Maxwell's equations

what the equation describes

Equation	What the equation describes
$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon}$	Charges produce electric field
$\nabla \cdot \mathbf{H} = 0$	No magnetic charges
$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t}$	Changing magnetic flux produces electric field
$\nabla \times \mathbf{H} = \mathbf{j} + \varepsilon \frac{\partial \mathbf{E}}{\partial t}$	Electric current and changing electric flux produce magnetic field

$$\mathbf{D} = \varepsilon \mathbf{E}$$

$$\mathbf{B} = \mu \mathbf{H}$$

Maxwell's equations

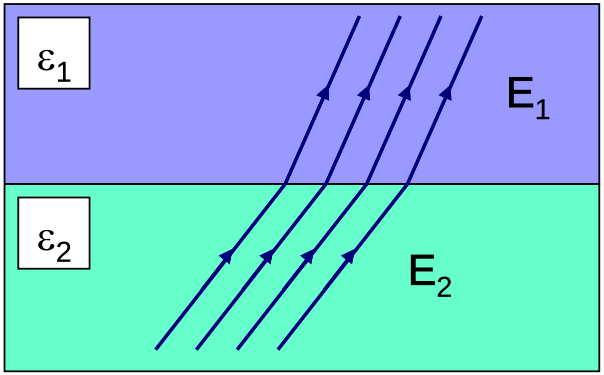
Charge neutrality, $\rho = 0$
No direct current, $\mathbf{j} = 0$
Nonmagnetic materials, $\mu_r = 1$ ($\mu = \mu_0$)

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon}$$
$$\nabla \cdot \mathbf{H} = 0$$
$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t}$$
$$\nabla \times \mathbf{H} = \mathbf{j} + \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \cdot \mathbf{E} = 0$$
$$\nabla \cdot \mathbf{H} = 0$$
$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}$$
$$\nabla \times \mathbf{H} = \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$

Boundary conditions

In inhomogeneous media consisting of several dielectrics, the field lines of E, H will experience discontinuity or bending at the boundary



The boundary conditions for E, H can be derived from Maxwell equations

normal components:

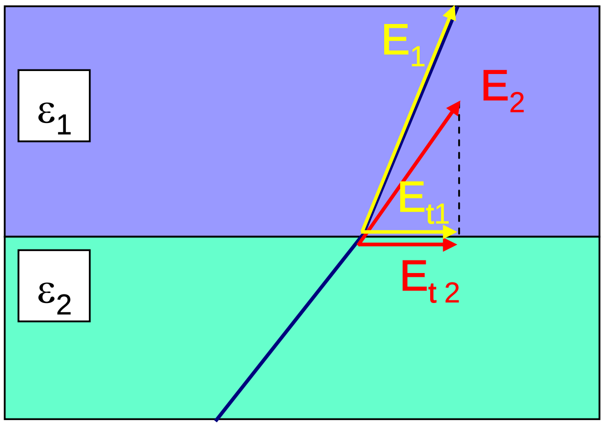
$$D_{n_1} = D_{n_2}$$

$$B_{n_1} = B_{n_2}$$

tangential components:

$$E_{t_1} = E_{t_2}$$

$$H_{t_1} = H_{t_2}$$



Electromagnetic waves

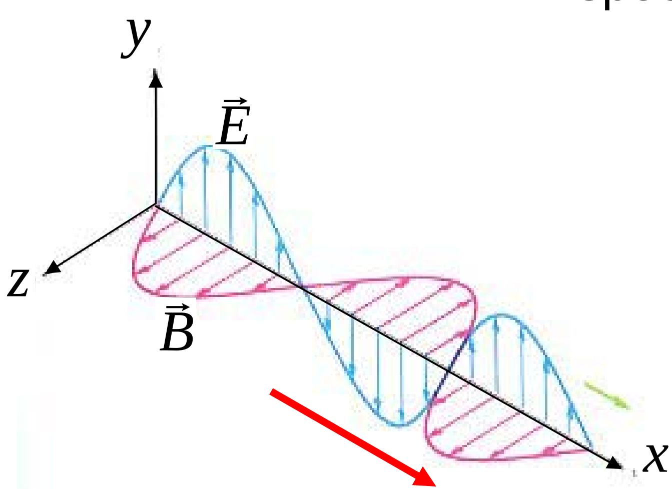
Maxwell's wave equations:
(in vacuum)

$$\frac{\partial^2 E}{\partial t^2} = \frac{1}{\mu_0 \varepsilon_0} \frac{\partial^2 E}{\partial x^2}$$

$$\frac{\partial^2 B}{\partial t^2} = \frac{1}{\mu_0 \varepsilon_0} \frac{\partial^2 B}{\partial x^2}$$

$E =$ electric field
$B =$ magnetic field
$\varepsilon_0 =$ permittivity (vacuum)
$\mu_0 =$ permeability (vacuum)

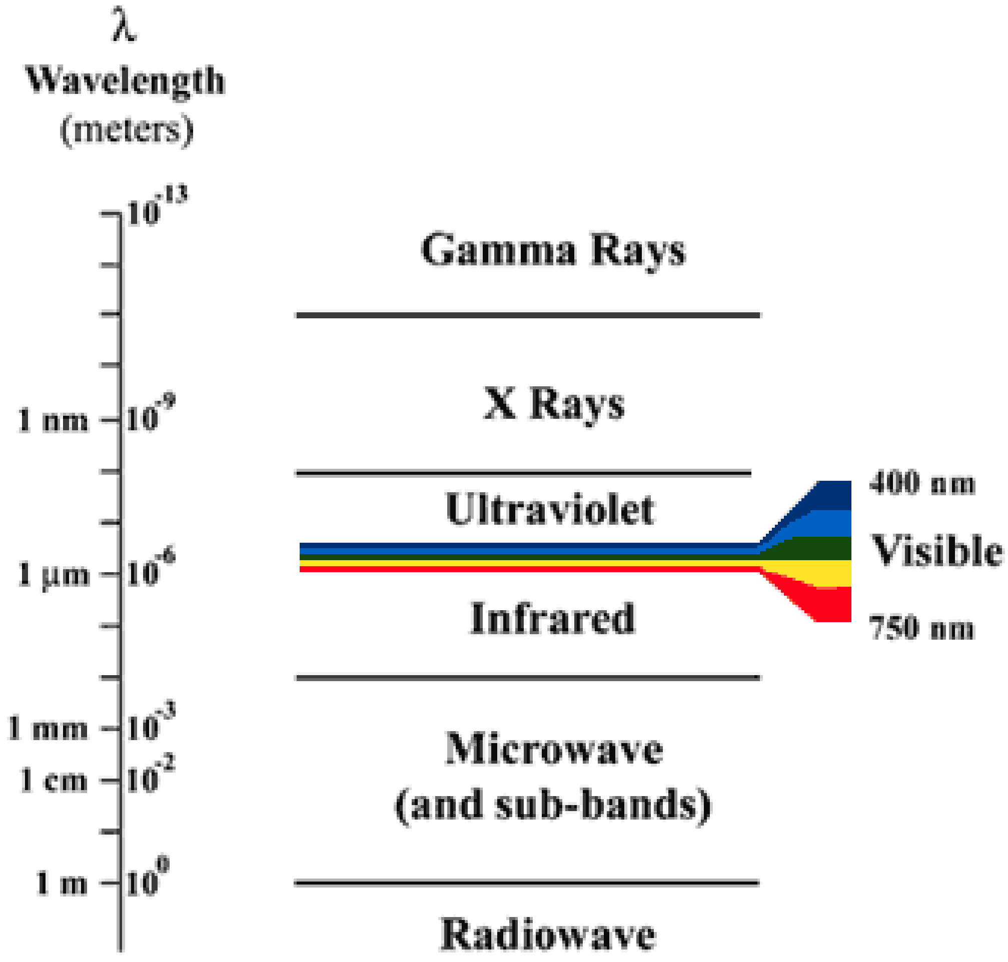
speed of light $c = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 3 \cdot 10^8 \text{ m/s}$



$$E(x,t) = E_0 \sin(\omega t - kx)$$

$$B(x,t) = B_0 \sin(\omega t - kx)$$

The electromagnetic spectrum



Electromagnetic waves in matter

vacuum:

$$\frac{\partial^2 E}{\partial t^2} = \frac{1}{\mu_0 \varepsilon_0} \frac{\partial^2 E}{\partial x^2}$$

$$\frac{\partial^2 B}{\partial t^2} = \frac{1}{\mu_0 \varepsilon_0} \frac{\partial^2 B}{\partial x^2}$$

matter:

$$\frac{\partial^2 E}{\partial t^2} = \frac{1}{\mu \varepsilon} \frac{\partial^2 E}{\partial x^2}$$

$$\frac{\partial^2 B}{\partial t^2} = \frac{1}{\mu \varepsilon} \frac{\partial^2 B}{\partial x^2}$$

permittivity: $\varepsilon = \varepsilon_r \varepsilon_0$ (ε_r = dielectric constant)

permeability: $\mu = \varepsilon_r \varepsilon_0$ (μ_r = relative permeability; $\mu_r \approx 1$)

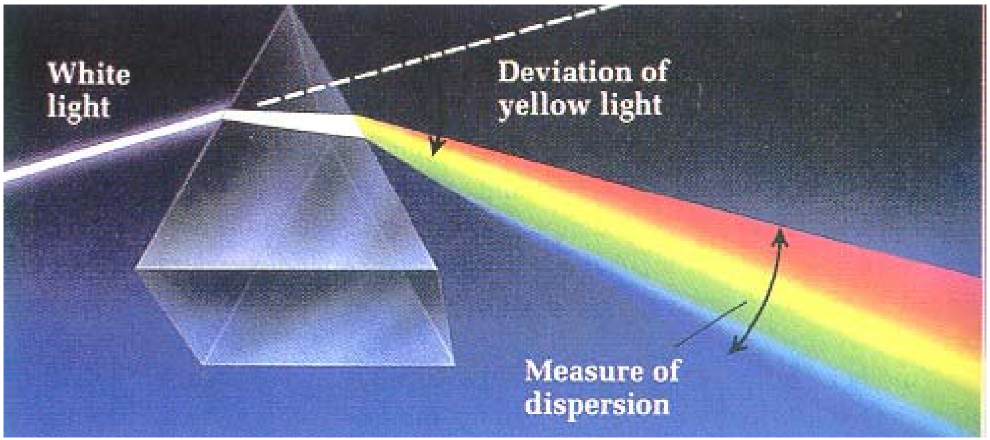
$$v = \frac{1}{\sqrt{\mu\varepsilon}} = \frac{1}{\sqrt{\mu_r \mu_0 \ \varepsilon_r \varepsilon_0}} = \frac{1}{\sqrt{\mu_0 \varepsilon_0}} \frac{1}{\sqrt{\mu_r \varepsilon_r}}$$

