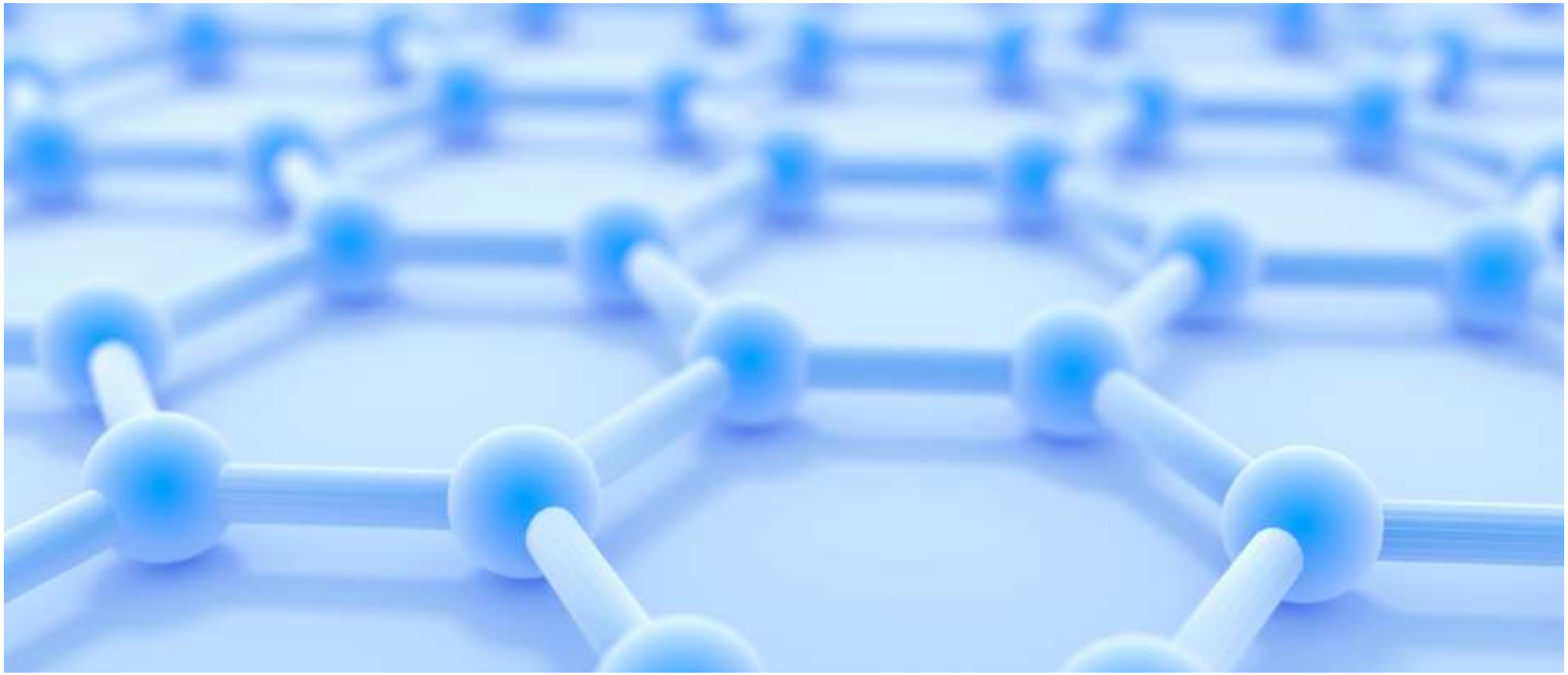
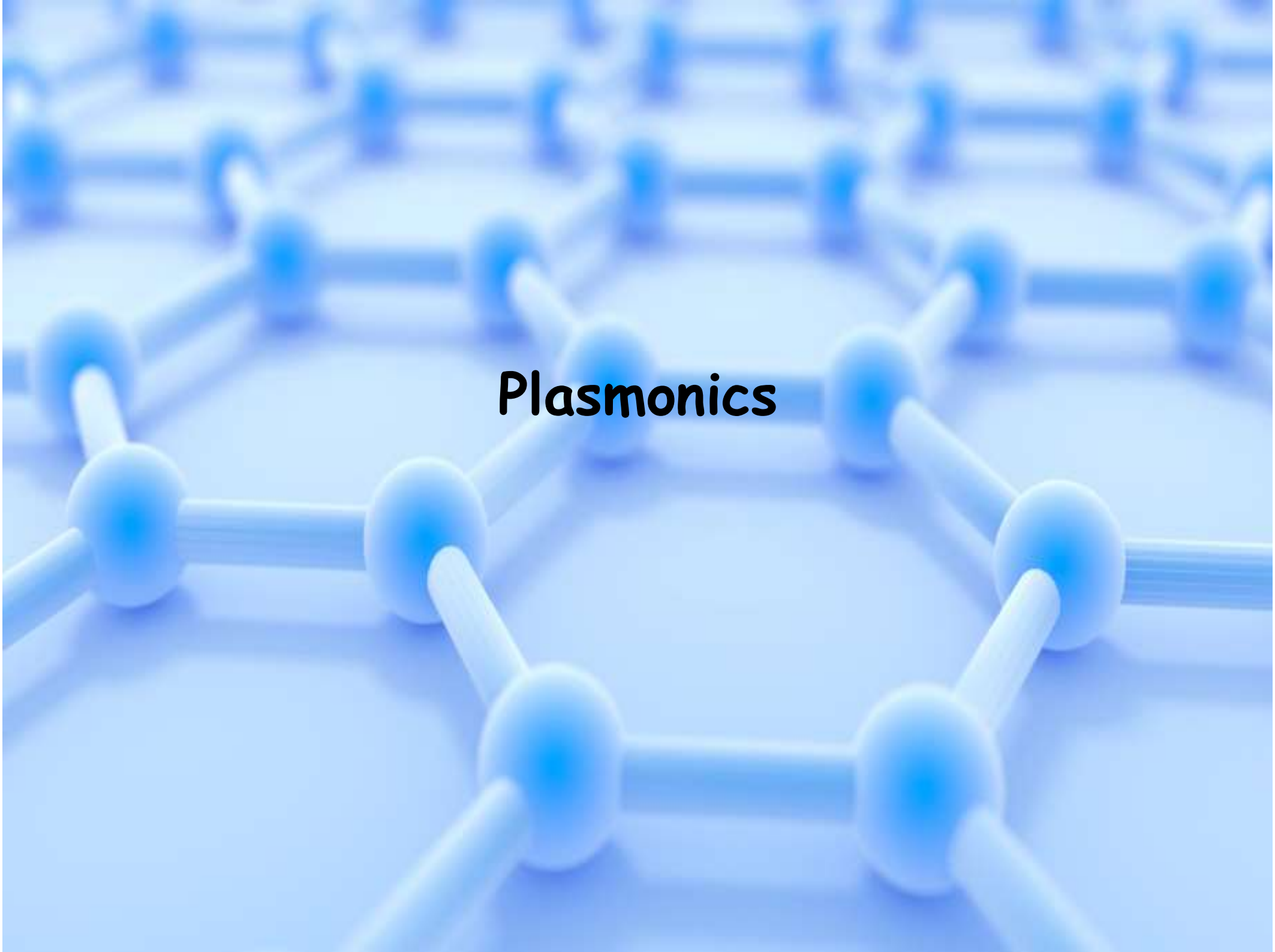


# Photonics

**Prof. Maria Antonietta Vincenti**
*Università degli Studi di Brescia*


Plasmonics

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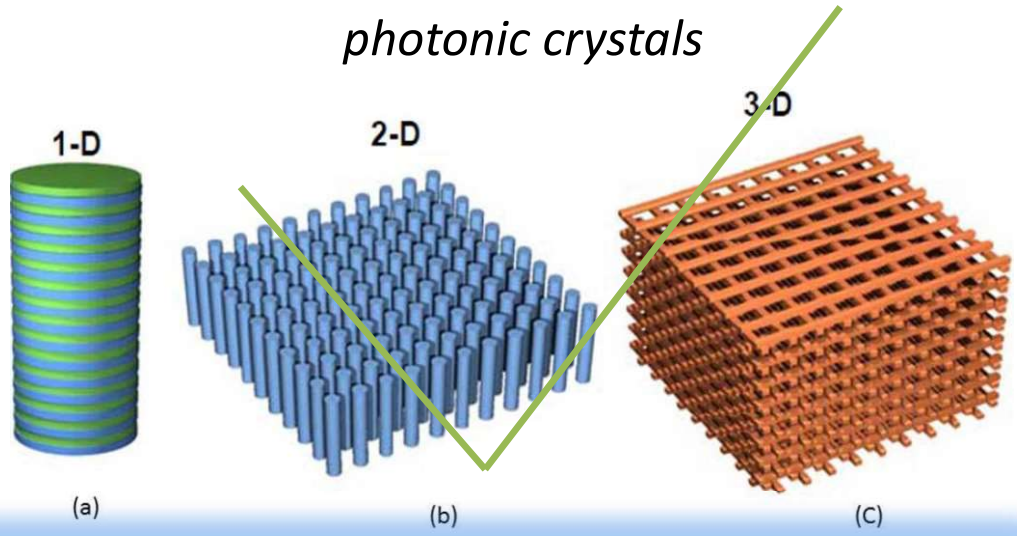
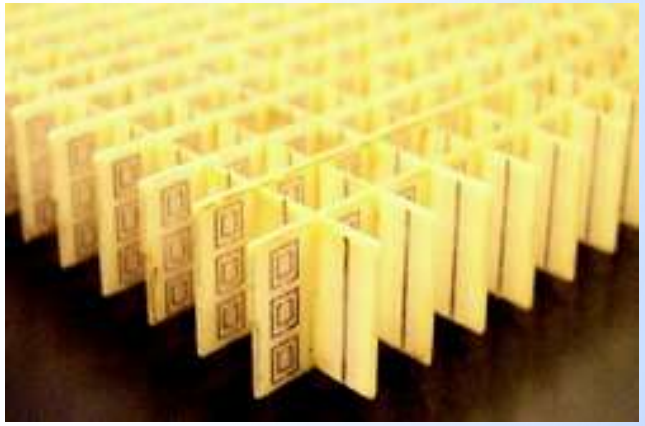
# Introduction

Scientists and researchers refuse to be confined by the materials refined from naturally occurring compounds and they are creating new materials or nanostructured materials that exhibit unusual electronic and optical properties.

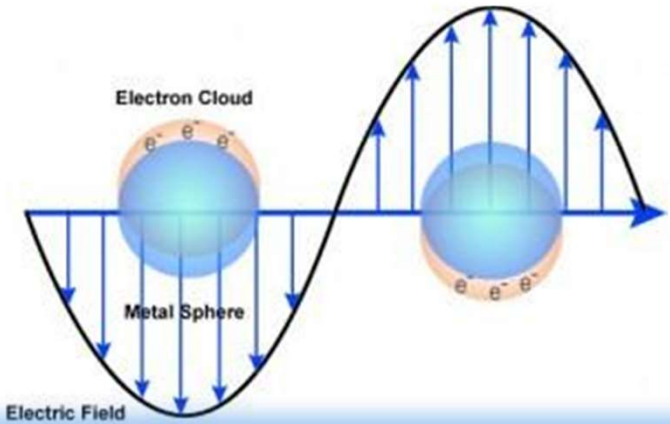
*photonic crystals*



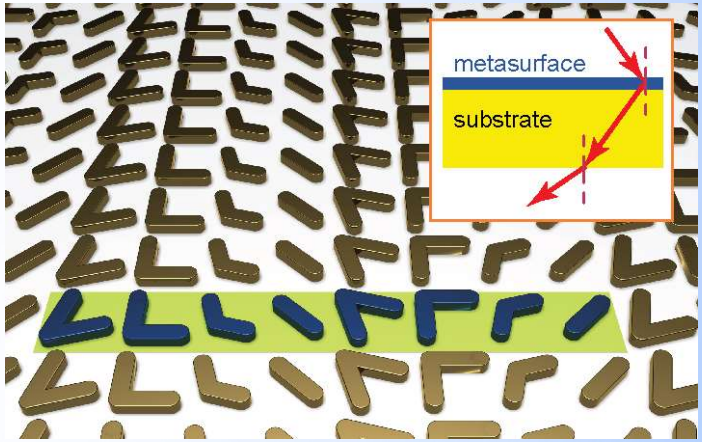

*metamaterials*



*plasmonics*




*metasurfaces*



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# Introduction

*Plasmonics* refers to a major topic in nanophotonics devoted to the optical phenomena resulting from the interaction of electromagnetic fields with conduction electrons in metals.

**Nanotechnology in Roman Times:**
**The Lycurgus Cup**

Plasmons of gold nanoparticles in glass reflect green light and transmit red light

The interest in plasmonic research is motivated by the rapid advancements in nanofabrication technologies and characterization tools, by the easier access to powerful and fast computational resources and by the progress in related research fields, e.g., metamaterials science. The existing and potential applications of plasmonic-based nanostructures are innumerable and span a wide range of fields, including energy harvesting, sensing devices, electro-optical devices, biomolecule detection, drug delivery, and many more.

