Surface Plasmon Polaritons (SPPs)
-
Introduction and basic properties

- Overview
- Light-matter interaction
- SPP dispersion and properties

Standard textbook:
- Heinz Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings
  Springer Tracts in Modern Physics, Vol. 111, Springer Berlin 1988

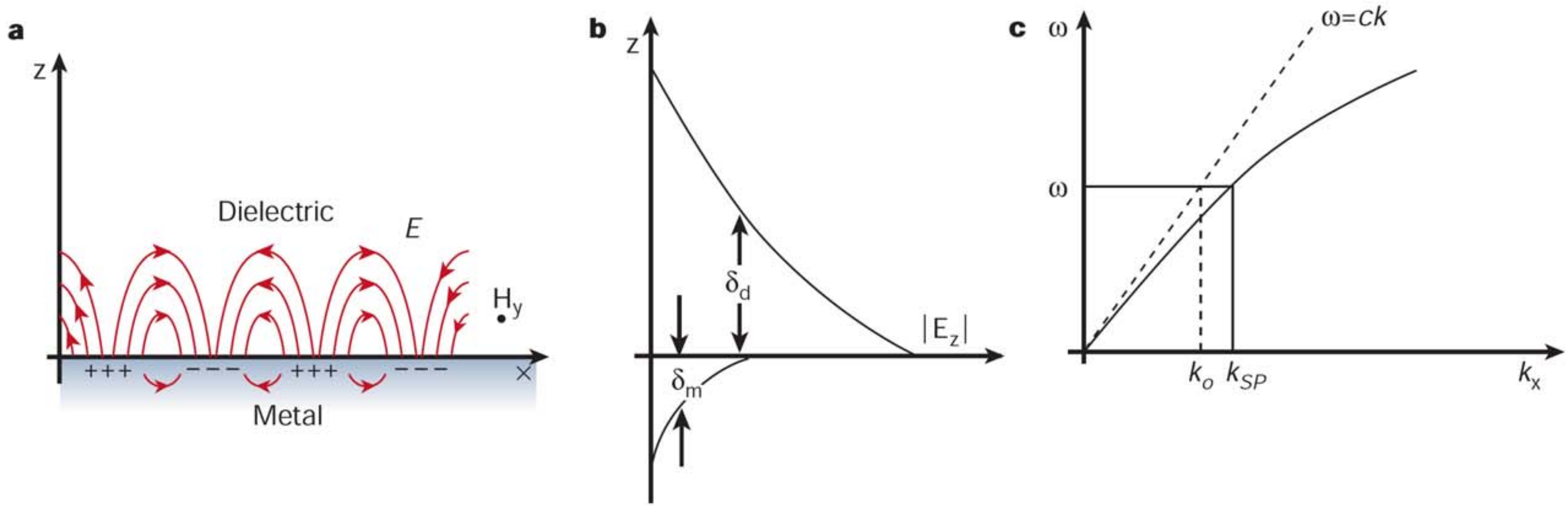
Overview articles on Plasmonics:
- A. Zayats, I. Smolyaninov, Journal of Optics A: Pure and Applied Optics **5,** S16 (2003)
- A. Zayats, et. al., Physics Reports **408,** 131-414 (2005)
- W.L.Barnes et. al., Nature **424,** 825 (2003)

Overview

Replace ‘slow’ electronic devices with ‘fast’ photonic ones

Photonic crystals

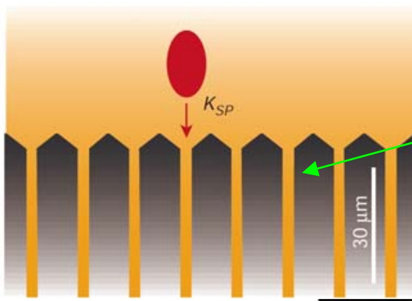
SPs is the way to concentrate and channel light using subwavelength structures



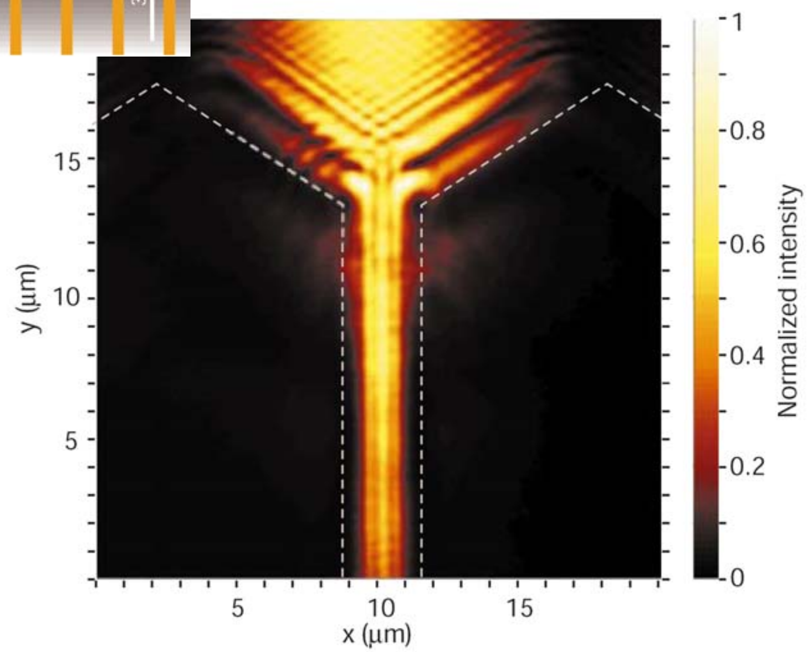
SPs structures at the interface between a metal and a dielectric material
Transverse magnetic in character → electric field normal to the surface
Perpendicular direction → evanescent field
Momentum mismatch in the SP dispersion curve

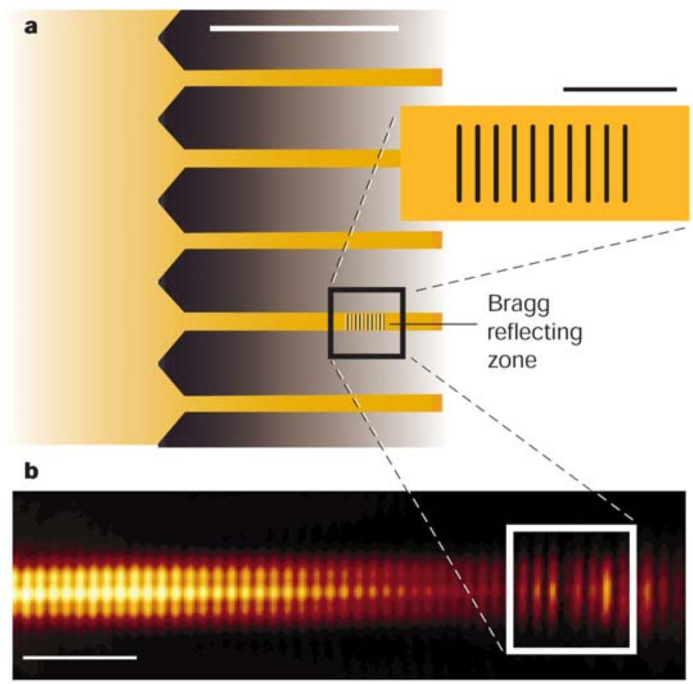
Overview

surface plasmon polariton optics (SPP)
Band-gap effects, SPP waveguiding along straight and bent line,



Gold stripes





Overview

enhanced optical transmission

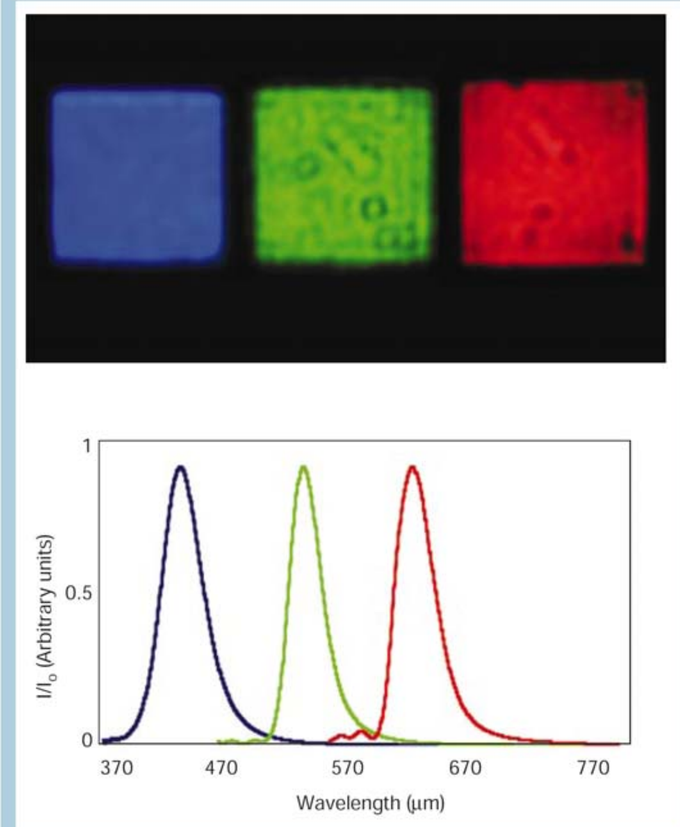


Figure 4 Normal incidence transmission for subwavelength holes. Normal incidence transmission images (top) and spectra (bottom) for three square arrays of subwavelength holes. For the blue, green and red arrays, the periods were 300, 450 and 550 nm, respectively, the hole diameters were 155, 180 and 225 nm and the peak transmission wavelengths 436, 538 and 627 nm. The arrays were made in a free standing 300 nm thick silver film (courtesy of A. Degiron, Université Louis Pasteur, France). Only the lowest order peak ($i,j = 0.1$ in equation (4)) of the spectrum of each array is shown as it dominates the colour seen. The figure shows that nanostructures can control the resonant wavelength of SP phenomena.

Elementary excitations and polaritons

Elementary excitations:
• Phonons (lattice vibrations)
• Plasmons (collective electron oscillations)
• Excitions (bound state between an excited electron and a hole)

Polaritons:
Commonly called coupled state between an elementary excitation and a photon
= light-matter interaction

Plasmon polariton: coupled state between a plasmon and a photon.

Phonon polariton: coupled state between a phonon and a photon.

Plasmons

- A plasmon is the quantum of the collective excitation of free electrons in solids.
- Electron plasma effects are most pronounced in free-electron-like metals.

The dielectric constant of such materials can be expressed as

$$\varepsilon_m(\omega) = 1 - \left(\omega_p / \omega \right)^2$$

$\omega < \omega_p \rightarrow \varepsilon_m < 0 \rightarrow$ wavevector of light in the medium is imaginary $\rightarrow$ no propagating electromagnetic modes

$\omega > \omega_p \rightarrow \varepsilon_m \rightarrow 1 \rightarrow$ altered by intraband transitions in noble metals

- A combined excitation consisting of a surface plasmon and a photon is called a surface plasmon polariton (SSP). → different nature, such as phonon–polariton, exciton–polariton, etc.

Plasmons

- free electrons in metal are treated as an electron liquid of high density $n \approx 10^{23}\,\mathrm{cm}^{-3}$
- longitudinal density fluctuations (plasma oscillations) at eigenfrequency ω_p
- quanta of volume plasmons have energy $\hbar\omega_p = \hbar\sqrt{\dfrac{4\pi ne^2}{m_0}}$, in the order 10eV

Volume plasmon polaritons

propagate through the volume for frequencies $\omega > \omega_p$

Surface plasmon polaritons

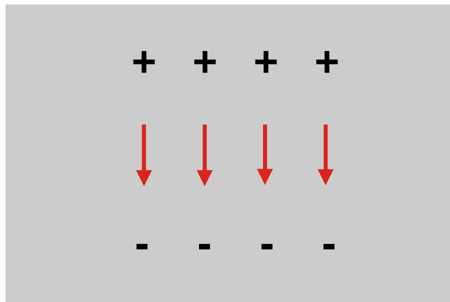
Maxell´s theory shows that EM surface waves can propagate also along a metallic surface with a broad spectrum of eigen frequencies

from ω = 0 up to $\omega = \omega_p / \sqrt{2}$

Particle (localized) plasmon polaritons

Plasmon resonance positions in vacuum

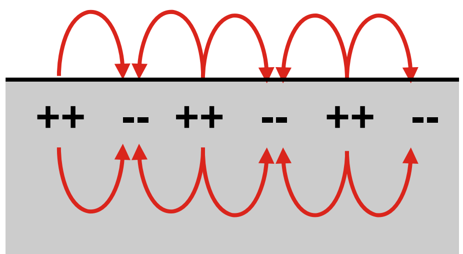
Bulk metal



ω_p

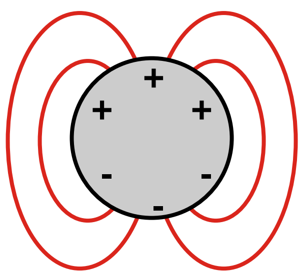
$\varepsilon = 0$

Metal surface



$\varepsilon = -1 \xrightarrow{\text{drude model}} \omega_p / \sqrt{2}$

Metal sphere
localized SPPs



$\varepsilon = -2 \xrightarrow{\text{drude model}} \omega_p / \sqrt{3}$

Surface Plasmon Photonics

Optical technology using
- propagating surface plasmon polaritons
- localized plasmon polaritons

Also called:
- Plasmonics
- Plasmon photonics
- Plasmon optics

Topics include:

Localized resonances/ local field enhancement	- nanoscopic particles - near-field tips
Propagation and guiding	- photonic devices - near-field probes
Enhanced transmission	- aperture probes - filters
Negative index of refraction and metamaterials	- perfect lens
SERS/TERS	- surface/tip enhanced Raman scattering
Molecules and quantum dots	- enhanced fluoresence

Nanophotonics using plasmonic circuits

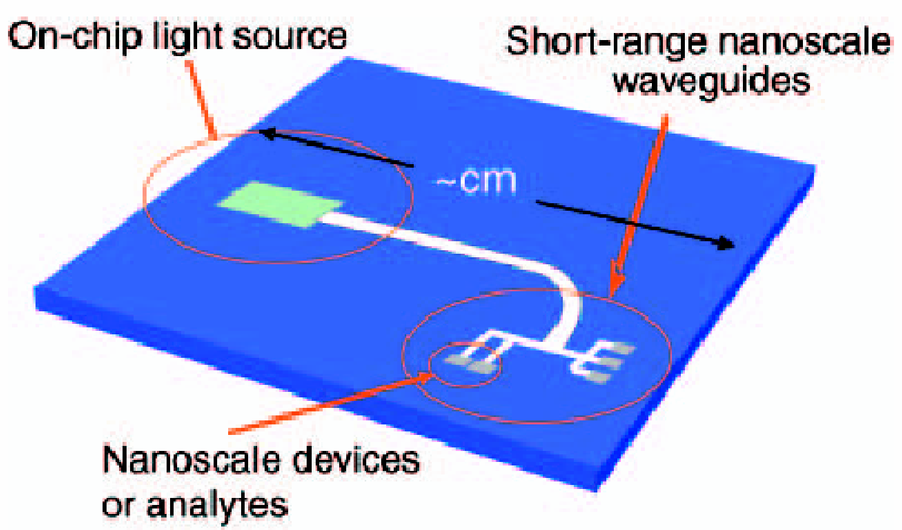
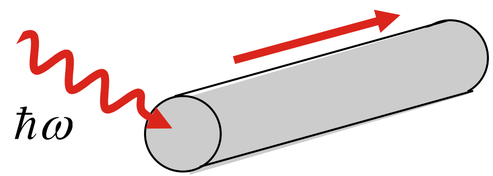


Figure 1. Schematic illustration of a chip-scale plasmonic interconnect network that enables both chip-scale propagation and subwavelength-scale operation. Architectures such as these would transport signals to and from active sources and detectors and efficiently couple into and out of nanometer-scale devices or analytes.

Atwater *et.al.*, MRS Bulletin **30**, No. 5 (2005)

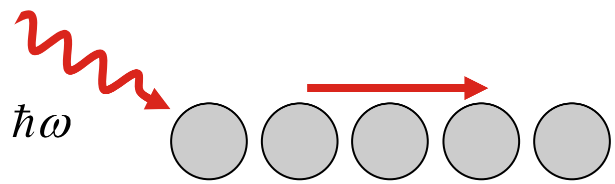
Nanoscale plasmon waveguides

- **Proposal by Takahara *et. al.* 1997**



Metal nanowire
Diameter << λ

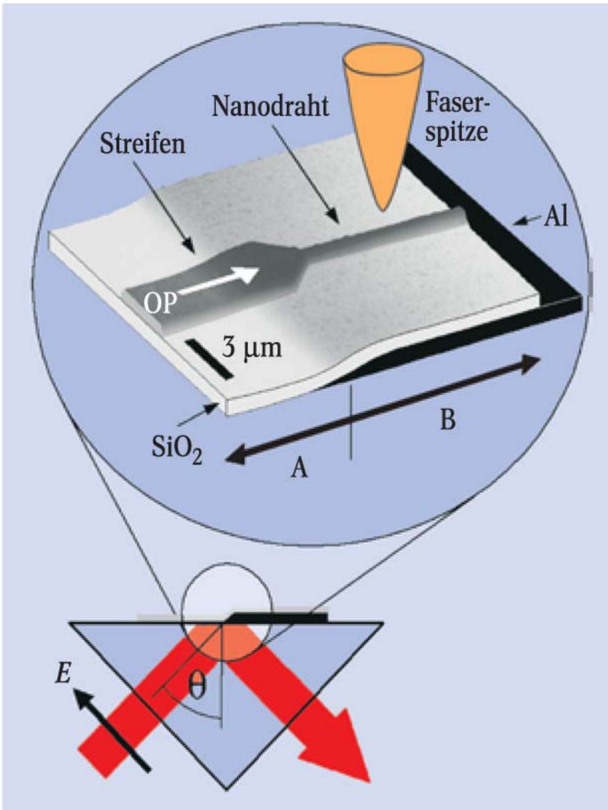
- **Proposal by Quinten *et. al.* 1998**

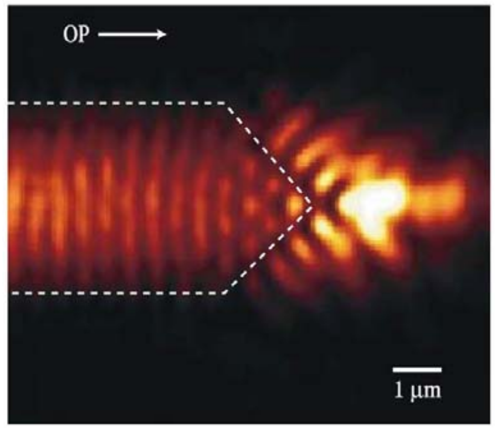


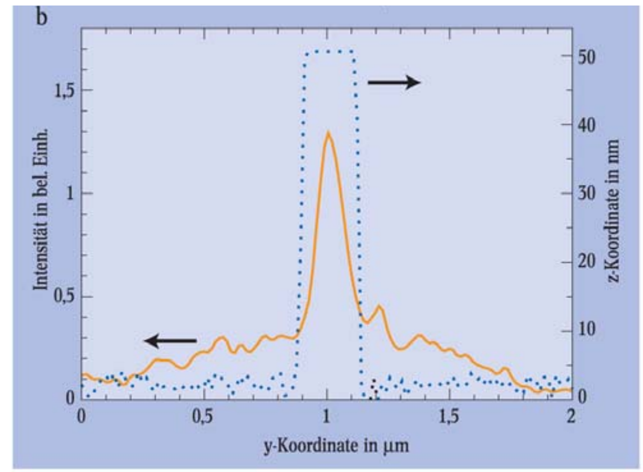
Chain of metal nanoparticles
Diameter and spacing << λ

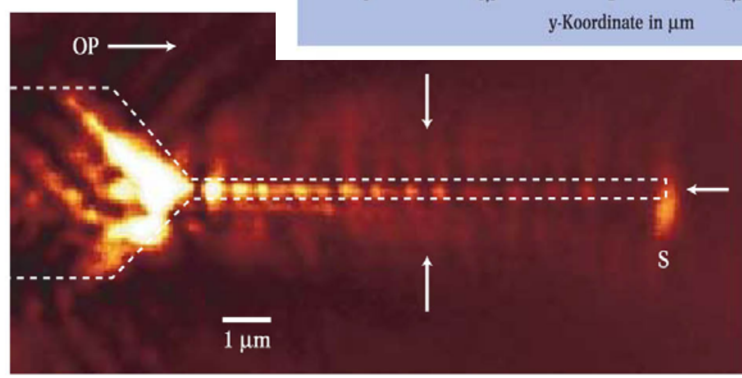
First experimental observation by Maier *et. al.* 2003

Subwavelength-scale plasmon waveguides







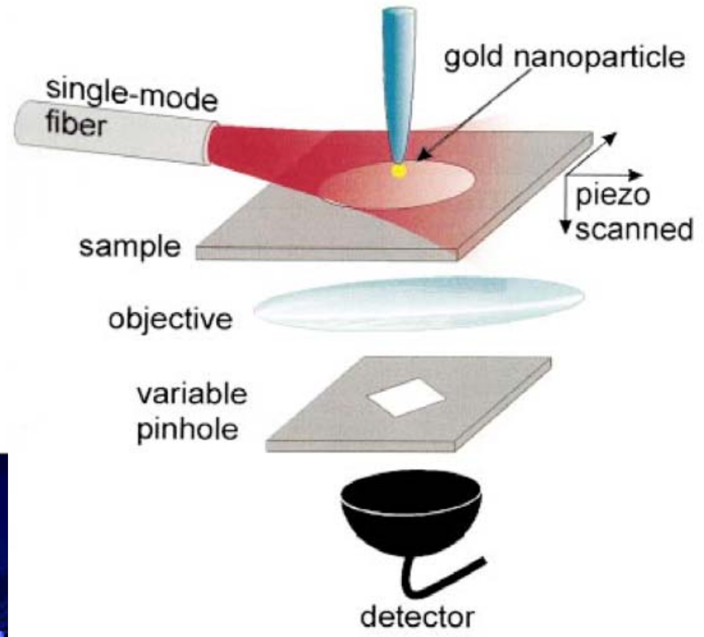


Krenn, Aussenegg, Physik Journal 1 (2002) Nr. 3

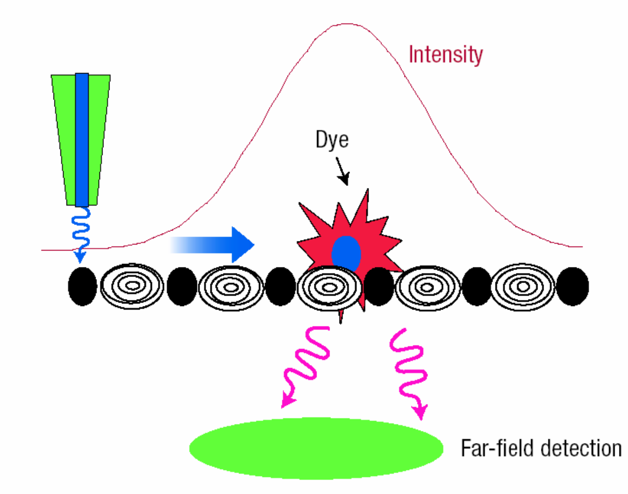
Some applications of plasmon resonant nanoparticles

