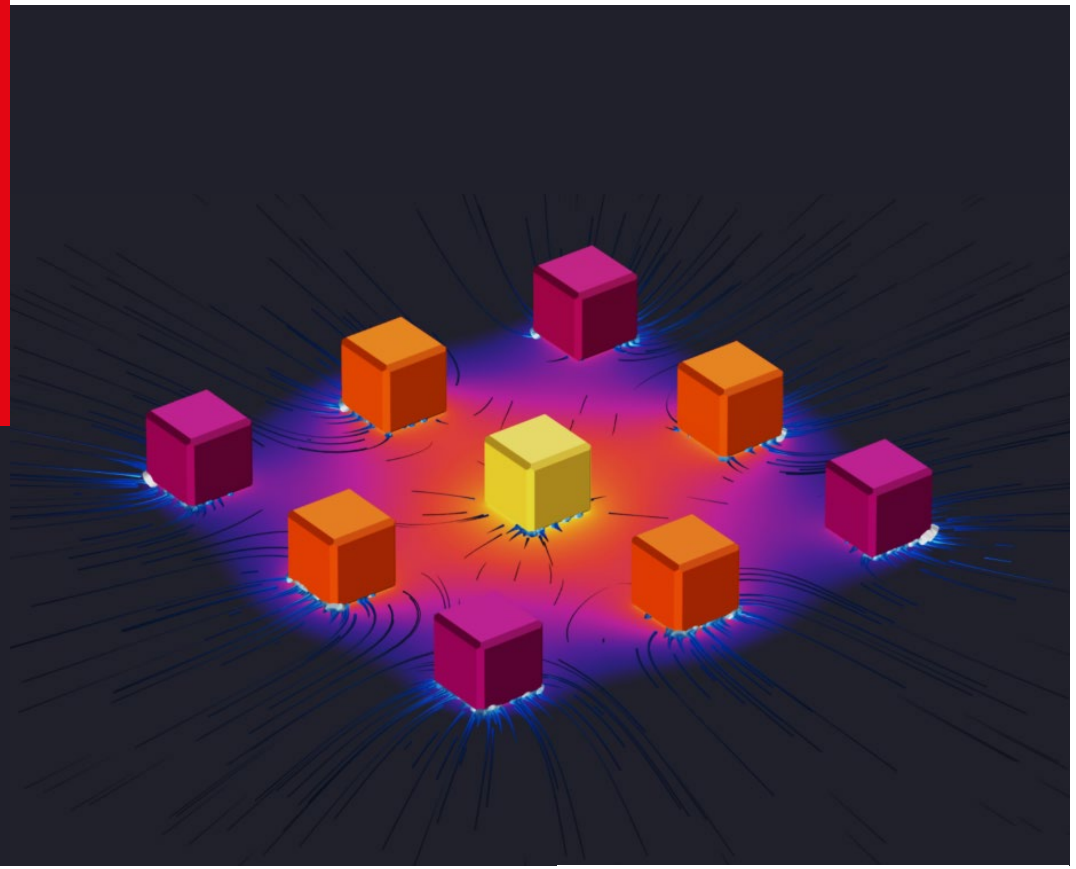
Nanoscale Heat Transfer (and Energy Conversion) ME469

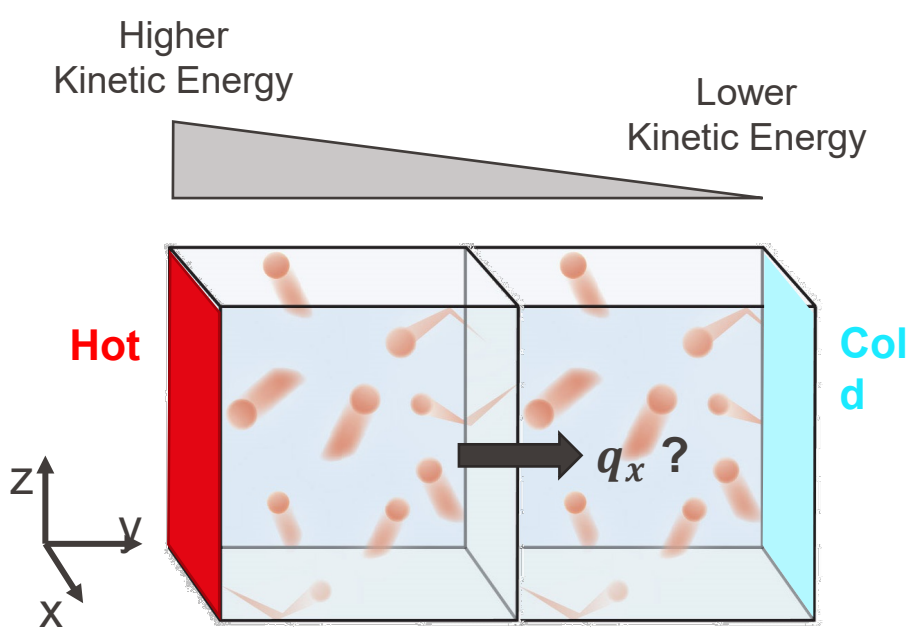
Instructor: Giulia Tagliabue



École polytechnique fédérale de Lausanne

Spring Semester

Energy Transport – Boltzmann Equation



Diffuse Transport
the phase of the carriers is unimportant

1. The **transient process** must be **slow compared to the relaxation time** of the carriers.
2. The temperature variation within one mean free path must be small compared to the absolute temperature
3. The **characteristic length** must be much **larger than the mean free path of the carrier**.

$$\vec{v} \cdot \nabla_r f + \frac{\vec{F}}{m} \cdot \nabla_v f = -\frac{f - f_0}{\tau}$$

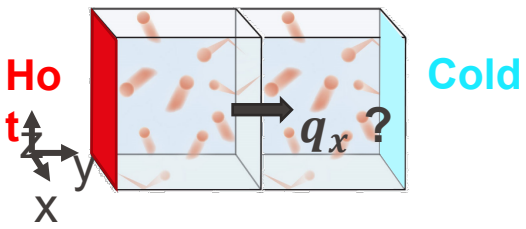
Phonons – Fourier Law and thermal conductivity

Molecules – Newton's Stress Law

Electrons – Ohm's Law and Thermoelectric Effects

Going Beyond with Nanoengineering

$L \ll \Lambda$



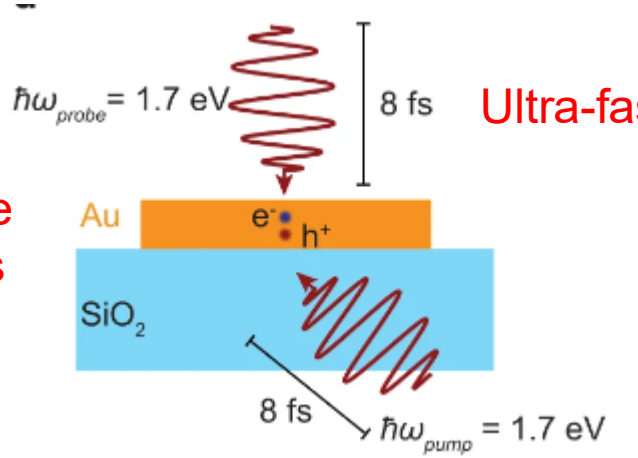
Diffuse Transport
the phase of the carriers is unimportant