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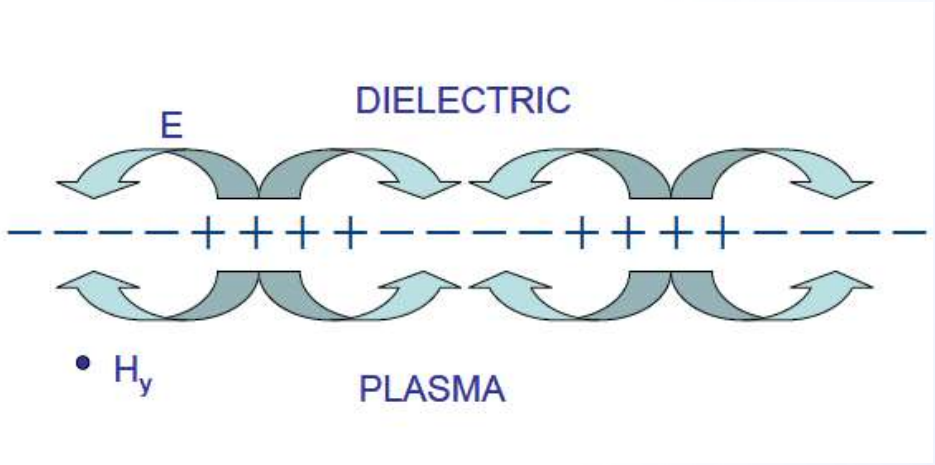
# Introduction

*Surface Plasmons are the collective vibrations of an electron gas (or plasma) surrounding the atomic lattice sites of a metal*.

When plasmons couple with a photon, the resulting particle is called a polariton. This polariton propagates along the surface of the metal until it decays, either by absorption, where the energy is converted into phonons, or by a radiative transition into a photon.




Surface plasmons can be excited by both electrons and photons. Excitation by electrons is created by shooting electrons into a metal. As the electrons scatter, energy is transferred into the plasma. The component of the scattering vector parallel to the surface results in the formation of a surface plasmon.

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# Optical Properties of metals

There are two kind of electrons in metal atoms:

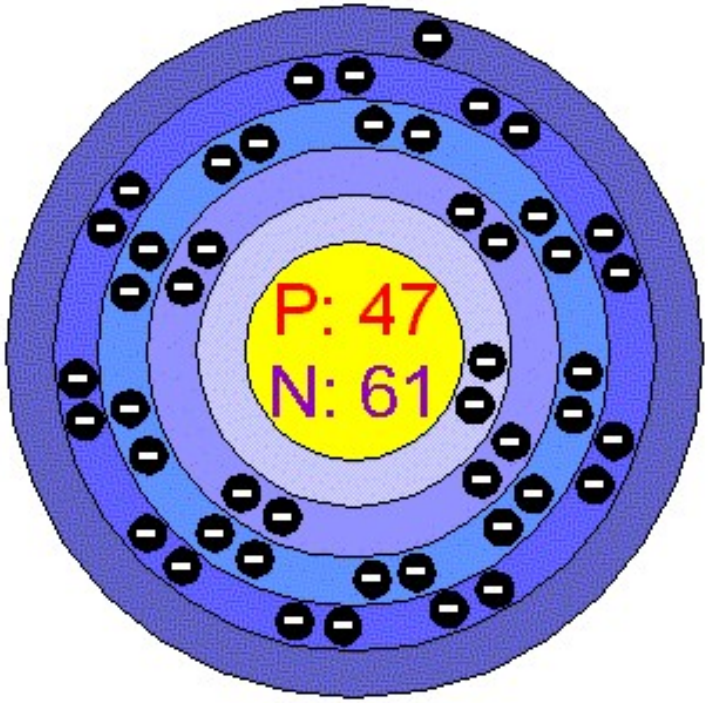
FREE ELECTRONS and BOUND ELECTRONS

Let's take a look for example at the electronic configuration of a silver atom:

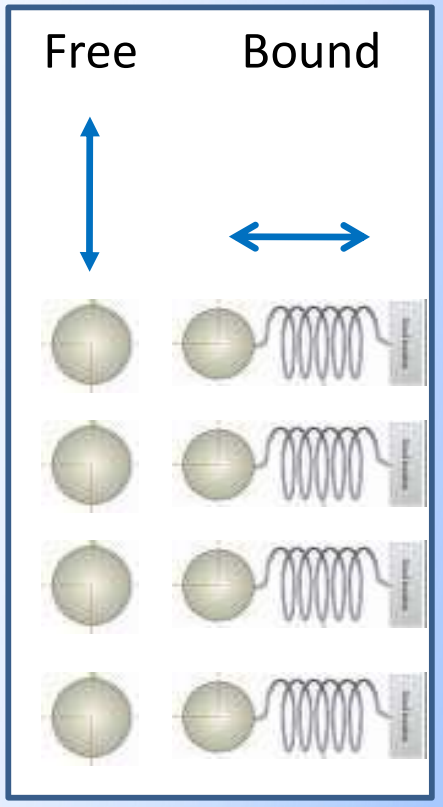
Valence and Free electrons

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6 4d^{10}\ 5s^1$

Tightly bound electrons
(contribute to material properties at X-ray wavelengths and beyond)




- ~1 free electron per atom
- up to 10 valence band electrons available. 4d orbital contributes to conductivity/dielectric constant at wavelengths in the visible range



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# Optical Properties of metals

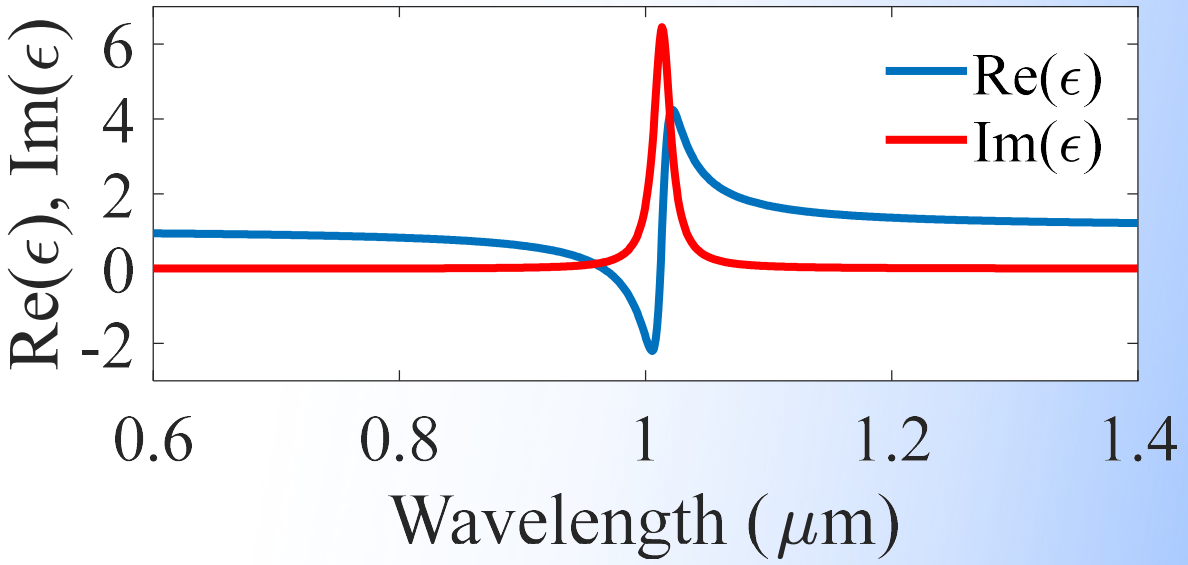
From the equation of motion of **BOUND** electrons:

$$m\frac{d^2\mathbf{r}}{dt^2}+m\gamma\frac{d\mathbf{r}}{dt}+K\mathbf{r}=-e\mathbf{E}$$

We got the Lorentz oscillator model for the dielectric permittivity:

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

$$\omega_p^2=\frac{Ne^2}{m}$$



# Optical Properties of metals

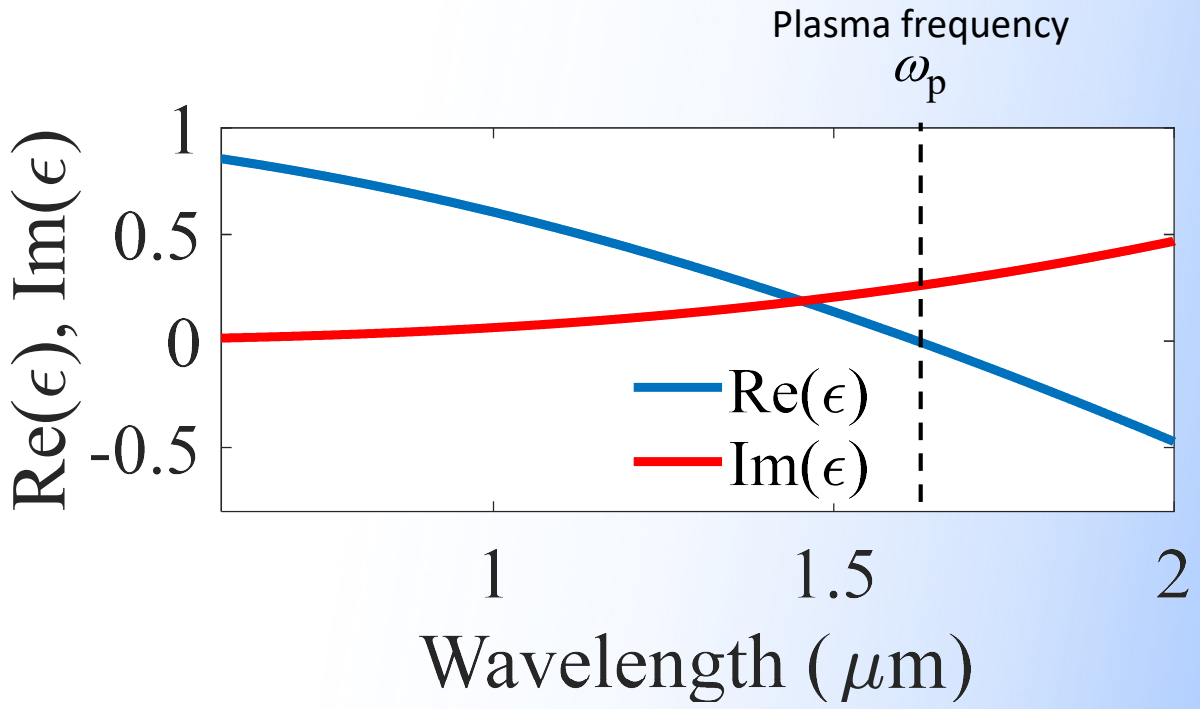
From the equation of motion of **FREE** electrons:

$$m\frac{d^2\mathbf{r}}{dt^2}+\frac{m}{\tau}\frac{d\mathbf{r}}{dt}=-e\mathbf{E}$$

We got the Drude oscillator model for the dielectric permittivity:

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

$$\omega_p^2=\frac{Ne^2}{m} \quad , \gamma=\frac{1}{\tau}$$



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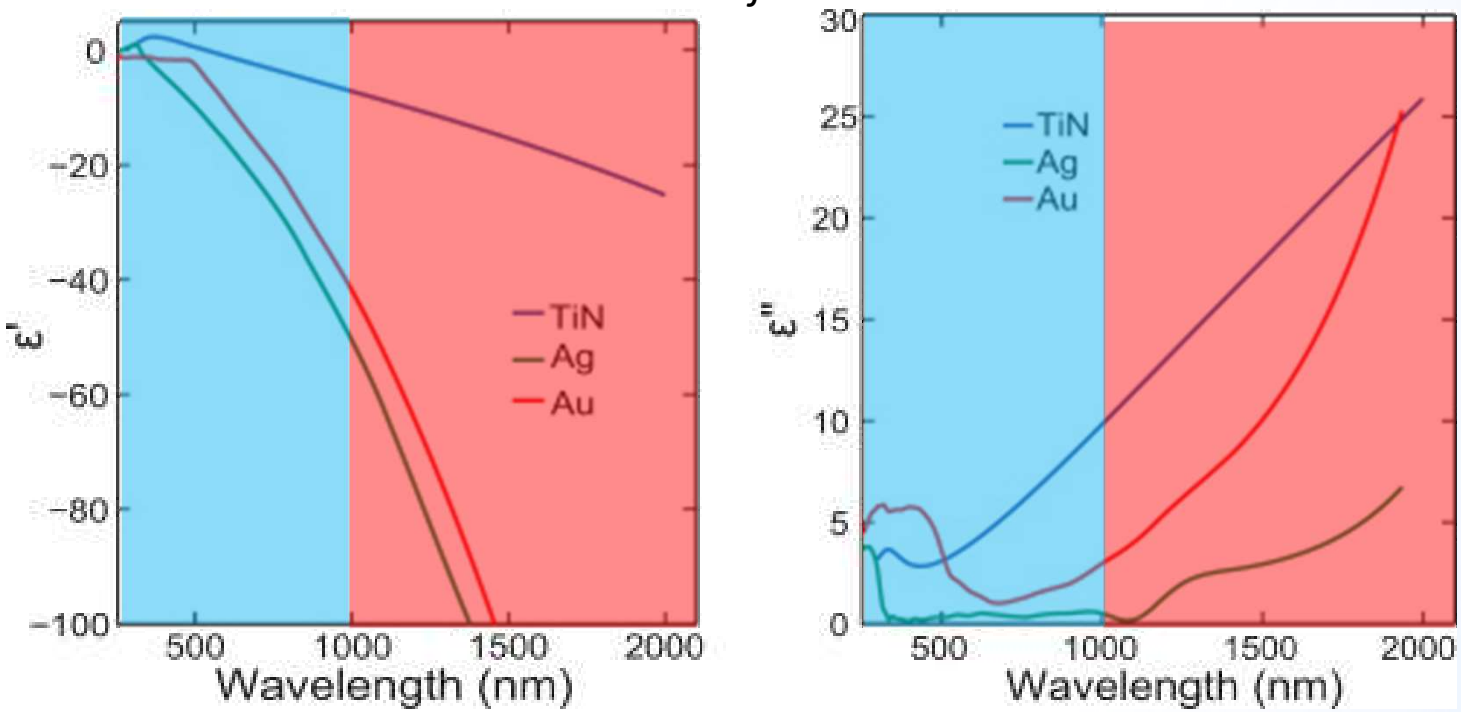
# Optical Properties of metals