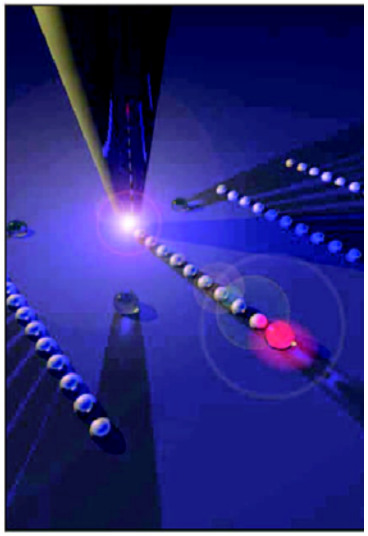
- **SNOM probes**
- **Sensors**
- **Surface enhanced Raman scattering (SERS)**

T. Kalkbrenner et.al., J. Microsc. **202**, 72 (2001)



- **Nanoscopic waveguides for light**





S.A. Maier *et.al.*, Nature Materials **2**, 229 (2003)

Light-matter interactions in solids

EM waves in matter
Lorenz oscillator
Isolators, Phonon polaritons
Metals, Plasmon polaritons

Literature:

- C.F.Bohren, D.R.Huffman, Absorption and scattering of light by small particles

- K.Kopitzki, Einführung in die Festkörperphysik

- C.Kittel, Einführung in die Festkörperphysik

EM-waves in matter (linear media) - definitions

Polarization

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \text{ with suszeptibility } \chi$$

Electric displacement

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi) \mathbf{E} = \varepsilon_0 \varepsilon \mathbf{E}$$

Complex refractive index

$$N = n + i\kappa = \sqrt{\varepsilon}$$

Complex dielectric function

$$\varepsilon = \varepsilon' + i\varepsilon'' = 1 + \chi$$

Relationship between *N* and ε

$$\varepsilon' = n^2 + \kappa^2$$

$$\varepsilon'' = 2n\kappa$$

EM-waves in matter (linear media) - dispersion

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{kr}-\omega t)}$$

$$\mathbf{B} = \mathbf{B}_0 e^{i(\mathbf{kr}-\omega t)}$$

wavevector $k = \frac{2\pi}{\lambda}$

frequency $\omega = 2\pi f$

Dispersion in transparent media without absorption:

$$\boxed{\omega = \frac{c}{\sqrt{\varepsilon}} k = \frac{c}{n} k}$$

$\mathbf{k}$ and ε are real

$\varepsilon > 0$

Dispersion generally:

$$\boxed{(\mathbf{k}\cdot\mathbf{k}) = \frac{\omega^2}{c^2}\varepsilon}$$

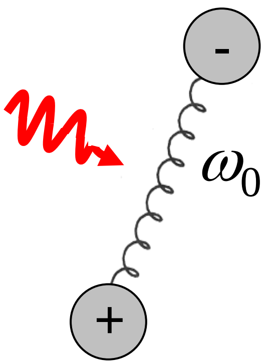
$\varepsilon(\omega)$ and thus $\mathbf{k} = \mathbf{k}' + i\mathbf{k}''$ are complex numbers!

$$\Rightarrow \boxed{\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{kr}-\omega t)} = \mathbf{E}_0 e^{i(\mathbf{k}'\mathbf{r}-\omega t)} e^{-\mathbf{k}''\mathbf{r}}}$$

propagating wave

exponential decay of amplitude

Harmonic oscillator (Lorentz) model



$$m\ddot{\mathbf{x}} + b\dot{\mathbf{x}} + K\mathbf{x} = e\mathbf{E} = e\mathbf{E}_0 e^{i\omega t}$$

$$\mathbf{x} = \frac{e/m}{\omega_0^2 - \omega^2 - i\gamma\omega}\mathbf{E} = Ae^{i\Theta}\frac{e\mathbf{E}}{m}$$

$$\mathbf{p} = e\mathbf{x} = \varepsilon_0 \alpha \mathbf{E}$$

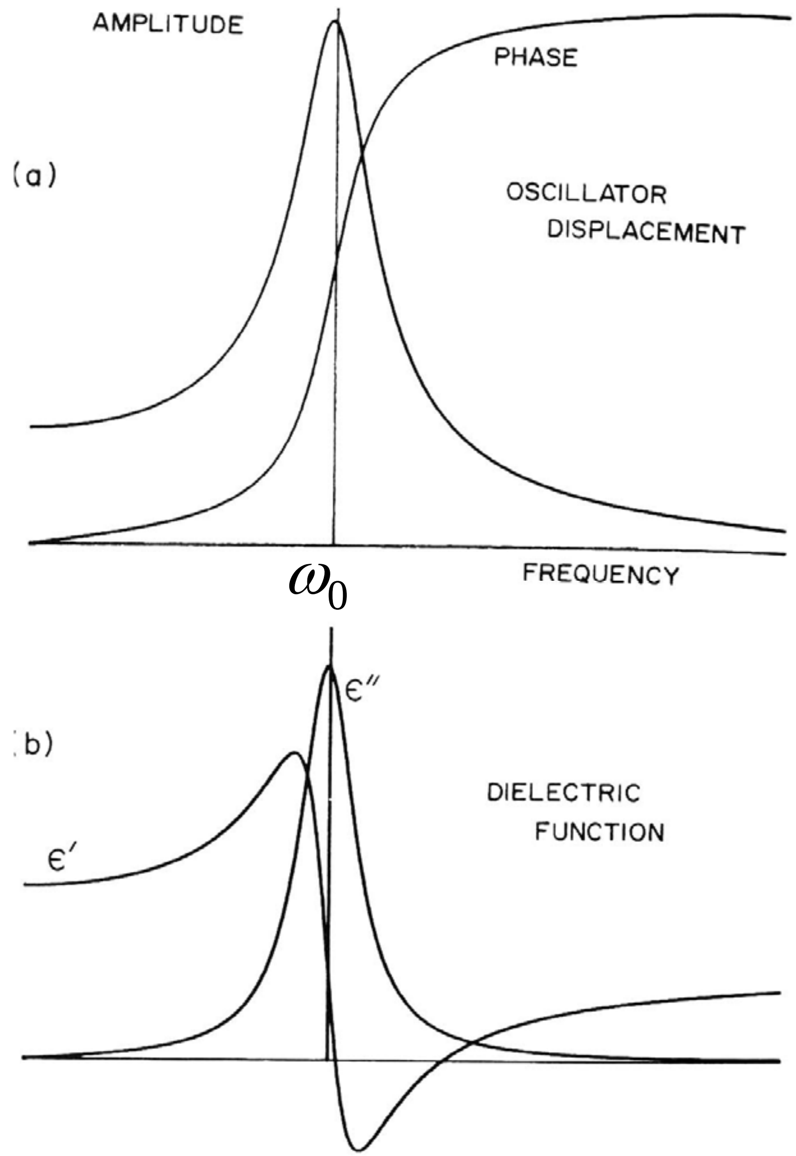
$$\mathbf{P} = N\mathbf{p} = \varepsilon_0 \chi \mathbf{E}$$

$$\boxed{\varepsilon = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}}$$

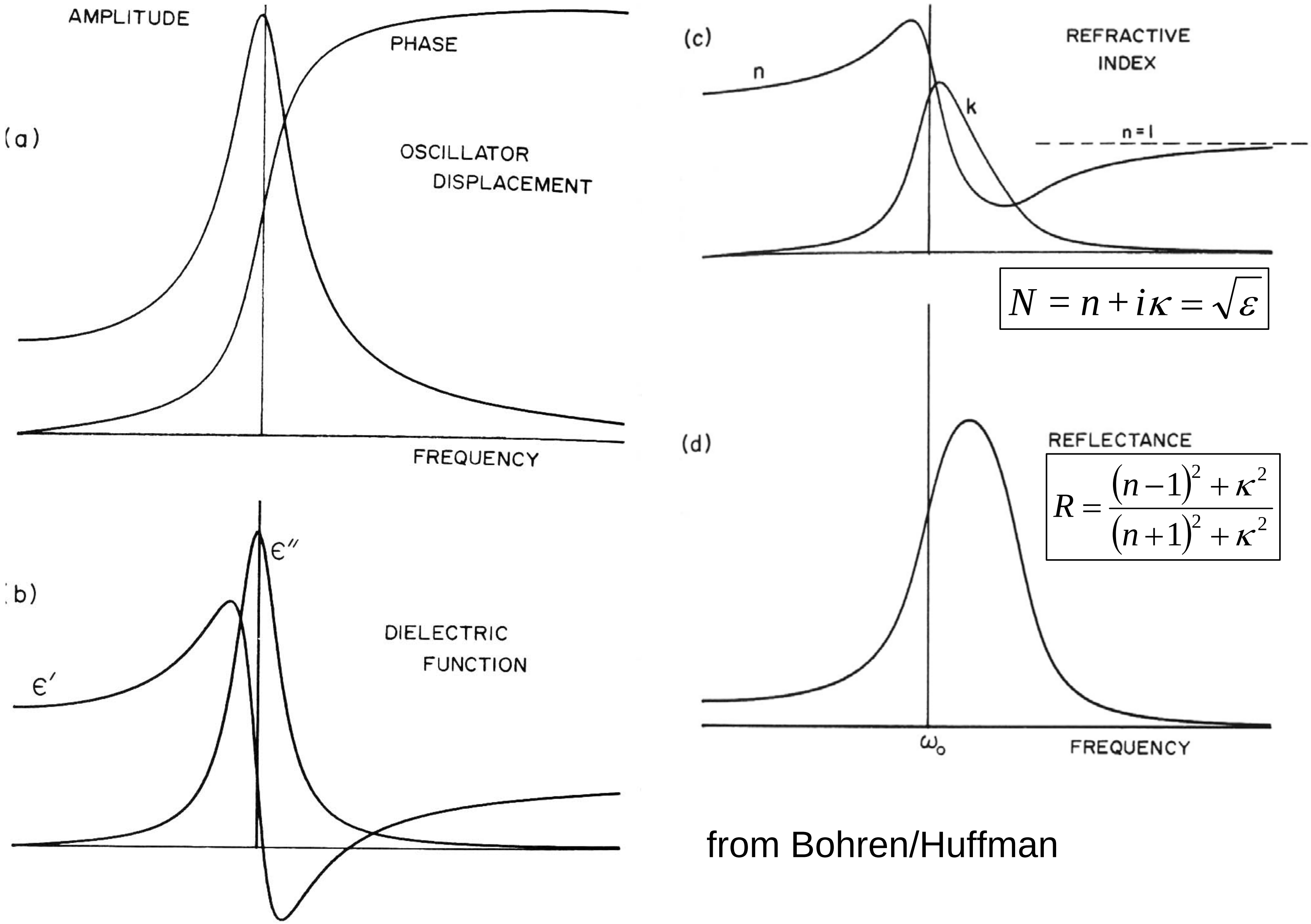
$\omega_0^2 = K/m$

$\gamma = b/m$

$\omega_p^2 = Ne^2/m\varepsilon_0$ plasma frequency



One-oscillator (Lorentz) model

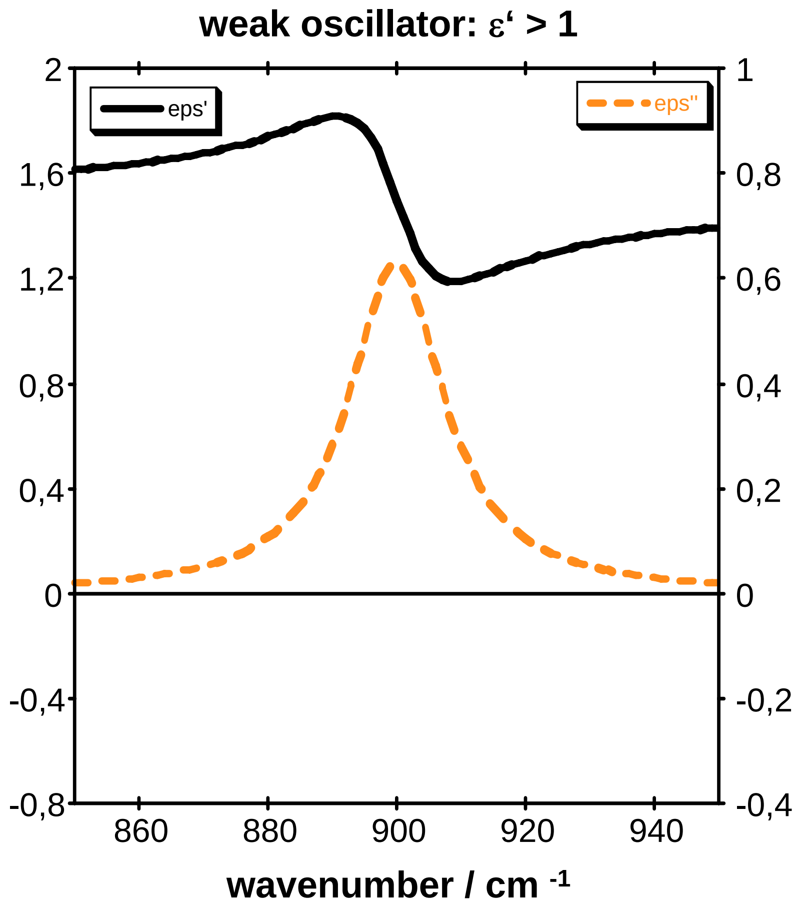


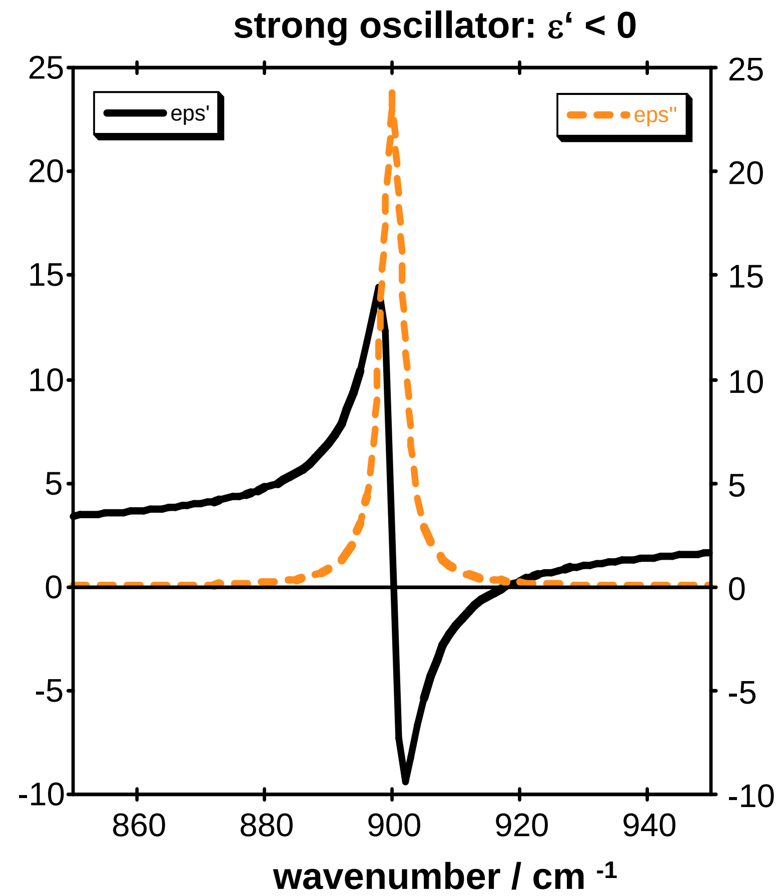
$$N = n + i\kappa = \sqrt{\varepsilon}$$

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}$$

from Bohren/Huffman

Weak and strong molecular vibrations





caused by: **molecular vibrations**

examples: PMMA, PS, proteins

crystal lattice vibrations

SiC, Xonotlit, Calcite, Si_3N_4

Optical properties of polar crystals

note:
lattice has transversal T and longitudinal L oscillations but only transversal phonons can be excited by light

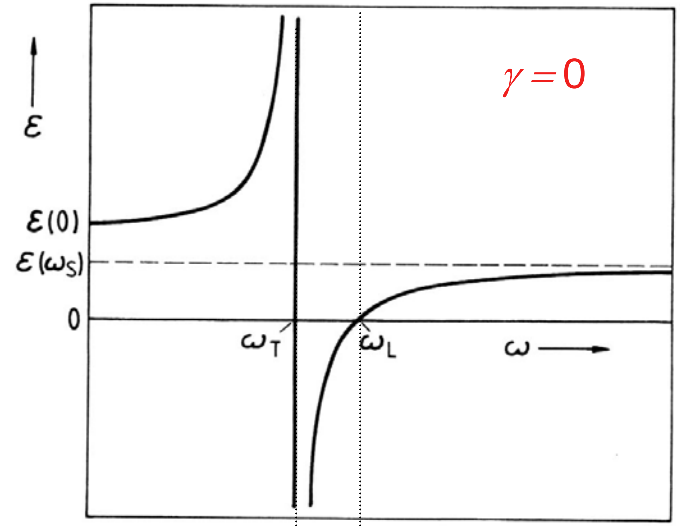
$$N = n + i\kappa = \sqrt{\varepsilon} \Rightarrow \begin{cases} \textbf{A} & \boxed{n = 0, \kappa = \sqrt{|\varepsilon|}} \\ \textbf{B} & \boxed{n = \sqrt{\varepsilon}, \kappa = 0} \end{cases}$$

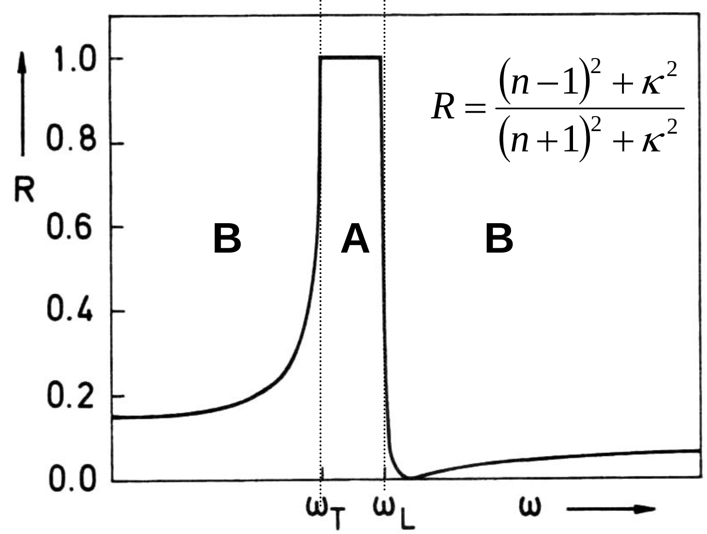
$$(\mathbf{k} \cdot \mathbf{k}) = \frac{\omega^2}{c^2}\varepsilon \Rightarrow \begin{cases} \textbf{A} & \boxed{k = i\frac{\omega}{c}\sqrt{|\varepsilon|}} \\ \textbf{B} & \boxed{k = \frac{\omega}{c}\sqrt{\varepsilon}} \end{cases}$$

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{kr} - \omega t)} \Rightarrow$$

A: total reflection

B: transmission and reflection





SiC - single oscillator model

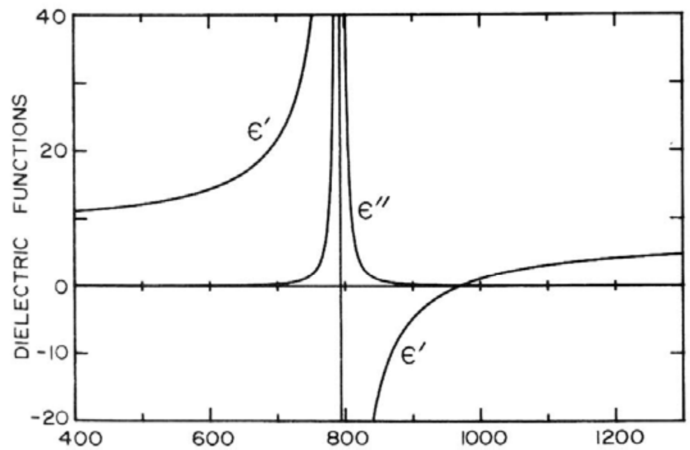
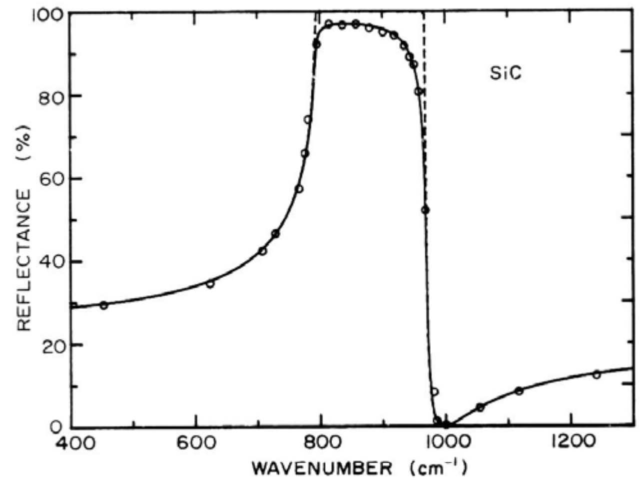
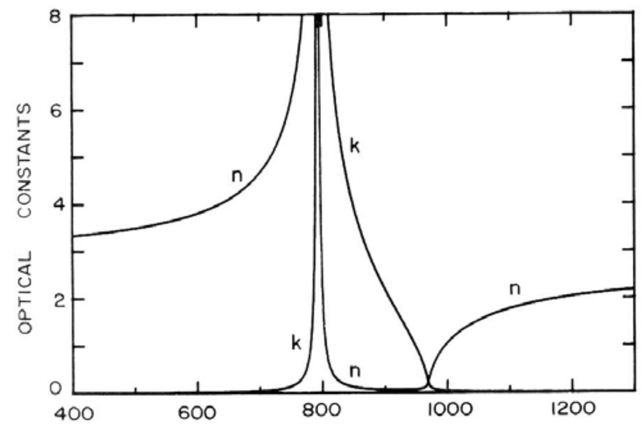


Figure 9.6 Measured reflectance (circles) of α-SiC. The solid curves are from (9.20) with $\omega_t = 793\ \mathrm{cm}^{-1}$, $\gamma = 4.76\ \mathrm{cm}^{-1}$, $\omega_p^2 = 2.08 \times 10^6\ \mathrm{cm}^{-2}$, and $\epsilon_{0e} = 6.7$; the dashed curve is for the same model with $\gamma = 0$. The wave number is $1/\lambda$.