Ballistic Transport
the phase of the carriers is important, interference effects are present (coherence)

1. The **transient process** is fast **compared to the relaxation time** of the carriers.

2. The **characteristic length is smaller than the mean free path of the carrier**.

Nanoscale Structures



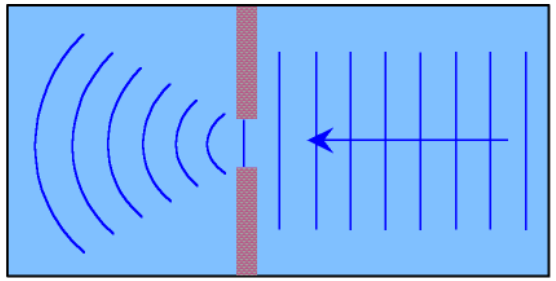
Ultra-fast Lasers

Nanophotonics – Manipulating Light at the Nanoscale

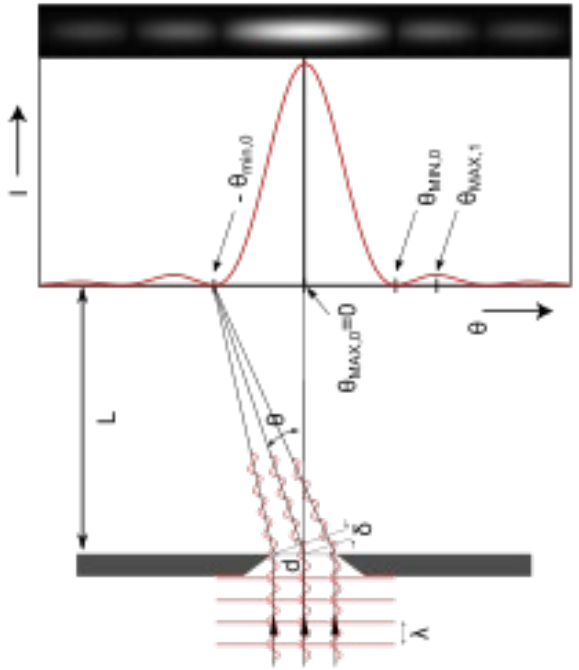
- **Why nanophotonics**
- **Optical resonances**
  - **Surface Plasmons and Mie resonators**
  - **From Nanoresonators to Metamaterials**
- Plasmonic catalysis and semiconducting metasurfaces
  - Plasmonic hot carrier dynamics & photochemistry
  - Interplay of absorption and charge transport – solar redox flow batteries
- Thermoplasmonics and Thermonanophotonics
  - Thermo-plasmonics for thermocatalysis
  - Thermo-plasmonics for solar evaporation/desalination
  - Thermonanophotonics for reconfigurable optical components
- Absorption/Emission Engineering
  - Near field heat transfer
  - Radiative cooling

Nanophotonics – Beyond the Diffraction Limit

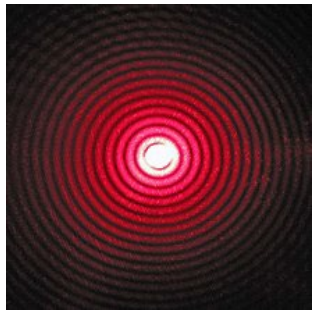
- Why we cannot see nanometer scale objects with an optical microscope?
- Because of diffraction of the electromagnetic waves!

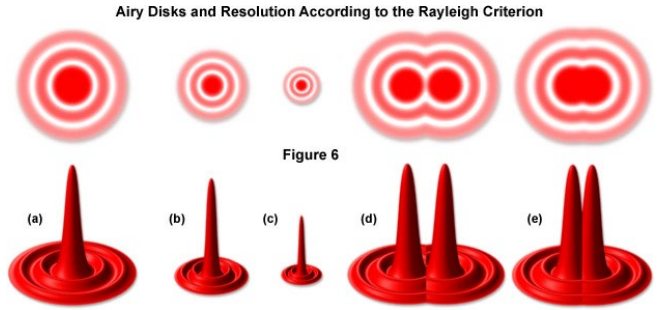


https://www.gcsescience.com/pwav44.htm



https://en.wikipedia.org/wiki/Diffraction

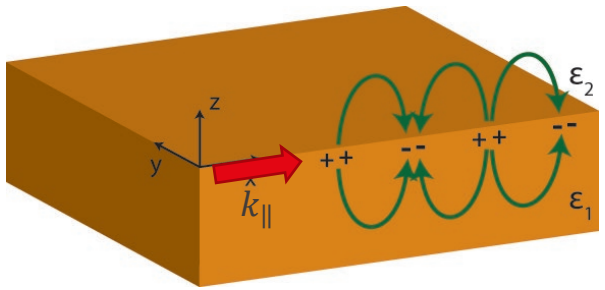




➡ For the same reason we cannot focus light to dimensions smaller than ~$\lambda/2$ (i.e. for green light 532nm -> ~250 nm)

Nanophotonic Engineering – Surface Polaritons and Optical Resonators

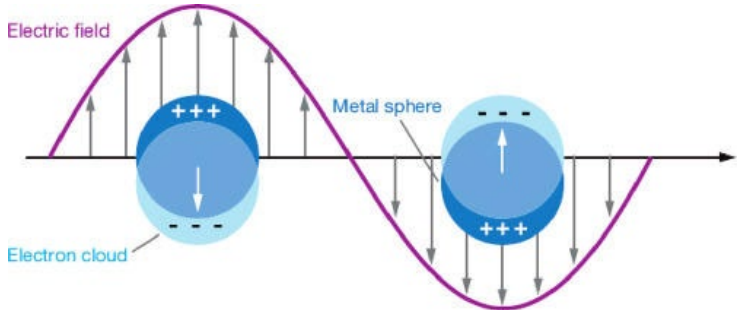
Surface Polaritons (SPs)



Quasiparticle originates from the strong-coupling of a photon with electrons (metal) or optical phonons (dielectric). The associated propagating wave is confined to an interface.