Silver, for example, has both bound and free electrons that contribute to its optical properties. Therefore, the RELATIVE permittivity of this metal (and many other similar metals such as gold, aluminum and copper) can be modeled as a superposition of Lorentz and Drude oscillators as follows:

$$\varepsilon = 1 - \frac{\omega_{\mathrm{pf}}^2}{\omega^2 - j\gamma_f \omega} - \sum_i \frac{\omega_{\mathrm{pb,i}}^2}{\omega^2 - \omega_{0b,i}^2 - j\gamma_{b,i}\omega}$$

Dispersion of silver, gold and titanium nitride permittivities

$\varepsilon = \varepsilon' - j\varepsilon''$




DRUDE-like dispersion in the infrared regime (free electrons dominate)

LORENTZ-like dispersion in the visible regime (bound electrons dominate)

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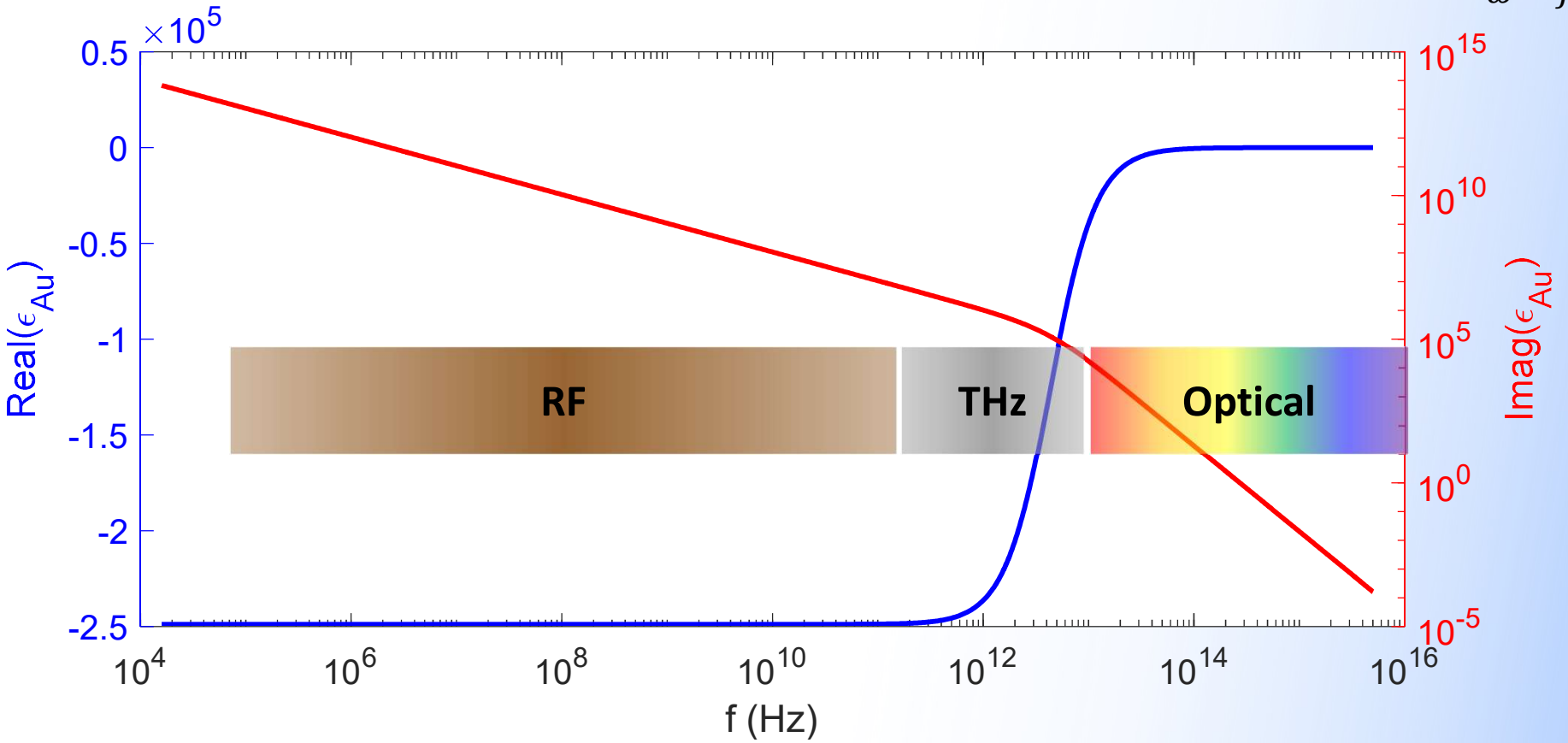
# Optical Properties of metals

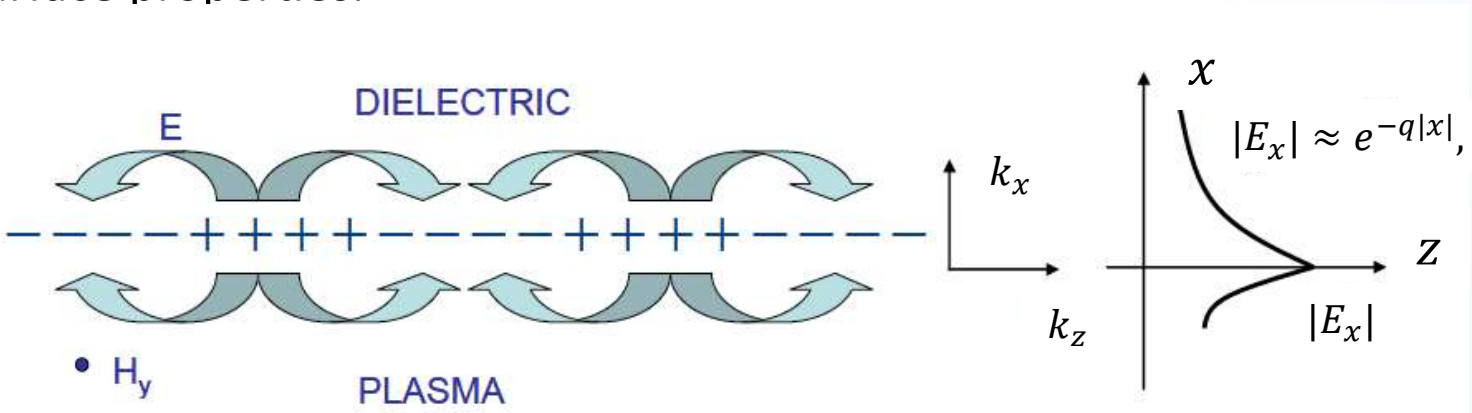
Let's look at a simple model for gold permittivity as a function of frequency $\varepsilon_{Au} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - j\gamma\omega}$




- **RF**: $\epsilon$ has very large imaginary part and the real part is negative → GOOD MIRROR (RF simply reflected and they do not penetrate much into metal)
- **THz**: Imaginary part and real part (negative) are both large and on the same order of magnitude → GOOD MIRROR (THz penetrates a lit bit more under the metal surface but the majority of the field is still reflected)
- **Optical**: Imaginary part is low and real part transitions from negative to positive!

# SPPs at metal-dielectric interfaces

The electron charges on a metal boundary (let's assume this boundary is at the plane x=0 and let's consider propagation of the SPP in the z direction) can perform coherent fluctuations called surface plasma oscillations. The frequency ω of these longitudinal oscillations is tied to its wavevector $k_z = k_{sp} = \beta$ by a dispersion relation $\omega(\beta)$. These charge fluctuations are accompanied by a mixed transversal and longitudinal electromagnetic field which disappears at x → ∞ and has its maximum at x = 0, therefore is a surface wave. This explain their sensitivity to surface properties.




$\epsilon_d$, for x>0

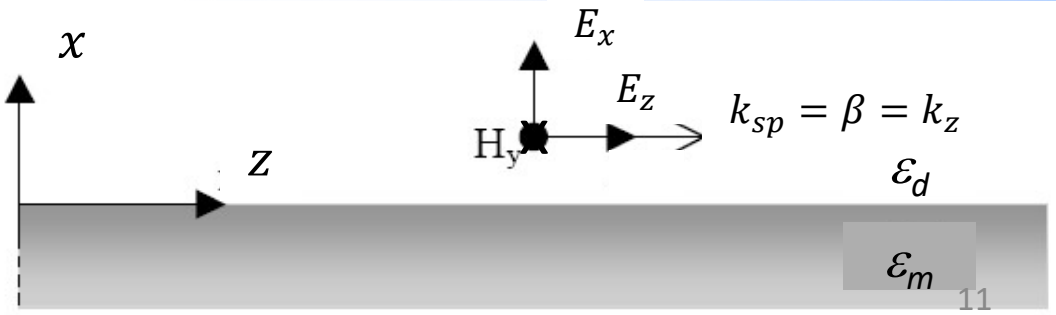
$\epsilon_m$, for x<0

$$\epsilon_m = \epsilon' - j\epsilon''$$

Where $\epsilon' < 0$, and $\epsilon''$ is very small

$$q^2 = -k_x^2$$

We will show that SPP is only possible for TM polarization. Hence, we consider a **TM polarized field**, propagating in the z direction as depicted in figure:



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# SPPs at metal-dielectric interfaces

Under TM excitation condition we can write the electromagnetic fields inside the dielectric material as:

$$\mathbf{H}^d(x,z,t) = \hat{y}Ae^{-q_d x}e^{-j(\beta z-\omega t)}$$

$$\mathbf{E}^d(x,z,t) = \hat{z}\left(\frac{jq_d}{\omega\varepsilon_0\varepsilon_d}\right)Ae^{-q_d x}e^{-j(\beta z-\omega t)} + \hat{x}\left(\frac{\beta}{\omega\varepsilon_0\varepsilon_d}\right)Ae^{-q_d x}e^{-j(\beta z-\omega t)}$$

Remember that the wavenumber component parallel to the interface, $\beta = k_z$, MUST be equal in the two regions (this comes from boundary conditions)

The same equations can be written also in the metal following this form:

$$\mathbf{H}^m(x,z,t) = \hat{y}Be^{q_m x}e^{-j(\beta z-\omega t)}$$

$$\mathbf{E}^m(x,z,t) = \hat{z}\left(\frac{-jq_m}{\omega\varepsilon_0\varepsilon_m}\right)Be^{q_m x}e^{-j(\beta z-\omega t)} + \hat{x}\left(\frac{\beta}{\omega\varepsilon_0\varepsilon_m}\right)Be^{q_m x}e^{-j(\beta z-\omega t)}$$

Notice the sign change! This allows an evanescent field of type $e^{-|qx|}$

# SPPs at metal-dielectric interfaces

Wavenumbers $q_d$ and $q_m$ quantify the decay of the field far from the surface in the dielectric and metal, respectively, and they are defined as follows (dispersion relation):

$$q_d = \sqrt{\beta^2 - k_d^2} \qquad q_m = \sqrt{\beta^2 - k_m^2} \qquad k_{m,d} = \omega / c\sqrt{\varepsilon_{m,d}} = k_0\sqrt{\varepsilon_{m,d}}$$

Since we are supposing a surface wave propagation in the z direction, the field MUST be evanescent both in the metal and dielectric side along the x direction. In the loss-less scenario ($\epsilon'' = 0$), $k_x^d = -jq_d$ and $k_x^m = -jq_m$ must be purely imaginary, with a positive imaginary part . In general $\epsilon'' > 0$, and this means that $k_x^d$ and $k_x^m$ are complex, but in order to have a surface wave we still need that the imaginary parts of $k_x^d$ and $k_x^m$ be positive. By imposing the continuity of the tangential component of the electric field ($E_z$) at the interface (x = 0) we have:

$$\frac{Aq_d}{\varepsilon_d} = -\frac{Bq_m}{\varepsilon_m}$$

From the continuity equation on the magnetic field follows:

$$A = B$$

So that in order to have a solution we must satisfy the following dispersion relation:

$$\frac{q_m}{q_d} = -\frac{\varepsilon_m}{\varepsilon_d}$$

**$\epsilon_m$ MUST have a negative real part in order to have a surface wave**
**Because $q_{m,d}$ required to be positive in an SPP**

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# SPPs at metal-dielectric interfaces

The resulting dispersion relation is:

$$k_z = \beta = k_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$

This is valid in general, even when $\epsilon_m = \epsilon' - j\epsilon''$ is complex. In this case $k_{sp}$ is a complex quantity ($k_{sp} = k'_{sp} - jk''_{sp}$), as well as $k_x^{d,m}$ and $q_{d,m}$ . In the low-absorption approximation ($\epsilon' \gg \epsilon''$), it is possible to write:

$$k'_{sp} \approx \frac{\omega}{c}\sqrt{\frac{\varepsilon' \varepsilon_d}{\varepsilon' + \varepsilon_d}} = k_0 n_{sp}$$

where $$n_{sp} = k'_{sp}/k_0 = \sqrt{\frac{\varepsilon' \varepsilon_d}{\varepsilon' + \varepsilon_d}} > \sqrt{\varepsilon_d}$$