$\gamma > 0$

General dispersion for nonconductor

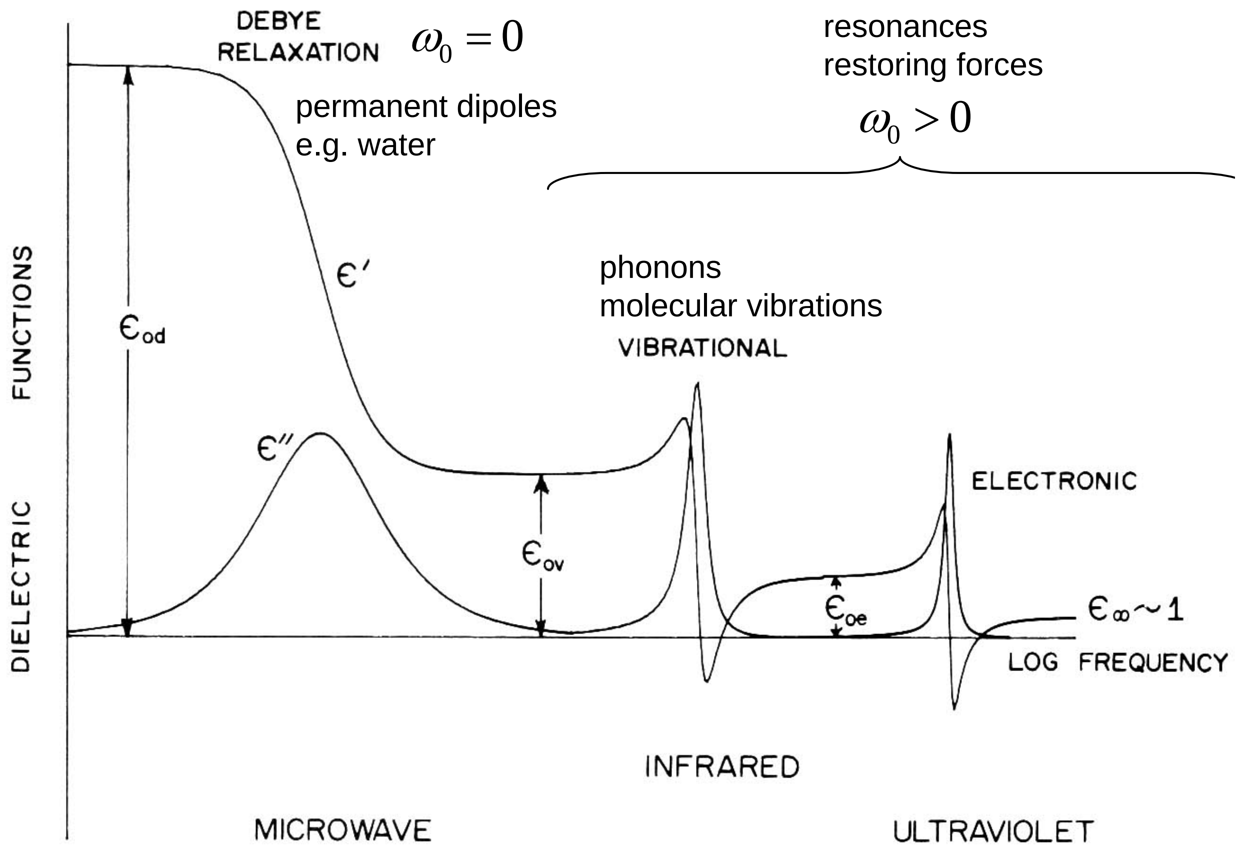
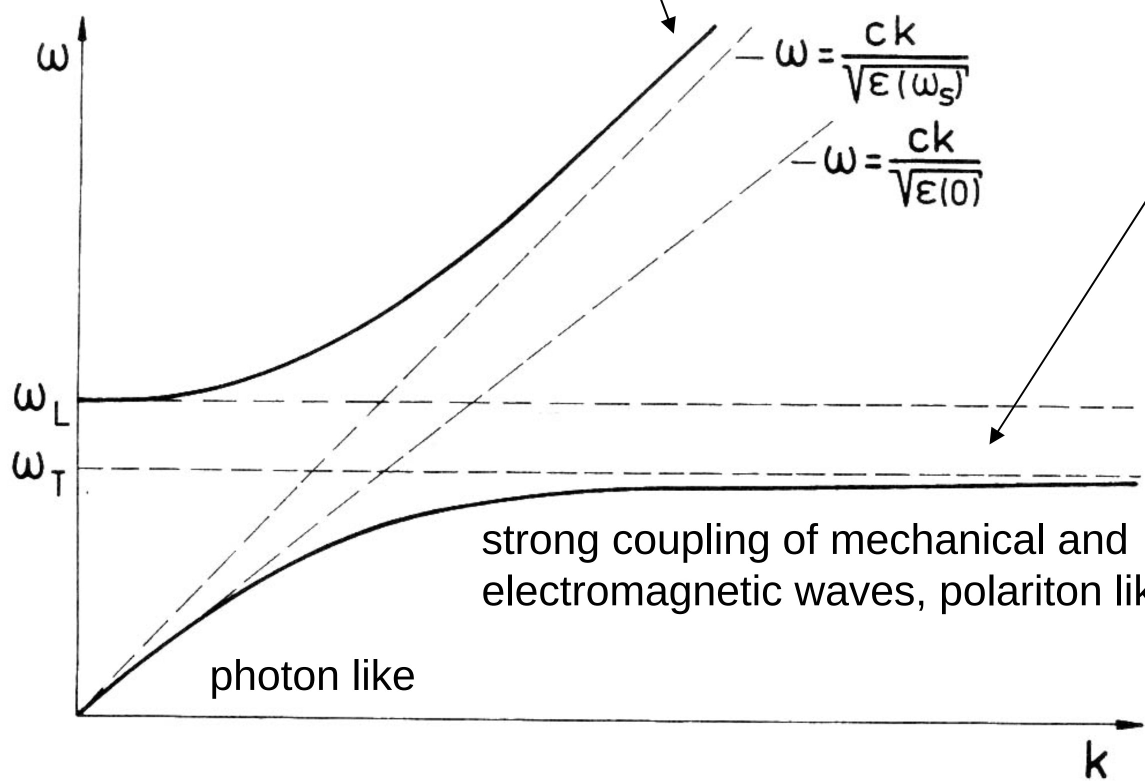


Figure 9.16 Schematic diagram of the frequency variation of the dielectric function of an ideal nonconductor.

Dispersion in polar crystals - phonon polaritons

Dispersion relation for $\gamma = 0$

$$k^2 = \frac{\omega^2}{c^2}\varepsilon = \frac{\omega^2}{c^2}\varepsilon(\omega_s)\frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2}$$



strong coupling of mechanical and electromagnetic waves, polariton like

photon like

$\gamma = 0$

between TO and LO there is no solution for real values ω and k

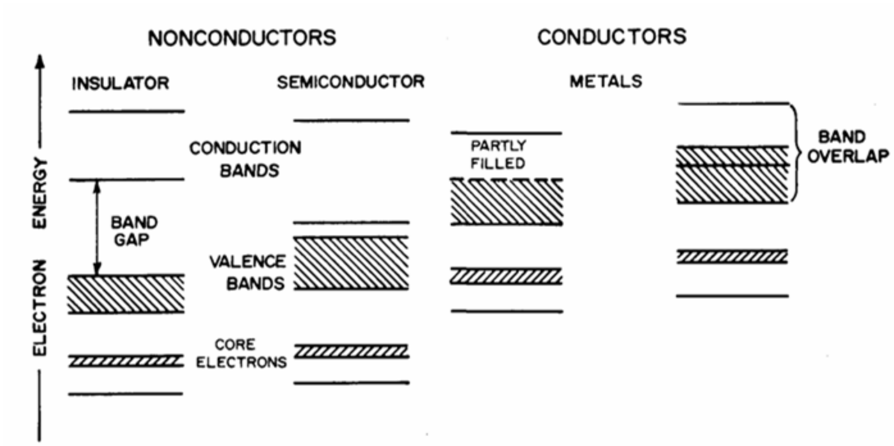
frequency gap:

$$E \propto e^{-i\omega t} e^{-kr}$$

no propagation

reflection

Metals - Drude model



$$m\ddot{x} + b\dot{x} + Kx = eE \quad \rightarrow \quad x = \frac{(e/m)\mathbf{E}}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$A = \frac{1}{\sqrt{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}}; \quad \theta = \tan^{-1}\frac{\gamma\omega}{\omega_0^2 - \omega^2}$$

$$\boldsymbol{p} = e\boldsymbol{x} \quad \rightarrow \quad \boldsymbol{P} = Ne\boldsymbol{x} = \frac{\omega_p^2 \varepsilon_0 \boldsymbol{E}}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\omega_p^2 = \frac{Ne^2}{m\varepsilon_0}; \quad \omega_0^2 = \frac{K}{m}$$

$$\Rightarrow \quad \varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\boldsymbol{P}(\omega) = \varepsilon_0 \chi(\omega) \boldsymbol{E}(\omega)$$

$$\mathbf{D}(\omega) = \varepsilon_0 \varepsilon(\omega) \boldsymbol{E}(\omega) = \varepsilon_0 \boldsymbol{E}(\omega) + \boldsymbol{P}(\omega) \quad \rightarrow \quad \varepsilon(\omega) = 1 + \chi(\omega)$$

Metals - drude model

- Intraband transitions
- longitudinal plasma oscillations
- $\omega_0 = 0$ i.e. no restoring force
- ω_P = plasma frequency

$$\varepsilon = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\omega_0 = 0$$

$$\boxed{\varepsilon = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma\omega}}$$

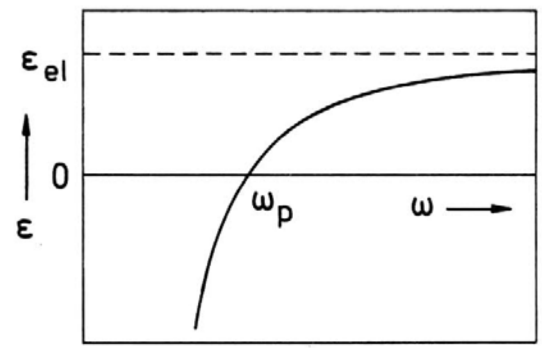
$$\begin{cases} \varepsilon' = 1 - \dfrac{\omega_p^2}{\omega^2 + \gamma^2} \approx 1 - \dfrac{\omega_p^2}{\omega^2} \\[2ex] \varepsilon'' = \dfrac{\omega_p^2 \gamma}{\omega\left(\omega^2 + \gamma^2\right)} \approx \dfrac{\omega_p^2 \gamma}{\omega^3} \end{cases}$$

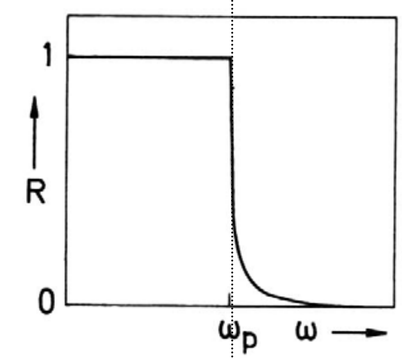
$\gamma = 0$

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{kr} - \omega t)}$$

$$\boxed{k = i\frac{\omega}{c}\sqrt{|\varepsilon|}} \qquad \boxed{k = \frac{\omega}{c}\sqrt{\varepsilon}}$$

$$\boxed{n = 0, \kappa = \sqrt{|\varepsilon|}} \qquad \boxed{n = \sqrt{\varepsilon}, \kappa = 0}$$





total reflection | transmission

$\omega >> \gamma = 1/\tau$ (1/ collision time)
collisions usually by electron-phonon scattering

generally:
$\gamma > 0$ leads to damping of transmitted wave $\boxed{n > 0,\ \kappa > 0}$

Aluminium

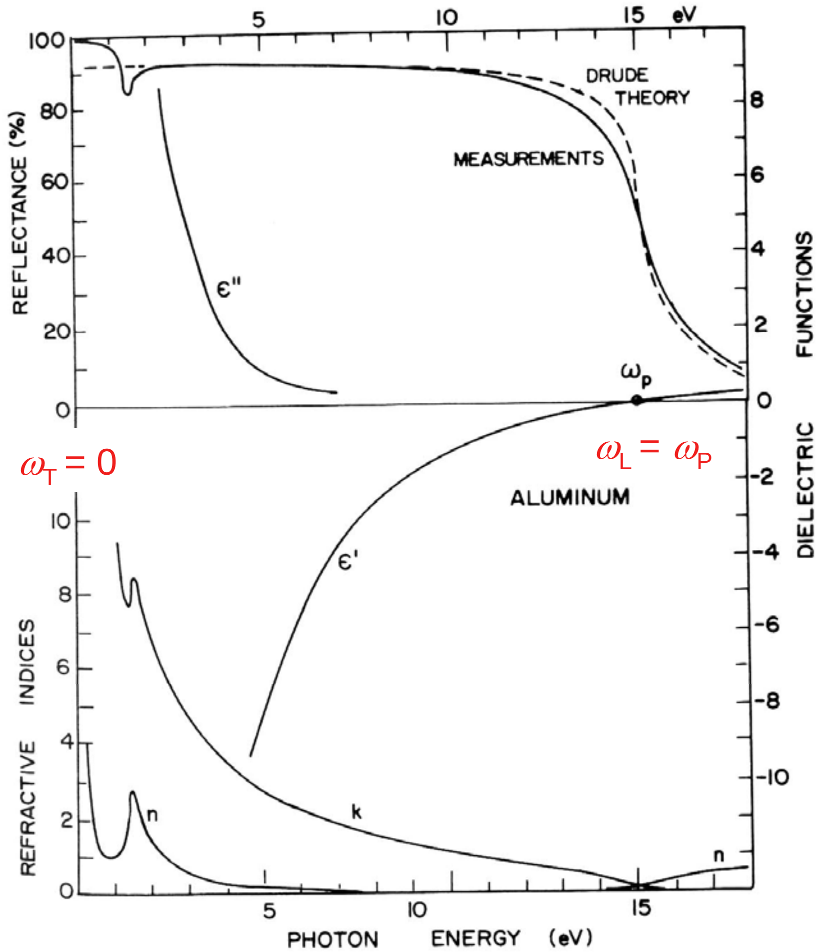


Figure 9.11 Measured reflectance of aluminum compared with the Drude theory. The dielectric function and refractive index are from Hagemann et al. (1974).

Metals - Drude model

- $\varepsilon_m(\omega_p) = 0 \rightarrow$ longitudinal field $\rightarrow$ bulk *plasma oscillation* caused by Coulomb forces.
- if $\gamma \neq 0$, $\varepsilon_m(\omega) = 0 \rightarrow \omega = \omega_p + i\gamma/2 \rightarrow$ *plasmon* is the quantum of plasma oscillation with energy $\hbar\,\omega_p$ and lifetime $\tau = 2/\gamma$.
- *plasmon* is not an electron but a collection of electrons.
- The damping constant γ is related to the average collision time $1/\tau \rightarrow$ interactions with the lattice vibrations: *electron-phonon scattering*.
- non conductor = metals at high frequencies: *intraband transitions* acts mainly at low frequencies $\rightarrow$ Drude model as well.
- at frequencies $\gg \omega_p$ metals are transparent: *ultraviolet transparency*.

Metals - Drude model

The Drude model needs to consider the effect of bound electrons → lower lying shells

Equation of motion has to include also the "restoring force"

$$m\ddot{x} + b\dot{x} + \alpha x = e\mathbf{E} \quad \rightarrow \quad \varepsilon_{Interband}(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\omega_0^2 = \frac{\alpha}{m}$$

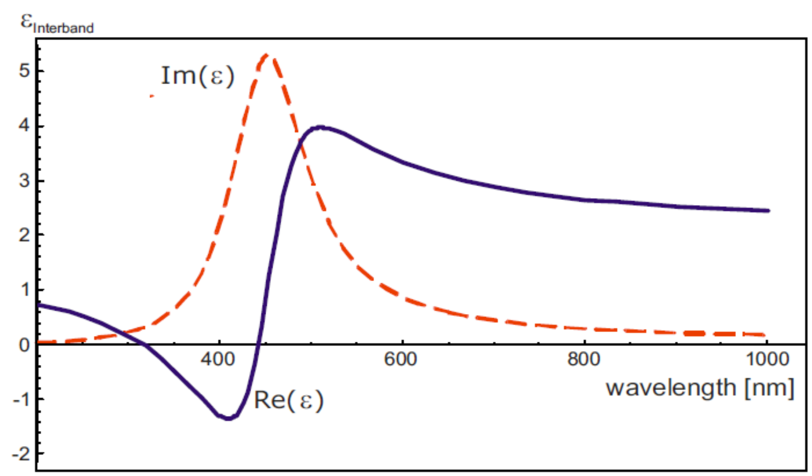
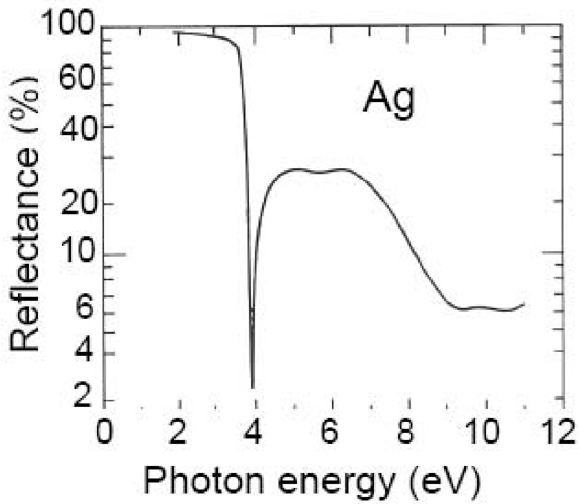


Figure 12.2: Contribution of bound electrons to the dielectric function of gold. The parameters used are $\tilde{\omega}_p = 45 \cdot 10^{14}\ s^{-1}$, $\gamma = 8.35 \cdot 10^{-16}\ s^{-1}$, and $\omega_0 = 2\pi c/\lambda$, with λ=450 nm. The solid blue line is the real part, the dashed red curve is the imaginary part of the dielectric function due to bound electrons.

Free and bound electrons in metals



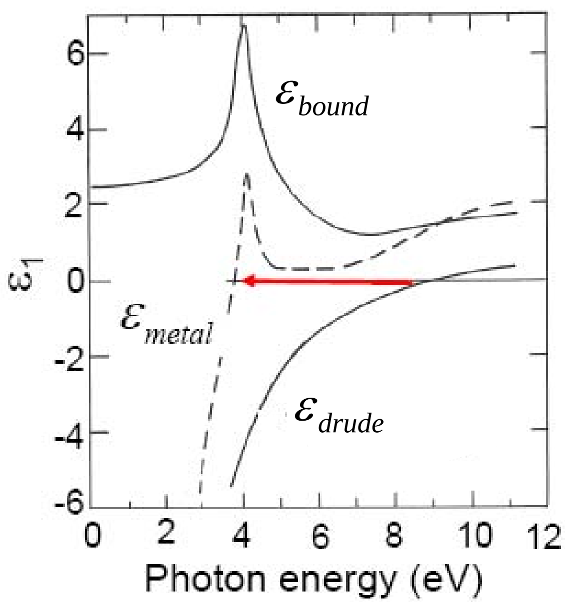
- Ag shows interesting feature in reflection

→ Both conduction and bound electrons

contribute to ε_{metal}

Bound electrons contribute like a Lorenz oscillator

$$\varepsilon_{metal} = \varepsilon_{drude} + \varepsilon_{bound}$$



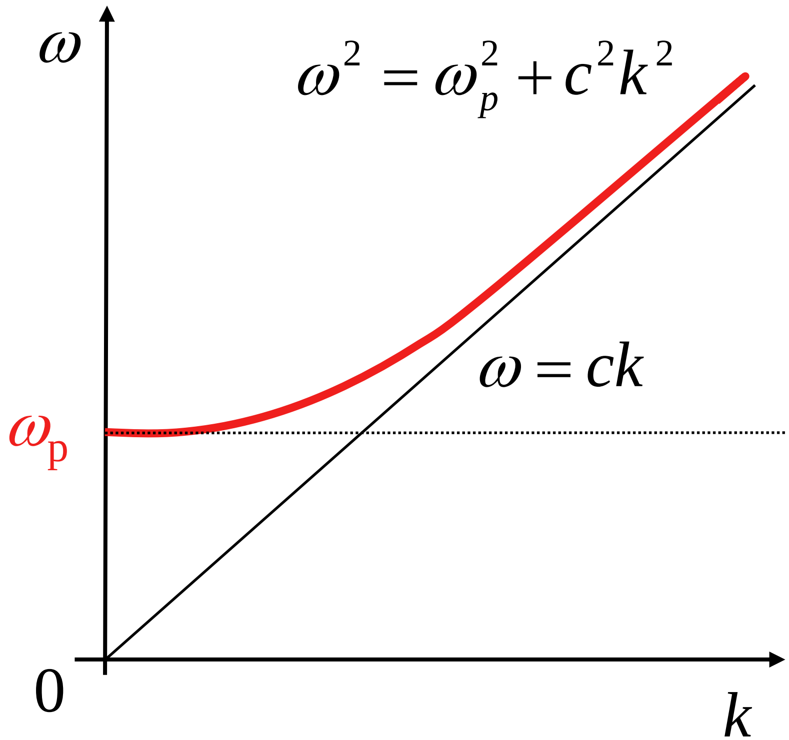
where

$$\varepsilon_{drude} = 1 - \frac{\omega_{p,d}^2}{\omega^2 - i\gamma_d \omega}$$

$$\varepsilon_{bound} = \sum_j \frac{\omega_{p,j}^2}{\omega_0^2 - \omega^2 - i\gamma_j \omega}$$

Metals - plasmon polaritons

Plasmon polariton dispersion (γ = 0)