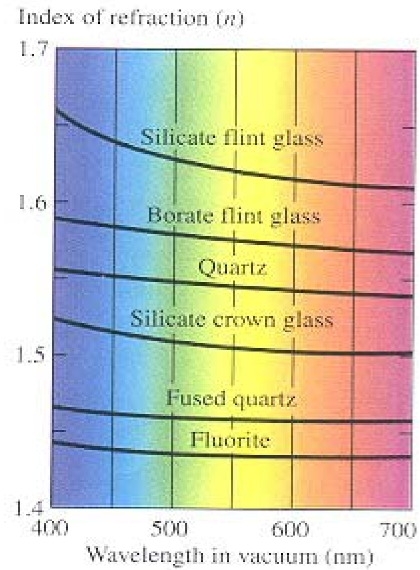
$\frac{1}{\sqrt{\mu_0 \varepsilon_0}} = c$

$\sqrt{\mu_r \varepsilon_r} = n$ refraction index

$$v = \frac{c}{n}$$

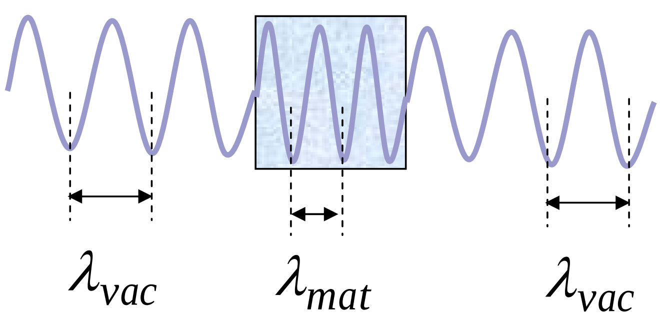
The dependence of the wave speed *v* and index of refraction *n* on the wavelength λ is called dispersion



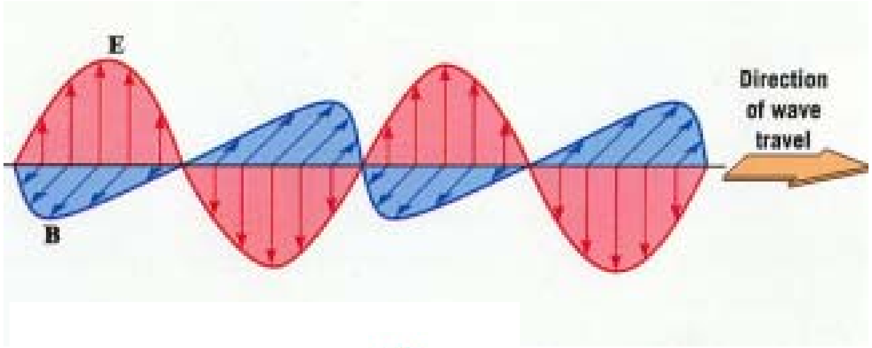


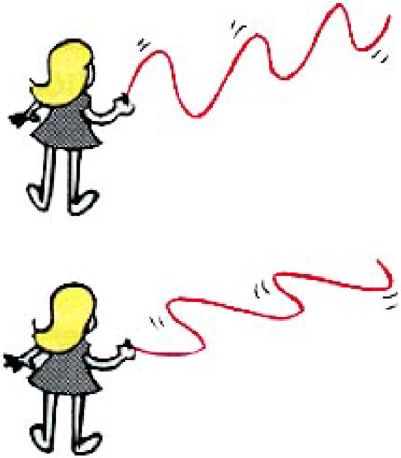
What is the wavelength of light in a medium with the refractive index *n*?

$$\lambda_{mat} = \frac{v}{c}\lambda_{vac} = \frac{\lambda_{vac}}{n}$$

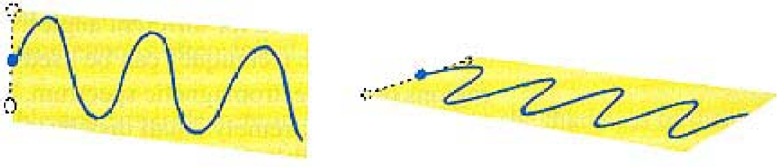


POLARIZATION



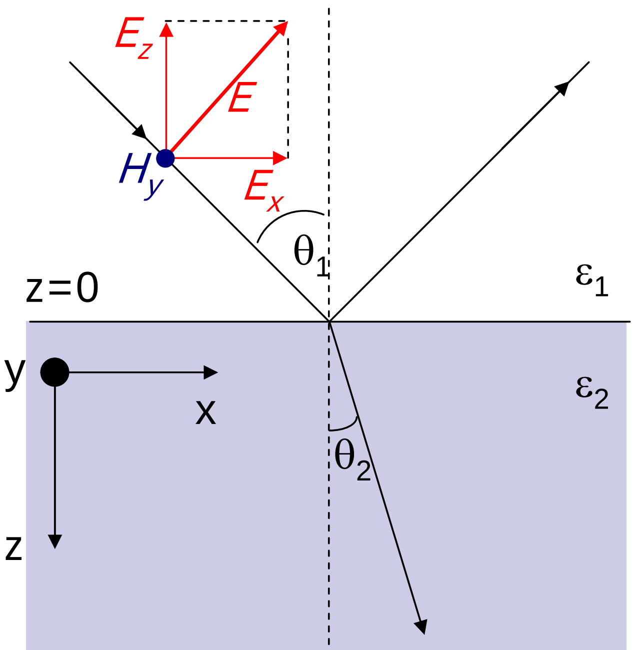


Illustrating vertical and horizontal polarized waves.

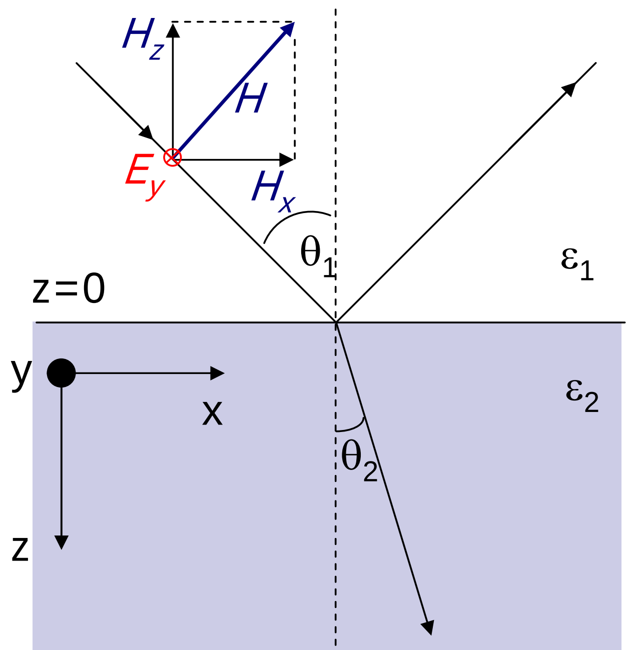


Plane Polarized Electromagnetic Waves

p-polarization:
E-field is parallel to the plane of incidence

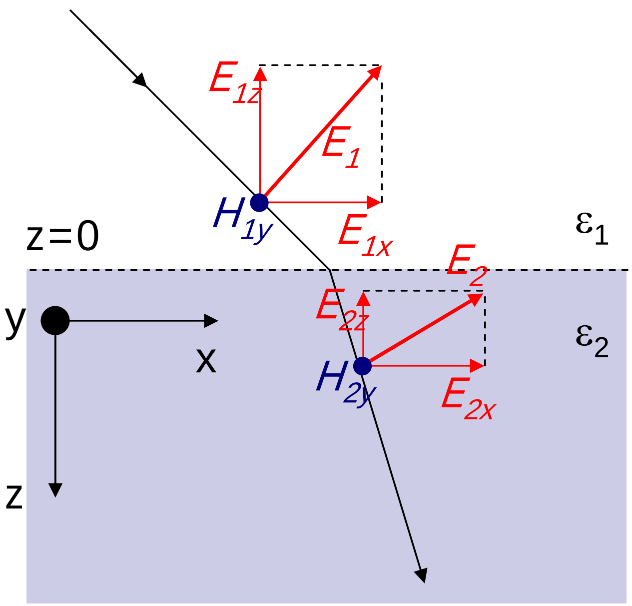


s-polarization:
E-field is perpendicular to the plane of incidence
(German *senkrecht* = perpedicular)



Any linearly polarized radiation can be represented as a superposition of p- and s-polarization.

p-polarized incident radiation will create polarization charges at the interface. We will show that these charges give rise to a surface plasmon modes



Boundary condition:

(a) transverse component of **E** is conserved,

$$E_{1x} = E_{2x}$$

(b) normal component of **D** is conserved

$$\mathbf{D} = \varepsilon\mathbf{E} = \varepsilon_0\mathbf{E} + \mathbf{P}$$

$$D_{1z} = D_{2z}$$

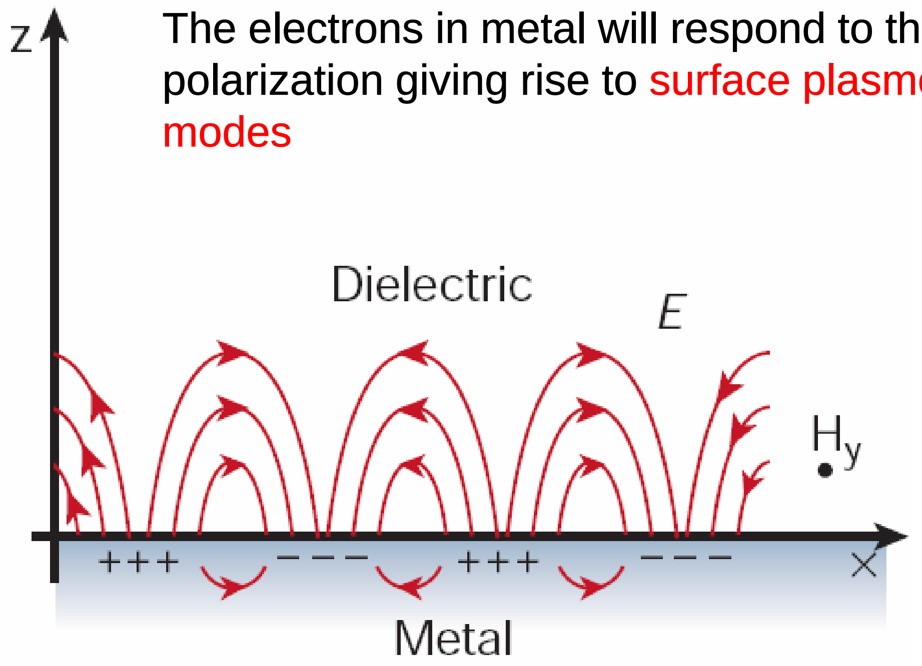
$$\varepsilon_0 E_{0z} + P_{1z} = \varepsilon_0 E_{0z} + P_{2z}$$