**Surface-plasmon effective refractive index**

Since we need $k'_{sp}$ to be real we must have: $\varepsilon' < 0$ and $|\varepsilon'| > \varepsilon_d$

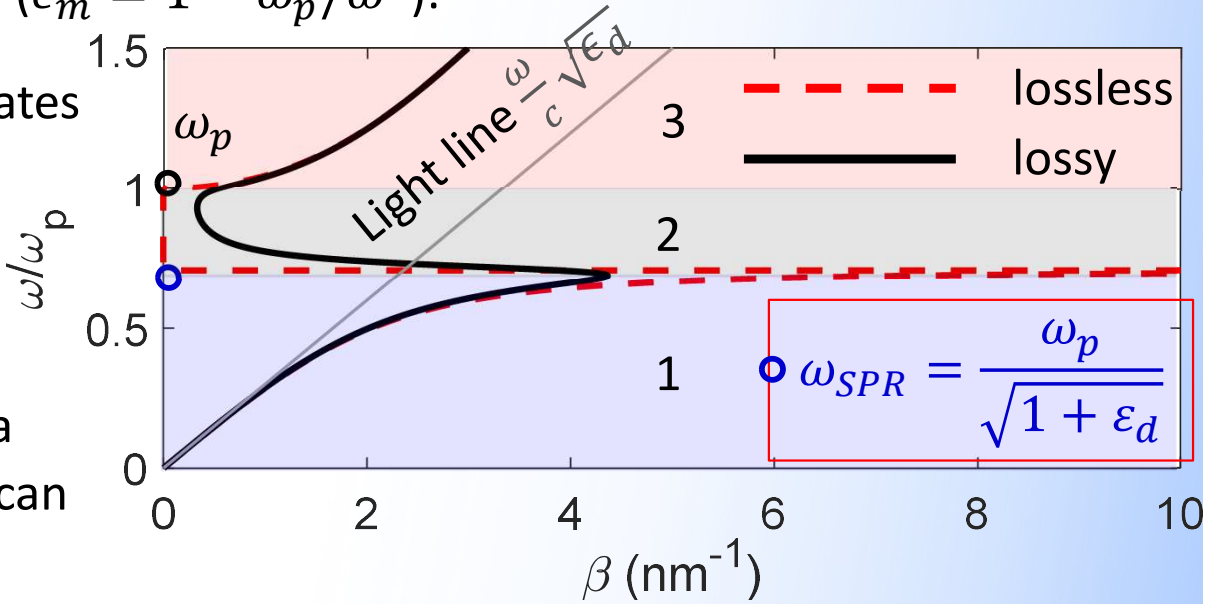
OBS: The requirement $\varepsilon' < 0$ condition occurs in metals and heavily doped semiconductors for frequencies below the plasma frequency $\omega_p$

For $\varepsilon' = -\epsilon_d$ , $n_{sp} \to \infty$. This condition occurs at a specific frequency that we call $\omega_{SP}$, and it is called **SURFACE PLASMON RESONANCE (SPR)**. At $\omega_{SPR}$, the plasmon becomes extremely confined. The effective wavelength $\lambda_0/n_{sp}$ of the SPP becomes extremely small. If there are losses, the absorption gets very large

# SPPs at a Drude-metal/dielectric interface

The SPP dispersion relation is represented in the following figure for the interface between a dielectric ($\epsilon_d$) and a lossless Drude metal ($\epsilon_m = 1 - \omega_p^2/\omega^2$):

1. For $\omega < \omega_{SPR}$ (blue), the SPP propagates in z and is confined in the x direction
2. For $\omega_p > \omega > \omega_{SPR}$ (grey), the SPP CANNOT propagate in the z ($\beta$ is imaginary)
3. For $\omega > \omega_p$ (red), the SPP becomes a **VOLUME PLASMON POLARITON** that can propagate in the volume of metal




**Three different regimes can be identified in the lossless scenario** ($\epsilon_m = 1 - \omega_p^2/\omega^2$): (i) for $\omega < \omega_{SPR}$, i.e., $\varepsilon_m < -\varepsilon_d$, the mode is an evanescent surface wave, i.e., a *surface plasmon polariton*, bound at the interface ($k_x^{d,m} = -jq_{d,m}$ purely imaginary, with $q_{d,m} > 0$) and propagates in the *z*-direction with a real $\beta = k_z = k_{sp}$ ; ii) in the region $\omega_p > \omega > \omega_{SPR}$ the mode has real $k_x^{d,m}$(purely imaginary $q_{d,m}$) and a purely imaginary $\beta = k_{sp} = k_z$, hence propagation is attenuated in the *z*-direction; (iii) for $\omega > \omega_p$ the mode becomes radiative since both $k_x^{d,m}$ and $k_z$ are real. The lossy case ($\gamma_f \neq 0$) is similar and it is reported (black curve) for comparison.

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# Surface plasmon polaritons at metal-dielectric interfaces

Under TE excitation condition we can write the fields inside the dielectric material as:

$$E^d(x,z,t) = \hat{y} A e^{-q_d x} e^{-j(\beta z - \omega t)}$$

$$H^d(x,z,t) = \hat{x} H_x^d + \hat{z}\left(\frac{-jq_d}{\omega\mu_0}\right) A e^{-q_d x} e^{-j(\beta z - \omega t)}$$

The same equations can be written also in the metal following this form:

$$E^m(x,z,t) = \hat{y} B e^{q_m x} e^{-j(\beta z - \omega t)}$$

$$H^m(x,z,t) = \hat{x} H_x^m + \hat{z}\left(\frac{jq_m}{\omega\mu_0}\right) A e^{q_m x} e^{-j(\beta z - \omega t)}$$

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# Surface plasmon polaritons at metal-dielectric interfaces

As previously done, we impose the continuity of tangential fields in x = 0

$$A = B$$

$$Aq_d = -Bq_m$$

Which can be combined in the equation:

$$A\left(q_d + q_m\right) = 0$$

Since $q_{d,m}$ must have same sign in order to have a surface wave, this implies that only the trivial (physically meaningless) solution is possible:

$$A = B = 0$$

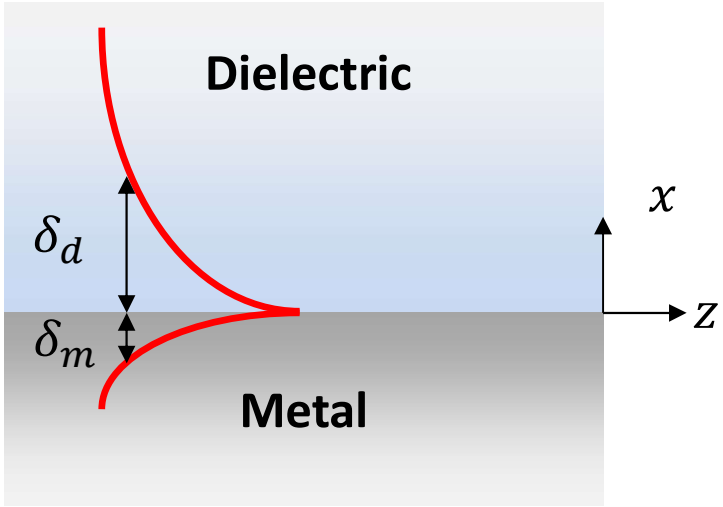
Surface Plasmons cannot be excited under TE polarization

# Penetration depth

In the metal and in the dielectric semi-infinite layers both $q_{d,m}$ greater than zero. The field amplitude of the plasmon decreases exponentially as:

$$\exp\left(-q_{d,m}|x|\right)$$

The penetration depth in a material (also known as the skin depth in a metal) is defined as the length at which the field intensity decreases of a factor of 1/e and can be defined as $\delta = 1/q$ .
It follows that:




$$\delta_d = 1/q_d \Rightarrow \delta_d = \frac{\lambda}{2\pi}\left(\left|\frac{\varepsilon_m' + \varepsilon_d}{\varepsilon_d^2}\right|\right)^{1/2}$$

$$\delta_m = 1/q_m \Rightarrow \delta_m = \frac{\lambda}{2\pi}\left(\left|\frac{\varepsilon_m' + \varepsilon_d}{\varepsilon_m'^2}\right|\right)^{1/2}$$

EXAMPLE: For a surface plasmon of wavelength 600 nm supported at a silver-air interface, the evanescent tail of the electromagnetic field extends for ~ 390 nm on the air side and ~24 nm on the silver side.

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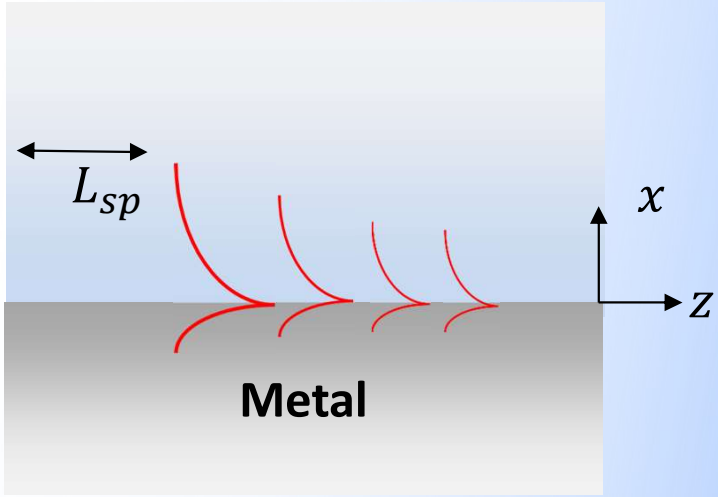
# Propagation length

Due to the ohmic losses inside the metal the surface plasmon propagation is attenuated also in the propagation direction (z-axis) at the metal-dielectric interface.

The propagation length is also defined as the distance at which the field intensity decays of a factor of 1/e of its maximum value, which means that the propagation length $L_{sp}$ is related to $Im(\beta) = k_{sp}^{''}$ by means of the following relation:

$$L_{sp} = \frac{1}{2k_{sp}^{''}} = \frac{c}{\omega} \frac{\sqrt{\left|\varepsilon_m^{'}\right|}\left(\left|\varepsilon_m^{'}\right| - \varepsilon_d\right)^{\frac{3}{2}}}{\varepsilon_d^{\frac{3}{2}} \varepsilon_m^{''}}$$




Of course, in the lossless case (metal with $\gamma_f = 0$ and $\epsilon'' = 0$ , $L_{sp} \to \infty$)

EXAMPLE: For a surface plasmon of wavelength $\lambda$ ~ 515 nm supported at a silver-air interface, the propagation length is approximately 500 μm.

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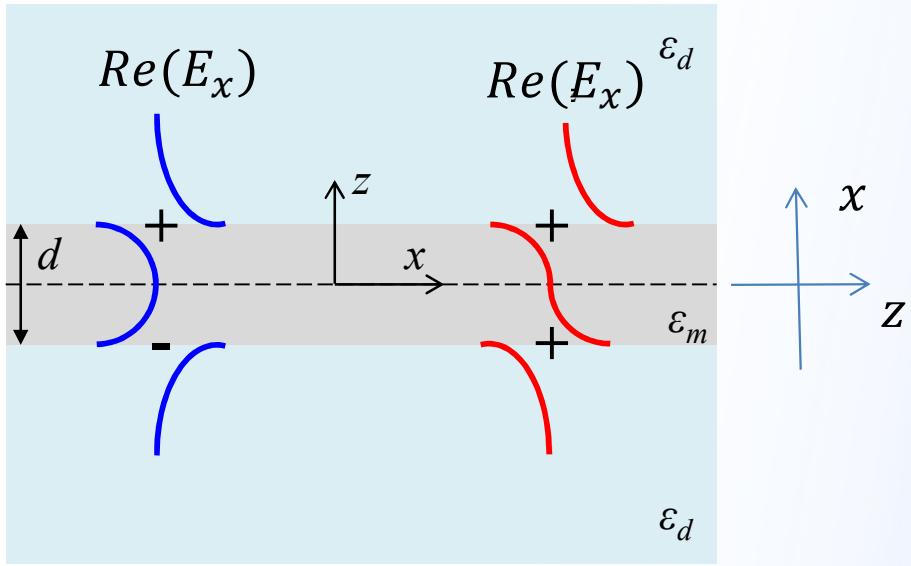
# Surface Plasmons on metallic thin films

Let's now consider the TM-polarized modes of a multilayer formed by a thin, metallic film with relative permittivity $\varepsilon_m$ and thickness $d$ surrounded by a dielectric medium with relative permittivity $\varepsilon_d$. The structure can be thought as a system of coupled waveguides. Each isolated interface is a waveguide that supports the propagation of a surface-plasmon polariton.

Symmetric

Antisymmetric




When the distance *d* between the two interfaces (i.e., the metal thickness) is of the order of the field penetration depth in the metal, the two surface waves are coupled through their evanescent tails. Because of the symmetry of the structure, the modes supported by the film can be either symmetric or antisymmetric with respect to the center of the film (plane *x*= 0).