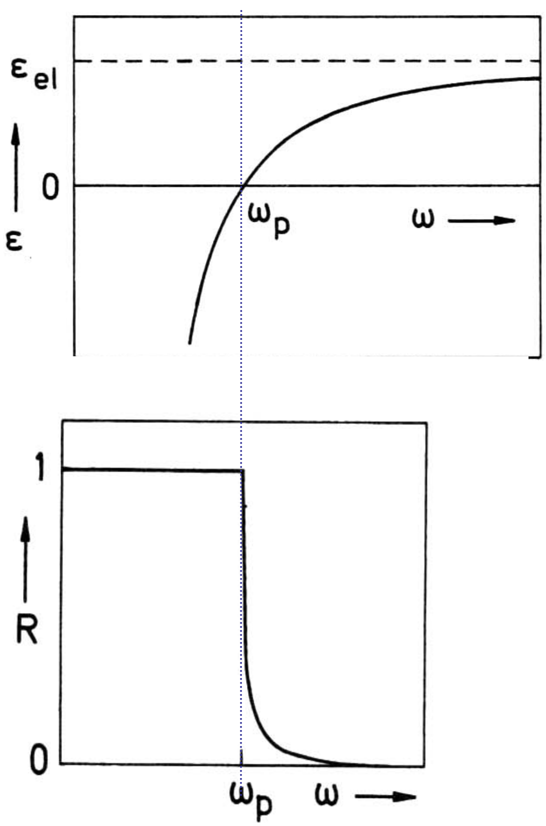
$E \propto e^{-i\omega t}e^{-kr}$

no propagation

reflection

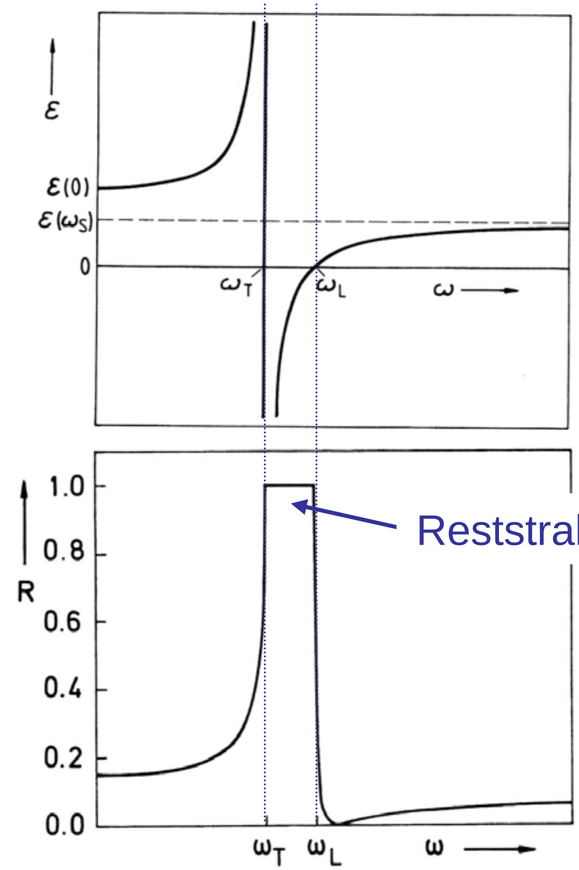
Dielectric function of metals and polar crystals

Metal
collective free electron oscillations (plasmons)
no restoring force



plasma frequency
(longitudinal oscillation)

Polar crystal
strong lattice vibrations (phonons)



Reststrahlenband

transversal optical
phonon frequency, TO

longitudinal optical
phonon frequency, LO

Surface Plasmon Polaritons (SPPs)
-
Introduction and basic properties

- Overview
- Light-matter interaction
- SPP dispersion and properties

Standard textbook:
- Heinz Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings
  Springer Tracts in Modern Physics, Vol. 111, Springer Berlin 1988

Overview articles on Plasmonics:
- A. Zayats, I. Smolyaninov, Journal of Optics A: Pure and Applied Optics **5,** S16 (2003)
- A. Zayats, et. al., Physics Reports **408,** 131-414 (2005)
- W.L.Barnes et. al., Nature **424,** 825 (2003)

SPP at metal/dielectric interfaces

From Maxwell's equations, combining the two curl eq. with $J_{ext}=\rho_{ext}=0$

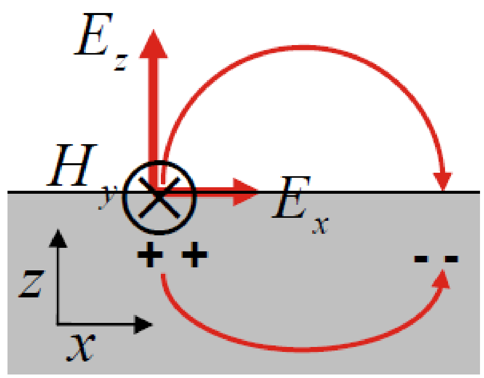
$$\nabla\times\nabla\times\boldsymbol{E}=-\mu_0\frac{\partial^2\boldsymbol{D}}{\partial t^2}\quad\rightarrow\quad\nabla^2\boldsymbol{E}-\frac{\varepsilon}{\boldsymbol{c}^2}\frac{\partial^2\boldsymbol{D}}{\partial t^2}=0$$

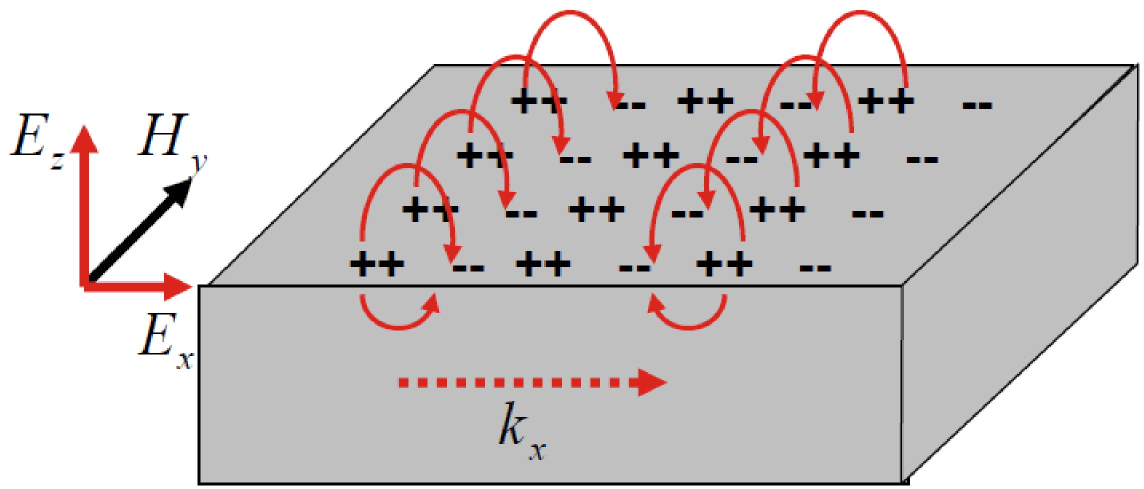
Assuming in general a harmonic time dependence

$$\boldsymbol{E}(\boldsymbol{r},t)=\boldsymbol{E}(\boldsymbol{r})e^{-i\omega t}\quad\rightarrow\quad\nabla^2\boldsymbol{E}-k_0^2\varepsilon\boldsymbol{E}=0$$

$$k_0=\frac{\omega}{c}$$

Helmholtz equation





SPP at metal/dielectric interfaces

In the defined geometry $\varepsilon = \varepsilon(z)$ → the propagating waves can be described as

$$\boldsymbol{E}(x,y,z) = \boldsymbol{E}(z)\,e^{i\beta x}$$

$\beta = k_x$ Propagation constant

→ inserted into the Helmholtz equation gives the wave equation

$$\frac{\partial^2 \boldsymbol{E}(z)}{\partial z^2} + \left(k_0^2 \varepsilon - \beta^2\right)\boldsymbol{E} = 0$$

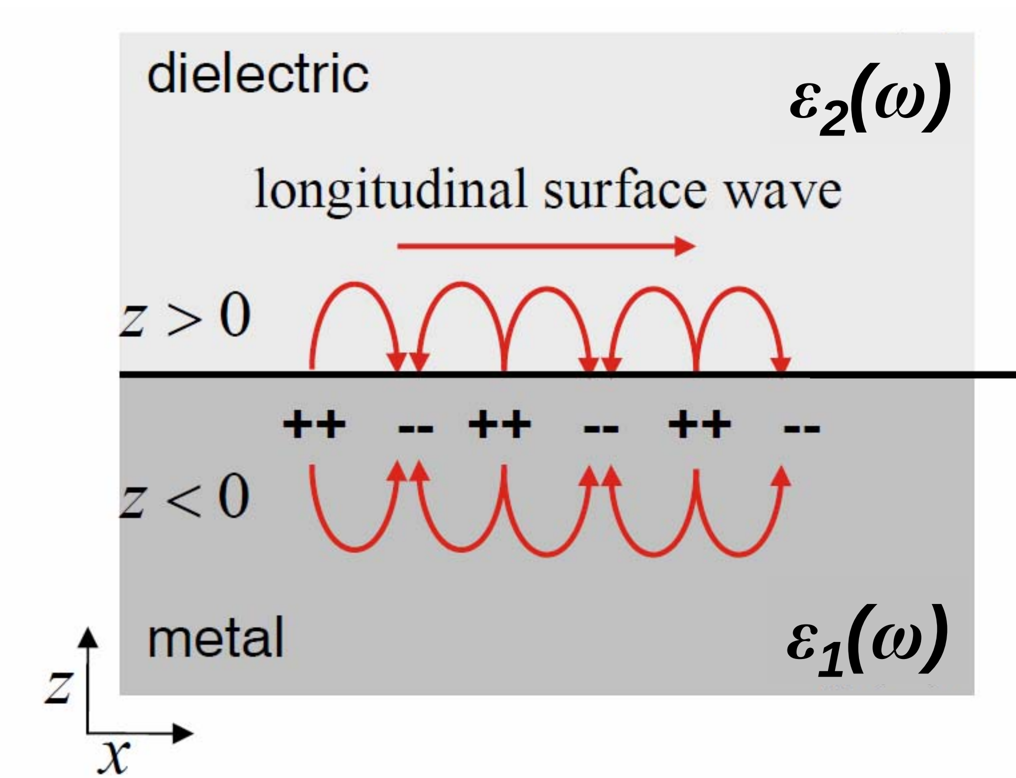
which is the starting point for any general guided EM modes

Two set of solutions

- TM or p modes → E_x, E_z and $H_y \neq 0$
- TE or s modes → H_x, H_z and $E_y \neq 0$

SPP at metal/dielectric interfaces

TM or p modes



$$H_y(z) = A_2 e^{i\beta x} e^{-ik_{2,z}z}$$

$$E_x(z) = iA_2 \frac{1}{\omega\varepsilon_0\varepsilon_2} k_2 e^{i\beta x} e^{-k_{2,z}z}$$

$$E_z(z) = -A_1 \frac{1}{\omega\varepsilon_0\varepsilon_2} e^{i\beta x} e^{-k_{2,z}z}$$

$$H_y(z) = A_1 e^{i\beta x} e^{k_{1,z}z}$$

$$E_x(z) = -iA_1 \frac{1}{\omega\varepsilon_0\varepsilon_1} k_1 e^{i\beta x} e^{k_{1,z}z}$$

$$E_z(z) = -A_2 \frac{1}{\omega\varepsilon_0\varepsilon_1} e^{i\beta x} e^{k_{1,z}z}$$

where Re[ε_1]<0 and 1/|k_z| defines the evanescent decay length $\perp$ to the interface
→ wave confinement

SPP at metal/dielectric interfaces

Continuity of $\varepsilon_i E_z$ → $A_1 = A_2$

Continuity of $E_{i,x}$ → $\dfrac{k_{2,z}}{k_{1,z}} = -\dfrac{\varepsilon_2}{\varepsilon_1}$

$H_{i,y}$ has to fulfill the wave eq. → $k_{1,z}^2 + k_0^2 \varepsilon_1 - \beta^2 = 0$, $k_{2,z}^2 + k_0^2 \varepsilon_2 - \beta^2 = 0$

$$\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

$$k_{i,z} = k_0 \sqrt{\frac{\varepsilon_i^2}{\varepsilon_1 + \varepsilon_2}}$$

Dispersion relations

Valid for both real and complex ε

TE or s modes

Continuity of E_y H_x →

$$A_1 \left(k_{1,z} + k_{2,z} \right) = 0 \quad \rightarrow \quad A_1 = A_2 = 0$$

SPP only exist for TM (p) polarization

SPP at metal/dielectric interfaces

The interface mode have to fulfill some conditions in order to exist

$$\mathrm{Im}[\varepsilon_i(\omega)] < \mathrm{Re}[\varepsilon_i(\omega)]$$

Propagating interface waves (The dispersion relation is valid) →

$$\beta \quad real \quad \Rightarrow \quad \varepsilon_1\varepsilon_2 \wedge (\varepsilon_1+\varepsilon_2) < 0 \quad or \quad \varepsilon_1\varepsilon_2 \wedge (\varepsilon_1+\varepsilon_2) > 0$$

β complex → damped propagation along the interface

Bound solution → vertical components are imaginary →

$$\varepsilon_1 + \varepsilon_2 < 0$$

$$\boxed{\varepsilon_1(\omega)\varepsilon_2(\omega) \wedge \left[\varepsilon_1(\omega)+\varepsilon_2(\omega)\right] < 0}$$

One of the dielectric functions must be negative and > than the other

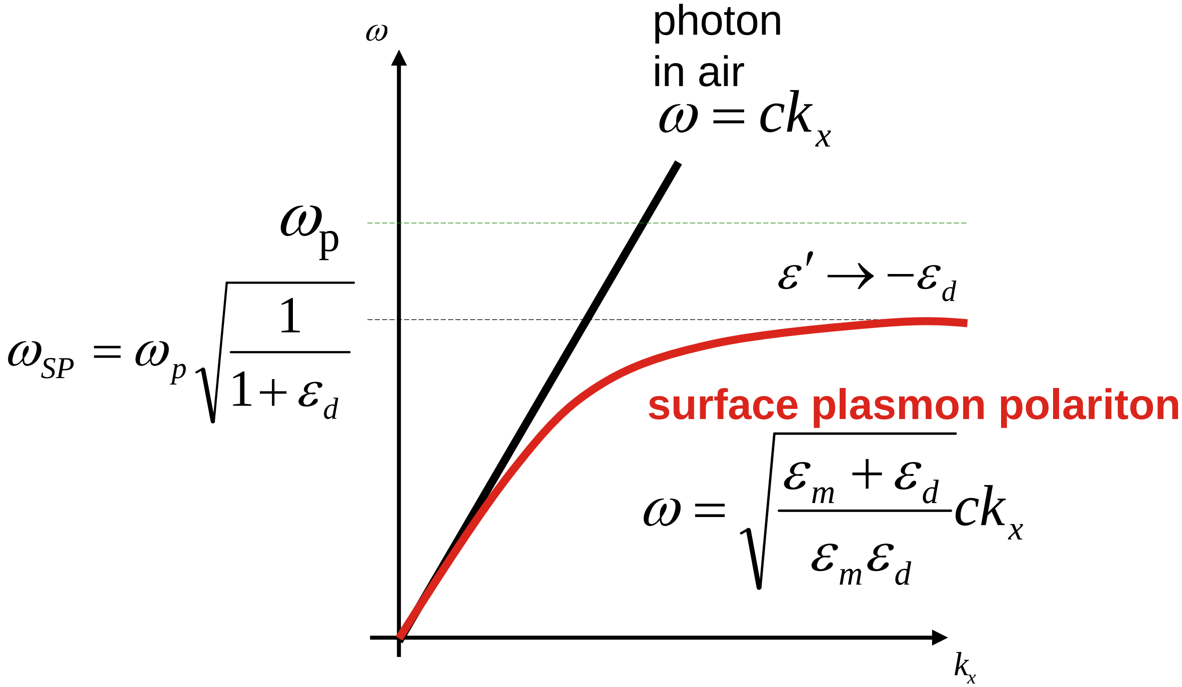
Dispersion relation of SPPs

$$\mathbf{E}_{\mathrm{SP}} = \mathbf{E}_0^{\pm} e^{i\left(k_x x \pm k_z z - \omega t\right)}$$

$$\boxed{k_x^2 = \left(\frac{\omega}{c}\right)^2 \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

$$\boxed{k_{zd}^2 = \left(\frac{\omega}{c}\right)^2 \frac{\varepsilon_d^2}{\left(\varepsilon_m + \varepsilon_d\right)}}$$

$$\boxed{k_{zm}^2 = \left(\frac{\omega}{c}\right)^2 \frac{\varepsilon_m^2}{\left(\varepsilon_m + \varepsilon_d\right)}}$$



$$\mathrm{Re}\left(\varepsilon_m\right) < 0 \text{ and } \left|\varepsilon_m\right| > \varepsilon_d \to \text{real } k_x$$

$$\Downarrow$$

k_{zd} and k_{zm} are imaginary

SPP at metal/dielectric interfaces

- surface plasmon polaritons are bound waves → SPP excitations lie on the right of the light line

- Radiation into metal occurs if $\omega > \omega_p$

- Between the bound and the radiative regime β is imaginary → no propagation

- for small k (<IR), β is close to k_0 and the light line

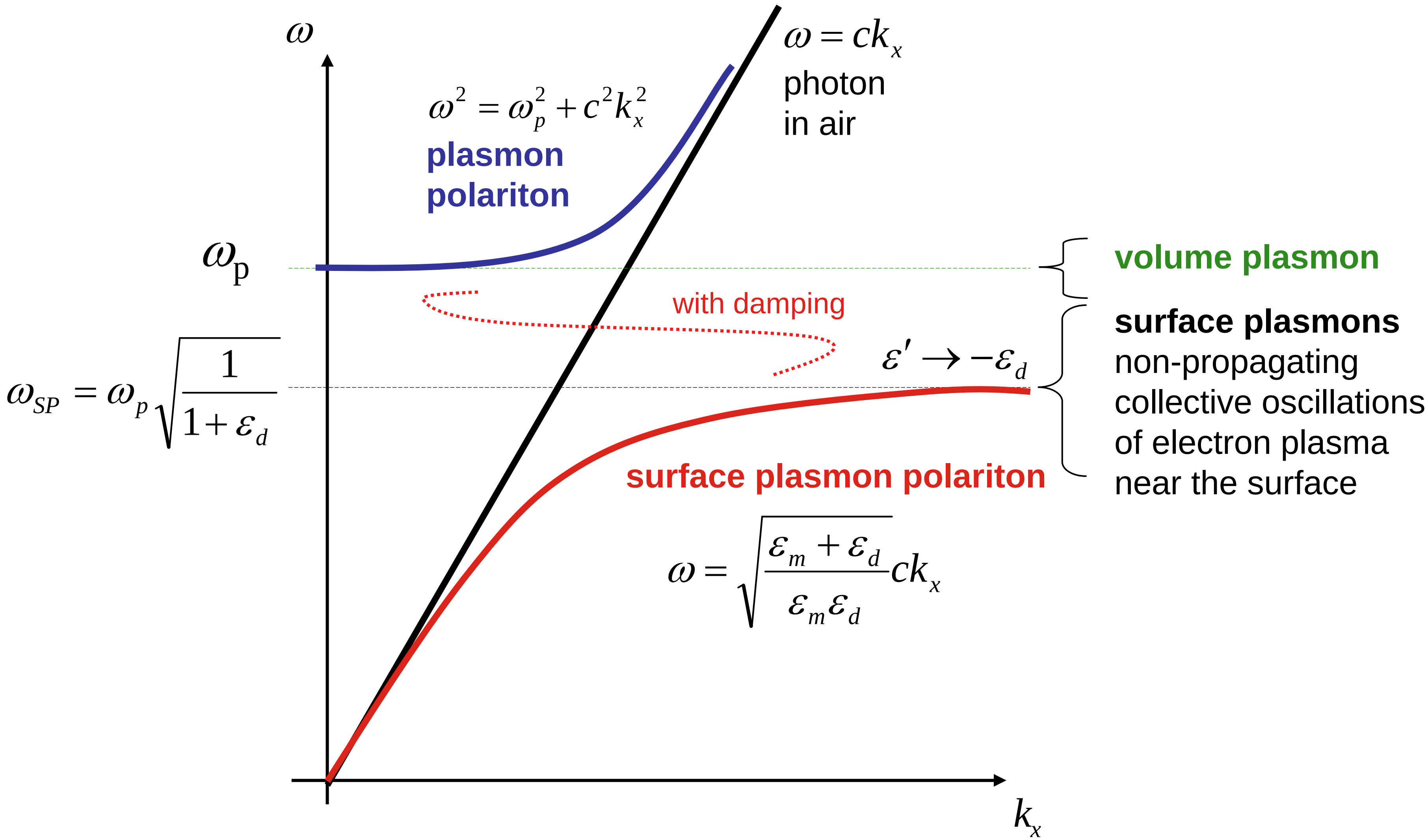
- for large k, $\omega_{sp} = \omega_p / (1+\varepsilon_2)^{1/2} \sim \omega_p / (2)^{1/2}$

- in the limit $\mathrm{Im}[\varepsilon_1(\omega)] = 0$, $\beta \to \infty$ and $v_g \to 0$ → the mode acquire an electrostatic character → *Surface Plasmon*

- but real metals suffer also from intraband transitions → *damping* and ε_1 is complex → the *quasibound regime* is allowed

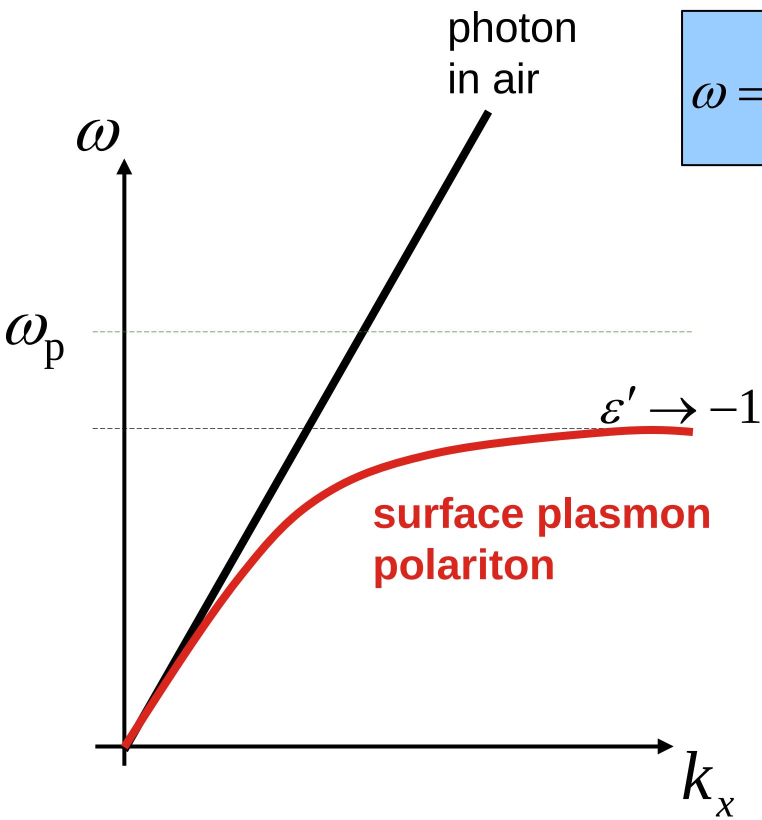
- at $\omega \sim \omega_{sp}$ → better confinement of the SPP but small propagation length (→ increased damping)

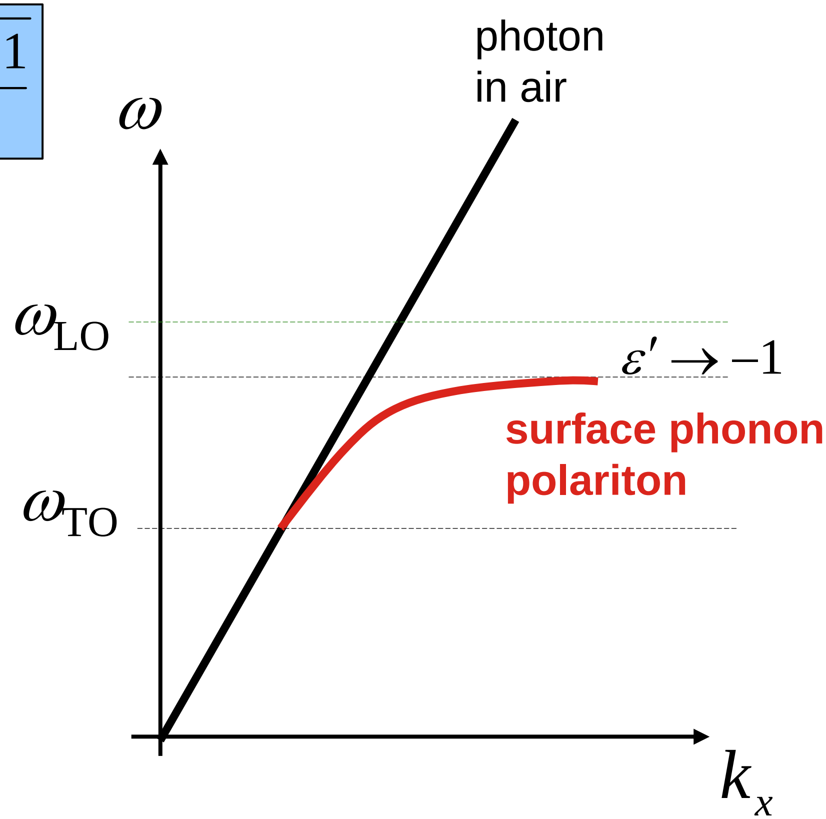
Volume vs. surface plasmon polariton



SP dispersion - plasmon *vs.* phonon

$$\omega = ck_x\sqrt{\frac{\varepsilon+1}{\varepsilon}}$$





Plasmon polaritons:

Light-electron coupling in
- metals
- semiconductors

Phonon polaritons:

Light-phonon coupling in polar crystals
- SiC, SiO_2
- III-V, II-VI-semiconductors

SP propagation length

metal/air interface

$$k_x = k_x' + ik_x'' = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m}{\varepsilon_m + 1}}$$

$$\mathbf{E}(x) = \mathbf{E}_0 e^{ik_x x} = \mathbf{E}_0 e^{ik_x' x} e^{-k_x'' x}$$

propagating term

exponential decay in x-direction

$$\boxed{L_x = \frac{1}{2k_x''}}$$

propagation length

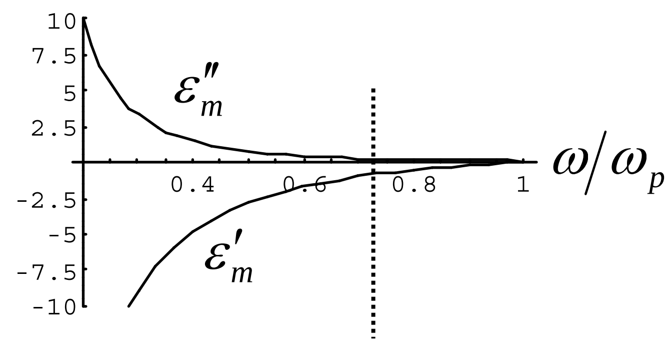
intensity !