- **Surface plasmon polariton (SPPs)**
- **Surface phonon polariton (SPhPs)**

Resonators (Nanoantennas)



An incident electromagnetic wave induces resonant responses in finite nanostructures. Metallic and dielectric resonators exhibit different types of modes that are called, respectively:

- **Localized surface plasmons (LSP)**
- **Mie resonances**

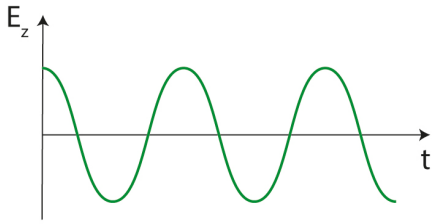
Evanescent Waves and SPPs

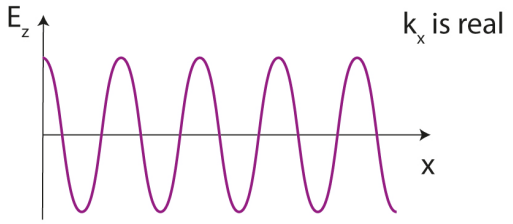
$$E_z = E_{z0} e^{i(k_x x - \omega t)}$$

$$H_y = -\frac{1}{c\mu} E_{z0} e^{i(k_x x - \omega t)}$$

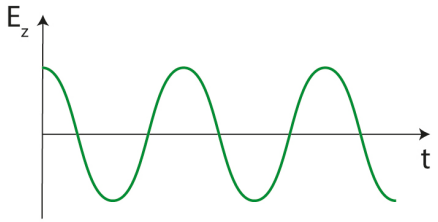
$$\langle \mathbf{S} \rangle = \frac{1}{2} \mathrm{Re}\{\mathbf{E} \times \mathbf{H}^*\}$$

Propagating wave

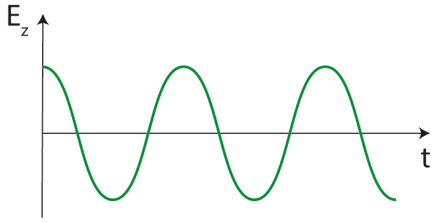




Decaying wave (absorption)



Evanescent wave

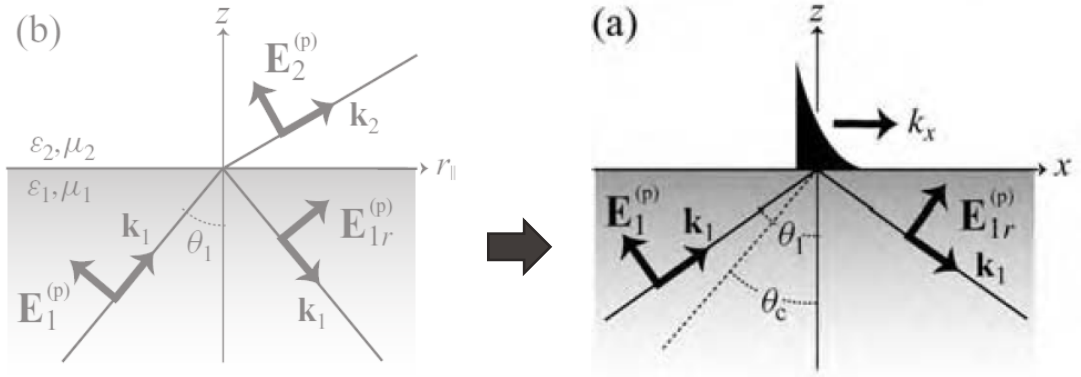


$$\langle S_x \rangle = \frac{1}{2} Re\left(i \frac{|k_x|}{\mu\omega} E_{z0}^2 e^{-2|k_x|x} \right) = 0$$

No energy is transferred by an evanescent wave along the evanescent direction !!

Evanescent Waves and SPs

We have encountered evanescent waves when we discussed total internal reflection. If $n_1 > n_2$ and $\theta > \theta_c$ we have an evanescent wave in medium 2.



For the evanescent wave we observe that:

$$\langle S \rangle_z = \frac{1}{2}\mathrm{Re}\left(E_x H_y^* - E_y H_x^*\right) = 0$$

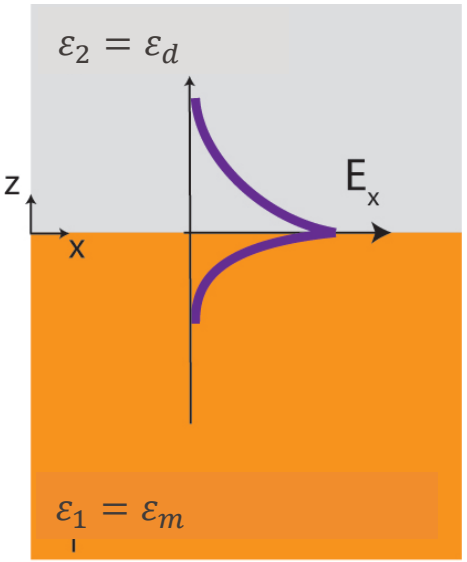
$$\langle \mathbf{S} \rangle_x = \frac{1}{2}\sqrt{\frac{\varepsilon_2 \mu_2}{\varepsilon_1 \mu_1}} \sin\theta_1 \left(\left|t^s\right|^2 \left|\mathbf{E}_1^{(s)}\right|^2 + \left|t^p\right|^2 \left|\mathbf{E}_1^{(p)}\right|^2 \right) \mathrm{e}^{-2\gamma z} \neq 0$$

➡ Although no energy is transported INTO medium 2, there is a net energy transport ALONG the interface

In the medium 1 the reflected wave is propagating, i.e. all the power is carried away from the interface.

➡ Can we completely “trap” energy at the interface ?
In other words, can we have a wave that is exponentially decaying on BOTH sides of the interface?

Surface Polaritons (SPs)



Goal: find the condition for the existence of a wave that propagates along an interface and decays exponentially away from it on BOTH sides of the interface

→ energy is transported SOLELY along the interface.

In regions of homogeneous dielectric properties, from Maxwell equations:

$\nabla^2\mathbf{E} + k_0^2\varepsilon\mathbf{E} = 0,$ $k_0 = \frac{\omega}{c}$ is the wave vector of the propagating wave in vacuum

We consider the case of two uniform materials that have an interface at $z = 0$. As the system is uniform along (x,y) we have:

$\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i\beta x}$ $\beta = k_x$ is called the *propagation constant*

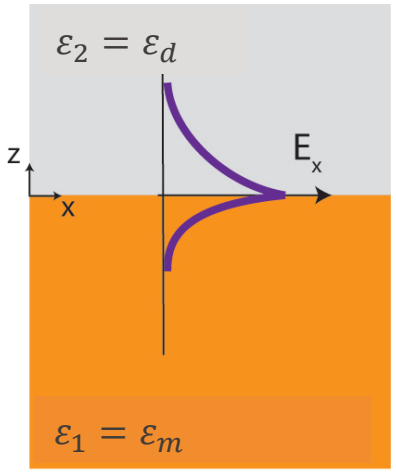
For time-harmonic fields, two solutions are possible:

$$TM: \begin{cases} \frac{\partial^2 H_y}{\partial z^2} + (k_0^2\epsilon - \beta^2)H_y = 0 \\ E_x = -i\frac{1}{\omega\epsilon_0\epsilon}\frac{\partial H_y}{\partial z} \\ E_z = -\frac{\beta}{\omega\epsilon_0\epsilon}H_y \end{cases} \qquad TE: \begin{cases} \frac{\partial^2 E_y}{\partial z^2} + (k_0^2\epsilon - \beta^2)E_y = 0 \\ H_x = i\frac{1}{\omega\mu_0}\frac{\partial E_y}{\partial z} \\ H_z = \frac{\beta}{\omega\mu_0}E_y \end{cases}$$