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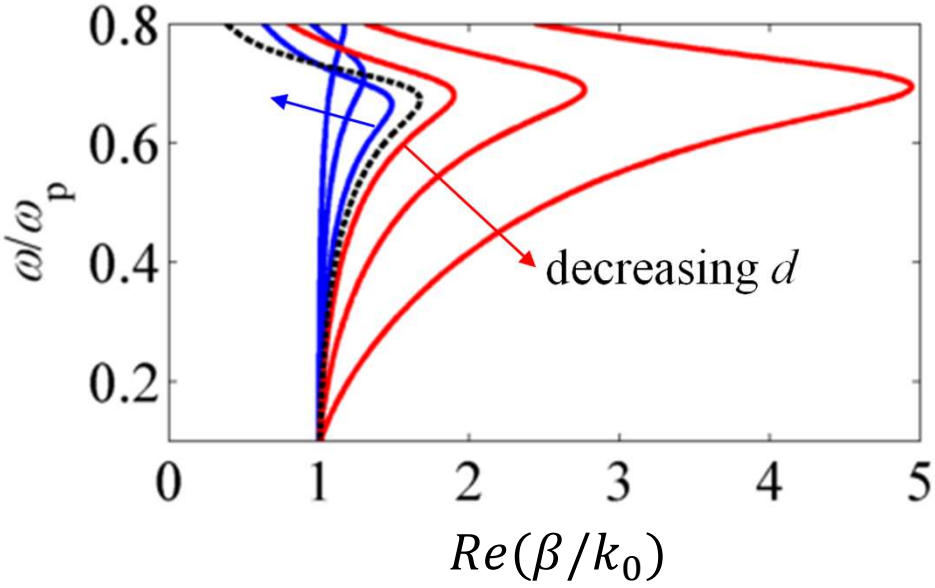
# Surface Plasmons on metallic thin films

The dispersion relations for the symmetric and the antisymmetric modes can be found in the usual way by setting the continuity of the tangential fields, and read as follows:

$$S: \varepsilon_m q_d + \varepsilon_d q_m \tanh\left(\frac{q_m d}{2}\right) = 0 \qquad A: \varepsilon_m q_d + \varepsilon_d q_m \coth\left(\frac{q_m d}{2}\right) = 0$$

The solutions in the complex $\omega - \beta$ plane are usually found numerically by minimizing the complex functions $|S|$ and $|A|$. For $d \to \infty$, i.e., when the film is very thick and two interfaces can be assumed as isolated, the dispersion relations of the two modes are equal and tend to the dispersion of the metal-dielectric surface-plasmon polariton. TE-polarization solutions are not allowed in any planar metal-dielectric structure as shown for the simple interface.




The figure shows the dispersion curves for the symmetric (blue curves) and antisymmetric (red curves) modes for *d*=20 nm, 40 nm and 80 nm, and assuming a lossy Drude model for the film with $\gamma = 0.1\,\omega_p$ and air ($\varepsilon_d = 1$) for the surrounding medium. Notice that $Re\left(\frac{\beta_S}{k_0}\right) < Re\left(\frac{\beta_{AS}}{k_0}\right)$, hence the symmetric extends more into air than in the metal. For this reason:

**The Symmetric mode is called LONG-RANGE SPP**

**The Asymmetric mode is called SHORT-RANGE SPP**

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# Excitation of surface plasmon polaritons

Surface plasmons can be excited by both ***electrons*** and ***photons***.

Excitation by electrons is created by shooting electrons into a metal. As the electrons scatter, energy is transferred into the plasma. The component of the scattering vector parallel to the surface results in the formation of a surface plasmon.

On the other hand any light source, e.g., a plane wave or a finite-cross section beam, impinging on the interface with the metal at any incidence angle cannot couple to a surface plasmon. The common techniques to bring evanescent fields near metal interfaces and achieve phase-matching to surface plasmons are based on prisms and gratings.


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# Prism coupling and grating coupling: How they work…

Prism coupling and grating coupling are two alternative techniques that are commonly used to excite surface plasmon polaritons, and more generally waveguides. Plasmons are indeed modes confined at a surface rather than inside a high-index core. Although the guiding mechanism behind SPP (coupling of free electrons to photons) is different from conventional dielectric waveguides (total internal reflection), the dispersion relation of SPP and guided modes is similar. Let's look at the prism and grating coupling for conventional waveguides first and then we move to excitation of SPP with the same techniques…

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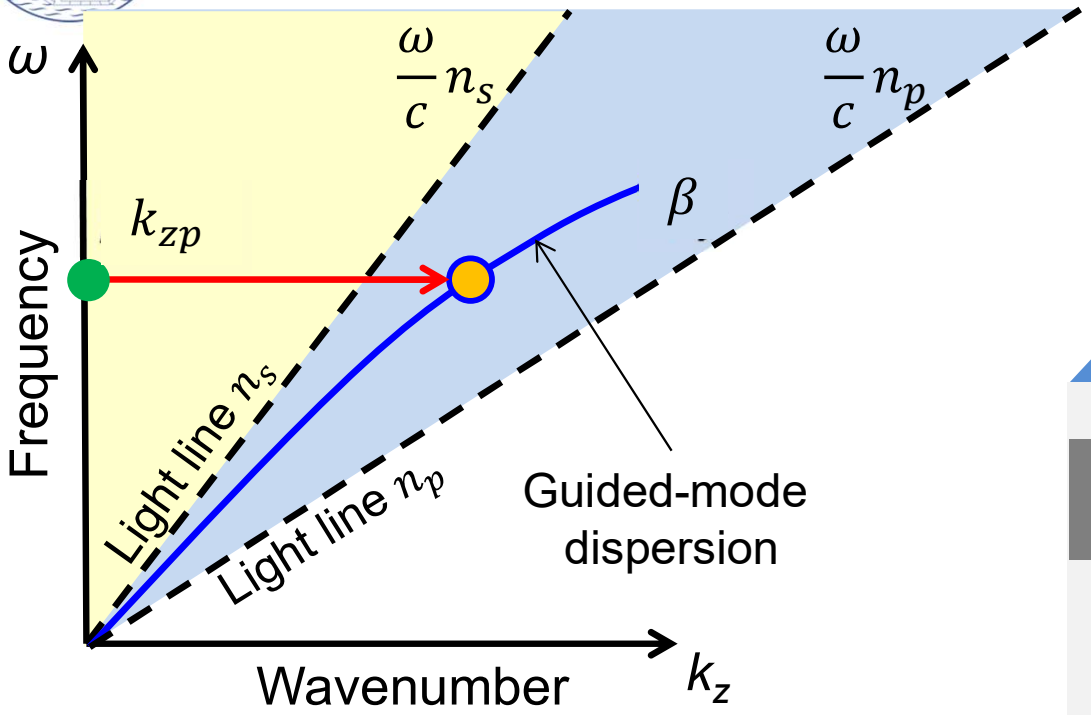
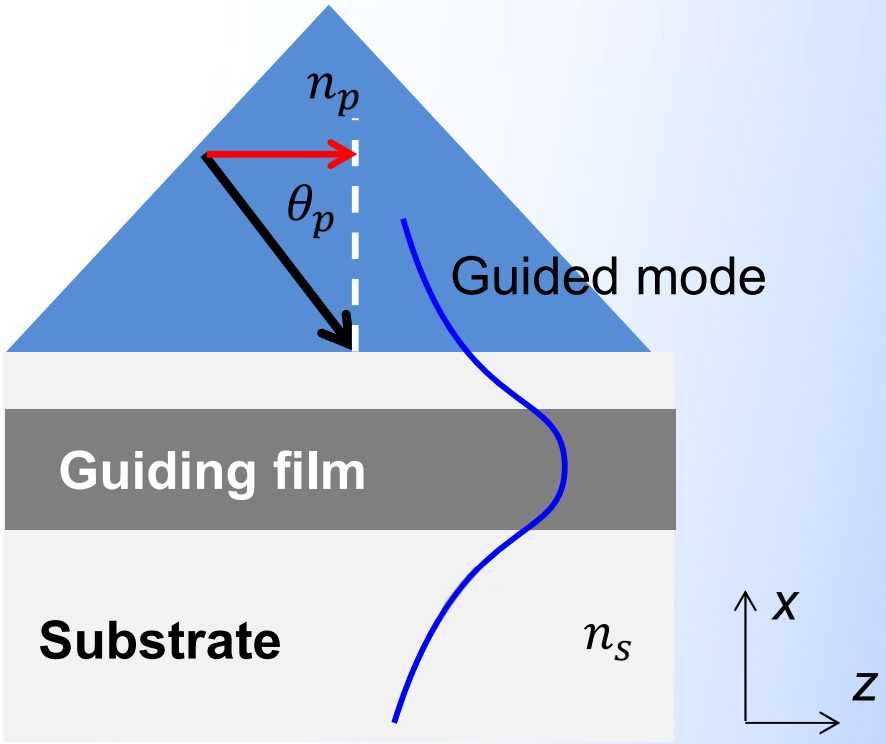
# Understanding prism coupling in the $\omega - k$ plane




In prism coupling, we excite the evanescent field that is required to match the field mode profile (the mode can be either a plasmon or, as in the figure, a mode guided by a slab). This can be achieved by introducing a prism in proximity to the guiding film. The prism index must be larger than the substrate/cover index, i.e., $n_p > n_s$. At this point, if the transverse momentum inside the prism, $k_{zp}$, matches the mode's propagation constant $\beta$, then the plane wave from the prism is coupled to the guided mode and light can propagate in the film. The phase-matching condition to excite the mode is:

$$k_{zp} = \frac{\omega}{c} n_p sin\theta_p = \beta = \frac{\omega}{c} n_{eff} \rightarrow \theta_p = \text{asin}(n_{eff}/n_p)$$

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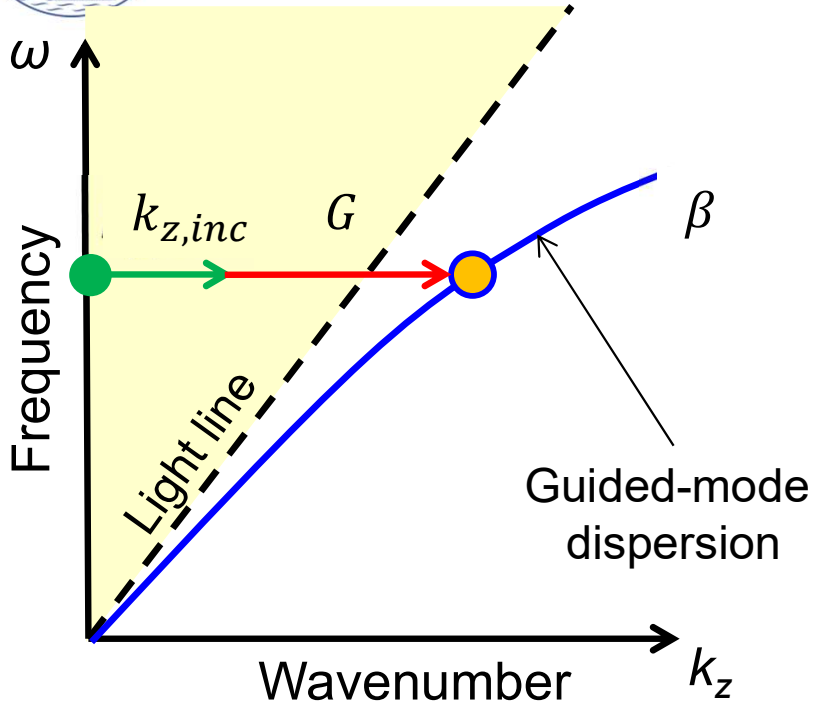
# Understanding grating coupling in the $\omega - k$ plane




Incident transverse wavenumber

$$k_{z,inc} = \frac{\omega}{c} n_d sin\theta$$

+

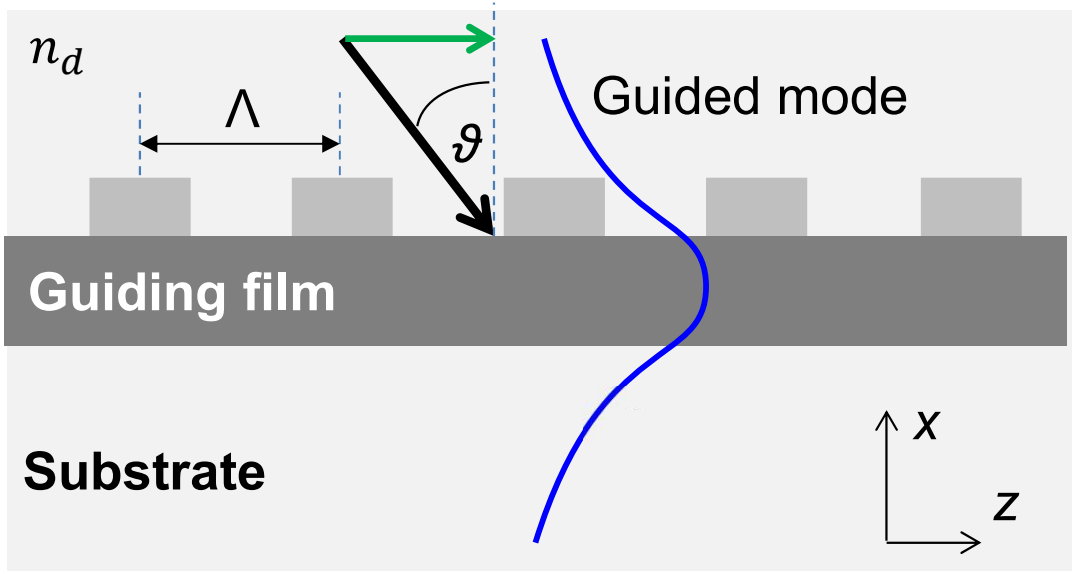
Lattice transverse momentum

$$G = \frac{2\pi m}{\Lambda}, \text{ where } m = \pm 1, \pm 2, \pm 3, \ldots$$

↓

Plane wave excitation of the guided mode

$$|k_{z,inc} + G| = \beta$$




*Note: The guided mode can be either a mode confined into a film (slab dielectric waveguide) or a plasmon (surface mode)*

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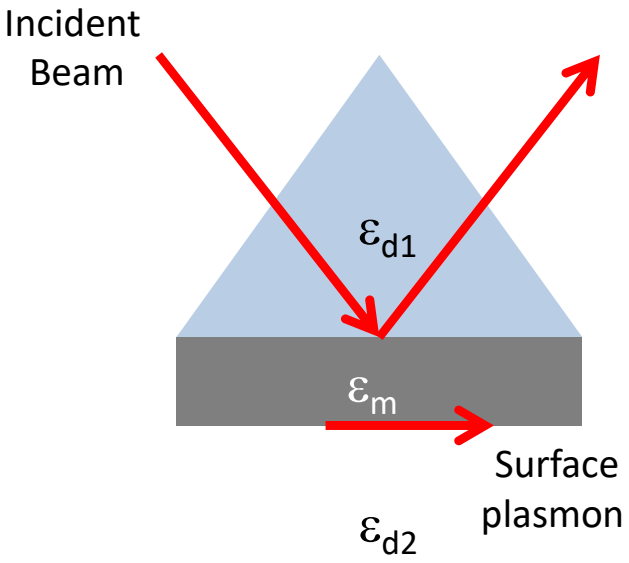
# Excitation of surface plasmons polaritons

In the *Kretschmann configuration* a metal film is deposited on a prism's face and a TM-polarized light source excites the film from the prism side at oblique incidence.