Example silver:

$$\lambda = 514.5\ \text{nm} : L_x = 22\ \mu\text{m}$$
$$\lambda = 1060\ \text{nm} : L_x = 500\ \mu\text{m}$$

$$\varepsilon_d = 1$$
$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$
$$\gamma = 0.2$$

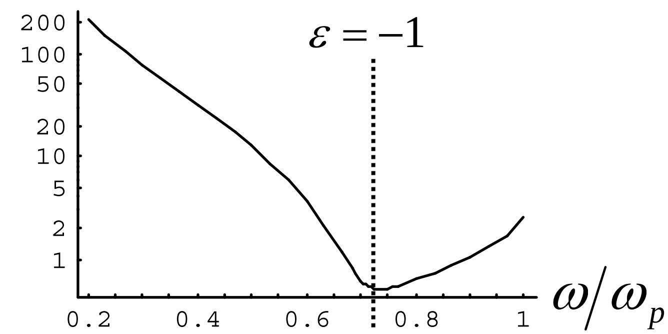
Drude model



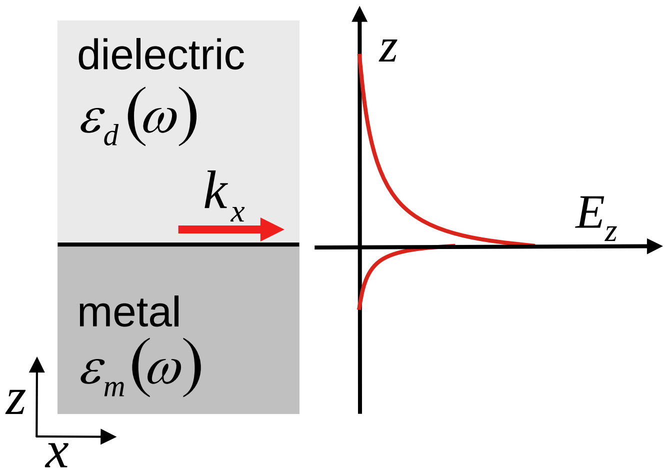
$L_x(\lambda_{vac})$

$$\omega_{SP} = \frac{\omega_p}{\sqrt{2}}$$

$$\varepsilon = -1$$



SPP field perpendicular to surface



$$\mathbf{E}(z) = \mathbf{E}_0 e^{-|\mathrm{Im}\, k_z||z|} \Rightarrow \boxed{L_z = \frac{1}{|\mathrm{Im}\, k_z|}}$$

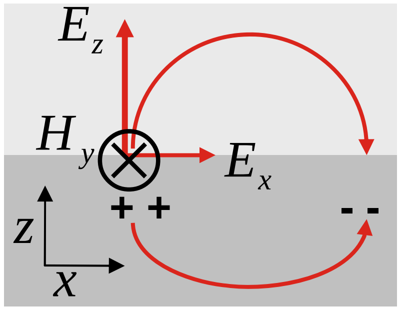
z-decay length (skin depth):

Examples:

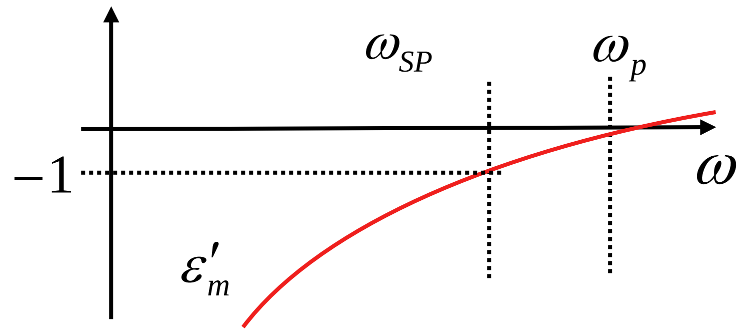
silver: $\lambda = 600\ \mathrm{nm} : L_{z,m} = 390\ \mathrm{nm}$ and $L_{z,m} = 24\ \mathrm{nm}$

gold: $\lambda = 600\ \mathrm{nm} : L_{z,m} = 280\ \mathrm{nm}$ and $L_{z,m} = 31\ \mathrm{nm}$

SPPs have transversal and longitudinal el. fields



The mag. field H is parallel to surface and perpendicular to propagation



El. field $\boxed{E_z = i\frac{k_x}{k_z}E_x}$

$$\frac{E_{zd}}{E_x} = i\sqrt{\frac{-\varepsilon_m}{\varepsilon_d}} \qquad \frac{E_{zm}}{E_x} = -i\sqrt{\frac{\varepsilon_d}{-\varepsilon_m}}$$

At large $|\varepsilon'_m|$ **values,**

the el. field in air/diel. has a strong transvers E_z component compared to the longitudinal component E_x

In the metal E_z is small against E_x

At large k_x, i.e. close to ε = - ε_d, both components become equal

$E_z = \pm iE_x$ (air: +i, metal: -i)

Dispersion and excitation of SPP

- SPP are 2D EM waves propagating at the interface conductor-dielectric (bound waves)
- $\beta > k_d$ → evanescent decay at both interfaces → confinement
- → SPP dispersion curve lies to the right of the light line
- → excitation by 3D light beams is not possible
- → phase-matching techniques are required

Excitation by charged particle impact

R. H. Ritchie, *Phys. Rev.* **106**, 874 (1957) → theoretical investigations of plasma losses in thin metallic films

→ predicted an additional loss at $\hbar\omega_p/(2)^{1/2}$

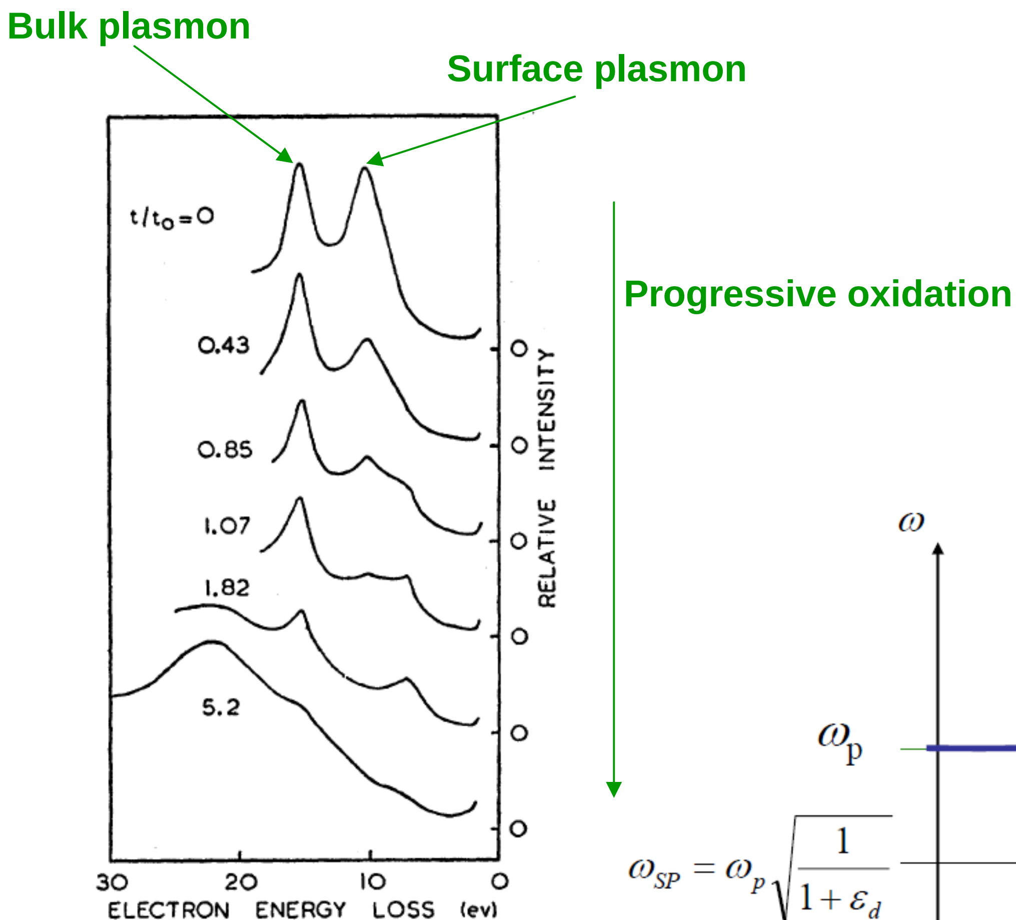
→ measured by C. J. Powell and J. B. Swan, *Phys. Rev.* **118**, 640 (1960)

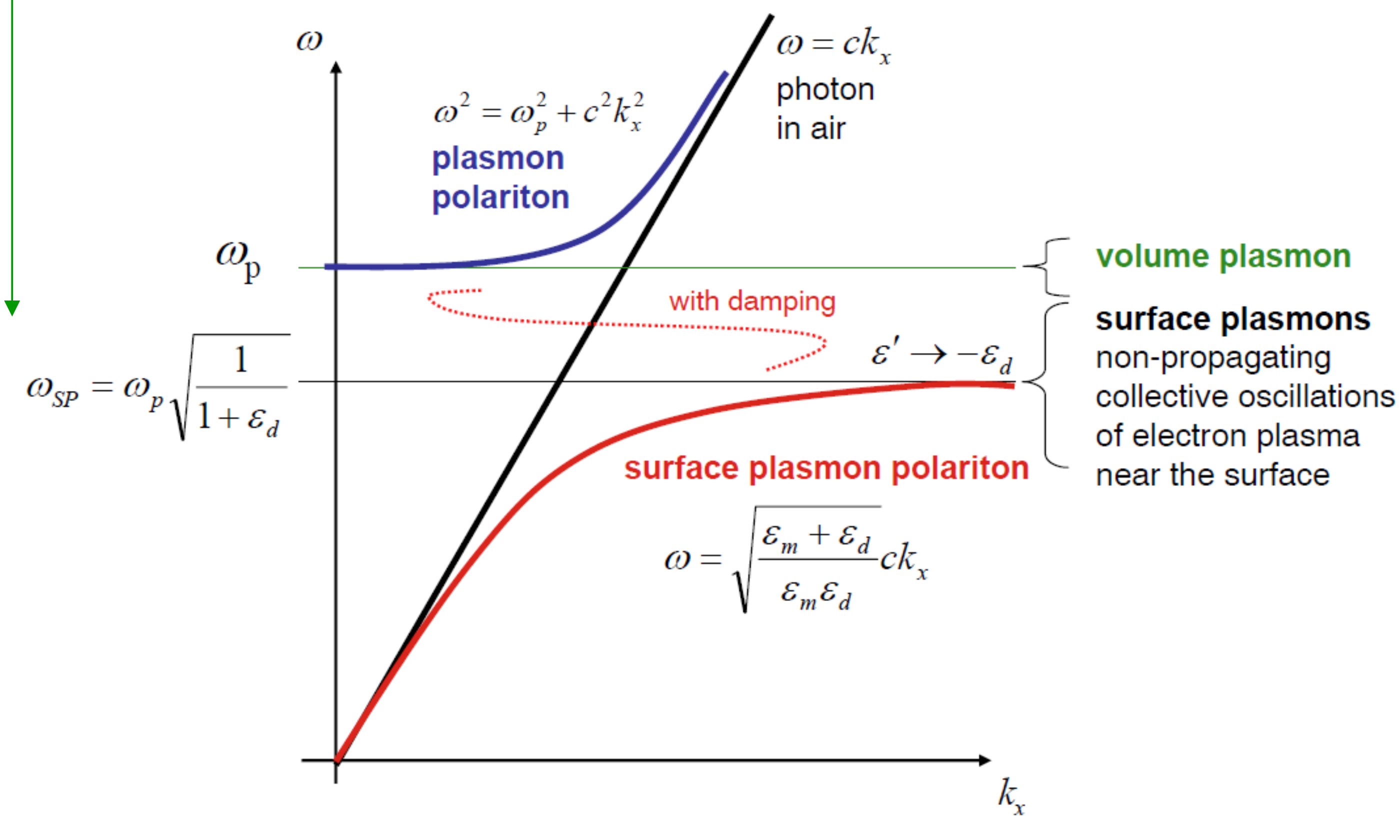
Quasi-static electromagnetic surface modes →

$$\varepsilon_m(\omega) + \varepsilon_d = 0 \wedge \varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad \Rightarrow \quad \omega_{sp} = \frac{\omega_p}{\sqrt{1+\varepsilon_d}}$$

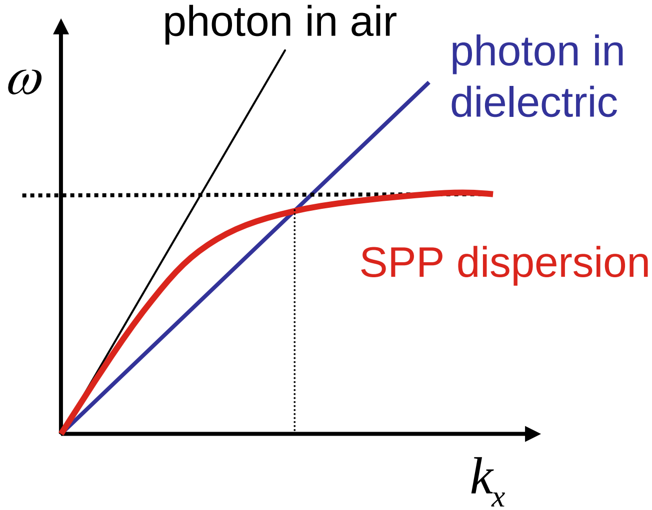
$$\Rightarrow \quad \beta \to \infty$$

Dispersion and excitation of SPP





Dispersion and excitation of SPPs



k of photon in air is always < k of SPP

⇩

no excitation of SPP is possible

in a dielectric k of the photon is increased

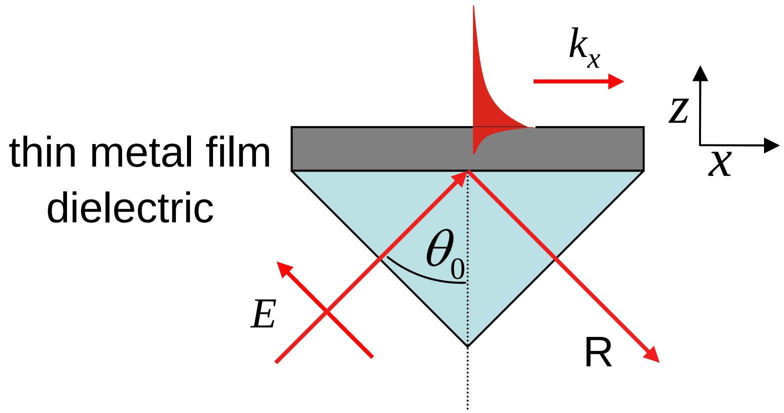
⇩

k of photon in dielectric can equal k of SPP

⇩

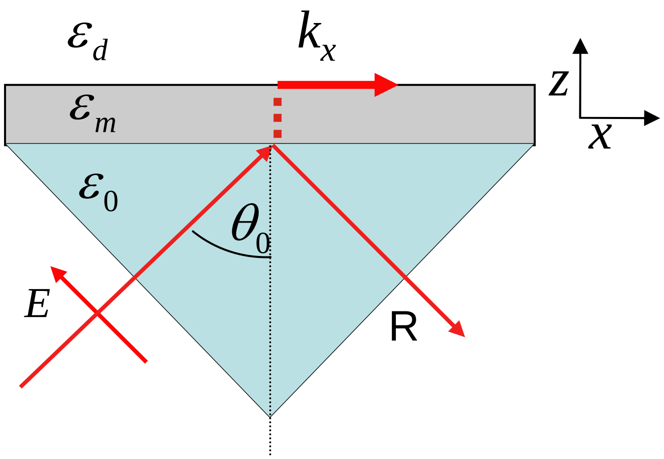
SPP can be excited by p-polarized light
(SPP has longitudinal component)

Kretschmann configuration



Excitation by ATR

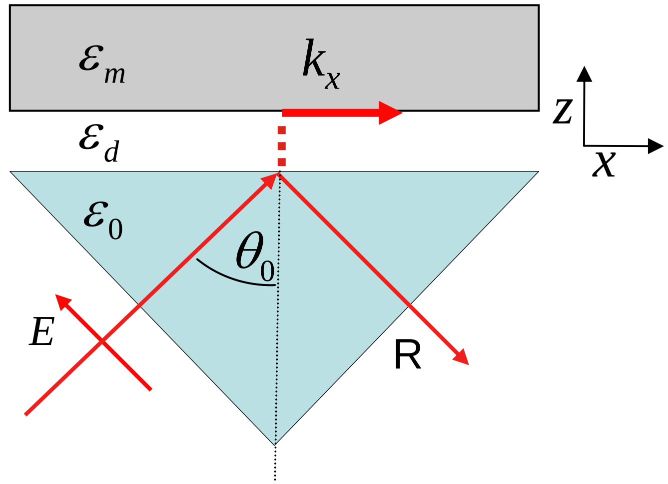
Kretschmann configuration



total reflection at prism/metal interface
-> evanescent field in metal
-> excites surface plasmon polariton at
interface metal/dielectric medium

metal thickness < skin depth

Otto configuration



total reflection at prism/dielectric medium
-> evanescent field excites surface plasmon
at interface dielectric medium/metal