creation of the polarization charges

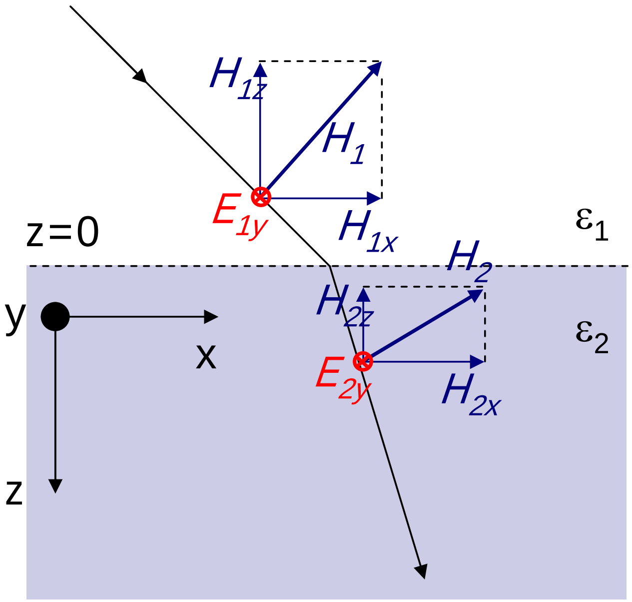
if one of the materials is metal, the electrons will respond to this polarization. This will give rise to surface plasmon modes

Polarization charges are created at the interface between two material.

The electrons in metal will respond to this polarization giving rise to surface plasmon modes



s-polarized incident radiation does not create polarization charges at the interface. It thus can not excite surface plasmon modes



Boundary condition (note that E-field has a transverse component only):

transverse component of E is conserved,

$$E_{1y} = E_{2y}$$

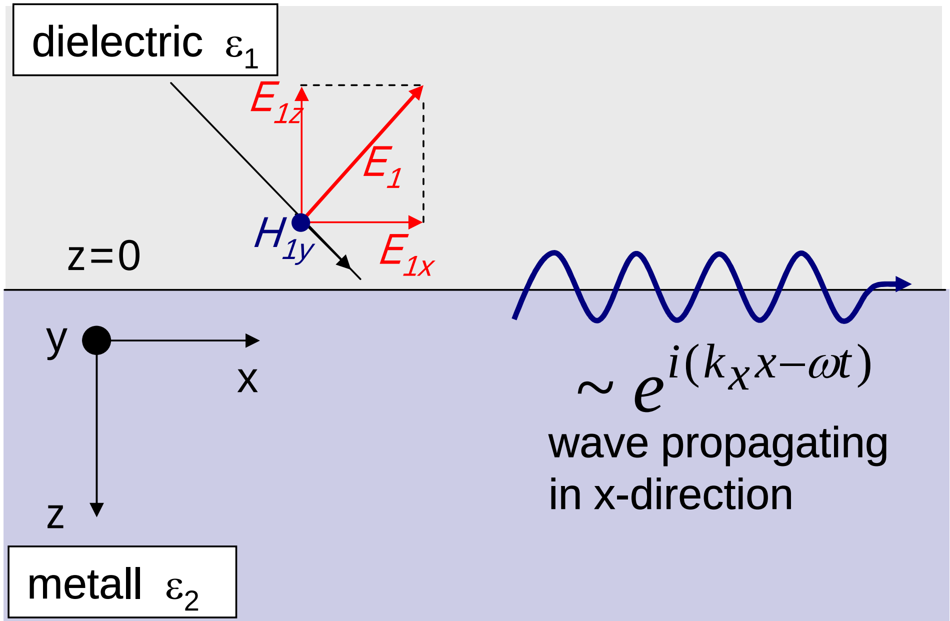
compare with p-polarization:

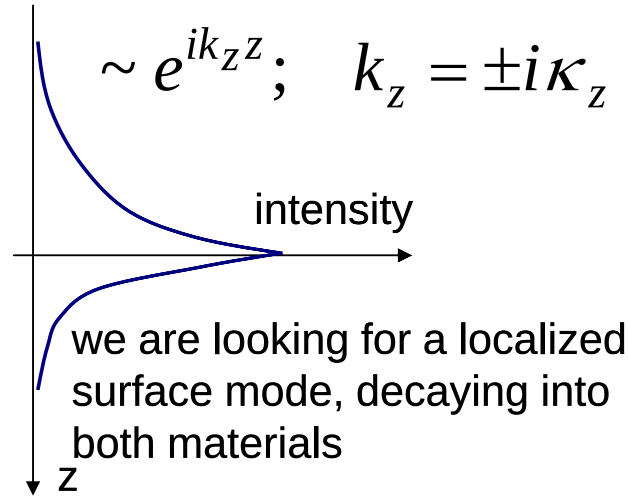
$$\varepsilon_0 E_{0z} + P_{1z} = \varepsilon_0 E_{0z} + P_{2z}$$

no polarization charges are created $\rightarrow$ no surface plasmon modes are excited!
In what follows we shall consider the case of p-polarization only

More detailed theory

Let us check whether p-polarized incident radiation can excite a surface mode



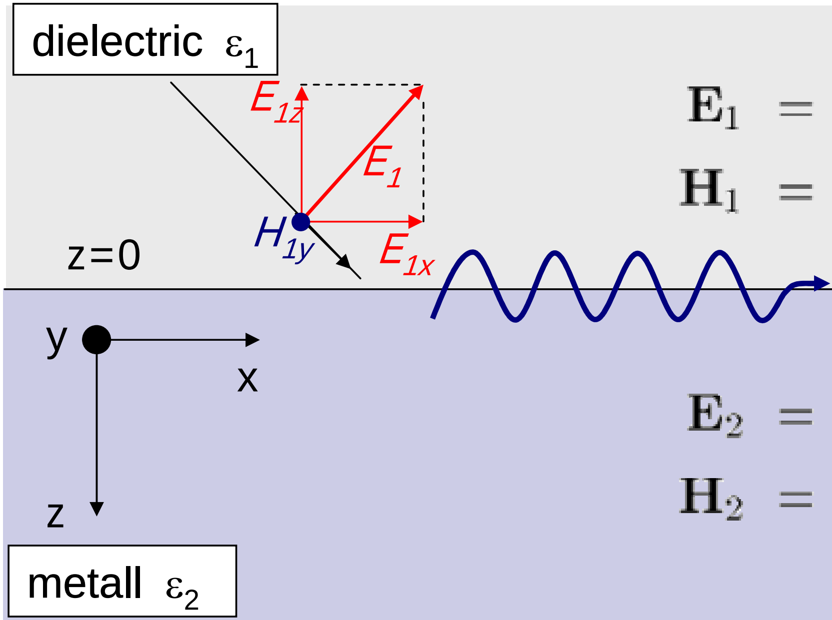


components of E-, H-fields: $E = (E_x, 0, E_z)$; $H = (0, H_y, 0)$

Thus, the solution can be written as

$$\mathbf{E} = (E_x, 0, E_y)\, e^{i(k_x x - \omega t)} e^{ik_z z}$$
$$\mathbf{H} = (0, H_y, 0)\, e^{i(k_x x - \omega t)} e^{ik_z z}$$

solution for a surface plasmon mode:



$$\mathbf{E}_1 = (E_{1x}, 0, E_{1y})\, e^{i(k_{1x}x-\omega t)} e^{ik_{1z}z}$$
$$\mathbf{H}_1 = (0, H_{1y}, 0)\, e^{i(k_{1x}x-\omega t)} e^{ik_{1z}z}$$

$$\mathbf{E}_2 = (E_{2x}, 0, E_{2y})\, e^{i(k_{2x}x-\omega t)} e^{ik_{2z}z}$$
$$\mathbf{H}_2 = (0, H_{2y}, 0)\, e^{i(k_{2x}x-\omega t)} e^{ik_{2z}z}$$

Let us see whether this solution satisfies Maxwell equation and the boundary conditions:

$$\nabla \cdot \mathbf{E} = 0$$
$$\nabla \times \mathbf{H} = \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$

+

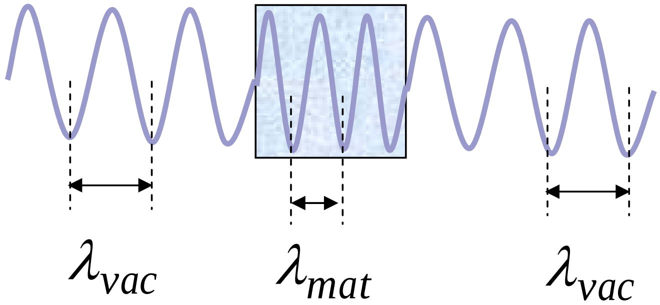
$$E_{1x} = E_{2x}$$
$$H_{y1} = H_{y2}$$

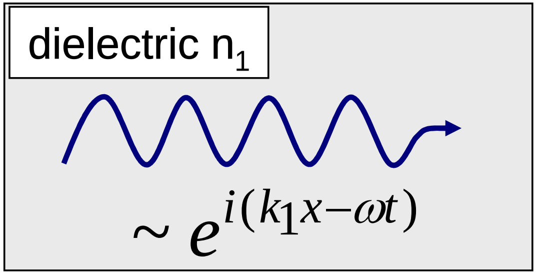
⇨

condition imposed on k-vector

$$\frac{\varepsilon_{r1}}{k_{1z}} = \frac{\varepsilon_{r2}}{k_{2z}}$$

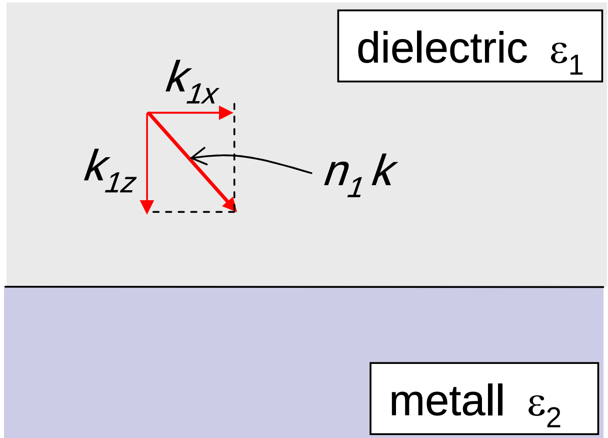
$$\lambda_{mat} = \frac{\lambda_{vac}}{n}; \quad n = \sqrt{\varepsilon}$$