In this asymmetric system two SPs are present, one pertaining to the air-metal interface and the other to the prism metal interface. Evanescent fields on the air side, and excitation of the air-metal SP, may be achieved only above the critical angle of incidence of the prism-air system, i.e., for internal incidence angles $\boldsymbol{\theta_i > \theta_c = \mathbf{asin}(1/n_{d1})}$. A quasi phase-matching to the dielectric-metal SP is obtained when $\boldsymbol{n_{d1}\mathbf{sin}(\theta_i) = n_{sp} = \mathbf{Real}\left[\sqrt{\varepsilon_m \varepsilon_{d2}/(\varepsilon_m+\varepsilon_{d2})}\right]}$.
The metal film should be semitransparent in order to allow tunneling of a portion of the light source from the prism side to the air side.

NOTE: The surface plasmon is observable as a dip in reflection at $\boldsymbol{\theta_i = asin(n_{sp}/n_{d1})}$ and it is due to the increased absorption in the metal film when the leaky SP is excited. Zero reflection or perfect absorption is achievable under critical coupling conditions, i.e., when the damping due to radiation leakage equals the damping due to absorption losses. This condition can be reached by properly choosing the metal film thickness.

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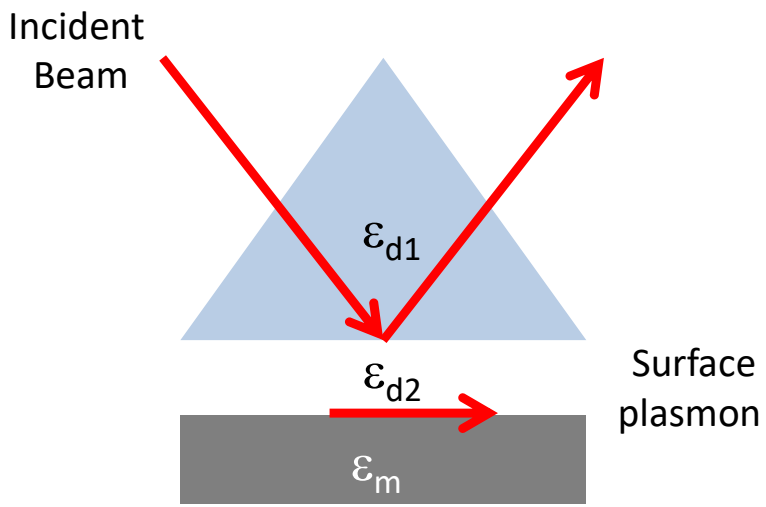
# Excitation of surface plasmon polaritons




In the *Otto configuration*, a sub-wavelength air gap between the metal surface and the prism allow the generation of evanescent fields at the prism-air interface above the critical angle $\theta_c$. If the air gap is thin enough, the evanescent tail reaches the metal surface and is able to couple to the air-metal SPP when $\theta_i = \theta_{SP}$. In the Otto configuration the thickness of the air gap is a critical parameter that influence the coupling strength to the SP. This geometry is particularly suitable for monitoring the surface quality and, in general, for all applications in which direct contact with metal must be avoided.

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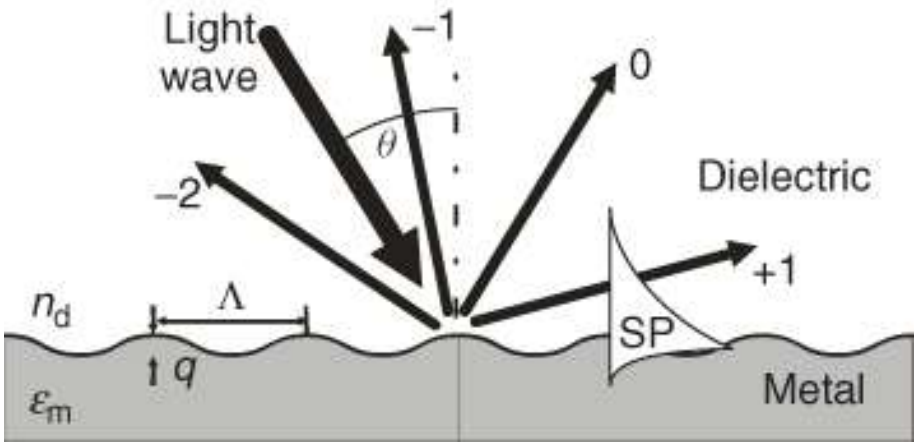
# Excitation of surface plasmon polaritons




Evanescent fields can be also obtained in gratings when a diffraction order assumes a wave vector larger than the incident radiation. A periodic perturbation on a metallic surface with periodicity $\Lambda$ introduce diffraction orders with parallel wave vector

$$\boldsymbol{k_0 n_d sin(\theta_i) \pm 2\pi m/\Lambda}$$

assuming light impinges on the structure from a medium with refractive index $n_d$ at an angle $\theta_i$ with respect to the normal to the patterned surface.

If one of these orders matches the SP wave vector, i.e., if

$$\boldsymbol{k_0 n_{sp} = k_0 n_d sin(\theta_i) \pm 2\pi m/\Lambda}$$

the SP is excited and a minimum in reflection occurs.

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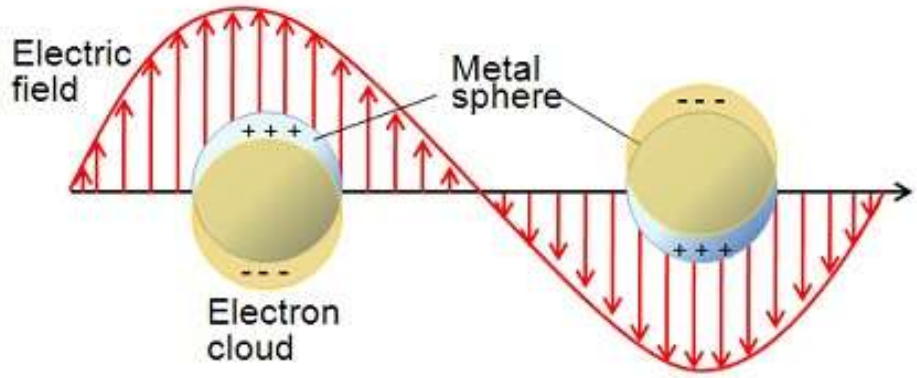
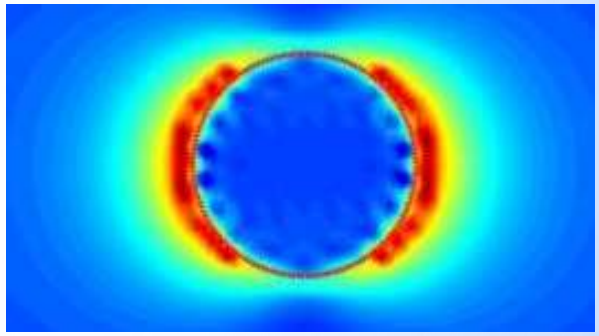
# Localized surface plasmons

While planar, metal-dielectric interfaces act as waveguides and support the propagation of surface waves coupled to the electron plasma, metallic nanostructures, i.e., small particles or nano-patterned metallic surfaces, may host non-propagating electromagnetic modes, also known as localized surface plasmons (LSPs). These modes induce resonances observable as peaks in the scattering and absorption.

The spectral position of the resonances depends on several factors: the metal permittivity, the permittivity of the surrounding dielectric, and the shape and size of the metallic nanostructure. A very simple scenario consists in a metallic, spherical nanoparticle much smaller than the wavelength of the interacting electromagnetic field.



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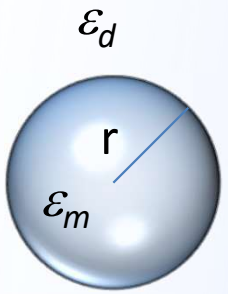
# Localized surface plasmons

The electrostatic approximation ($\omega \rightarrow 0$) provides a good description of the problem in the near field region of the particle (for $kr << 1$) and a simple prediction of the resonant frequency.
For a spherical, metallic particle with radius r and relative permittivity $\varepsilon_m$ in a homogeneous dielectric background with relative permittivity $\varepsilon_d$, the solutions of the Laplace equation for the potential, $\nabla^2\varphi = 0$, inside and outside the particle are given by:

$$\varphi_{in} = -\frac{3\varepsilon_d}{\varepsilon_m+2\varepsilon_d} E_0 r\cos(\theta)$$

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




In these expressions $\mathbf{p} = \varepsilon_0\varepsilon_d\alpha\mathbf{E}_0$ is the dipole moment associated to the spherical nanoparticle and $\alpha = 4\pi R^3 \frac{\varepsilon_m-\varepsilon_d}{\varepsilon_m+2\varepsilon_d}$ is its polarizability, **r** is the position vector (with amplitude R = $|\mathbf{r}|$), $\mathbf{E}_0$ the applied (static) electric field and $\theta$ the angle between $\mathbf{E}_0$ and **r**.

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# Localized surface plasmons

The electric field distribution is evaluated as $\mathbf{E} = -\nabla\varphi$ and its expressions inside and outside the particle are, respectively:

$$E_{in} = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0$$

$$E_{out} = E_0 + \frac{\mathbf{3n(n\cdot p) - p}}{4\pi\varepsilon_0\varepsilon_d r^3}$$

where $\mathbf{n} = \mathbf{r}/r$ is the radial unit vector. Both the inside and outside fields diverge when the particle polarizability becomes singular, i.e., when $\varepsilon_m + 2\varepsilon_d = 0$. If the relative background permittivity $\varepsilon_d$ is positive, the singularity is only possible for particles with negative relative permittivity $\varepsilon_m$. However, the presence of losses in the particle prevents the fields from diverging, resulting in a resonance at the frequency that satisfies the condition :

$$\boldsymbol{Re(\varepsilon_m) = -2\varepsilon_d}$$

The latter is sometimes referred to as Frohlich condition or **Frohlich resonance**. It is interesting to note that in the electrostatic approximation ($R \ll \lambda \rightarrow \infty$), the localized surface plasmon resonance associated with the Frohlich condition depends solely on the particle and surrounding medium permittivities. This behavior is at the basis of plasmonic sensing devices. In such sensors the presence or absence of organic/inorganic media around the particle alters the effective permittivity $\varepsilon_d$ and may be detected as a frequency shift of the plasmonic resonance. Since $|\varepsilon_m|$ gets larger when the frequency decreases (normal chromatic dispersion) an increase in the surrounding permittivity $\varepsilon_d$ results in a typical red-shift of the plasmonic resonance.

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# Localized surface plasmons

Geometrical features like particle size and shape play an important role in establishing the spectral position of the localized plasmon resonance. For simple geometries, such as ellipsoidal particles, analytical expressions of polarizability and cross sections can be retrieved in the electrostatic approximation.

If we assume $R_1$, $R_2$, and $R_3$ the ellipsoid semi-axes in the *x*,*y*, and *z* directions, and $R_1 \geq R_2 \geq R_3$, the electrostatic problem in elliptical coordinates leads to the following expression for the anisotropic polarizability:

$$\alpha_j = 4\pi R_1 R_2 R_3 \frac{\varepsilon_m - \varepsilon_d}{3\varepsilon_d + 3L_j(\varepsilon_m - \varepsilon_d)} \quad , j = 1,2,3$$

Where $L_j$ is a geometrical factor given by the integral:

$$L_j = \frac{R_1 R_2 R_3}{2} \int_0^\infty [(R_j^2 + q) f(q)]^{-1} dq$$

$$f(q) = \sqrt{(q + R_1^2)^2 + (q + R_2^2)^2 + (q + R_3^2)^2}.$$

Only two of the geometrical factors are independent since $L_1 + L_2 + L_3 = 1$.