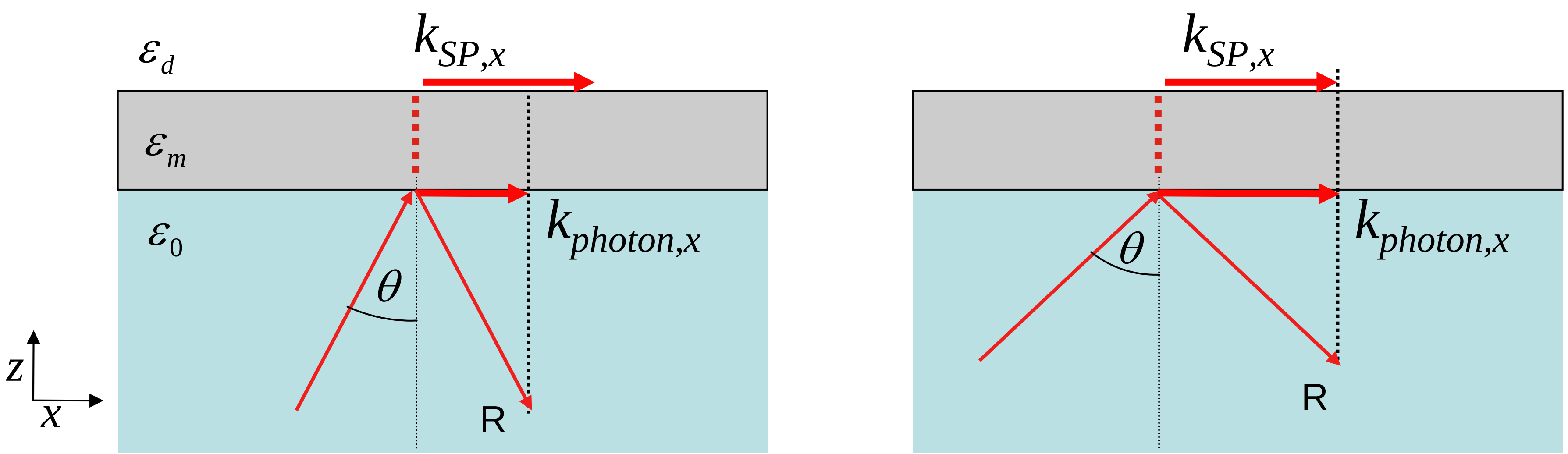
usful for surfaces that should not be damaged
or for surface phonon polaritons on thick crystals

distance metal – prism of about λ

ATR: Attenuated Total Reflection

Excitation by ATR

SPP excitation requires $k_{photon,x} = k_{SP,x}$



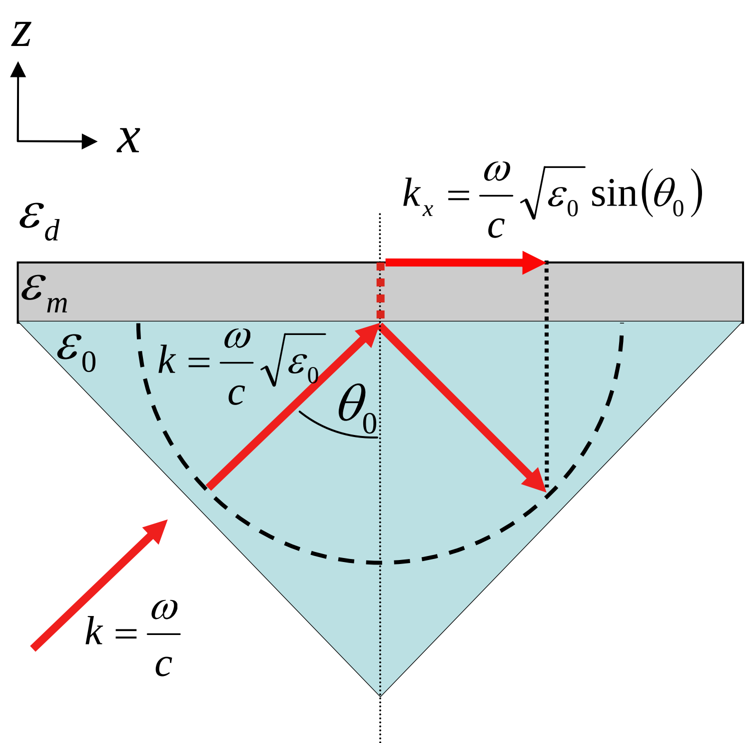
$k_{photon,x} < k_{SP,x}$

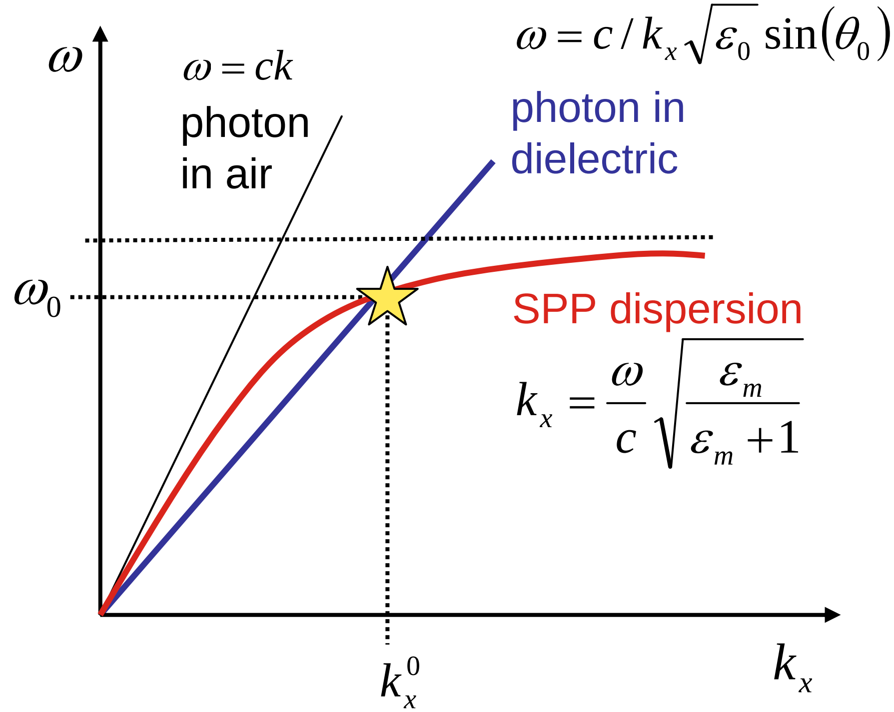
$k_{photon,x} = k_{SP,x}$

→ **no SPP excitation**

→ **SPP excitation**

Excitation by Kretschmann configuration



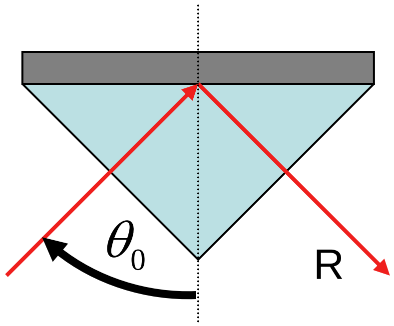


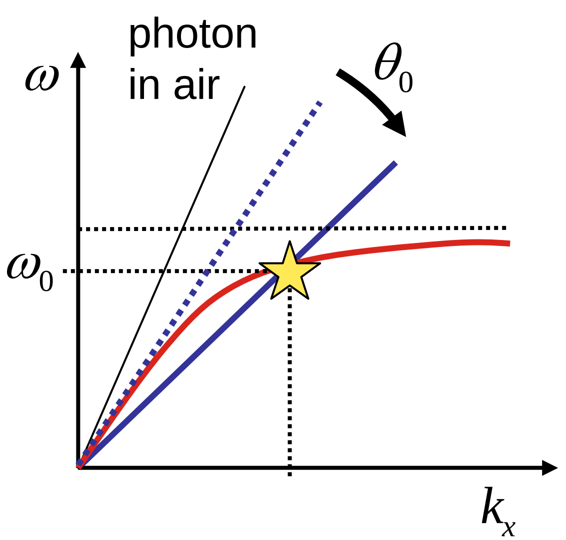
$$\boxed{\frac{\omega_0}{k_x^0} = c\sqrt{\frac{\varepsilon_m + 1}{\varepsilon_m}} = \frac{c}{\sqrt{\varepsilon_0}\sin(\theta_0)}}$$

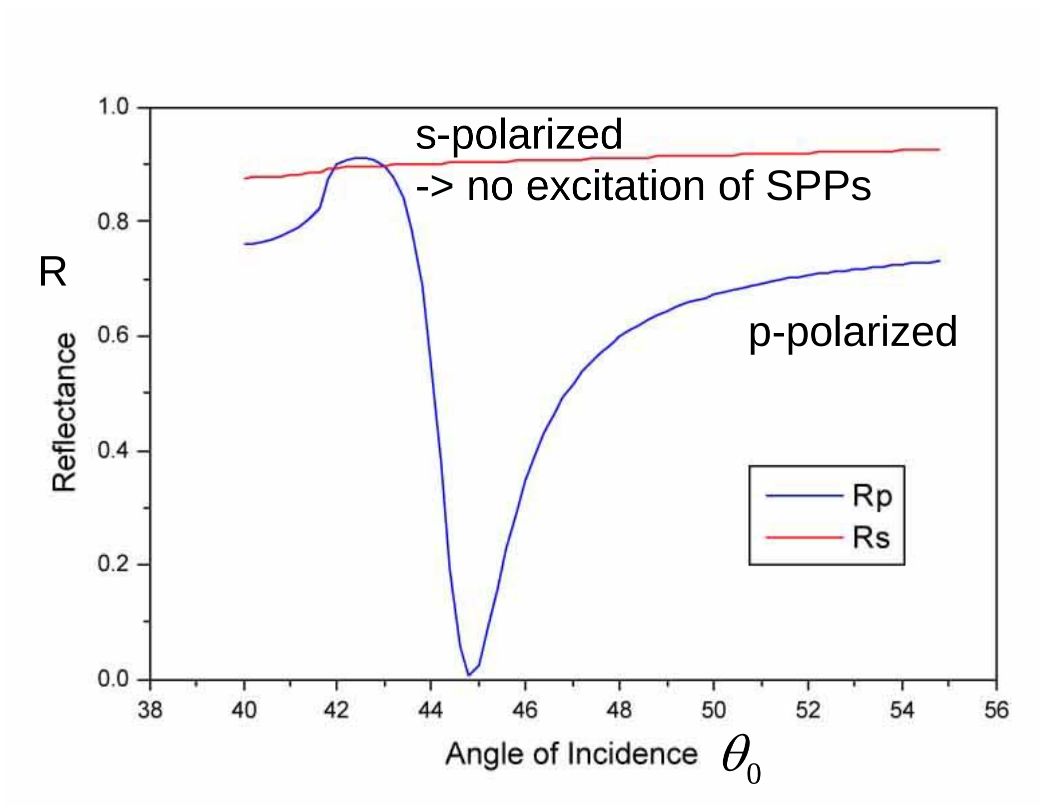
Resonance condition

Kretschmann configuration – angle scan

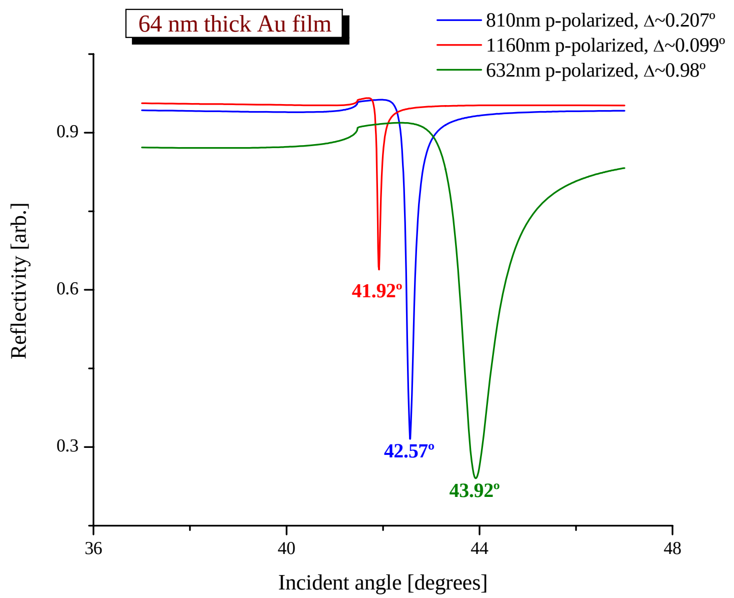
illumination freq. ω_0= const.

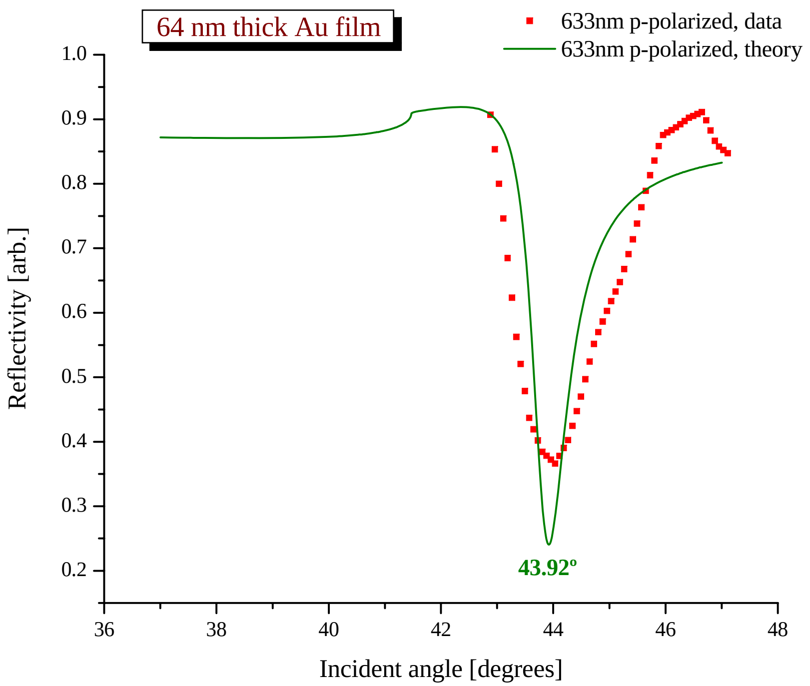




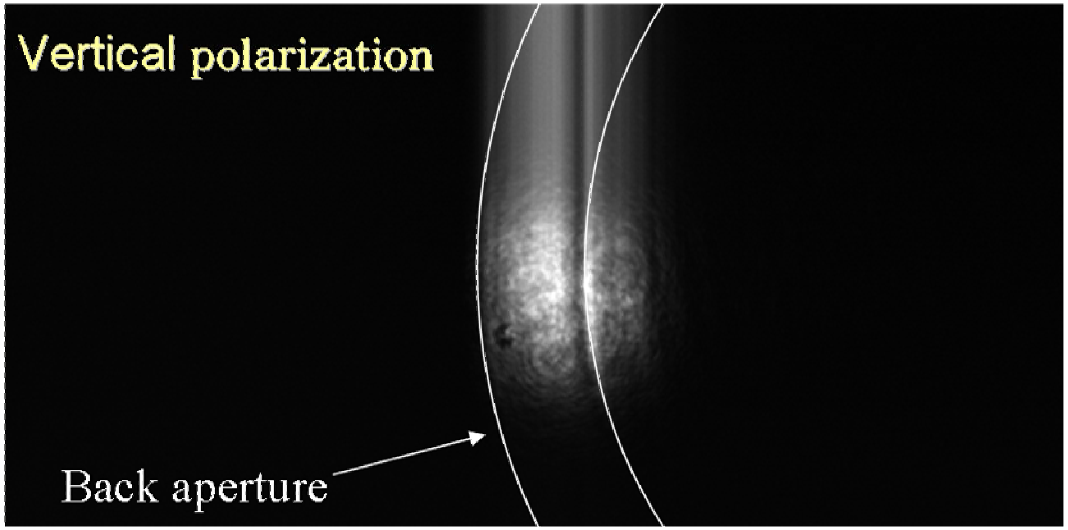


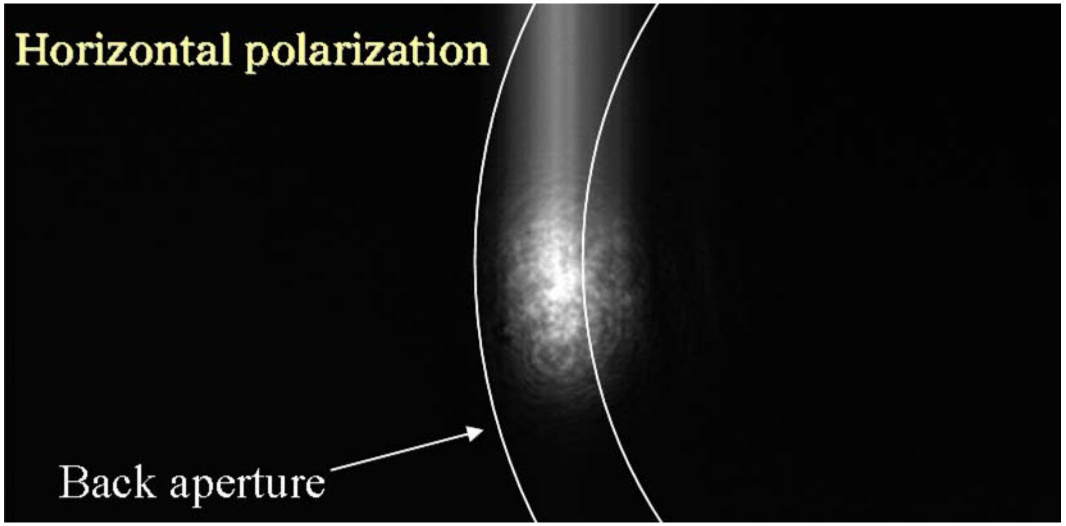
Dispersion and excitation of SPP





HeNe SPP excitation at Au-air interface (ATR)





Methods of SPP excitation

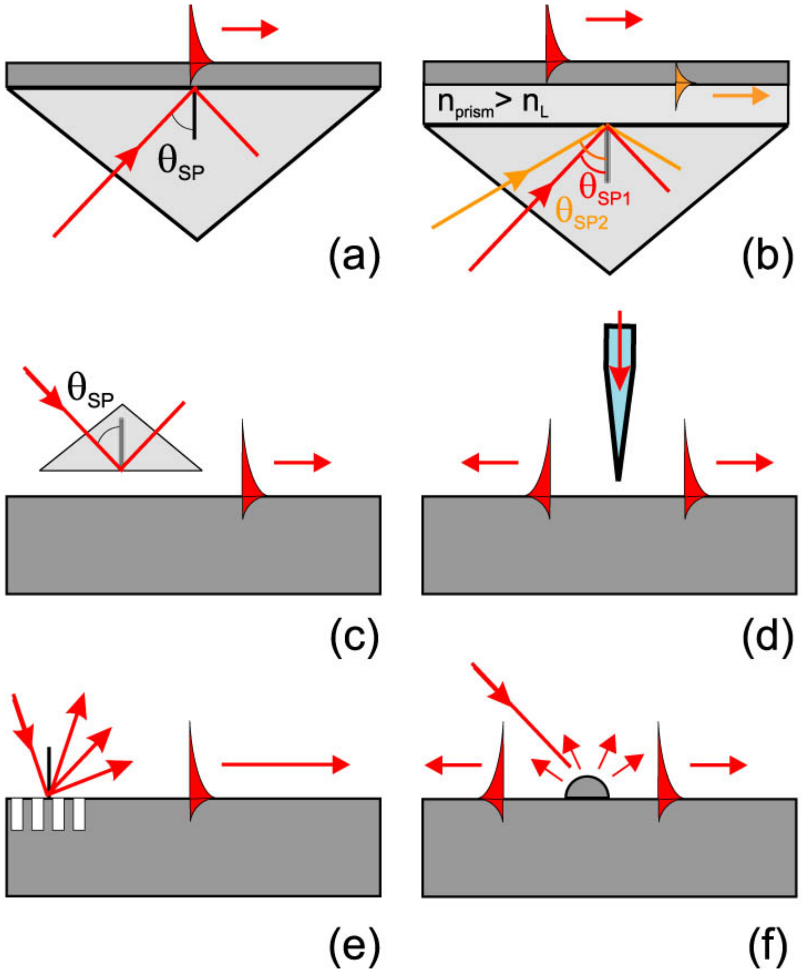
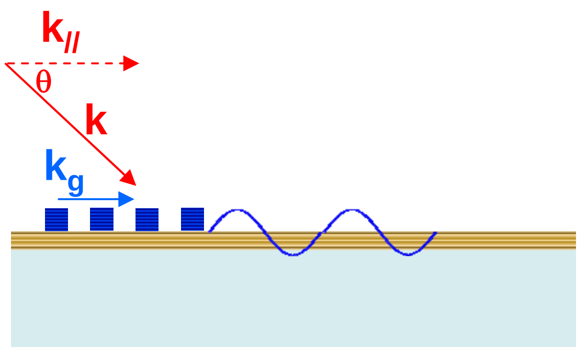


Figure 3. SPP excitation configurations: (a) Kretschmann geometry, (b) two-layer Kretschmann geometry, (c) Otto geometry, (d) excitation with an SNOM probe, (e) diffraction on a grating, and (f) diffraction on surface features.

$n_{prism} > n_L$!!

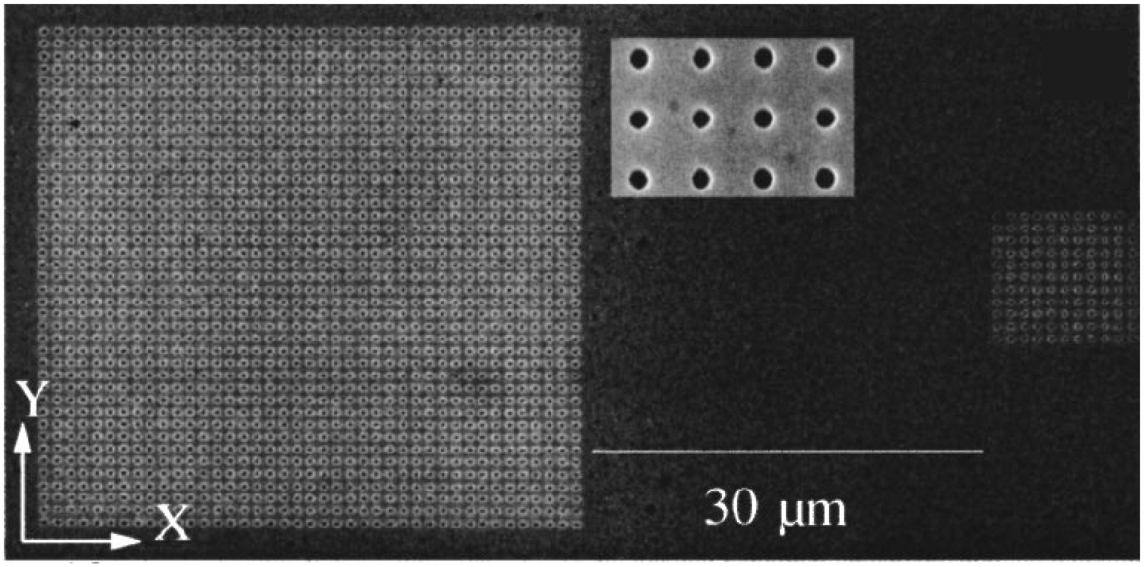
Dispersion and excitation of SPP

Excitation by grating coupling



$$k_{//} = k\sin\theta$$

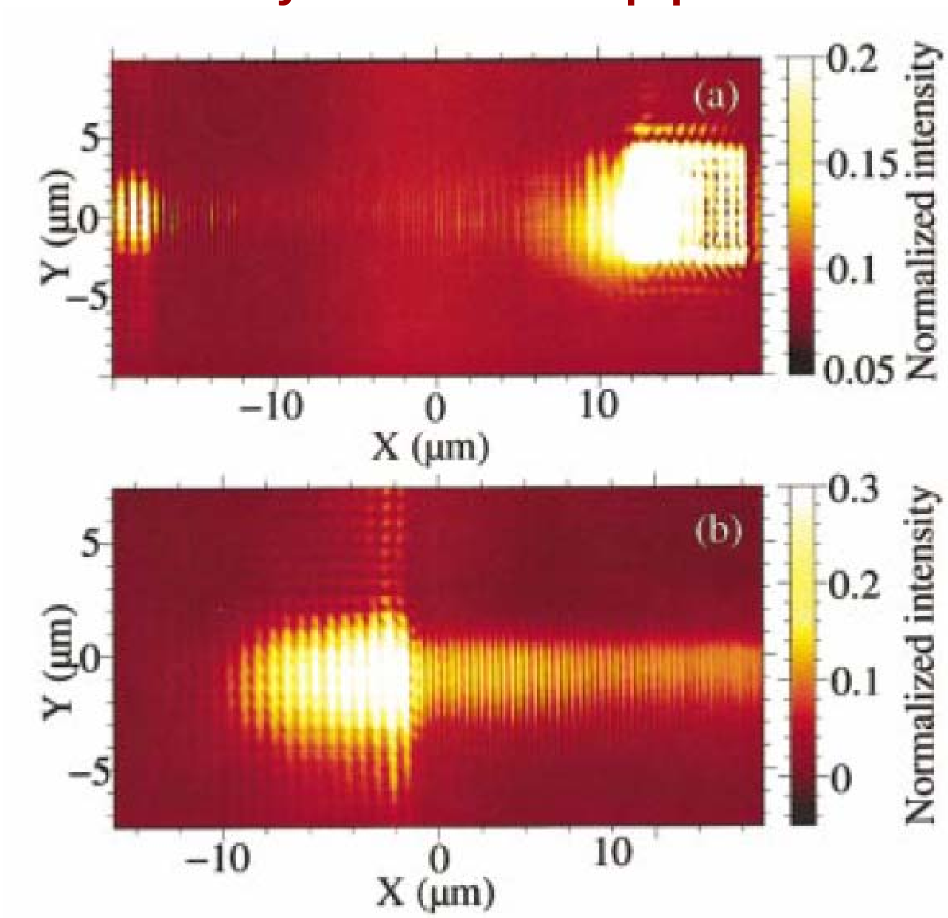
$$k_g = \frac{2\pi}{a}\nu = g\nu \quad \rightarrow \quad \beta = k\sin\theta + g\nu$$