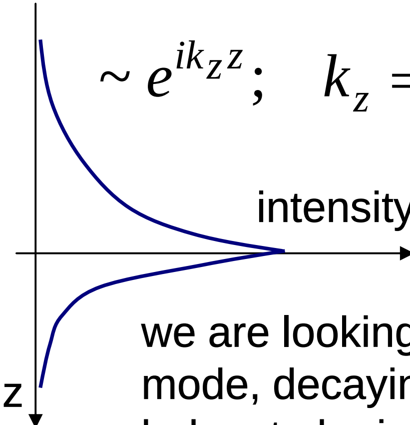


wave vector in vacuum

$$k_1 = \frac{2\pi}{\lambda_1} = \frac{2\pi\, n_1}{\lambda} = n_1 k$$



$$\sim e^{ik_z z}; \quad k_z = \pm i\kappa_z$$



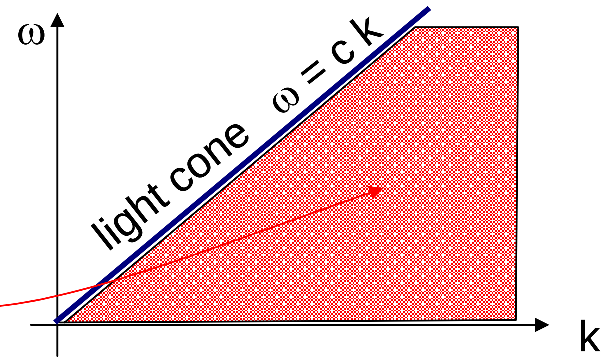
we are looking for a localized surface mode, decaying into both materials → k_z has to be imaginary

$$(n_1 k)^2 = k_{1x}^2 + k_{1z}^2$$

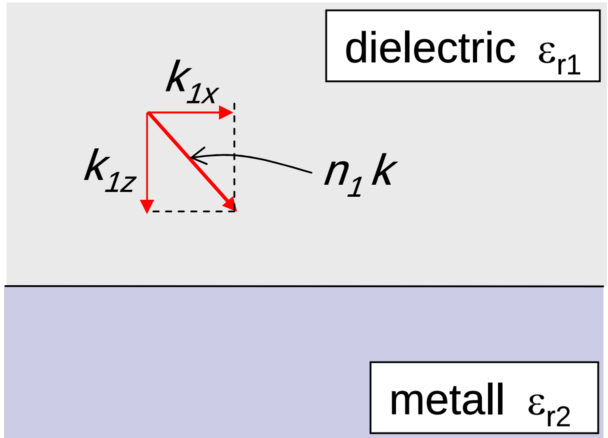
$$k_{1z} = \pm\sqrt{(n_1 k)^2 - k_{1x}^2}$$

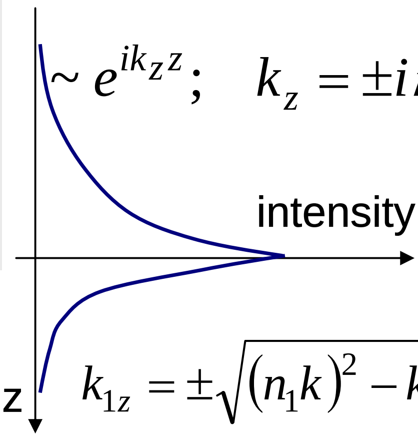
$$(n_1 k)^2 - k_{1x}^2 < 0$$

$$k_{1x} > n_1 k$$



The plasmonic dispersion curve lies beyond the light cone, therefore the direct coupling of propagating light to plasmonic states is difficult! ☹





$$\sim e^{ik_z z}; \quad k_z = \pm i\kappa_z$$

$$k_{1z} = \pm\sqrt{(n_1 k)^2 - k_{1x}^2}$$

sign of k_z:

$$k_{1z} = -\sqrt{(n_1 k)^2 - k_{1x}^2}$$

$$k_{2z} = +\sqrt{(n_1 k)^2 - k_{2x}^2}$$

k_{1z} and k_{2z} are of opposite signs!

recall the condition imposed on k-vector:

$$\frac{\varepsilon_{r1}}{k_{1z}} = \frac{\varepsilon_{r2}}{k_{2z}}$$

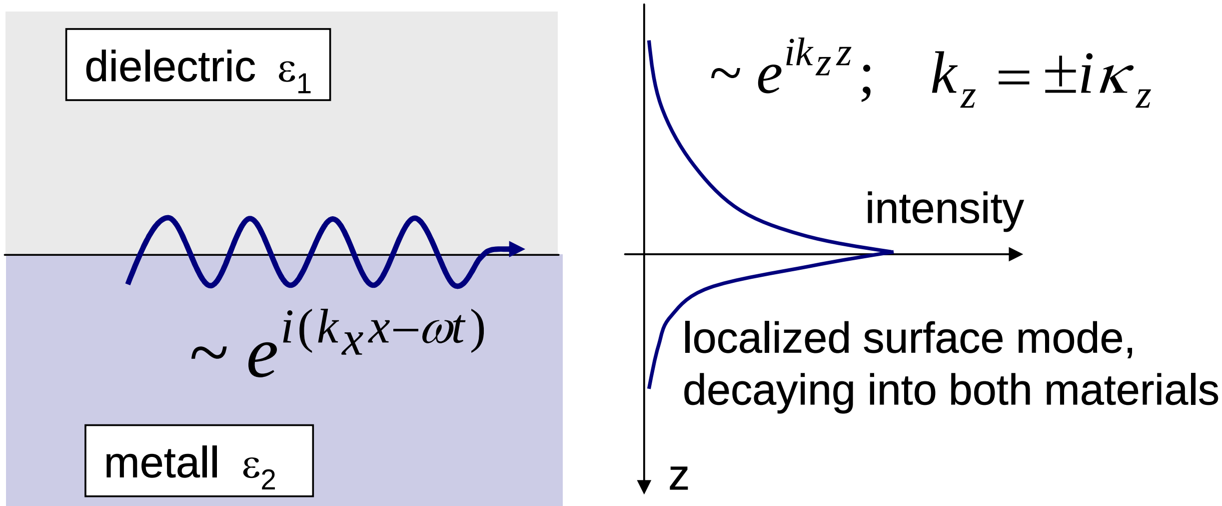
⇨

because k_{1z} and k_{2z} are of opposite signs, this condition will be satisfied only if ε_{r1} and ε_{r2} are of opposite signs. This is the case when one material is dielectric $\varepsilon_{r1} > 0$, and the second material is metal, $\varepsilon_{r1} < 0$.

also, recall the condition

$$k_{2x}^2 > (n_2 k)^2 = \varepsilon_{r2} k^2$$

this condition is always satisfied for metals, where $\varepsilon_{r2} < 0$



$$
\begin{aligned}
\mathbf{E} &= (E_x, 0, E_y)\, e^{i(k_x x - \omega t)} e^{ik_z z} \\
\mathbf{H} &= (0, H_y, 0)\, e^{i(k_x x - \omega t)} e^{ik_z z}
\end{aligned}
$$

Thus, we have established that on the surface between a metal and dielectric one can excite a localized surface mode. This localized mode is called a surface plasmon

What is the wavelength of the surface plasmon $\lambda = \dfrac{2\pi}{k}$?

let us find *k:*

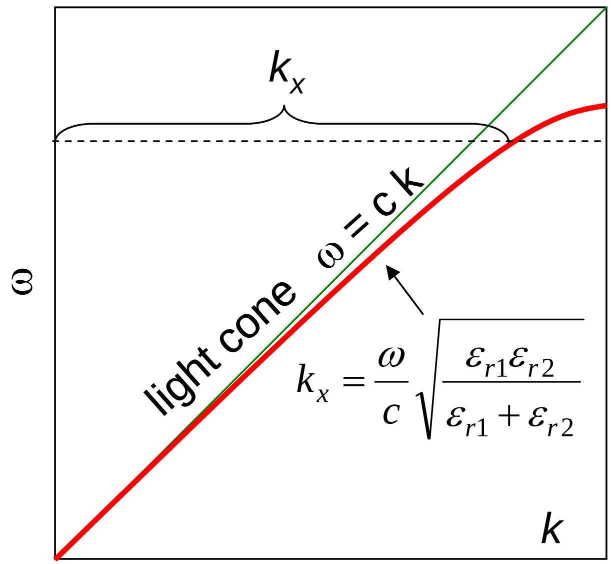
$$\frac{\varepsilon_{r1}}{k_{1z}} = \frac{\varepsilon_{r2}}{k_{2z}}$$

substitute

$$k_{1z} = -\sqrt{(n_1 k)^2 - k_{1x}^2}$$

$$k_{2z} = +\sqrt{(n_1 k)^2 - k_{2x}^2}$$

$$k_x = k\sqrt{\frac{\varepsilon_{r1}\varepsilon_{r2}}{\varepsilon_{r1} + \varepsilon_{r2}}}$$



The surface plasmone mode always lies beyond the light line, that is it has greater momentum than a free photon of the same frequency ω

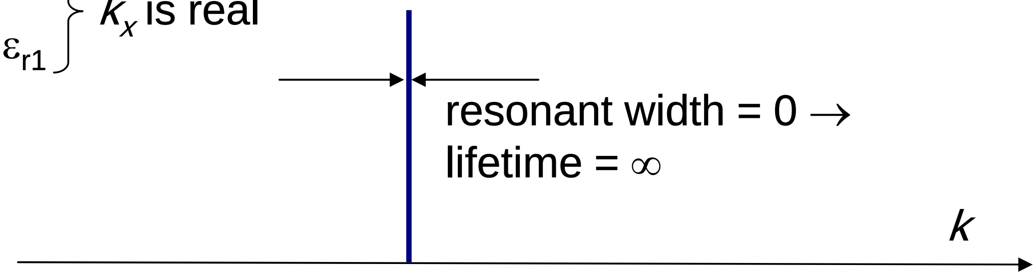
$$k_x = k\sqrt{\frac{\varepsilon_{r1}\varepsilon_{r2}}{\varepsilon_{r1}+\varepsilon_{r2}}}$$

Ideal case: ε_{r1} and ε_{r2} are real (no imaginary components = no losses)