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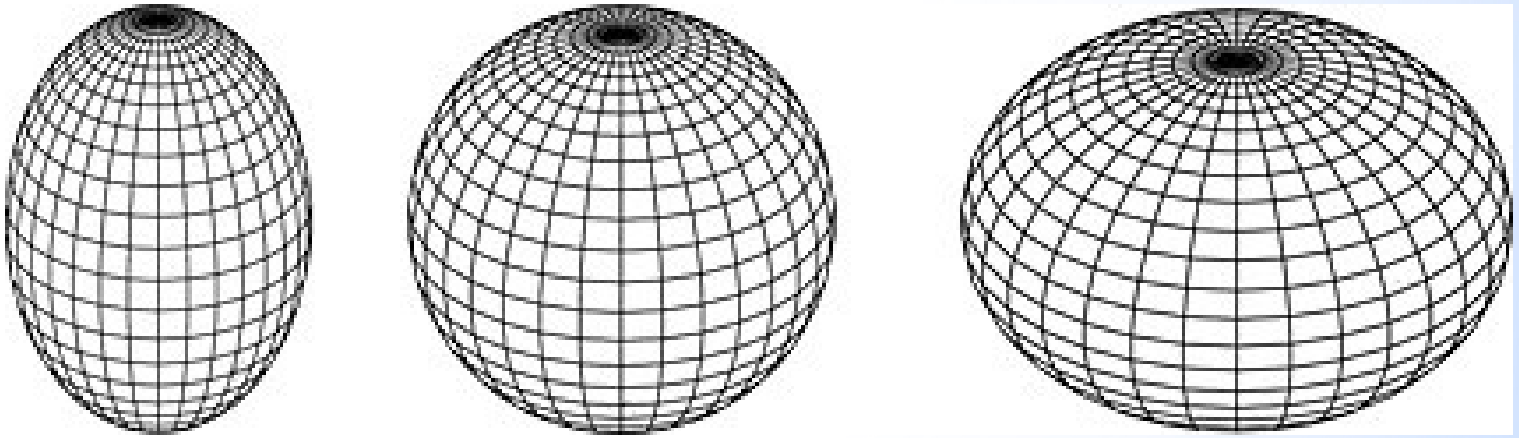
# Localized surface plasmons

Note that $L_1 = L_2 = L_3 = 1/3$ for a sphere, whereas for a generic ellipsoid $L_1 \leq L_2 \leq L_3$. Spheroids are special ellipsoids with two equal semi-axis. Cigar-shaped spheroids, known as *prolates*, have $R_2 = R_3$ and $L_2 = L_3$ , and are obtained by rotating an ellipse about its major axis. *Oblates* (pancake-shaped spheroids) have $R_1 = R_2$ and $L_1 = L_2$ and are obtained by rotating an ellipse around its minor axis.

*prolate* *spheroid* *oblate*



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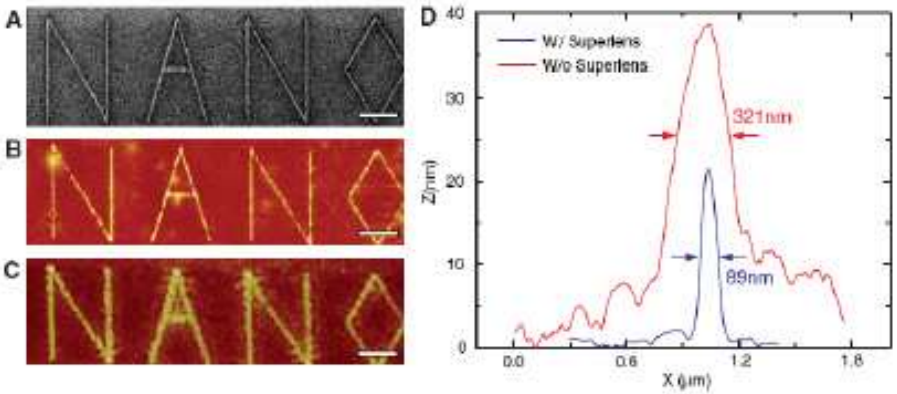
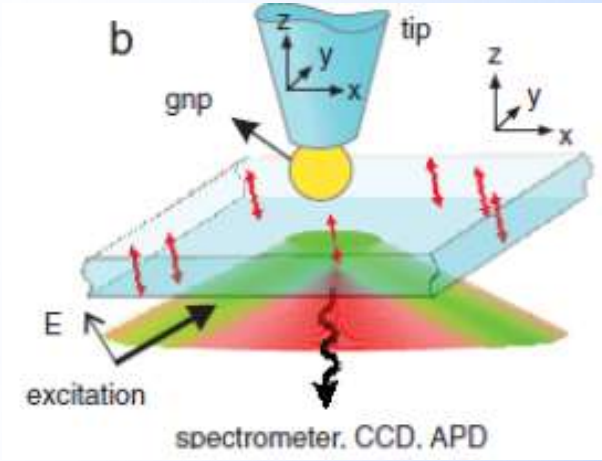
# Surface Plasmons Based devices

## Superlens



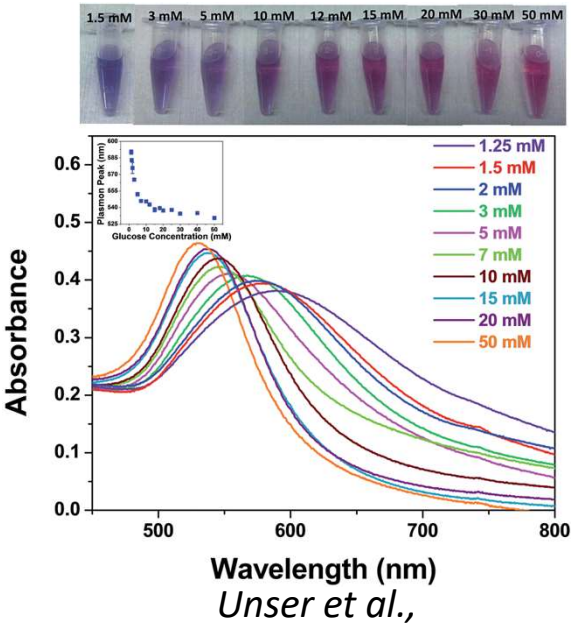

N. Fang et al., Science, **308** (2005) 534.

## Single molecule fluorescence enhancement



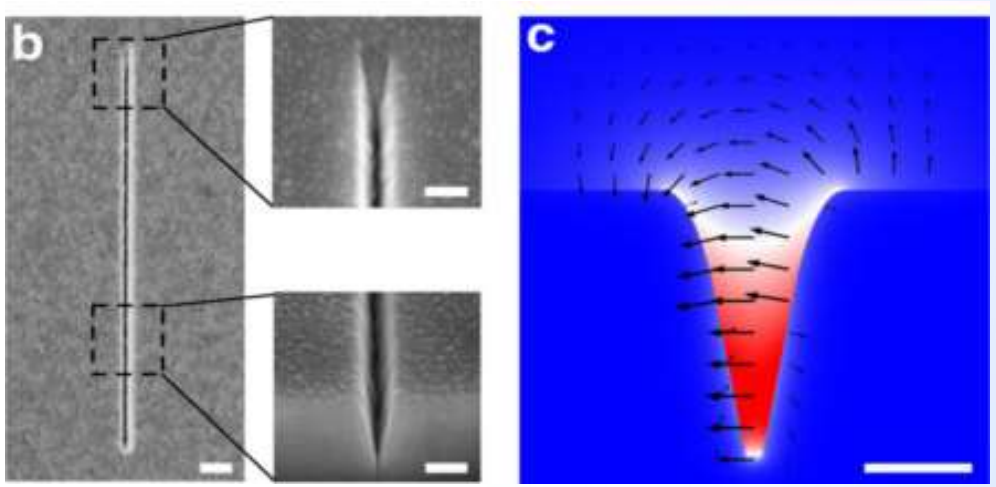

S. Kühn et al.,
*Phys. Rev. Lett.* 97, 1-4 (2006).

## Plasmonic Glucose Sensor




*Unser et al.,*
*Analyst* 140, 590-599 (2015)

## V-groove plasmonic waveguide




E. Bermúdez-Ureña et al.,
*Nature Communications* 6, 7883 (2015)

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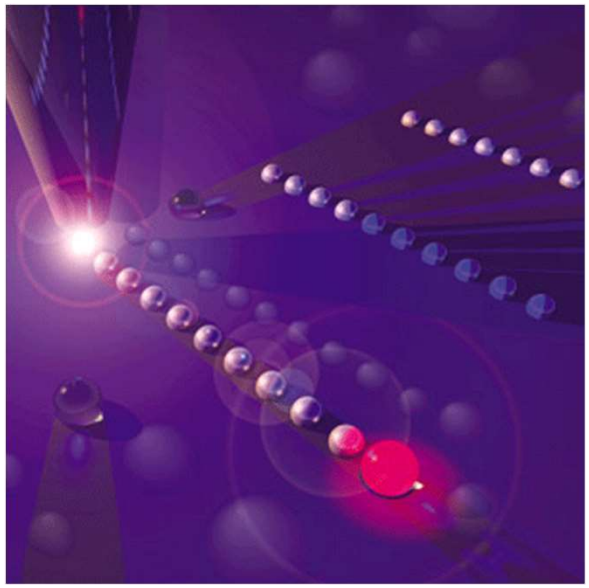
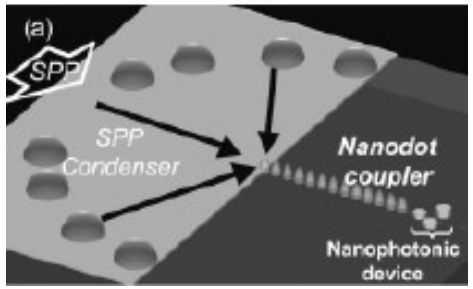
# Surface Plasmons Based devices

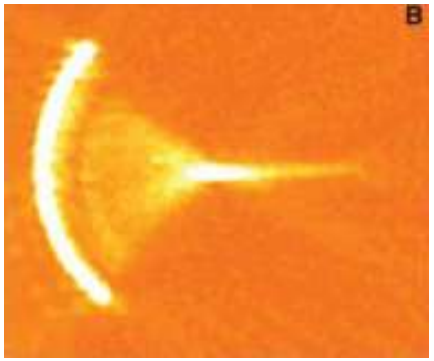
## Plasmonic nanoparticles waveguide



*S. Maier et al.*
*Nature Materials* 2, 229–232 (2003)

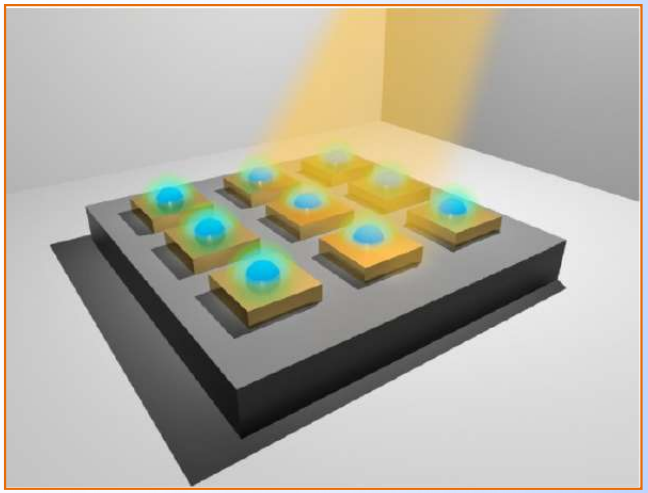
## Plasmonic coupler



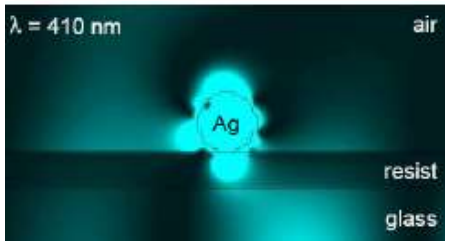

W. Nomura et al.,
Appl. Phys. Lett., 86 181108 (2005)

## Plasmonic Grating sensor



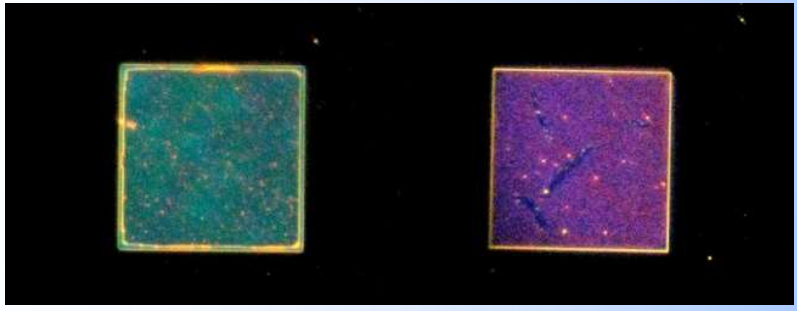
*Grande et al.*
*Opt. Express 19, 21385-21395 (2011)*

## Plasmonic printing


P. G. Kik et al.,
Proc. Of SPIE, 4810 (2002) 7.

## Plasmonic Grating sensor



*Vincenti et al.*
*Appl. Phys. Lett. 100, 201107 (2012)*

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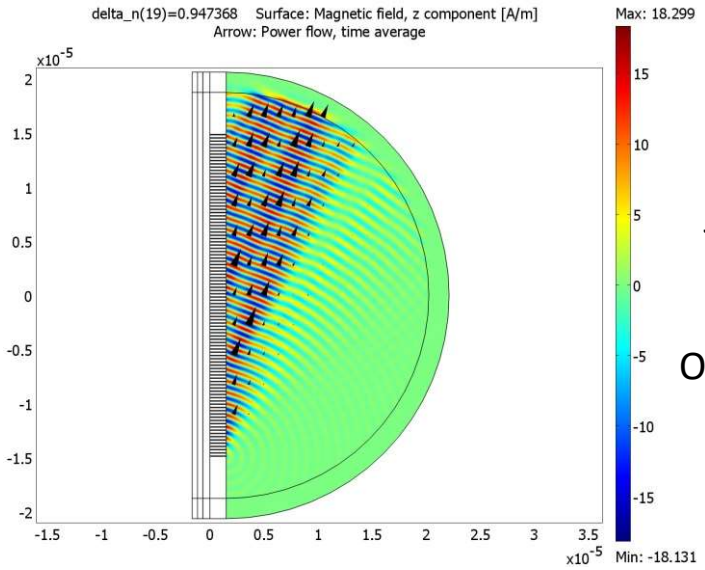
# Surface Plasmons Based devices

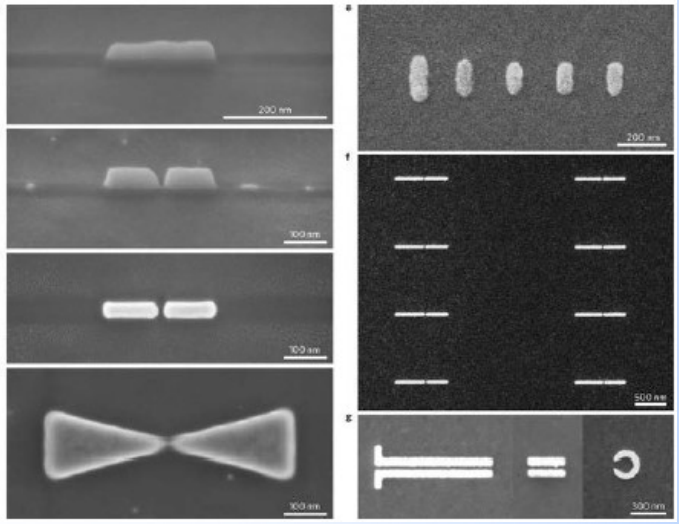
## Plasmonic Beam steering




M.A. Vincenti et al,
JOSAB 26, 301-307 (2009).