Surface Polaritons (SPs)

Note: we are looking for a **wave that decays exponentially on BOTH sides of the interface**

We consider first the TM-wave solution, and impose this additional constraint:



k_{z2} is imaginary $\rightarrow ik_{z2} = k_d$

k_x is complex $\rightarrow$ **β**

k_{z1} is imaginary $\rightarrow ik_{z2} = k_m$

$$z > 0 \begin{cases} H_y(z) = A_d e^{i\beta x} e^{-k_d z} \\ E_x(z) = iA_d \frac{1}{\omega\epsilon_0\epsilon_d} k_d e^{i\beta x} e^{-k_d z} \\ E_z(z) = -A_d \frac{\beta}{\omega\epsilon_0\epsilon_d} e^{i\beta x} e^{-k_d z} \end{cases}$$

$$z < 0 \begin{cases} H_y(z) = A_m e^{i\beta x} e^{k_m z} \\ E_x(z) = -iA_m \frac{1}{\omega\epsilon_0\epsilon_m(\omega)} k_m e^{i\beta x} e^{k_m z} \\ E_z(z) = -A_m \frac{\beta}{\omega\epsilon_0\epsilon_m(\omega)} e^{i\beta x} e^{k_m z} \end{cases}$$

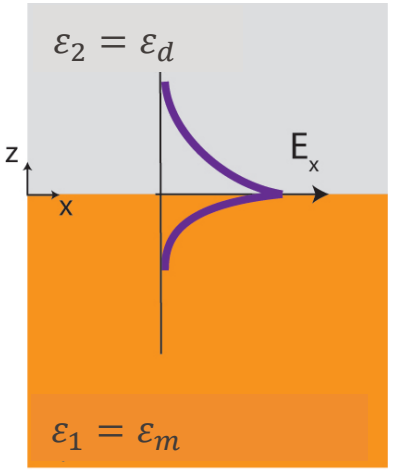
Exponential decay!

$$\Rightarrow \begin{cases} A_d = A_m \\ \frac{k_d}{k_m} = -\frac{\epsilon_d}{\epsilon_m(\omega)} \end{cases}$$

A wave that propagates only along the interface, i.e. an SP, can exist only if the sign of the permittivity of the two materials is opposite.
→ An SPP exists at a metal ($\boldsymbol{\varepsilon_m < 0}$) dielectric ($\boldsymbol{\varepsilon_d > 0}$) interface
→ An SPhP exists at a polar semiconductor ($\boldsymbol{\varepsilon_m < 0}$) dielectric ($\boldsymbol{\varepsilon_d > 0}$) interface close to a phonon resonance

Starting from the TE-wave solution results in a condition that cannot be satisfied.

Surface Polaritons (SPs) – Dispersion relation



$$\begin{aligned} k_m^2 &= \beta^2 - k_0^2 \epsilon_m(\omega) \\ k_d^2 &= \beta^2 - k_0^2 \epsilon_d \end{aligned} \quad \Rightarrow \quad \beta = \sqrt{\frac{\epsilon_m(\omega)\epsilon_d}{\epsilon_m(\omega) + \epsilon_d}}$$

To find the dispersion relation we need to know the dielectric function of the medium ***m***.

Metals

To a first approximation, the dielectric function can be described by the Drude-model for a metal:

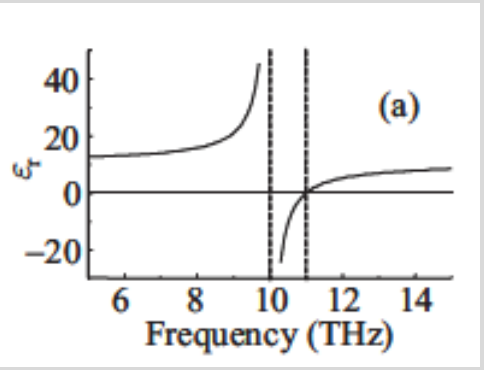
$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}.$$

where:

$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}$ is the *plasma frequency* of the free electron gas.