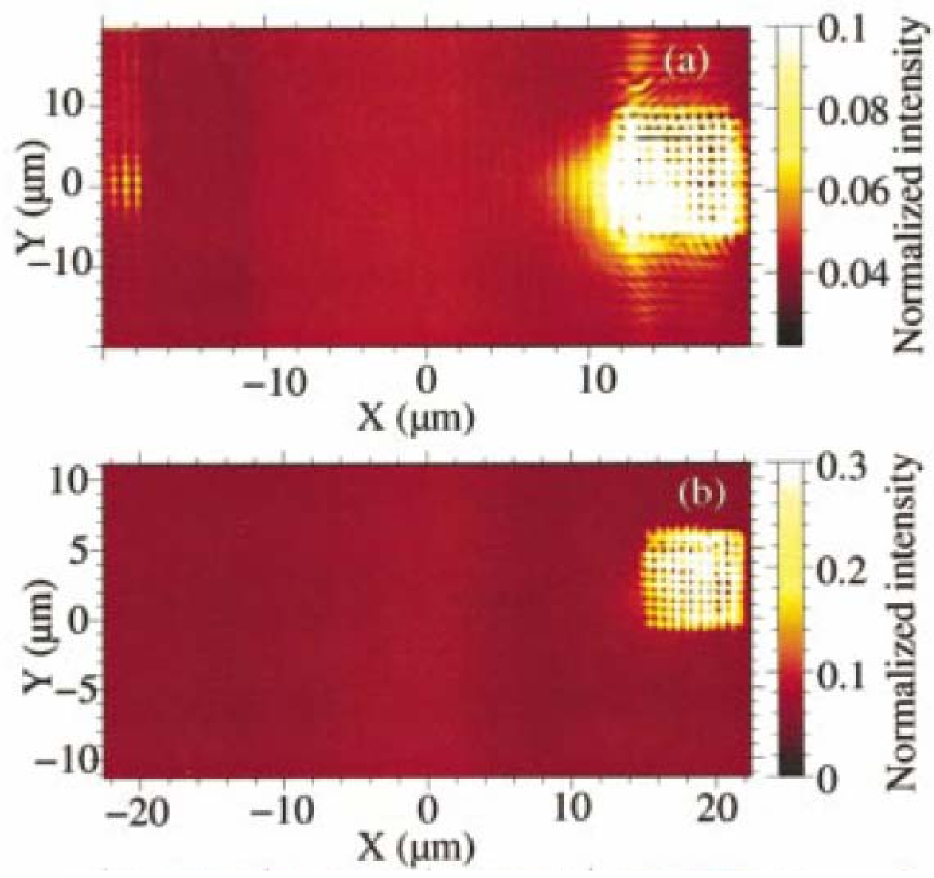
E. Devaux, T. W. Ebbesen, J.C. Weeber, A. Dereux, *Appl. Phys. Lett.* **83**, 4936 (2003)

Dispersion and excitation of SPP

Periodicity a = 760 nm & p-pol beam



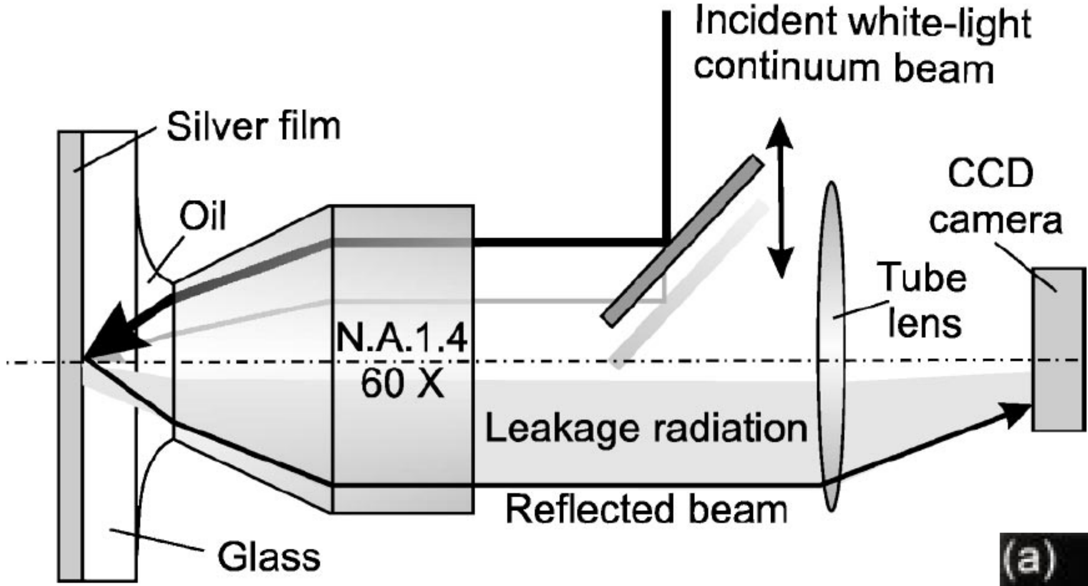
Periodicity a = 760 nm & s-pol beam

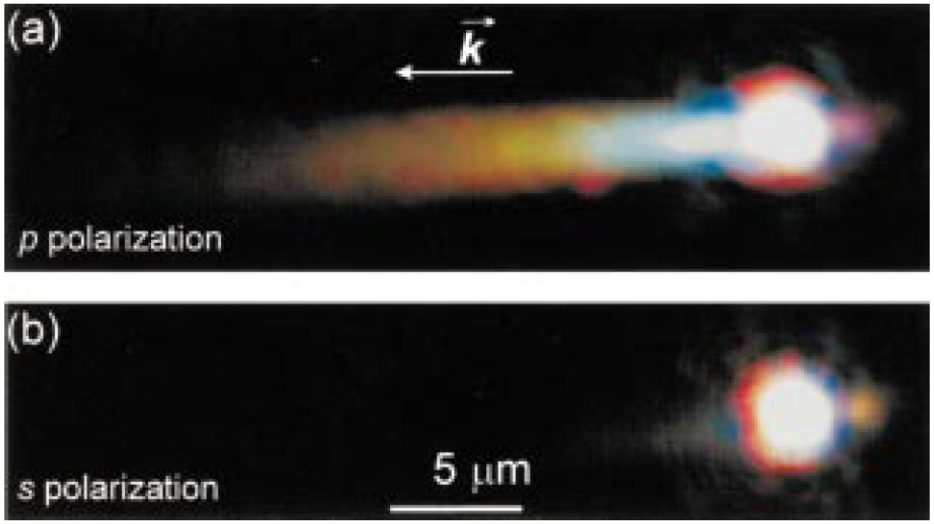


Periodicity a = 700 nm & p-pol beam

Dispersion and excitation of SPP

Excitation by highly focused optical beams



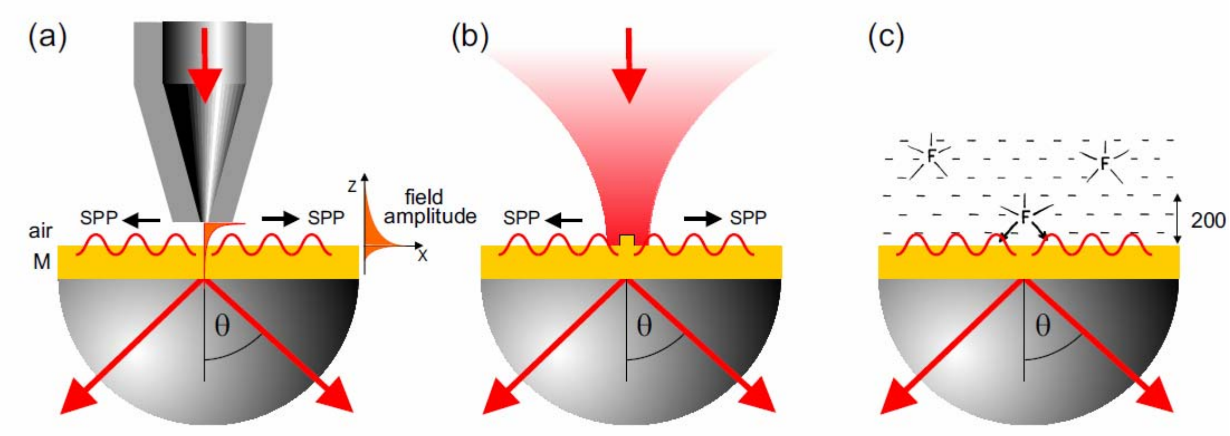


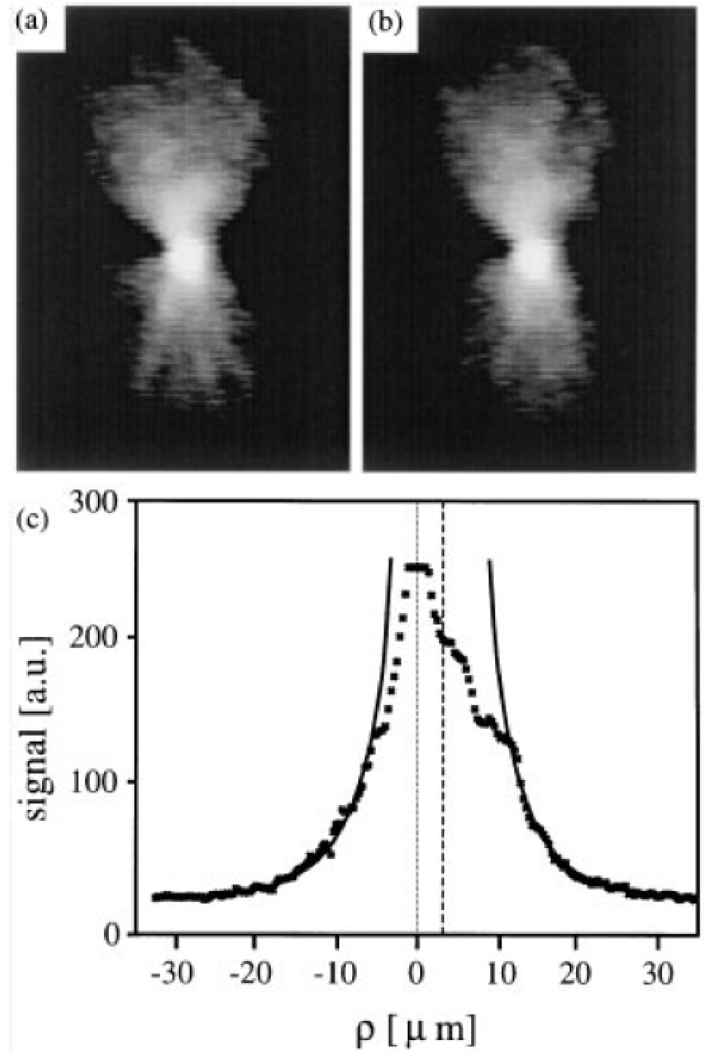
$$\theta_{SPP} = \arcsin\left(\beta / nk_0 \right) > \theta_c$$

A. Bouhelier and G. P. Wiederrecht, *Opt. Lett.* **30**, 884 (2005)

Dispersion and excitation of SPP

Near-field excitation



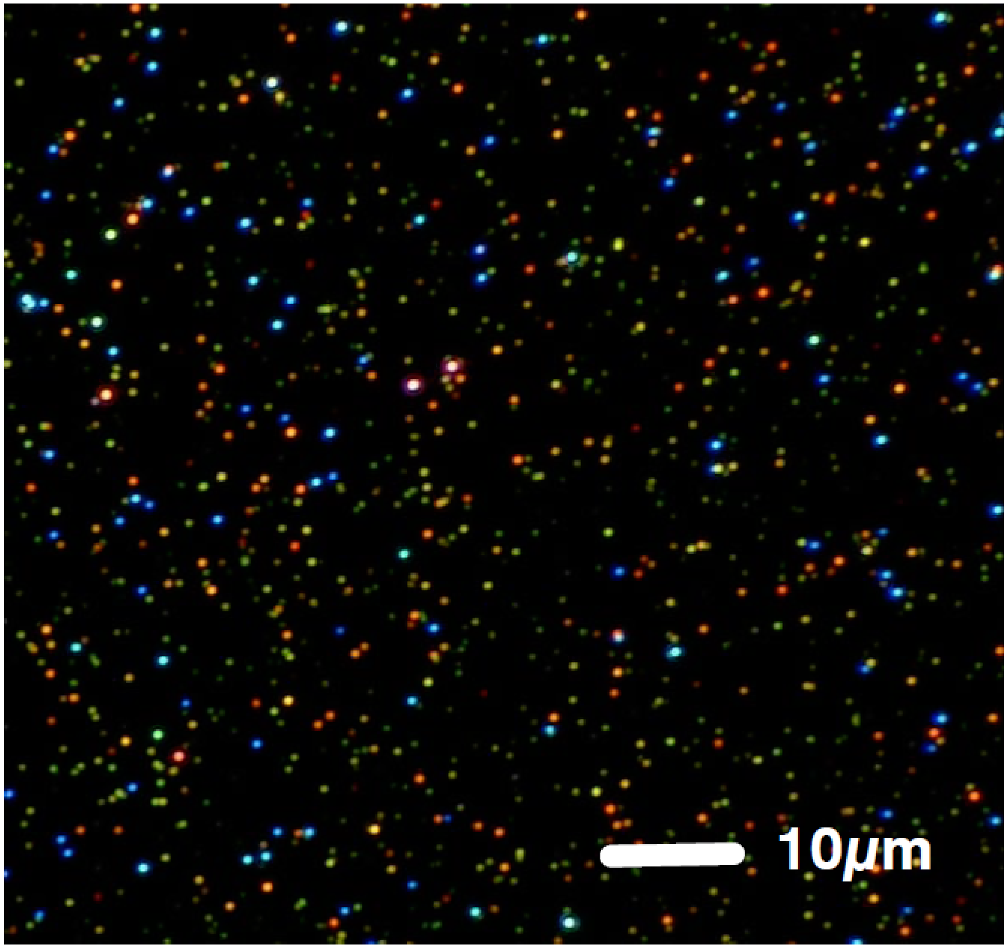


Small aperture → wavevector components $k_0 < \beta < k$ → phase matched excitation

B. Hecht, H. Bielefeld, L. Novotny, Y. Inouye, D. W. Pohl *Phys. Rev. Lett.* **77**, 1889 (1996)

Localized Surface Plasmon

Overview

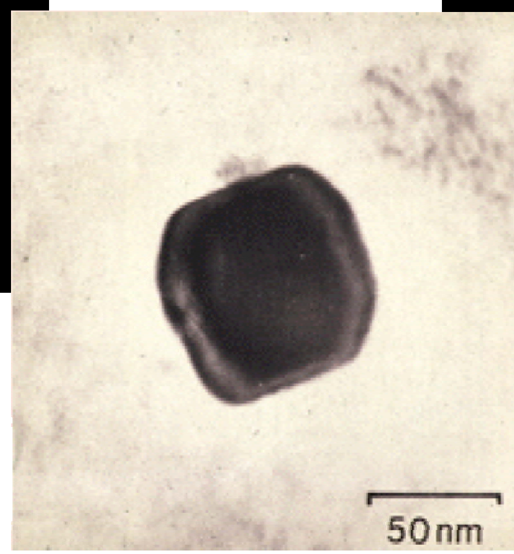


True color image of a sample containing gold and silver nanospheres as well as gold nanorods photographed with a dark field microscope.
Each dot corresponds to light scattered by an individual nanoparticle at the plasmon resonance. The resonance wavelength varies from blue (silver nanospheres) via green and yellow (gold nanospheres) to orange and red (nanorods).

Localized Surface Plasmon

Overview

Illuminated from inside



Illuminated from outside

Lycurgus cup

Localized Surface Plasmon

Overview

Localized Surface Plasmon

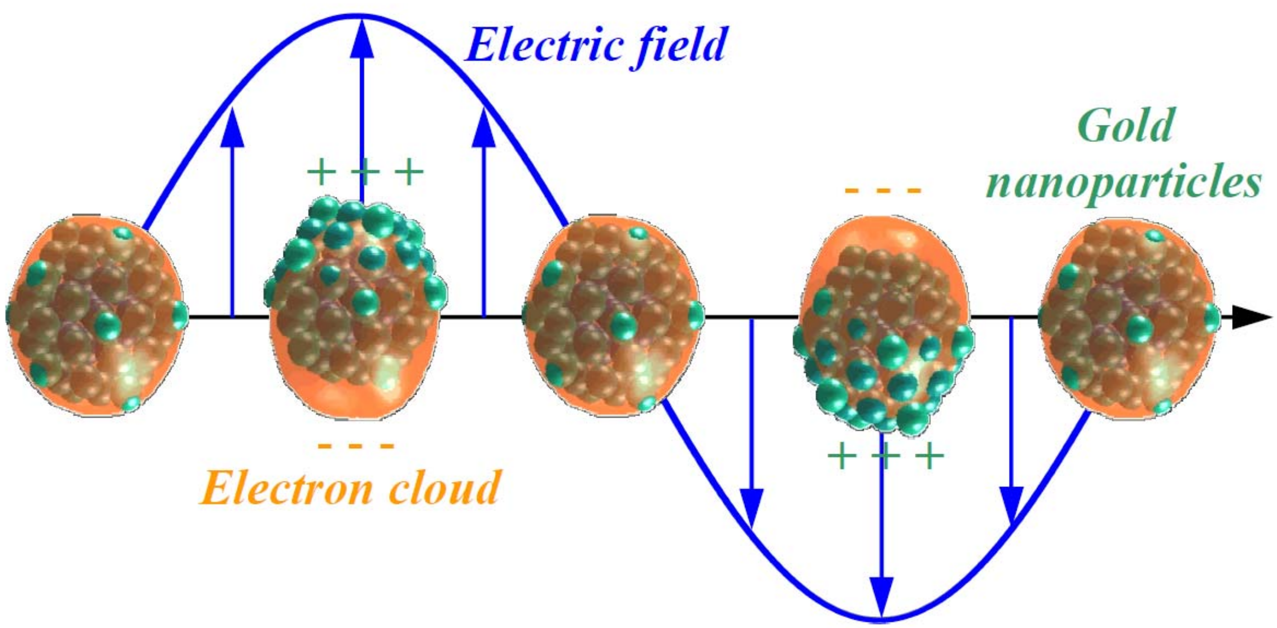
- SPP are 2D, dispersive EM waves propagating at the interface conductor-dielectric
- SP are non-propagating collective oscillations of electron plasma near the surface
- LSP are non-propagating excitations of the conduction electrons of a metallic nanostructure coupled to an EM field.

Localized Surface Plasmon

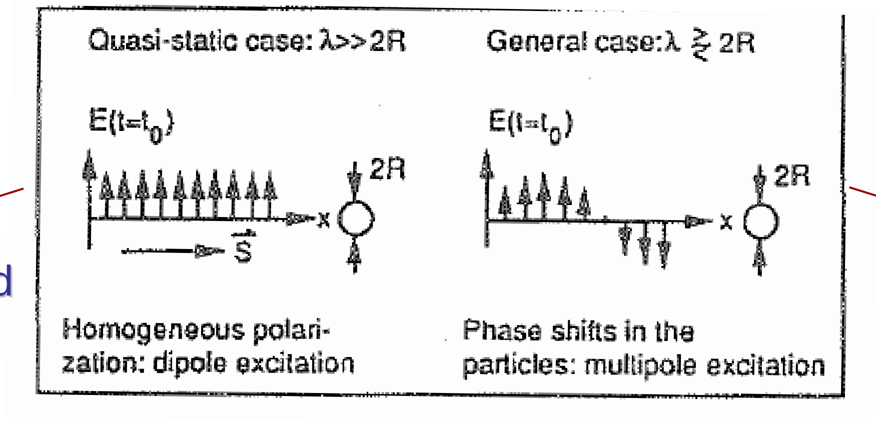
- The curved surface of the nanostructure act as a restoring force → immobile positively charged core ion

- The curved surface of the nanostructure allows the excitation of the LSP by 3D light

- The resonance falls into the visible region for Au and Ag nanoparticles



Localized Surface Plasmon



Particle in an electrostatic field → nanoparticle acts as an electric dipole

Mie Theory → rigorous electrodynamic approach

Drude Free Electron Model

$$m_e \frac{\partial^2 \mathbf{r}}{\partial t^2} + m_e \Gamma \frac{\partial \mathbf{r}}{\partial t} = e\mathbf{E}_0 e^{-iwt} \qquad \Gamma = \frac{v_F}{l}$$

	Au	Ag	Cu
n/m^{-3}	$5.90 \cdot 10^{28}$	$5.76 \cdot 10^{28}$	$8.45 \cdot 10^{28}$
$\sigma/(\Omega\,\mathrm{m})^{-1}$	$4.9 \cdot 10^{7}$	$6.6 \cdot 10^{7}$	$6.5 \cdot 10^{7}$
m^*/m_e	0.99	0.96	1.49
$\hbar\omega_p/\,\mathrm{eV}$	9.1	9.1	8.8
$\tau/\,\mathrm{fs}$	29	40	40

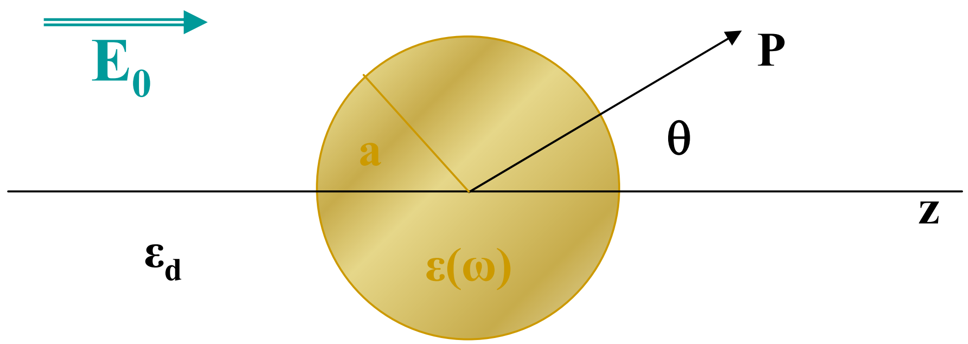
v_F → Fermi velocity (about 1.4 nm/fs in the case of Au and Ag)
l is the electron mean free path (l_{Au}=42 nm and l_{Ag}=52 nm at 273K)