Dielectric: $\varepsilon_{r1} > 0$

Metal: $\varepsilon_{r2} < 0$, $|\varepsilon_{r2}| >> \varepsilon_{r1}$

} k_x is real



$$k_x = k\sqrt{\frac{\varepsilon_{r1}\varepsilon_{r2}}{\varepsilon_{r1}+\varepsilon_{r2}}}$$

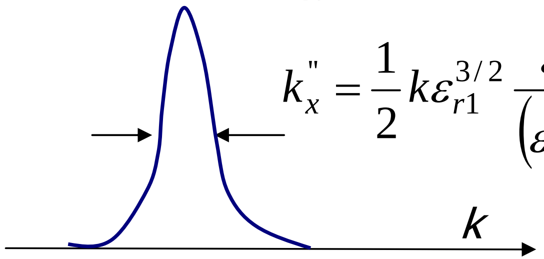
Realistic case: ε_{r1} is real, and ε_{r2} is complex,

$$\varepsilon_{r2} = \varepsilon'_{r2} + i\varepsilon''_{r2}$$ ← imaginary part describes losses in metal

$$k_x = k\sqrt{\frac{\varepsilon_{r1}\varepsilon_{r2}}{\varepsilon_{r1}+\varepsilon_{r2}}} = k\sqrt{\frac{\varepsilon_{r1}\left(\varepsilon'_{r2}+i\varepsilon''_{r2}\right)}{\varepsilon_{r1}+\left(\varepsilon'_{r2}+i\varepsilon''_{r2}\right)}}$$

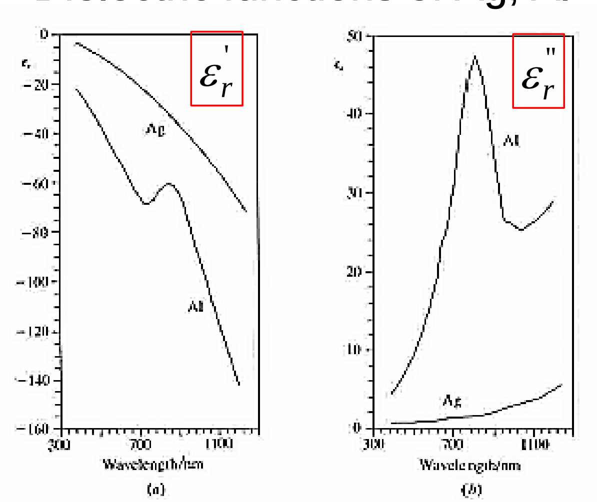
$$= \ldots = k'_x + ik''_x$$

resonant width (gives rise to losses)

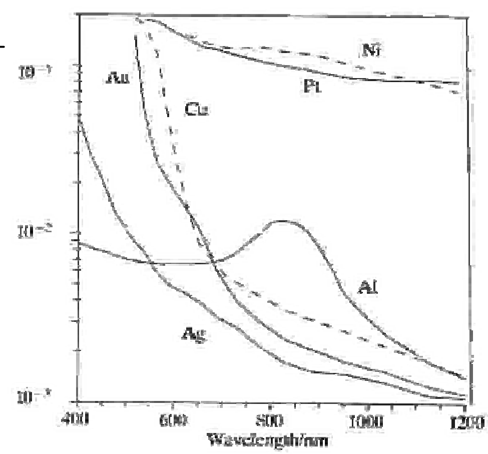


$$k''_x = \frac{1}{2}k\varepsilon_{r1}^{3/2}\frac{\varepsilon''_{r2}}{\left(\varepsilon'_{r2}\right)^2}$$

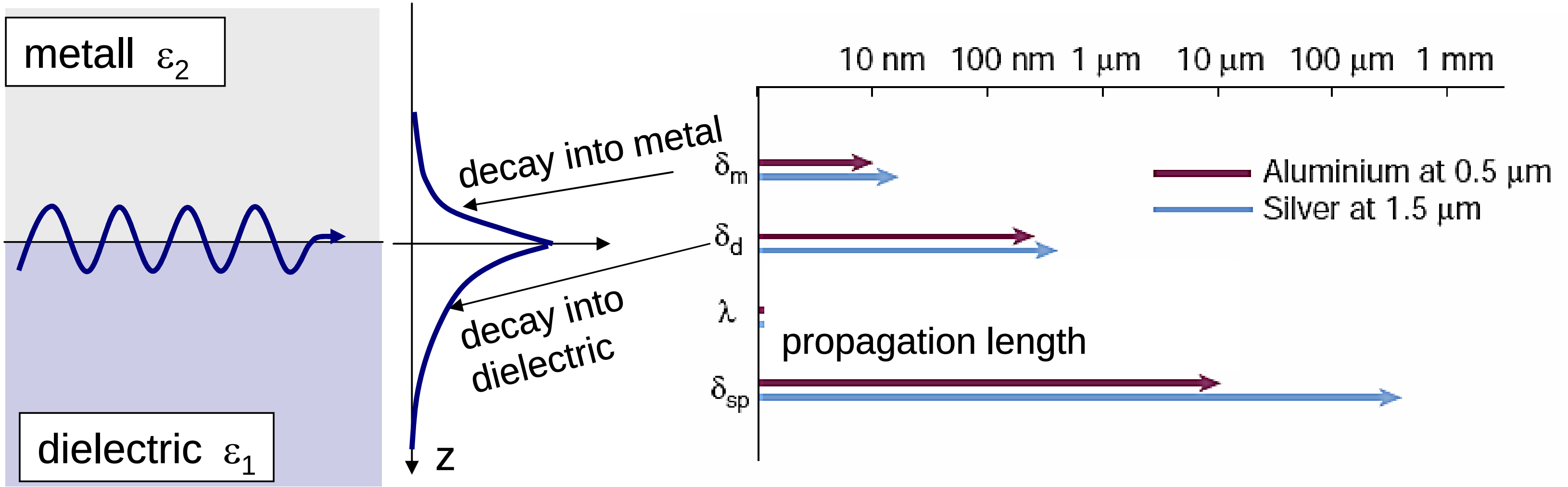
Dielectric functions of Ag, Al



$$\frac{\varepsilon''_{r2}}{\left(\varepsilon'_{r2}\right)^2}$$

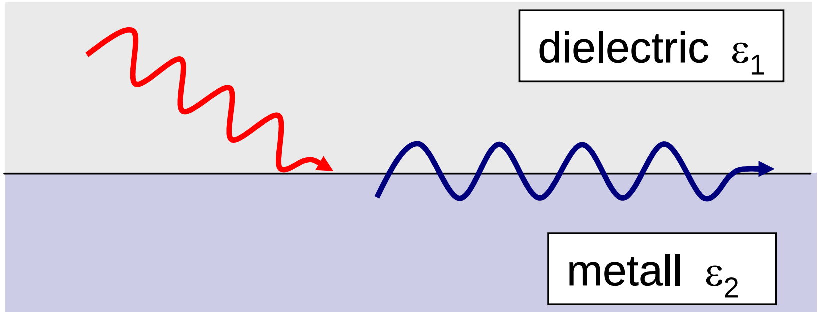


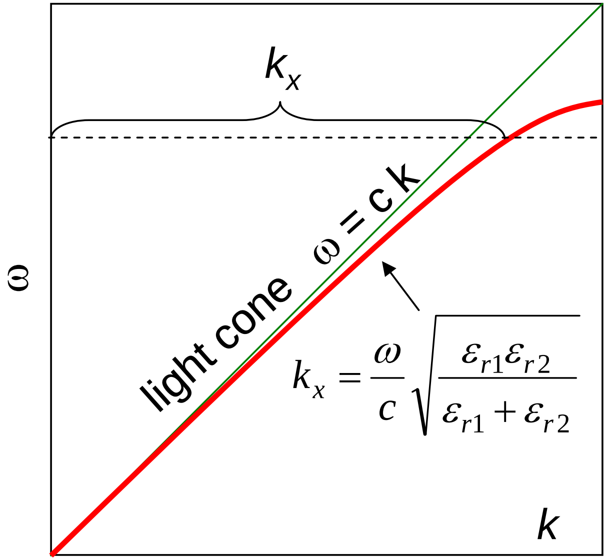
surface plasmon length scales:



How to excite a surface plasmon?

is it possible to excite a plasmon mode by shining light on a dielectric/metal interface?



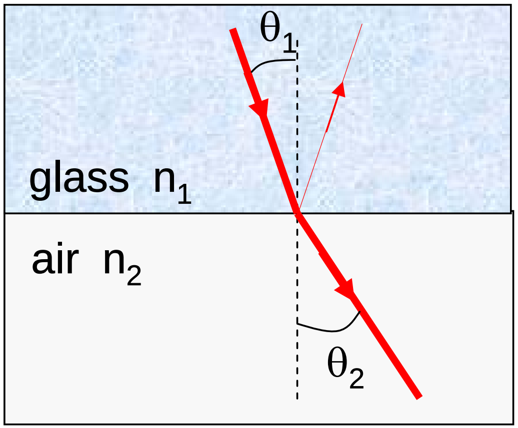


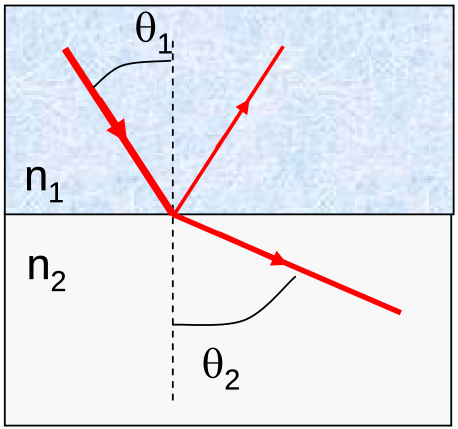
The surface plasmone mode always lie beyond the light line, that is it has greater momentum than a free photon of the same frequency ω.

This makes a direct excitation of a surface plasmon mode impossible!