$\gamma = 1/\tau$ Collision frequency

Polar Semiconductors

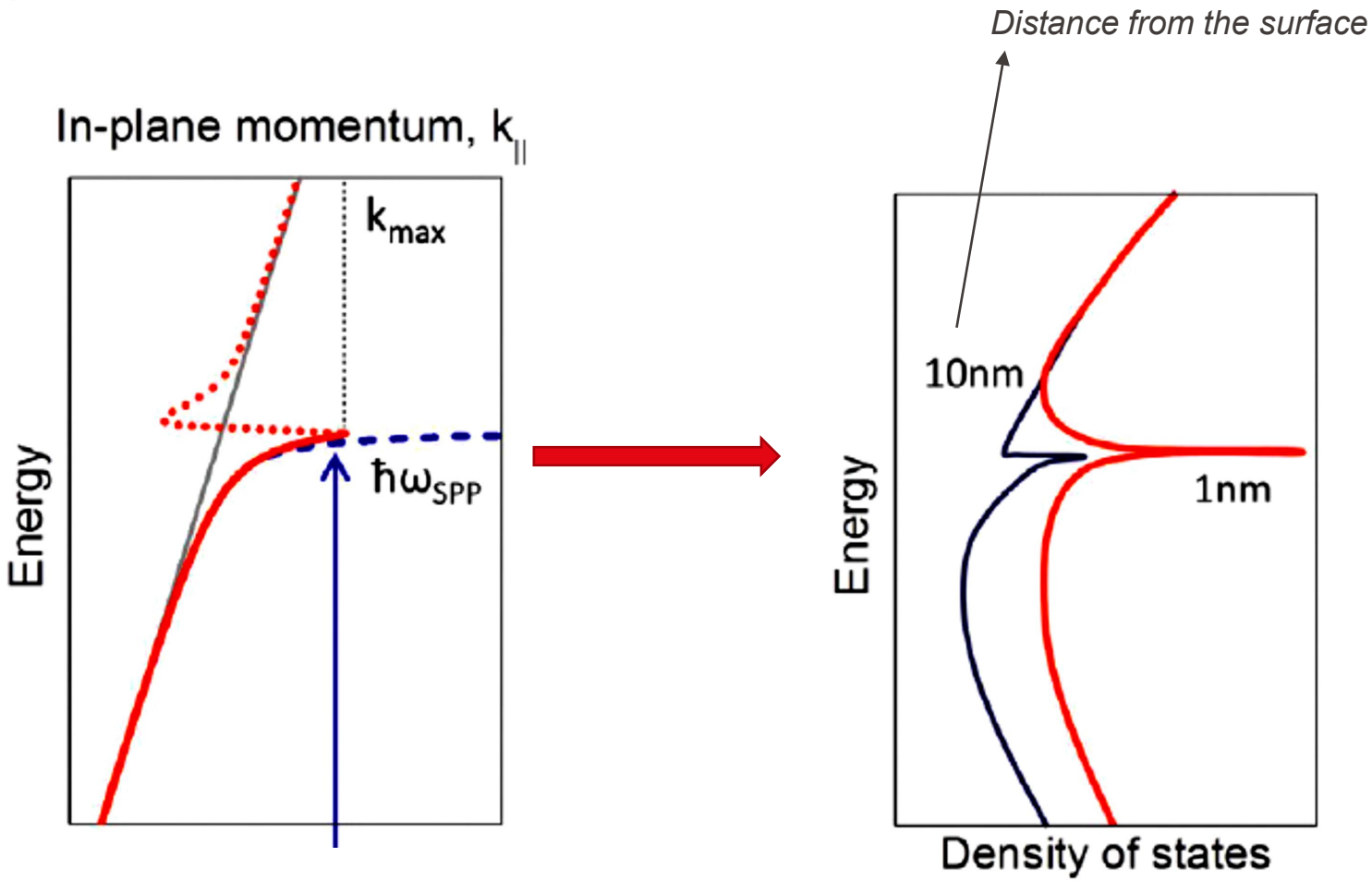


Fox, Mark.; Optical Properties of Solids

Surface Plasmon Polaritons (SPPs)

$$\beta = \sqrt{\frac{\epsilon_m(\omega)\epsilon_d}{\epsilon_m(\omega)+\epsilon_d}} \qquad \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}.$$

- An SPP cannot be excited by a planar wave impinging onto the surface due to momentum matching conditions!!
- An SPP is very sensitive to the surrounding environment (ε_d)



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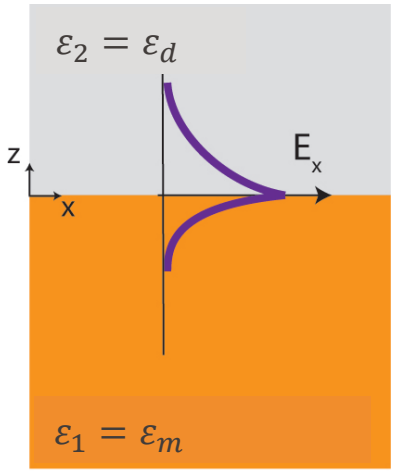

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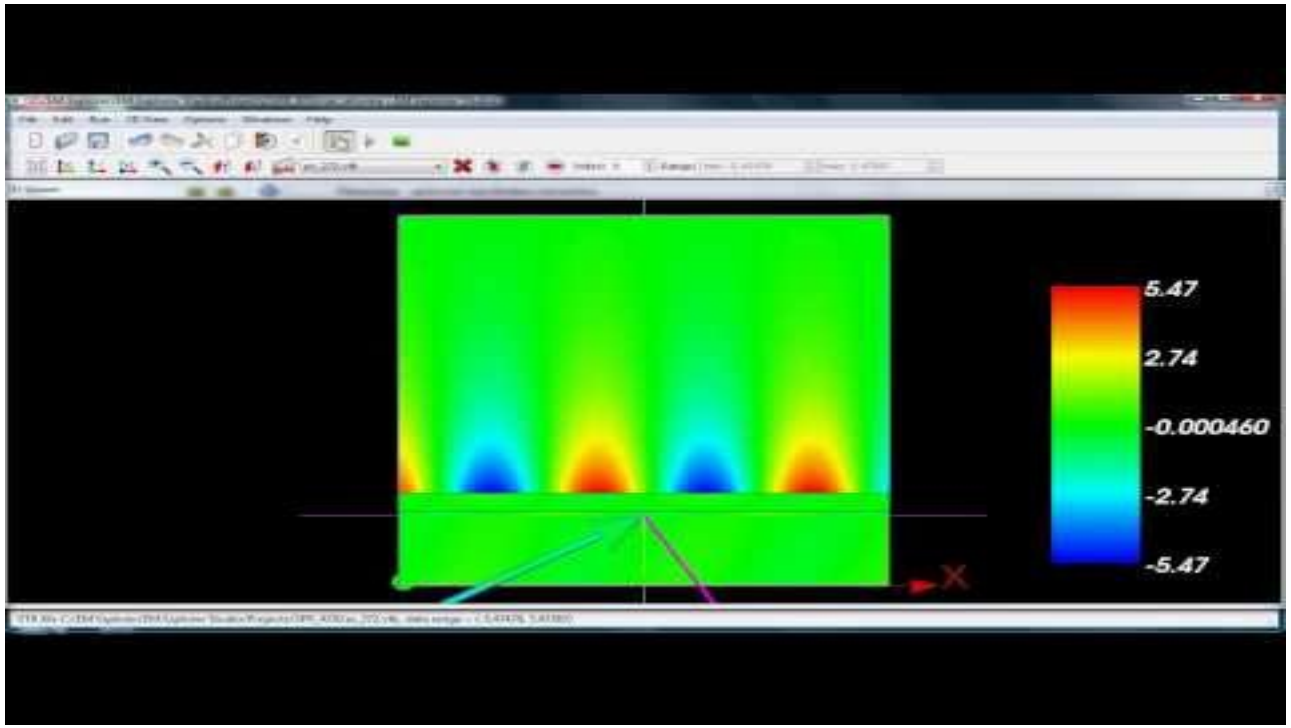
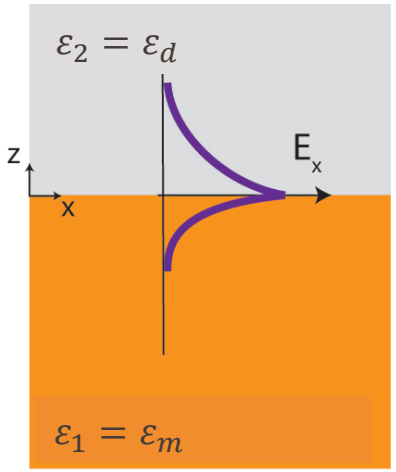
k_x is complex $\rightarrow$ **β**

k_{z1} is imaginary $\rightarrow ik_{z2} = k_m$



Surface Plasmon Polaritons (SPPs)