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

it is not possible to ignore the contribution to the dielectric function of the ***interband transitions***

Localized Surface Plasmon

Sub-wavelength metal particles



electrostatic approach →
Laplace equation for the electric potential + boundary conditions

$$\nabla^2 \Phi = 0 \quad \rightarrow \quad \mathbf{E} = -\nabla\Phi$$

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

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

Applied field

Oscillating dipole field

Localized Surface Plasmon

$$\mathbf{E} = -\nabla\Phi \quad \rightarrow$$

$$\mathbf{E_{in}} = \frac{3\varepsilon_d}{\varepsilon + 2\varepsilon_d}\mathbf{E}_0$$

$$\mathbf{E_{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}}{4\pi\varepsilon_0\varepsilon_d}\frac{1}{r^3}$$

$$\Phi_{out} = -E_0 r\cos\theta + \frac{\mathbf{p}\cdot\mathbf{r}}{4\pi\varepsilon_0\varepsilon_d r^3}$$

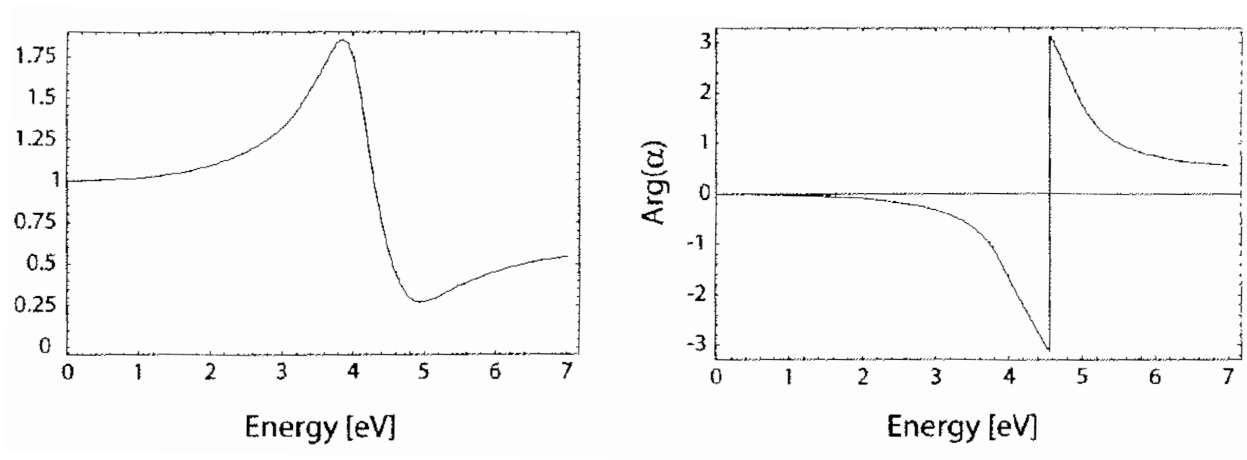
$$\mathbf{p} = \varepsilon_0\varepsilon_d\alpha\mathbf{E}_0$$

$$\mathbf{p} = 4\pi\varepsilon_0\varepsilon_d a^3\frac{\varepsilon - \varepsilon_d}{\varepsilon + 2\varepsilon_d}\mathbf{E}_0$$

Localized Surface Plasmon

$$\alpha = 4\pi a^3 \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d}$$

Complex polarizability of a sub-wavelength diameter
in the electrostatic approximation



Localized Surface Plasmon

$$\left|\varepsilon(\omega)+2\varepsilon_d\right|\rightarrow 0$$

Complex polarizability enhancement

$$\boxed{\mathrm{Re}\left[\varepsilon(\omega)\right]=-2\varepsilon_d \qquad if\ \ \mathrm{Im}\left[\varepsilon(\omega)\right]\ is\ small}$$

Fröhlic condition

Geometry	*Resonance condition*	*Resonance frequency*
Bulk metal	$\varepsilon_1(\omega)=0$	$\omega_1=\omega_p$
Planar surface	$\varepsilon_1(\omega)=-1$	$\omega_1=\omega_p/\sqrt{2}$
Thin film	$\frac{\varepsilon(\omega)+1}{\varepsilon(\omega)-1}=\pm e^{-k_x d}$	$\omega_1=\omega_p\sqrt{(1\pm\exp(-k_x t))/2}$
Sphere (quasi-static)	$\varepsilon_1(\omega)=-2$	$\omega_1=\omega_p/\sqrt{3}$
Ellipsoid (quasi-static)	$\varepsilon_1(\omega)=-(1-L)/L$	$\omega_1=\omega_p L$

Localized Surface Plasmon

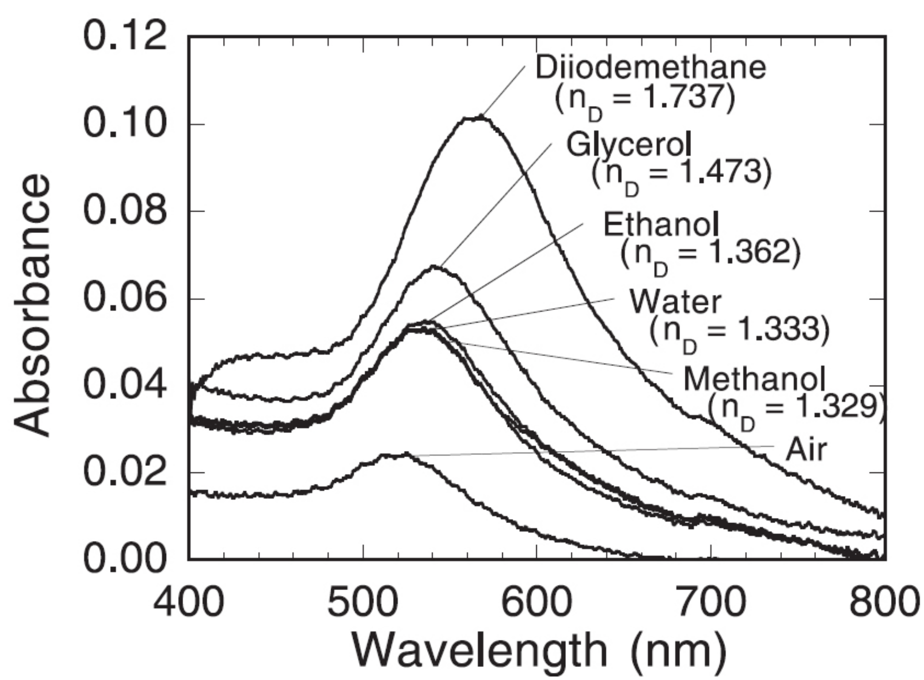
Corresponding absorption & scattering cross sections calculated via the Pointing vector from the full EM field associated with an oscillating dipole

$$\sigma_{sca} = \frac{k^4}{6\pi}|\alpha|^2 = \frac{8\pi}{3}k^4 a^6 \left|\frac{\varepsilon(\omega)-\varepsilon_d}{\varepsilon(\omega)+2\varepsilon_d}\right|^2$$

$$\sigma_{abs} = k\,\mathrm{Im}(\alpha) = 4\pi k a^3\,\mathrm{Im}\left[\frac{\varepsilon(\omega)-\varepsilon_d}{\varepsilon(\omega)+2\varepsilon_d}\right]$$

$$\boxed{\sigma_{ext} = \sigma_{sca} + \sigma_{abs}}$$

$$I_{ext}(\omega) = \frac{I_0(\omega)}{S}\sigma_{ext}(\omega)$$



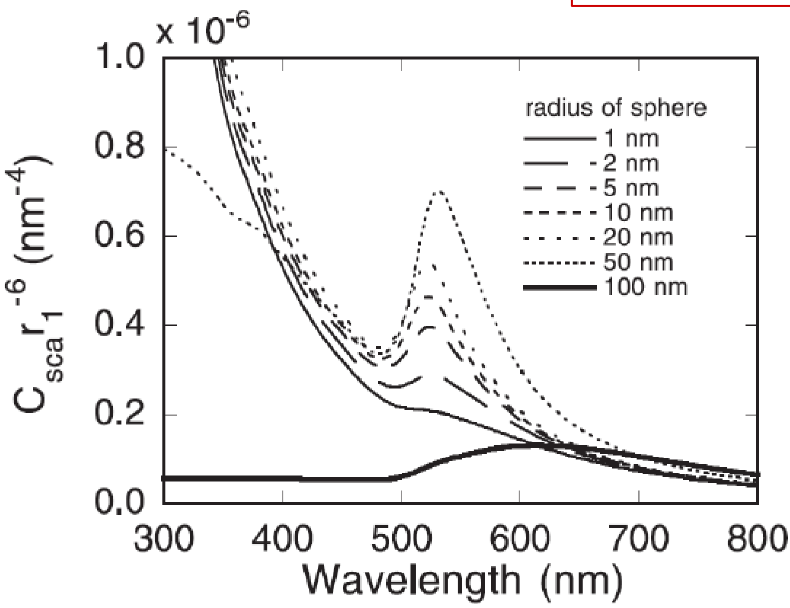
Localized Surface Plasmon

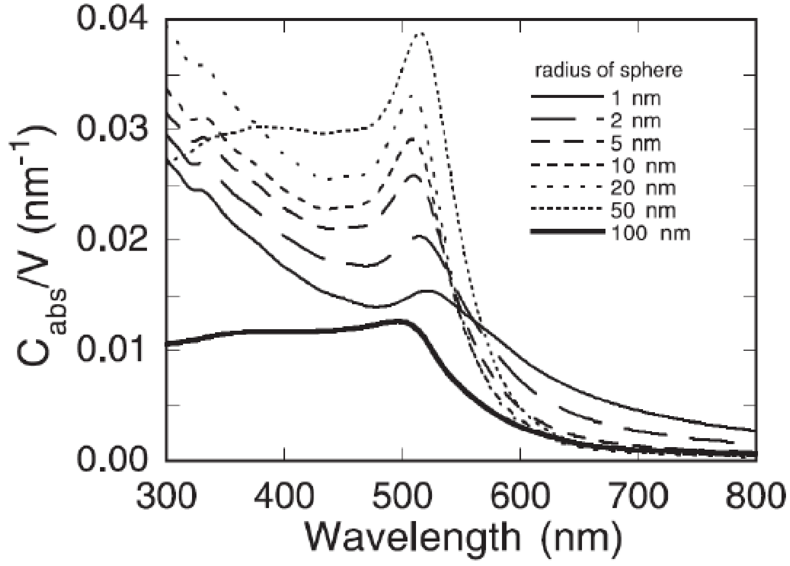
Corresponding absorption & scattering cross sections calculated via Mie Theory in the case of large particles where the electrostatic approx. brakes down and the retardation effects are to be considered

$$\sigma_{sca} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2+|b_n|^2\right)$$

$$\sigma_{ext} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\mathrm{Re}(a_n+b_n)$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca}$$





Localized Surface Plasmon

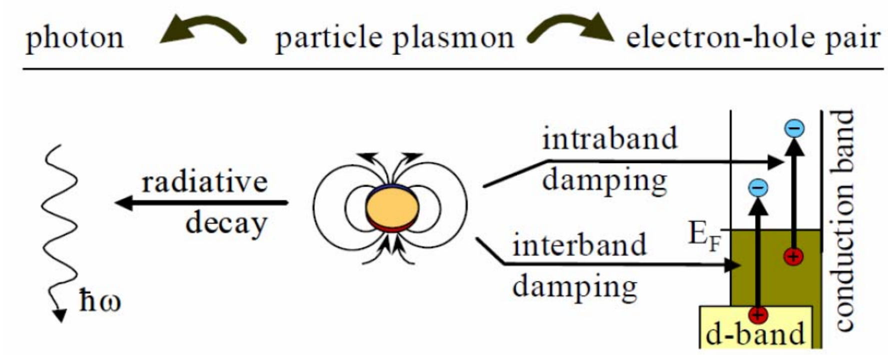
Damping mechanism

In a quasi-particle picture, damping is described as population decay → radiative (by emission of a photon), or nonradiative

Drude-Sommerfeld model → plasmon is a superposition of many independent electron oscillations

Nonradiative damping → due to a dephasing of the oscillation of individual electrons (scattering events with phonons, lattice ions, other conduction or core electrons, the metal surface, impurities, etc.)

Pauli-exclusion principle, the electrons can only be excited into empty states in the conduction band → inter- and intraband excitations by electron from either the d-band or the conduction band



$$\Gamma = \frac{2\hbar}{T_2}$$

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

Decay time (radiative & non energy loss processes)

Pure dephasing time (elastic collisions)

$$T_2^* \gg T_1 \quad \rightarrow \quad T_2 = 2T_1$$

$$5\,fs \le T_2 \le 10\,fs$$

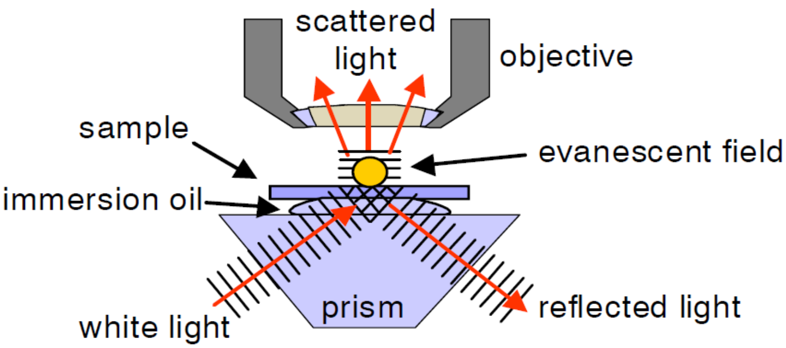
$$\tau_{\mathrm{rad}} \leftrightarrow Q_{\mathrm{sca}}, \quad \tau_{\mathrm{nonrad}} \leftrightarrow Q_{\mathrm{abs}}, \quad \tau_{\mathrm{tot}} \leftrightarrow Q_{\mathrm{ext}}$$

Localized Surface Plasmon

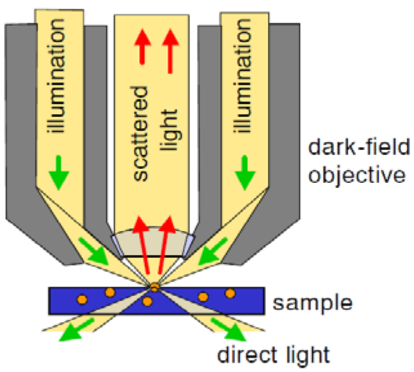
Damping mechanism for very small nanoparticles (< 10nm)

$$\Gamma = \Gamma_{bulk} + A\frac{v_F}{R}$$

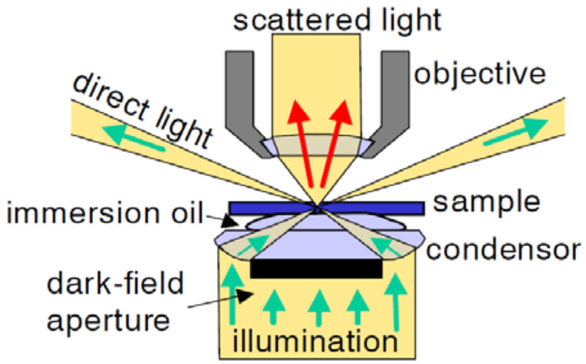
Experimental methods



Total Internal Reflection Microscopy (TIRM)



Dark Field Microscopy in reflection

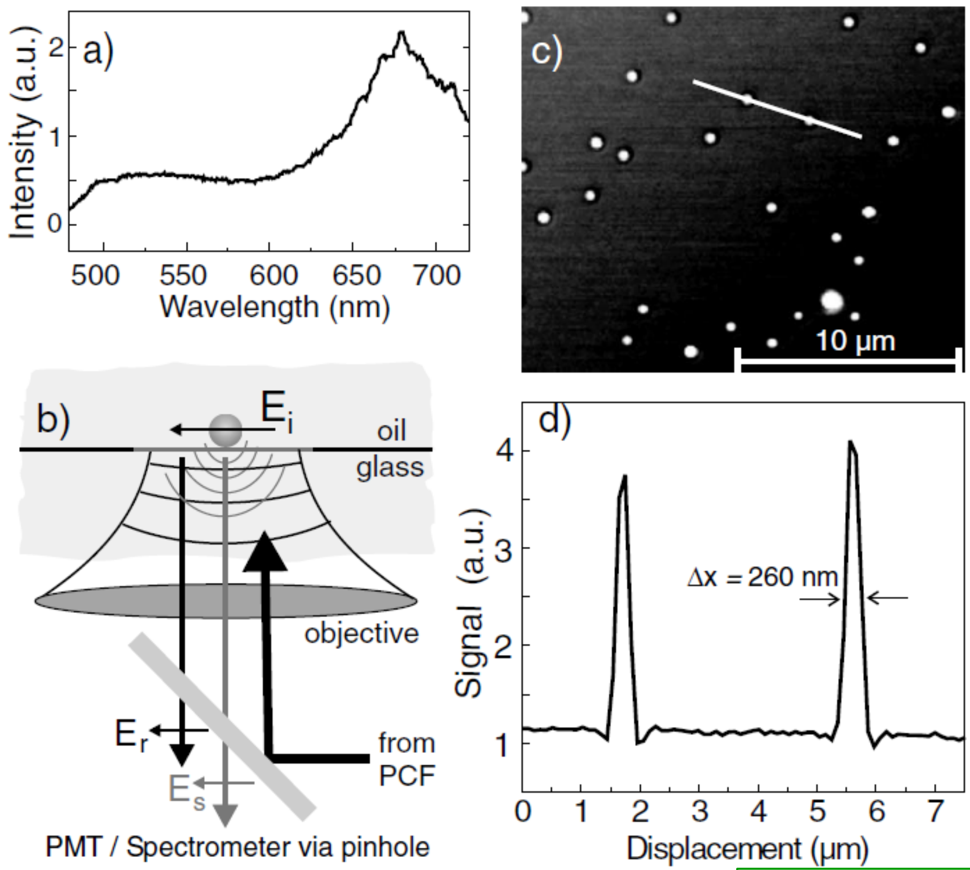


Dark Field Microscopy in transmission

Localized Surface Plasmon

Detection and Spectroscopy of Gold Nanoparticles Using Supercontinuum White Light Confocal Microscopy

K. Lindfors, T. Kalkbrenner, P. Stoller, V. Sandoghdar, *PRL* **93**, 037401-1 (2004)



$$E_r = rE_i e^{-\pi/2}$$

$$E_s = sE_i = |s| e^{i\varphi} E_i$$

$$\rightarrow s(\lambda) = \eta\alpha(\lambda) = \eta\varepsilon_d \frac{\pi D^3}{2} \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d}$$

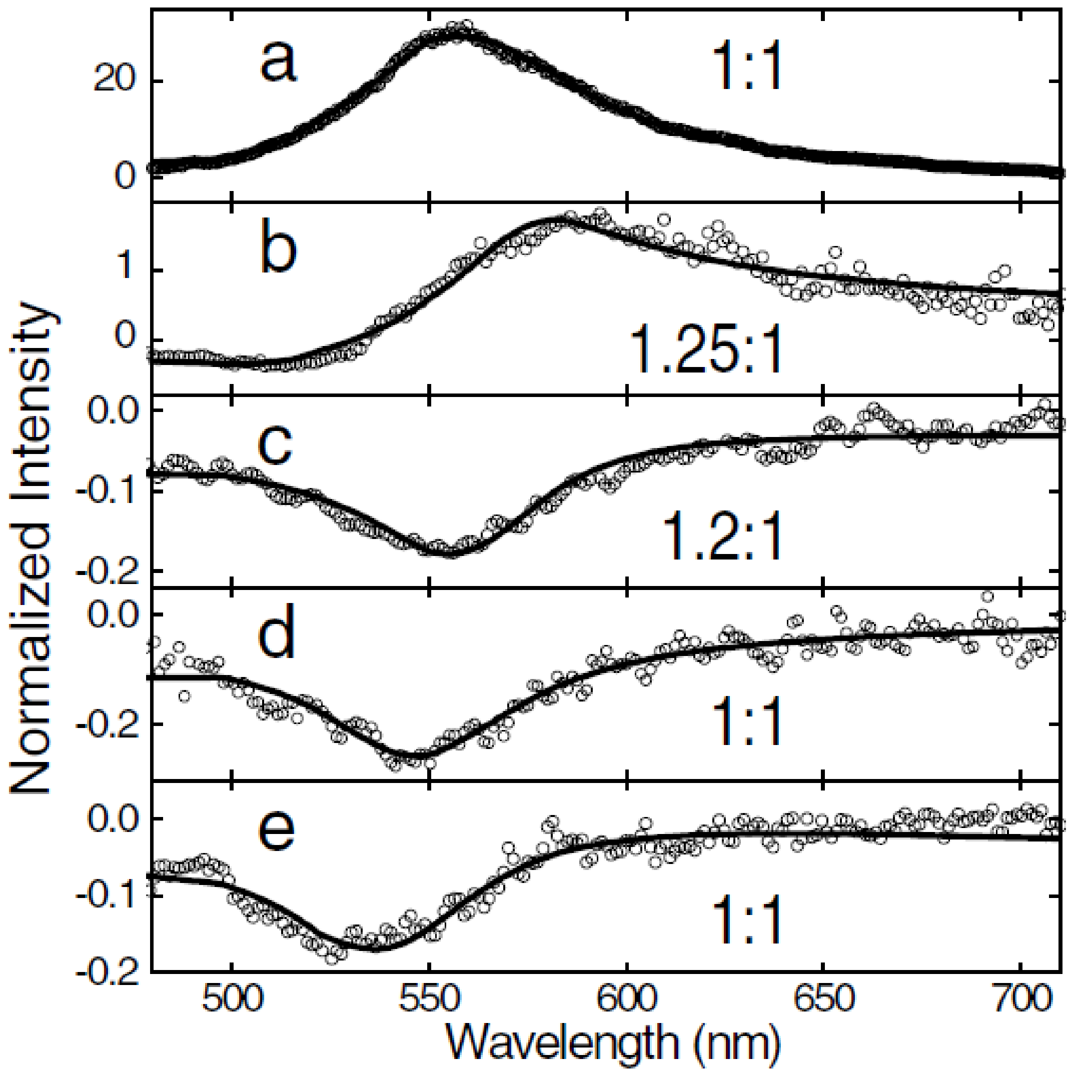
$$\downarrow$$

$$I_m = |E_r + E_s|^2 = |E_i|^2 \left\{ r^2 + |s|^2 - 2r|s|\sin\varphi \right\}$$

$$\downarrow$$

$$\boxed{\sigma(\lambda) = \frac{I_m(\lambda) - I_r(\lambda)}{I_r(\lambda)} = \frac{\eta^2}{r^2}|\alpha(\lambda)|^2 - 2\frac{\eta}{r}|\alpha(\lambda)|\sin\varphi}$$

Localized Surface Plasmon



(a) 60 ± 12 nm
(b) 31 ± 6 nm
(c) 20 ± 4 nm
(d) 10.3 ± 1.0 nm
(e) 5.4 ± 0.8 nm

Localized Surface Plasmon