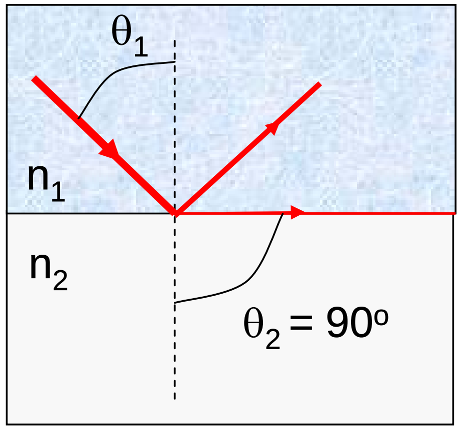
Total internal reflection

Snell's law of refraction: $n_2 \sin\theta_2 = n_1 \sin\theta_1$ $\quad n_2 < n_1 \Rightarrow \dfrac{\sin\theta_2}{\sin\theta_1} = \dfrac{n_1}{n_2} > 1$





Total internal reflection

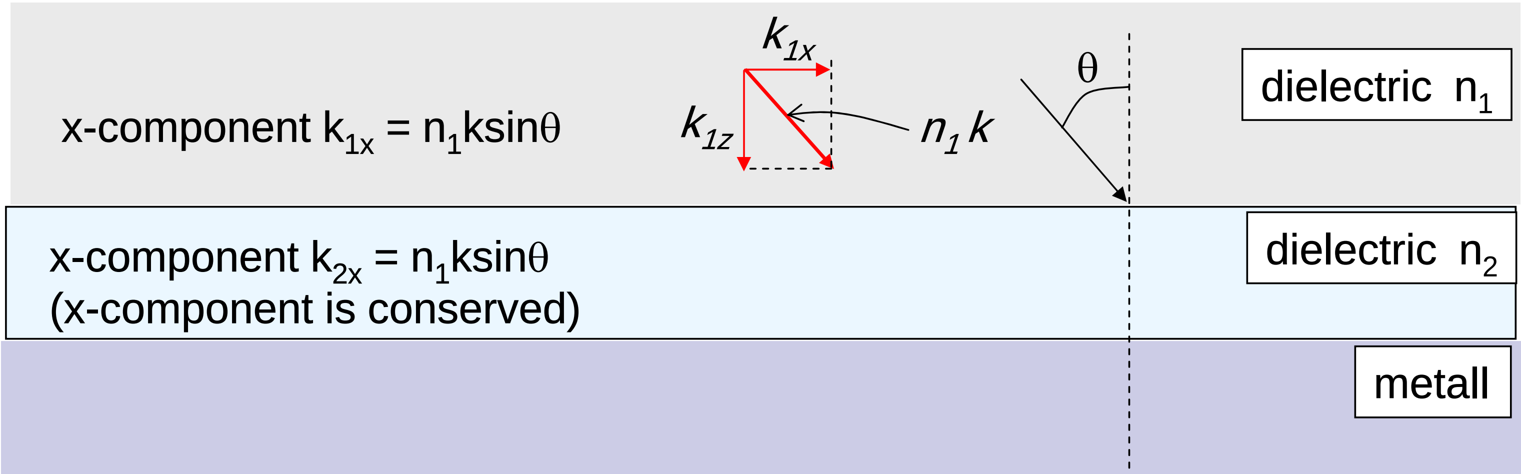


critical angle of the total internal reflection:

$$\theta_2 = 90^0 \Rightarrow$$

$$\sin\theta_c = \frac{n_2 \sin 90^0}{n_1} = \frac{n_2}{n_1}$$

Otto geometry

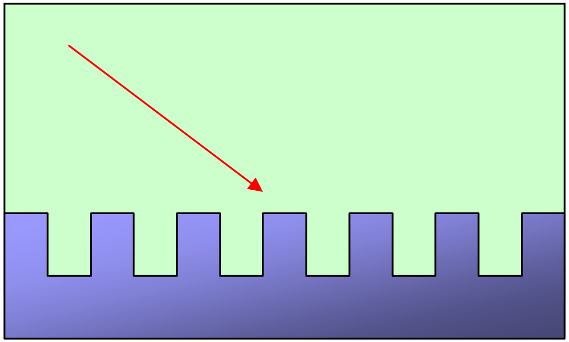


to excite a plasmon mode in the region 2:

$k_{2x} > n_2 k$

$$n_1 k \sin\theta > n_2 k \quad \Rightarrow \quad \sin\theta > \frac{n_2}{n_1}$$ condition for the total internal reflection!

Utilization of a grating to excite a plasmon mode



The grooves in the grating surface break the translation invariance and allow k_x of the outgoing wave to be different from that of the incoming wave

$$\underbrace{k_x \text{ (outgoing)}}_{k_{\text{plasmon}}} = \underbrace{k_x \text{ (incoming)}}_{nk \sin\theta} \pm \underbrace{NG}_{\text{reciprocal lattice vectors}}, \quad \text{where } G = 2\pi/d$$

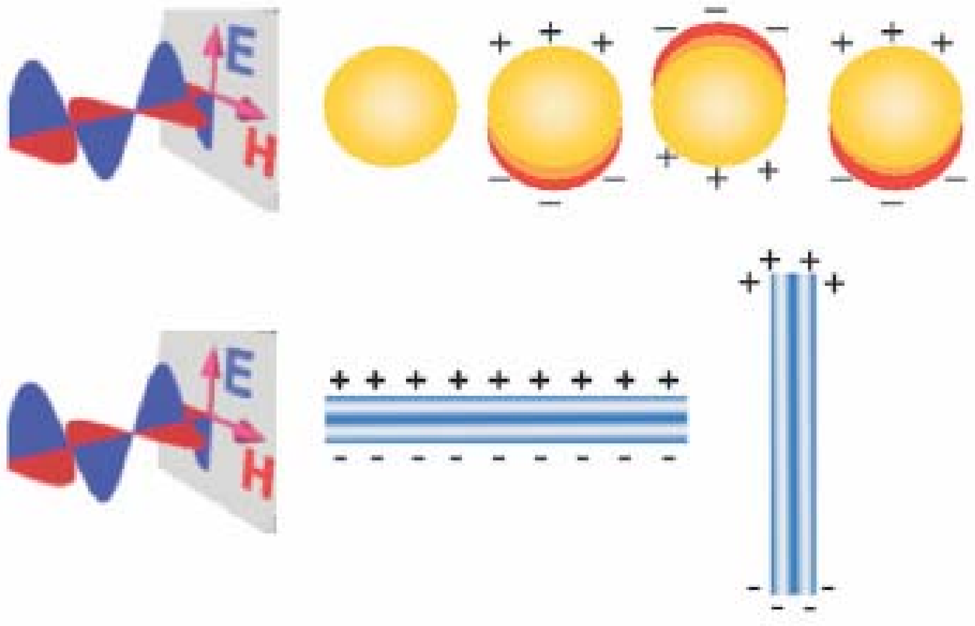


Fig. 2 (Top) Schematic drawing of the interaction of an electromagnetic radiation with a metal nanosphere. A dipole is induced, which oscillates in phase with the electric field of the incoming light. (Bottom) Transverse and longitudinal oscillation of electrons in a metal nanorod.

Mie Theory for SPR of Spherical Nanoparticles

$$\sigma_{ext}(\lambda) = \frac{24\pi^2 r^3 \varepsilon_{\mathrm{med}}^{3/2}}{\lambda} \left\{ \frac{\varepsilon''(\lambda)}{[\varepsilon'(\lambda) + 2\varepsilon_{\mathrm{med}}]^2 + [\varepsilon''(\lambda)]^2} \right\}$$

σ :	extinction cross section
λ :	wavelength
r :	particle radius
$\varepsilon_{\mathrm{med}}$:	medium dielectric constant
ε' :	real part of metal dielectric constant
ε'' :	imaginary part of metal dielectric constant

C. F. Bohren, D. R. Huffman, *Absorption and Scattering*

Correc tions due to surface scattering for particles with at least one dimension smaller than the electron mean free path

$$\varepsilon = \varepsilon_F + \varepsilon_B$$

Free electron contribution — **Bound contribution**

Drude Model

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

- ω_p → **Plasmon frequency**
- γ → **Plasmon width**

$$\gamma = \gamma + A\frac{v_F}{L_{eff}}$$

- v_F → **Fermi velocity**
- L_{eff} → **Average chord length in the spheroid**

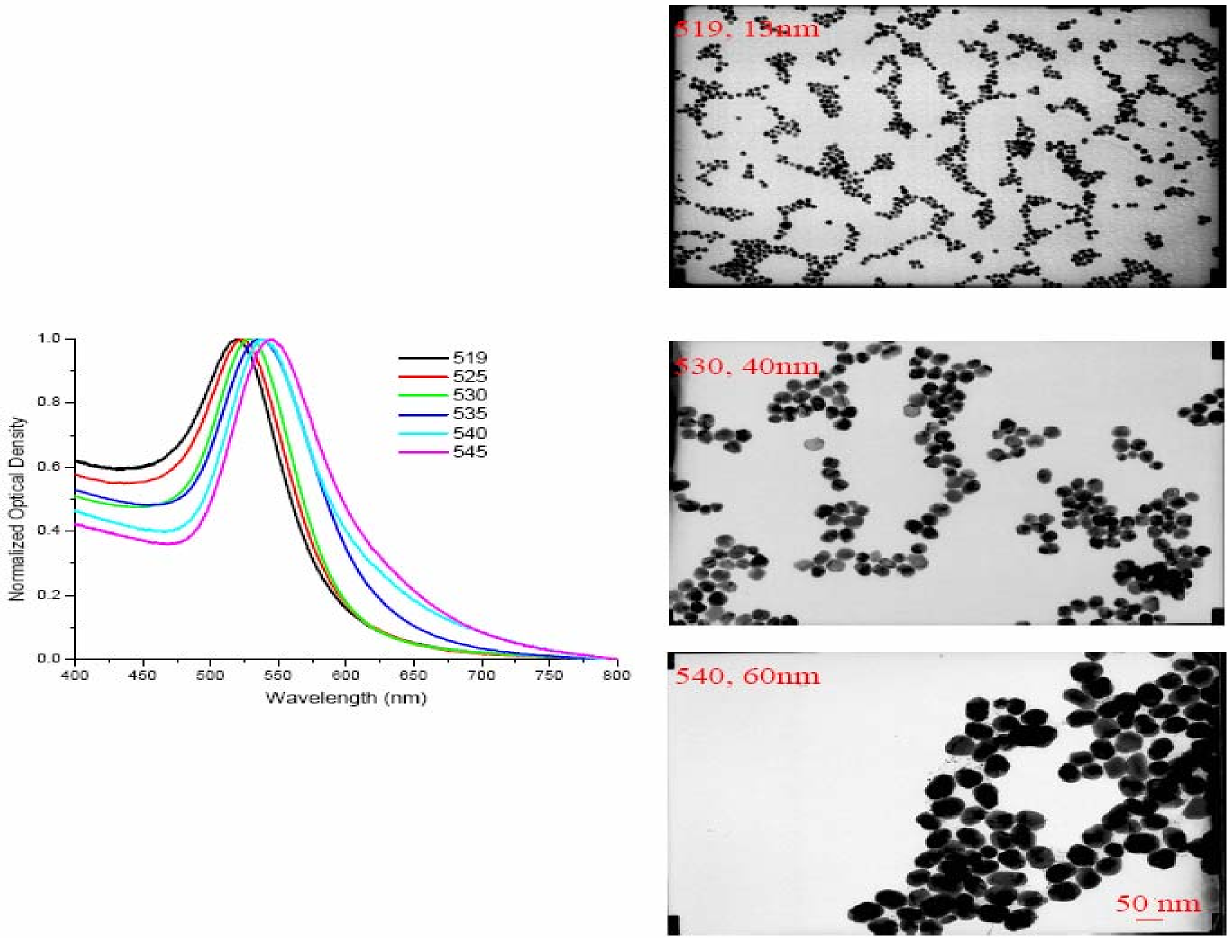


Figure 1-3: Surface plasmon absorption spectra (left) and TEM (right) of spherical gold nanoparticles in different sizes. The surface plasmon absorption maximum is weakly dependant on the size of the nanospheres.