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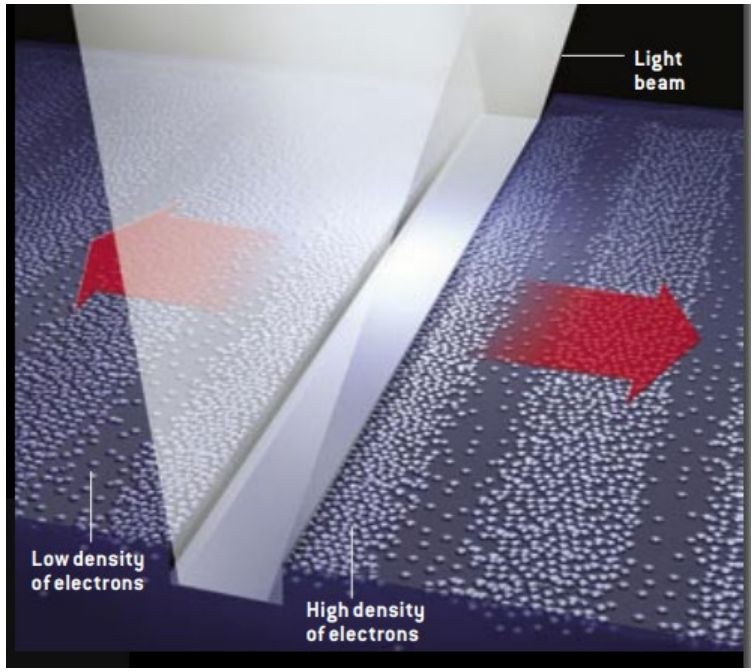
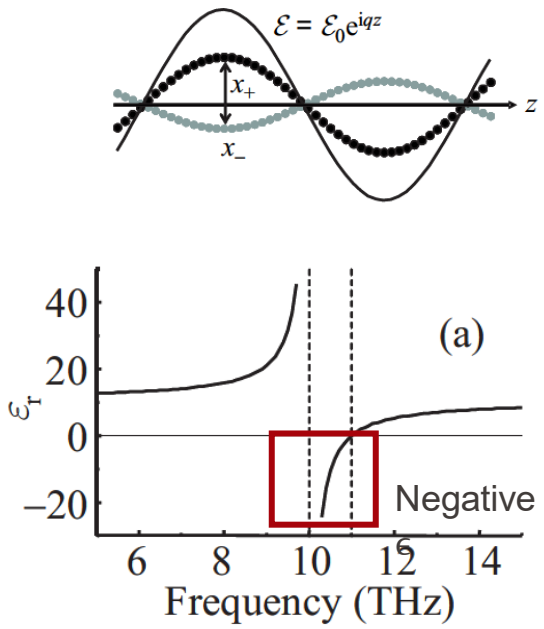


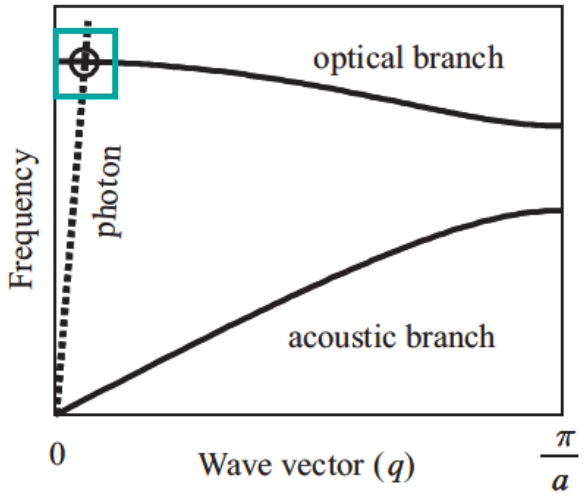
Atwater, The promise of plasmonics, Scientific American 2007

Plasmons are quanta of plasma oscillations. For a solid, these correspond to electron density oscillations.

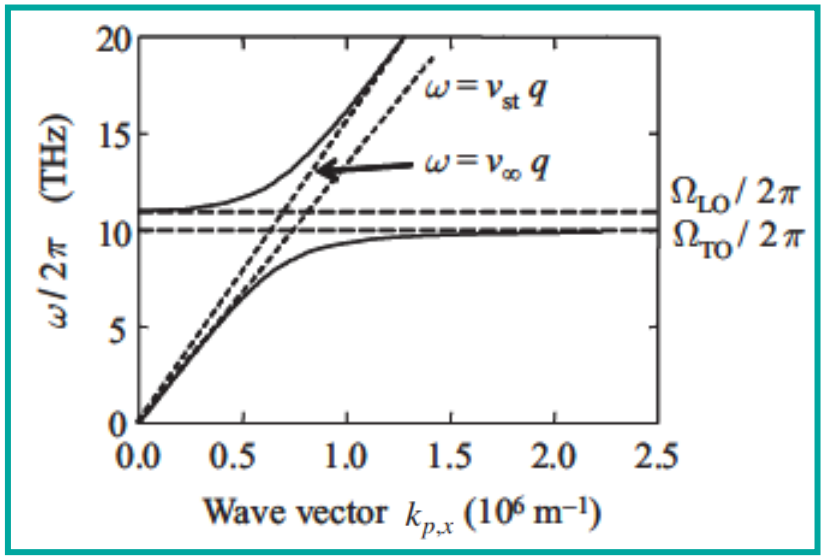
Surface plasmons are coherent oscillations of electron density at the interface between a metal and a dielectric.

Surface Phonon Polaritons (SPhPs)





$$k_{p,x} = k'_{p,x} + ik''_{p,x} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_\parallel \varepsilon_\perp - \varepsilon_\perp}{\varepsilon_\parallel \varepsilon_\perp - 1}}$$



- Because of the momentum matching between a photon and an optical phonon, in principle excitation of a transverse optical phonon by a photon is possible.
- In reality, close to the intersection point, a **strong-coupling effect** occurs that splits the resonance into two new modes, altering the dispersion curve (think of two coupled masses that oscillate)

➢ A phonon polariton mode gets excited and propagates along the interface

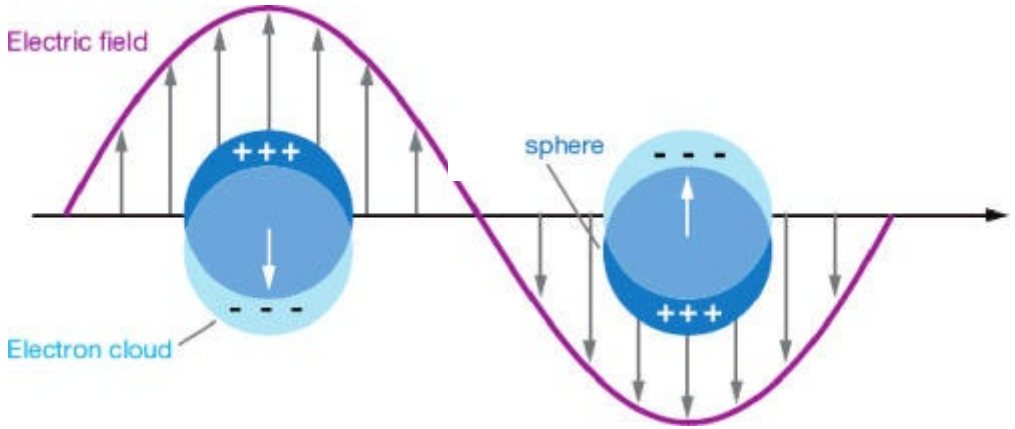
➢ The modified dispersion curve increases the DOS

Fox, Mark.; Optical Properties of Solids

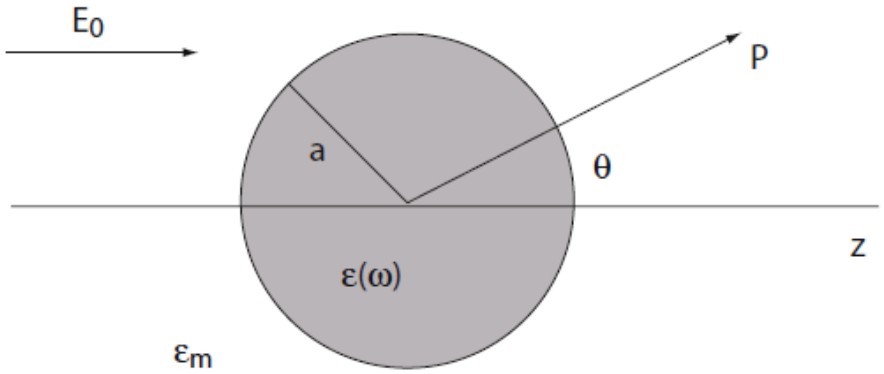
Resonant Modes of a Nanosphere

While SPs have a continuous dispersion relations, finite nanostructures support discrete resonance modes.