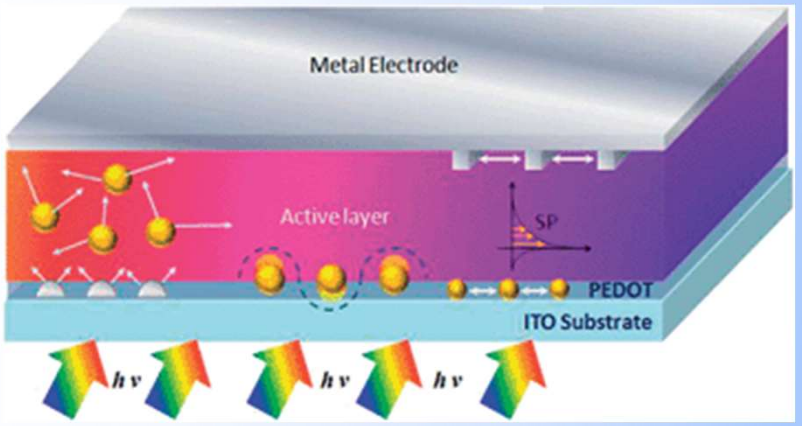
D. de Ceglia et al.,
Optics Letters 37, 271 (2012).

## Nanoantennas



*L. Novotny, Niek van Hulst,*
*Nature Photonics 5, 83–90(2011)*

## Plasmonic solar cell




*Chou et al,*
*Nanoscale* 6, 8444-8458 (2014)

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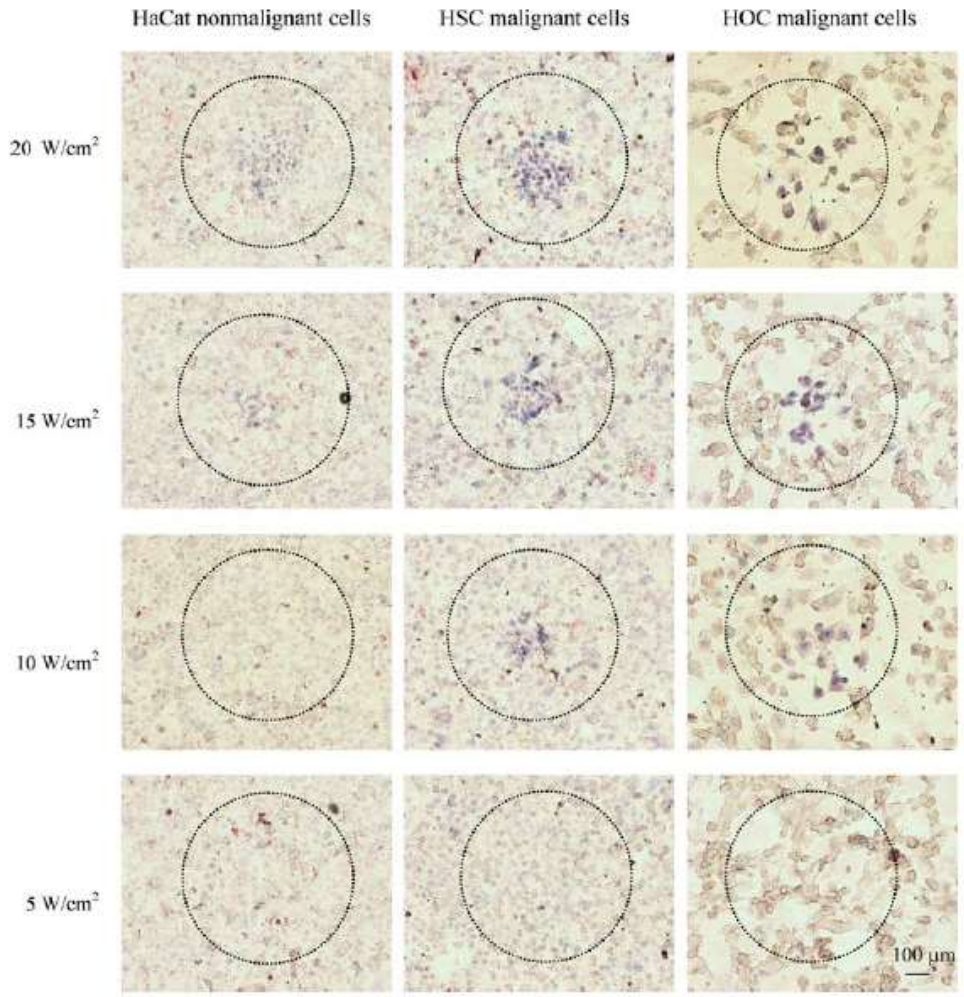
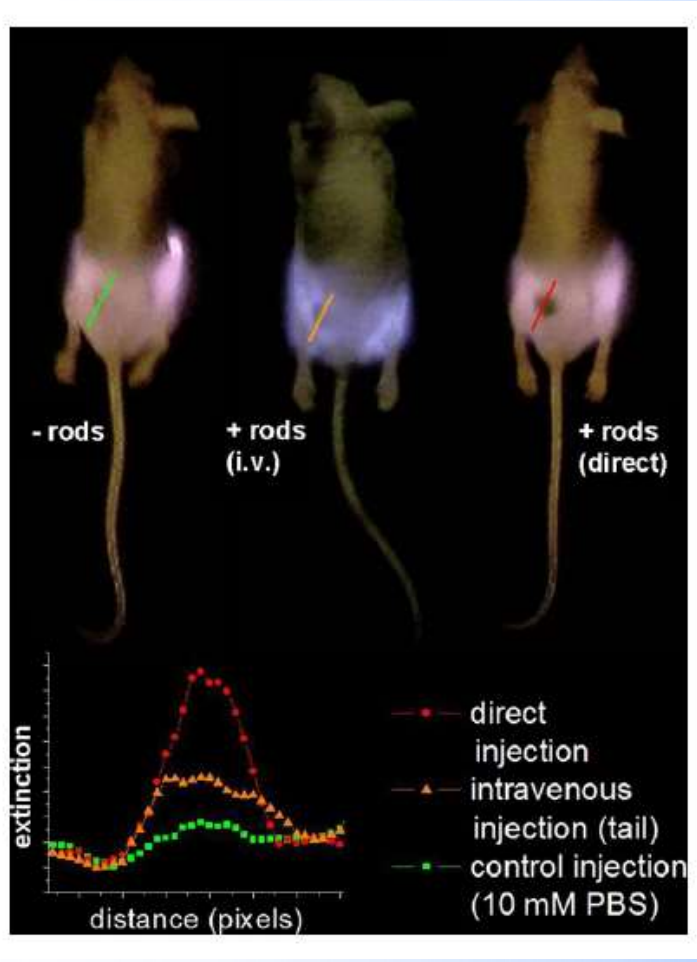
# Surface Plasmons Based devices

**Cancer therapy**

plasmonic phototermal therapy may make some cancer cells more sensitive to radiation or harm other cancer cells that radiation cannot damage




*Huang et al., Lasers Med Sci (2008) 23:217–228*




*Dickerson et al, Cancer Letters 269 (2008) 57–66*

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# Surface Plasmons Based devices

**Drug delivery**

Metal nanoshells and nanoparticles can be “loaded” with drugs that can be selectively released under specific light excitation

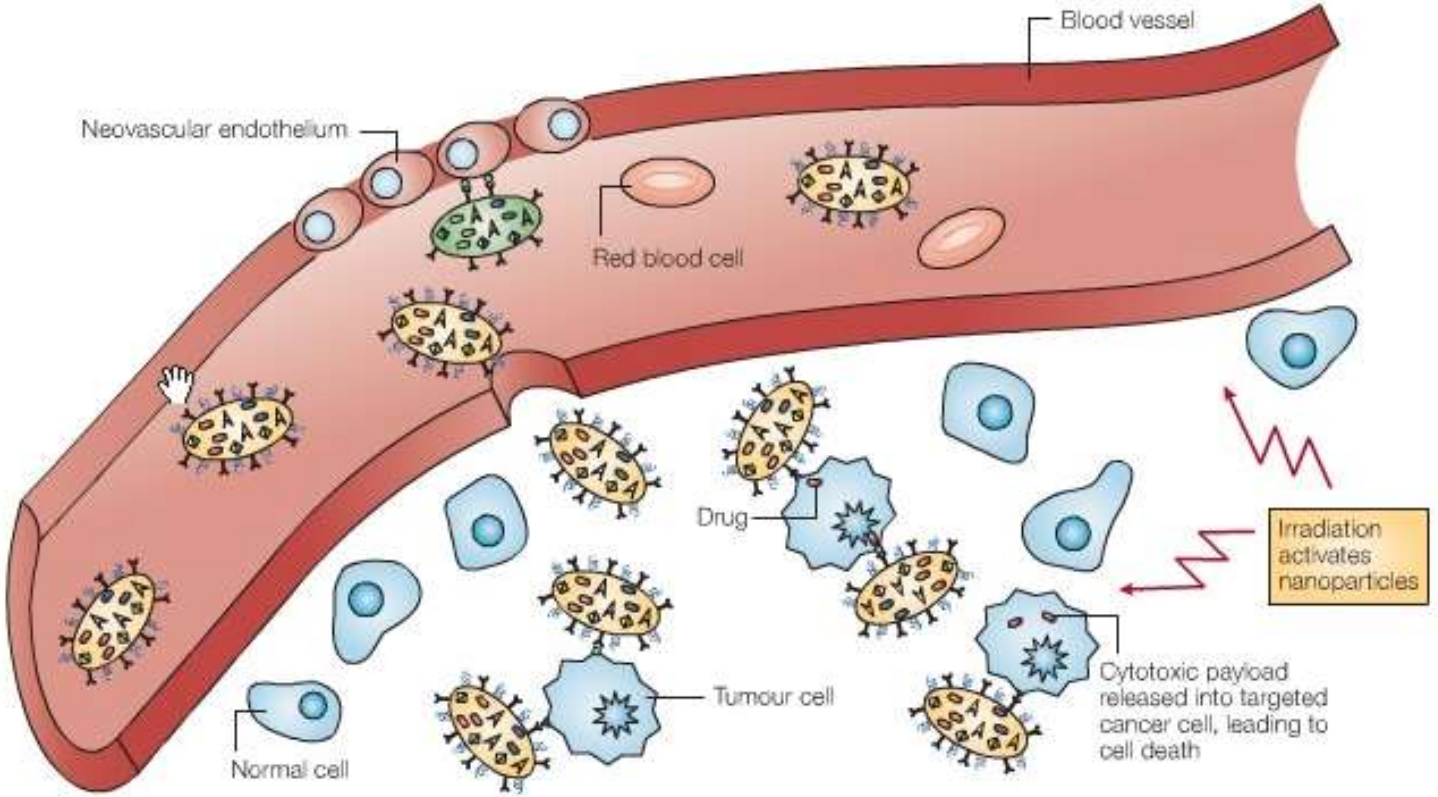


Figure 4 | **Multicomponent targeting strategies.** Nanoparticles extravasate into the tumour stroma through the fenestrations of the angiogenic vasculature, demonstrating targeting by enhanced permeation and retention. The particles carry multiple antibodies, which further target them to epitopes on cancer cells, and direct antitumour action. Nanoparticles are activated and release their cytotoxic action when irradiated by external energy. Not shown: nanoparticles might preferentially adhere to cancer neovasculature and cause it to collapse, providing anti-angiogenic therapy. The red blood cells are not shown to scale; the volume occupied by a red blood cell would suffice to host 1–10 million nanoparticles of 10 nm diameter.

*Maurizio Ferrari, Nature Reviews Cancer 5, 161 (2005)*