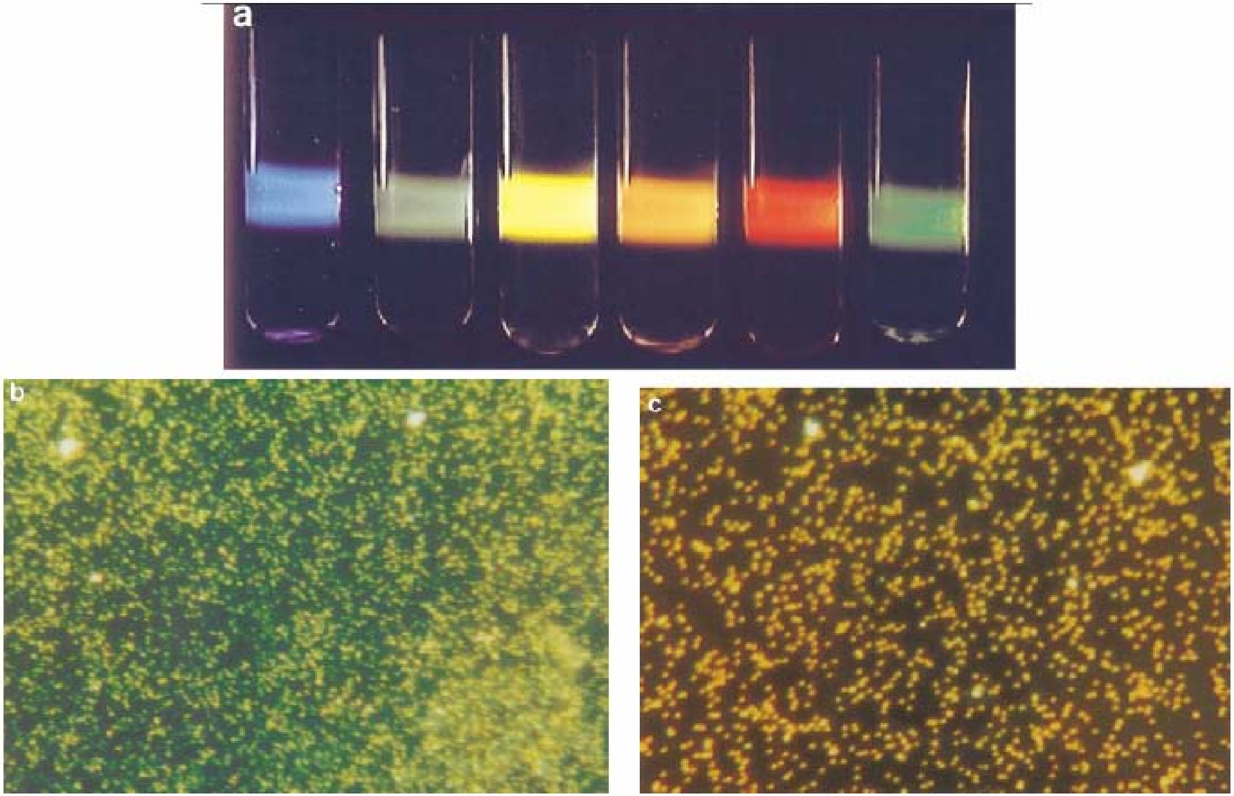


Figure 1-8: a: the gold nanoparticles of different sizes irradiated by a beam of white light, b: the light scattering imaging of 58 nm gold nanoparticles, c: the light scattering imaging of 78 nm gold nanoparticles (5).

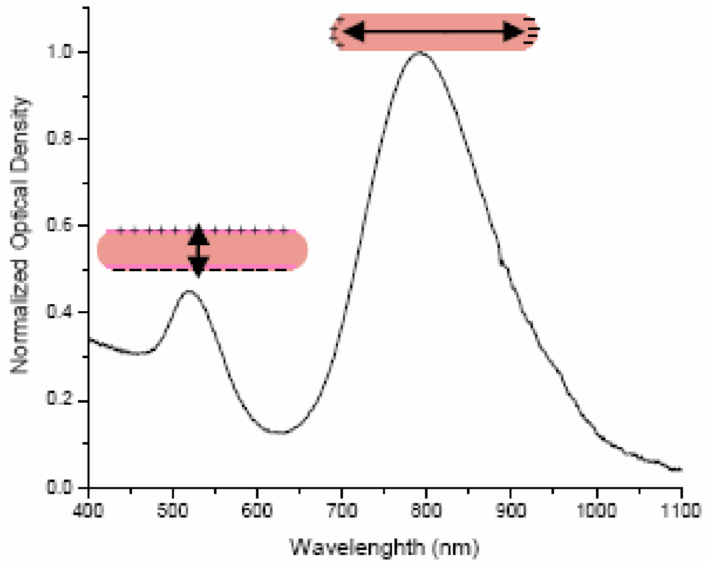


Figure 1-5: Typical surface plasmon absorption spectrum of gold nanorods. The strong long wavelength band in the near infrared region around 800 nm is due to the longitudinal oscillation of electrons and the weak short wavelength band in the visible region around 520 nm is due to the transverse electronic oscillation.

$$\sigma_{ext}(\lambda) = \frac{2\pi V \varepsilon_{\text{med}}^{3/2}}{3\lambda} \sum_j \frac{(1/P_j^2)\varepsilon''}{\left(\varepsilon' + \frac{1-P_j}{P_j}\varepsilon_{\text{med}}\right)^2 + (\varepsilon'')^2}$$

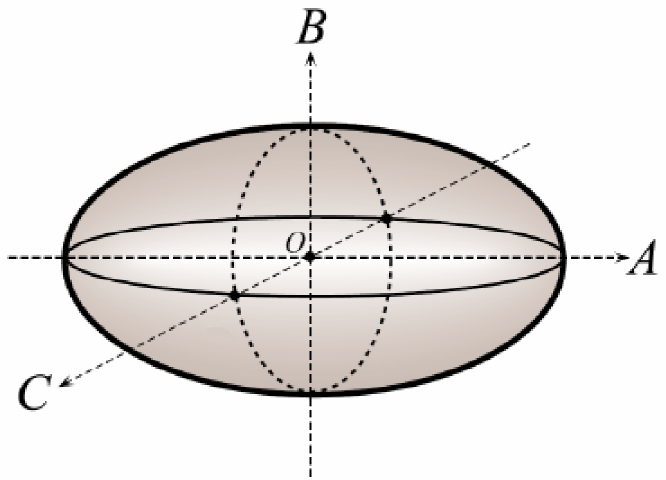
$$(A > B = C)$$

$$P_A = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1\right]$$

$$P_B = P_C = \frac{1-P_A}{2}$$

$$e = \sqrt{1-\left(\frac{B}{A}\right)^2}$$

aspect ratio $R = \frac{A}{B}$



S. Link, M. B. Mohamed, M. A. El-Sayed, *J. Phys.*

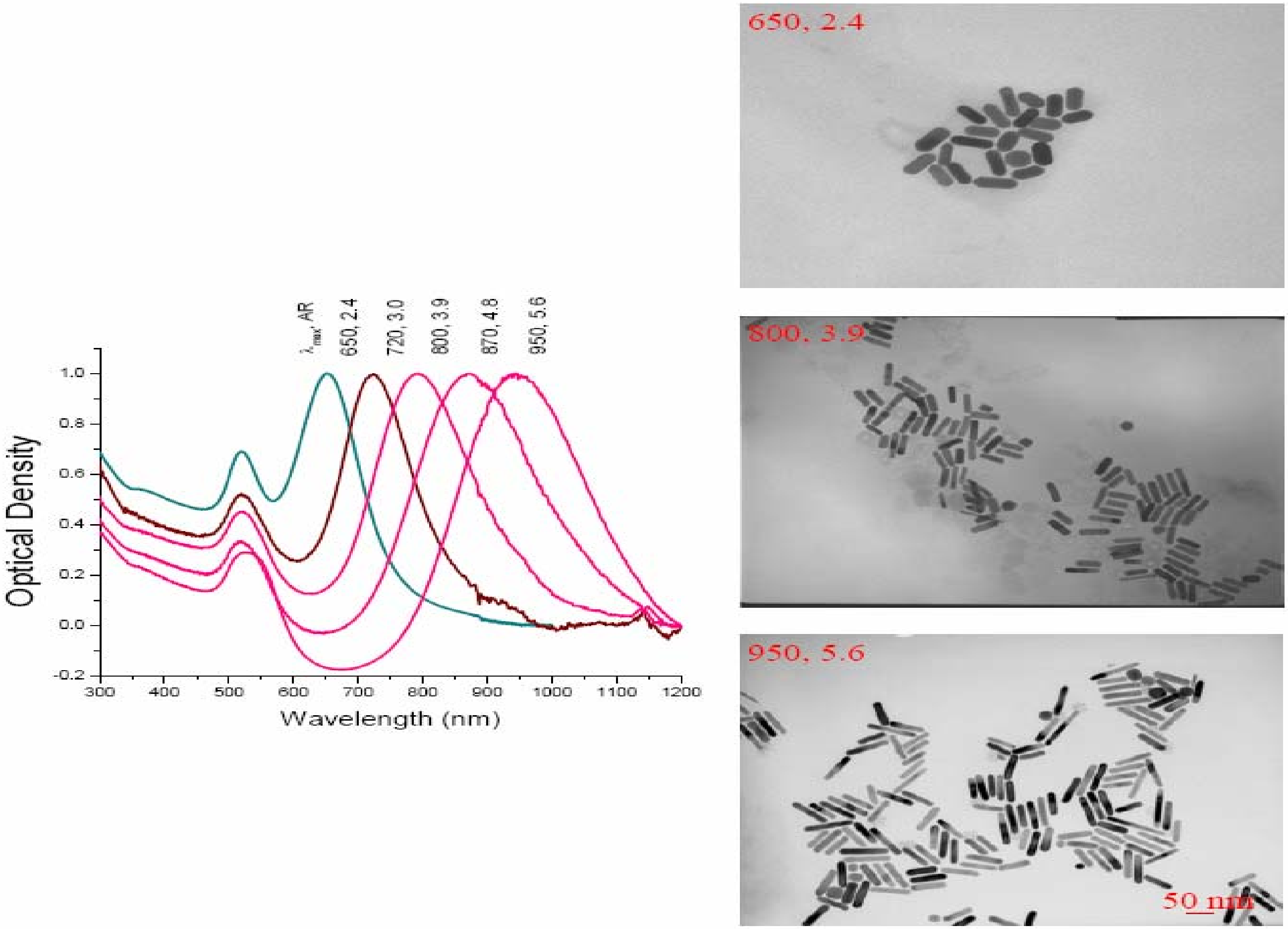


Figure 1-6: The absorption spectra of gold rods of different aspect ratios (left) and TEM of the rods with aspect ratios at 2.4, 3.9 and 5.6.