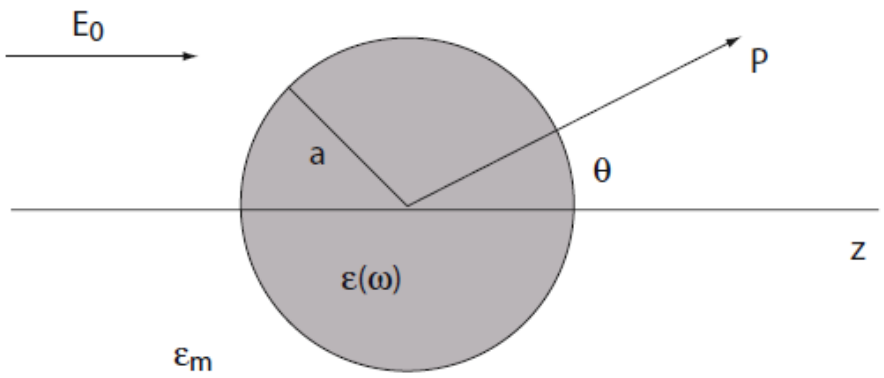
What are the resonance modes of a metallic or dielectric nanosphere, much smaller than the wavelength of light ($d \ll \lambda$) ?



electrostatic approximation



Localized Surface Plasmons (LSP)



$$\mathbf{E} = E_0\hat{\mathbf{z}} \qquad \nabla^2\Phi = 0 \Rightarrow \mathbf{E} = -\nabla\Phi$$

$$\Phi(r,\theta) = \sum_{l=0}^{\infty}\left[A_l r^l + B_l r^{-(l+1)}\right] P_l(\cos\theta)$$

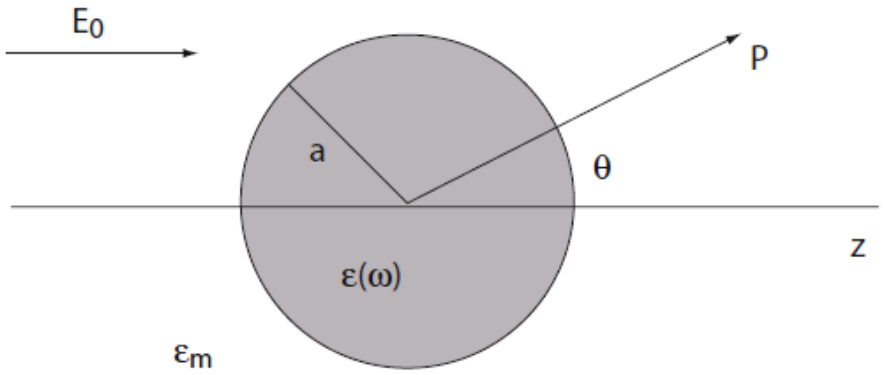
where $P_l(\cos\theta)$ are the Legendre Polynomials of order l, and θ the angle between the position vector $\mathbf{r}$ at point P and the z-axis

The field must remain finite everywhere. In addition there are three boundary conditions:
(i) $r \to \infty$ then $\Phi_{out} \to -E_0 z = -E_0 r\cos\theta$
(ii) tangential components of the electric field are continuous at the surface of the sphere
(iii) normal component of the displacement field are continuous at surface of the sphere.

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

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

Localized Surface Plasmons (LSP)



We re-write the potential outside as:

Dipole mode

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

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

We then define: $\mathbf{p} = \varepsilon_0\varepsilon_m\alpha\mathbf{E}_0$ $\quad \alpha = 4\pi a^3 \dfrac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}$ polarizability

We then calculate:

$$\mathbf{E}_{\text{in}} = \frac{3\varepsilon_m}{\varepsilon+2\varepsilon_m}\mathbf{E}_0$$

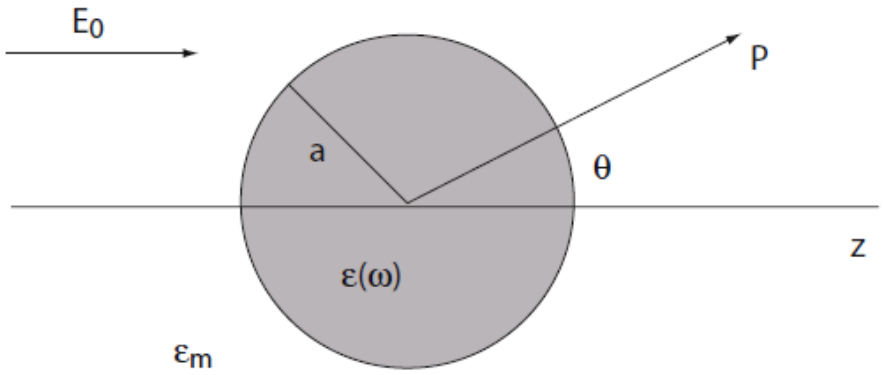
$$\mathbf{E}_{\text{out}} = \mathbf{E}_0 + \frac{3\mathbf{n}(\mathbf{n}\cdot\mathbf{p})-\mathbf{p}}{4\pi\varepsilon_0\varepsilon_m}\frac{1}{r^3}.$$

When $\text{Re}[\varepsilon(\omega)] = -2\varepsilon_m$

The polarizability exhibits a resonance and the field is greatly enhanced.
The resonance frequency is very sensitive to the environment!

