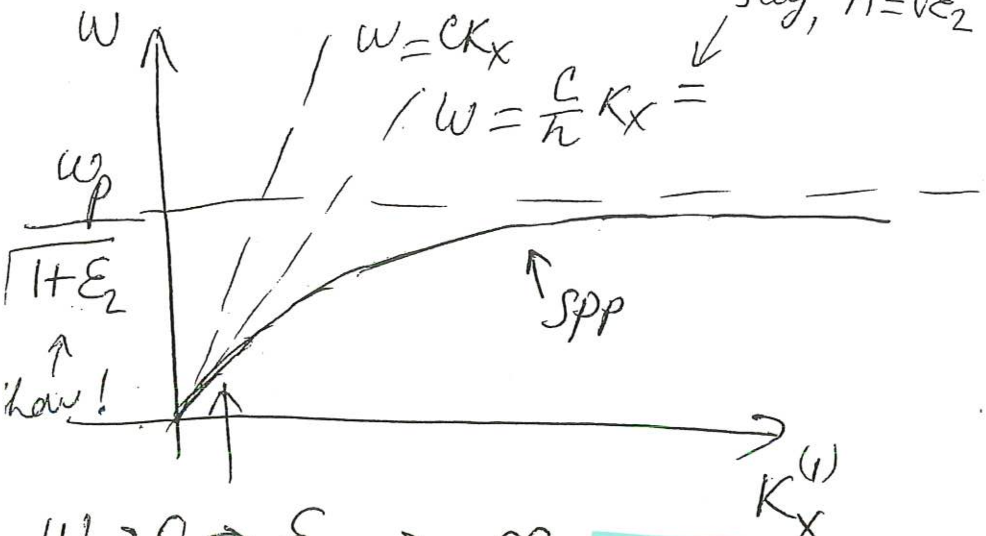
SPP propagation length $\frac{1}{2K_x''} \Rightarrow$ 60 μm (Ag), 10 μm (Au)

mode confinement Ag/air $\Rightarrow \left(\frac{1}{K_{1z}'}, \frac{1}{K_{2z}''}\right) = (23\,nm, 42$

Au/air $\Rightarrow \left(\frac{1}{K_{1z}''}, \frac{1}{K_{2z}''}\right) = (28\,nm, 328\,nm)$

Excitation of SPP

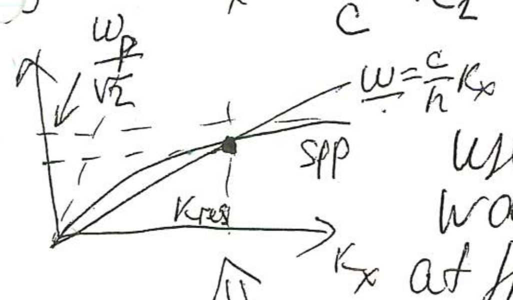
$|K'_x| \gg |K''_x|$; consider K'_x vs ω $\Rightarrow$ dispersion relation



$\omega \to 0 \Rightarrow \varepsilon_1 \to -\infty$
$\Downarrow$
$K_x \to \frac{\omega}{c}\sqrt{\varepsilon_2}$

$K \to \infty \Rightarrow \varepsilon_1 + \varepsilon_2 \to 0$
$\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega^2}$
$\omega = \frac{\omega_p}{\sqrt{1+\varepsilon_2}}$ $\quad K_{x\to 0}$ $\frac{\omega}{c}\sqrt{\varepsilon_2}$

• for a given $\hbar\omega$ K_x is always larger than $\frac{\omega}{c}$! $\Rightarrow$ Can't excite SPP from free space!



use evanescent waves created at the interface with medium with $n > 1$
$\Uparrow$
$\Downarrow$

Otto configuration $\qquad$ Kretschmann $\quad K_x > n\omega/c$

TIR $\quad (\theta > \theta_c)$ $\Rightarrow$