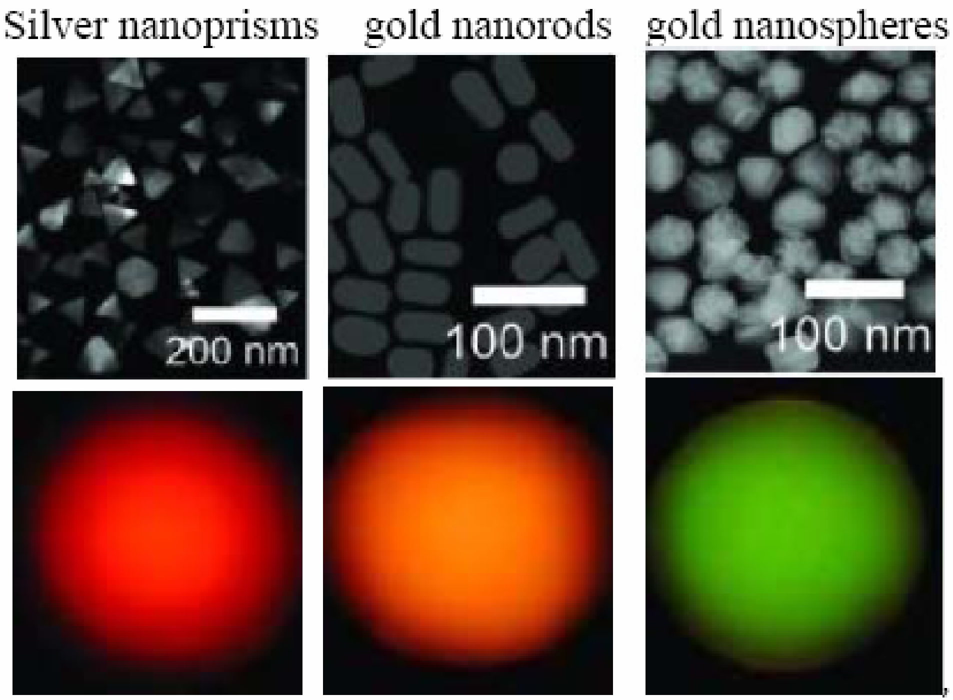


Figure 1-10: Light scattering of silver nanoprisms, gold nanorods, and gold nanospheres (26).

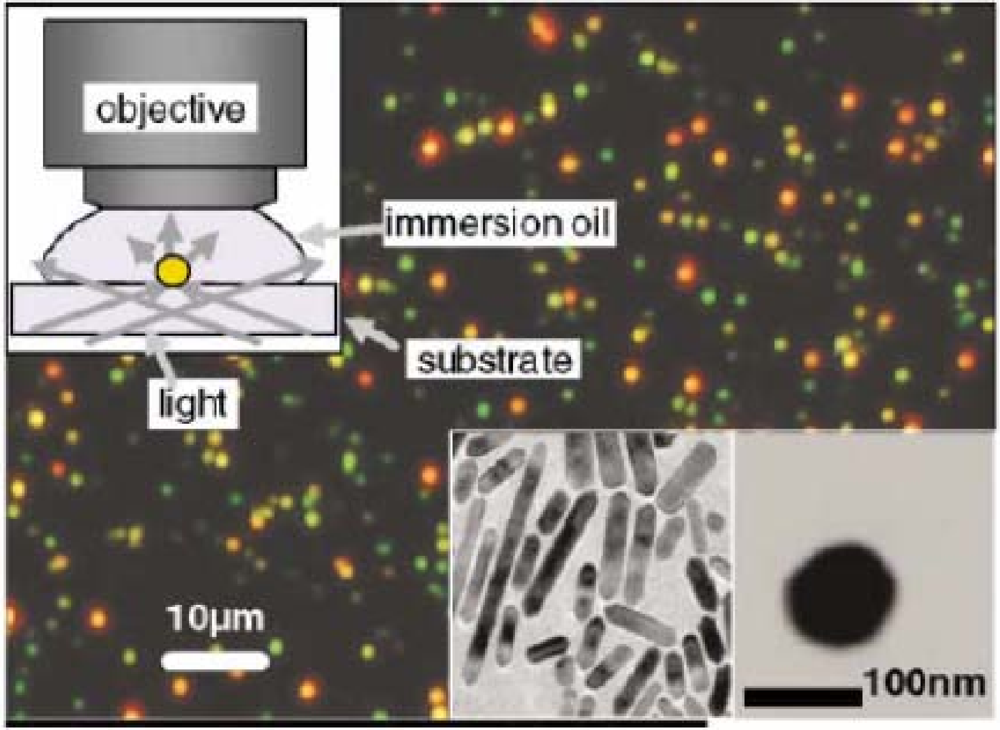


Figure 1-9: True color photograph of a sample of gold nanorods (red) and 60 nm nanospheres (green) in dark-field illumination (inset upper left). Bottom right: TEM images of a dense ensemble of nanorods and a single nanosphere (25).

Luster decorated XVI century Renaissance pottery, Gubbio, Italy
Image and information from the ***National Gallery of Art, Washington, DC***

Padovani et al.,
J. Appl. Phys. 2003, *93*, 10058 .

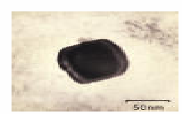
NPs = nano particles

The Lycurgus Cup, Roman glass IV century
Image and information from the ***British Museum***

Illuminated from outside => green

Illuminated from inside => red

70% silver and 30 % gold



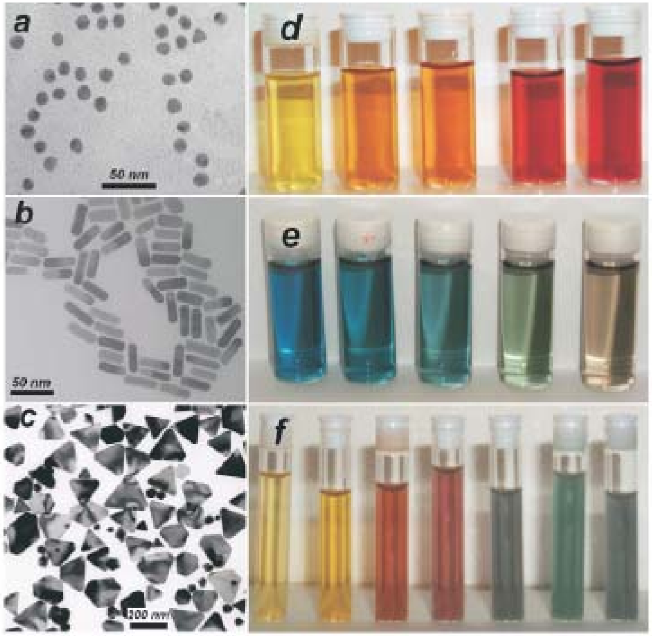


Fig. 1 Left: Transmission electron micrographs of Au nanospheres and nanorods (a,b) and Ag nanoprisms (c, mostly truncated triangles) formed using citrate reduction, seeded growth, and DMF reduction, respectively. Right: Photographs of colloidal dispersions of AuAg alloy nanoparticles with increasing Au concentration (d), Au nanorods of increasing aspect ratio (e), and Ag nanoprisms with increasing lateral size (f).

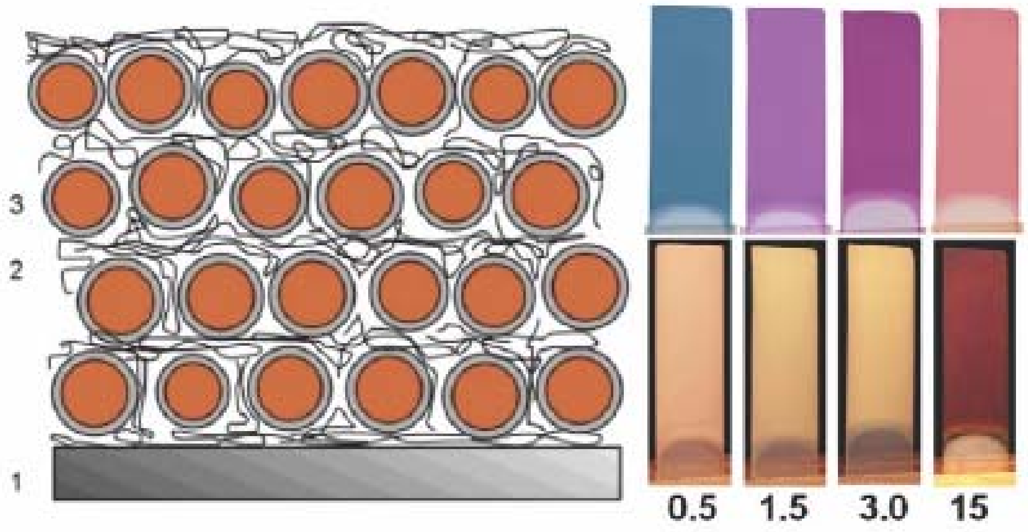


Fig. 3 Left: Schematic drawing of a multilayer film formed by layer-by-layer assembly of SiO_2-coated Au nanoparticles (1 = glass substrate; 2 = cationic polyelectrolyte; 3 = nanoparticles). Right: Photographs of transmitted (top) and reflected (bottom) colors from Au@SiO_2 multilayer thin films with varying silica shell thickness.

$$\varepsilon_{av} = \varepsilon_m \frac{\varepsilon(1+2\phi)+2\varepsilon_m(1-\phi)}{\varepsilon(1-\phi)+\varepsilon_m(2+\phi)} \qquad (6)$$

where ϕ is the metal volume fraction, ε_m is the dielectric function of the surrounding medium, and ε is the complex dielectric function of the nanoparticles. The transmittance, T,