Dipolar surface

Localized Surface Plasmons (LSP)



For an oscillating electric field, the dipole response is:

$$\mathbf{H} = \frac{ck^2}{4\pi}(\mathbf{n}\times\mathbf{p})\frac{e^{ikr}}{r}\left(1-\frac{1}{ikr}\right)$$

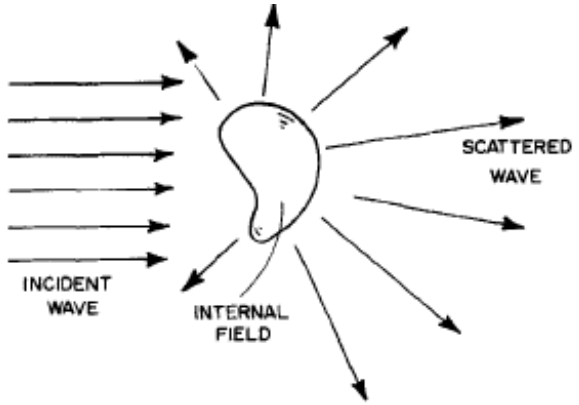
$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0\varepsilon_m}\left\{k^2(\mathbf{n}\times\mathbf{p})\times\mathbf{n}\frac{e^{ikr}}{r}+\left[3\mathbf{n}(\mathbf{n}\cdot\mathbf{p})-\mathbf{p}\right]\left(\frac{1}{r^3}-\frac{ik}{r^2}\right)e^{ikr}\right\}$$

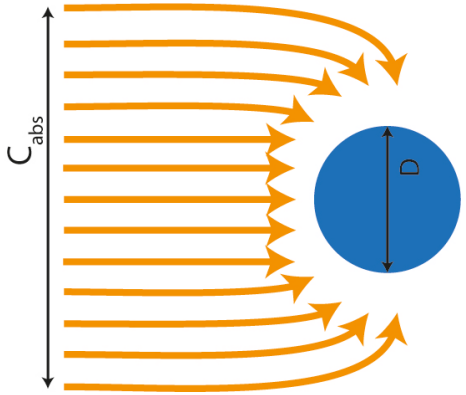
where $\mathbf{p}(t) = \varepsilon_0\varepsilon_m\alpha\mathbf{E}_0e^{-i\omega t}$

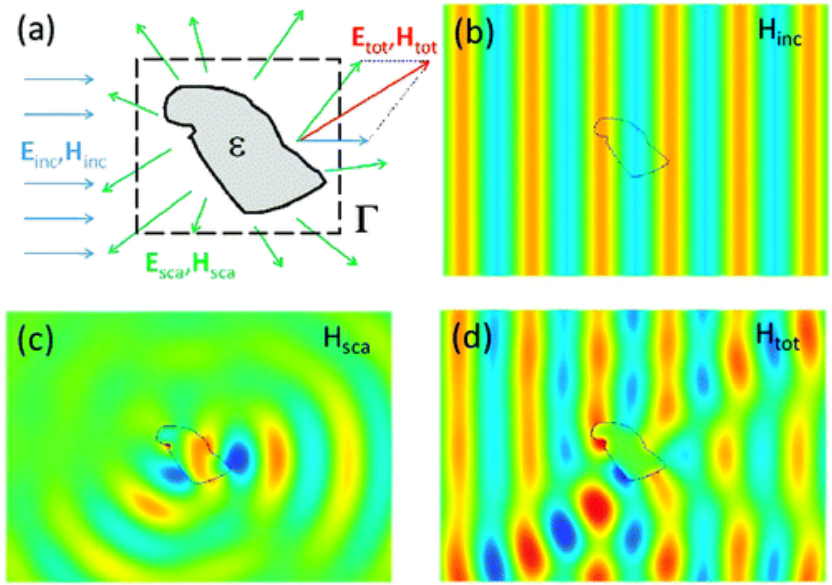
Even for an oscillating electric field the static polarizability plays a major role in the response of a nanosphere much smaller than the wavelength of light.

Localized Surface Plasmons (LSP)

Extinction = Scattering + Absorption







Chem. Rev. 2011, 111, 6, 3888–3912

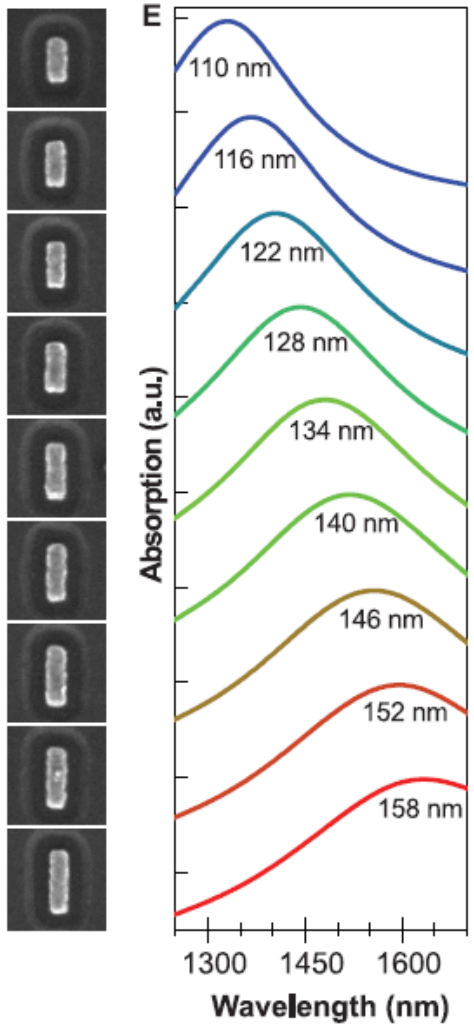
$$C_{sca} = \frac{k^4}{6\pi}|\alpha|^2 = \frac{8\pi}{3}k^4 a^6 \left|\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\right|^2$$

$$C_{abs} = k\,\mathrm{Im}[\alpha] = 4\pi k a^3 \mathrm{Im}\left[\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\right]$$

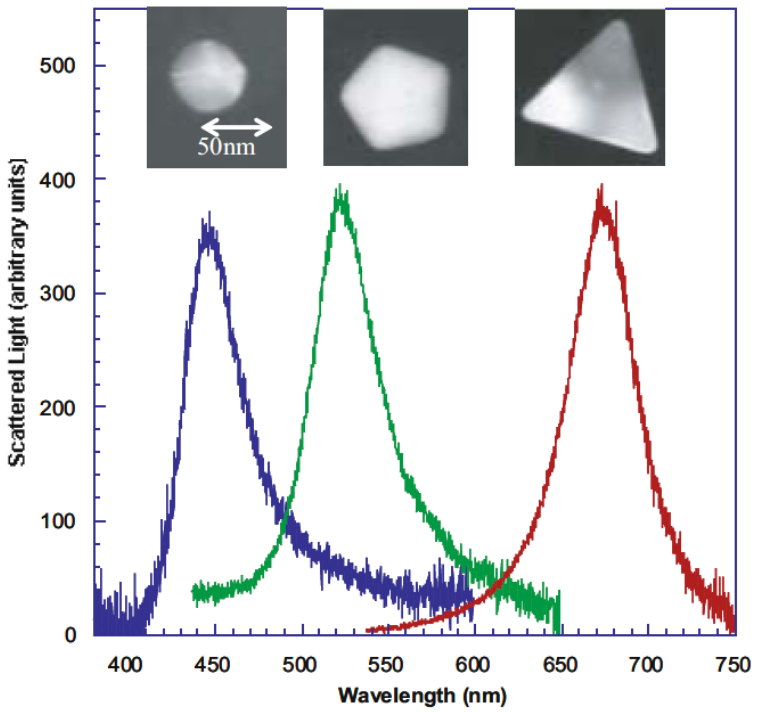
$$C_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2} V \frac{\varepsilon_2}{[\varepsilon_1 + 2\varepsilon_m]^2 + \varepsilon_2^2}$$

Localized Surface Plasmons (LSP)

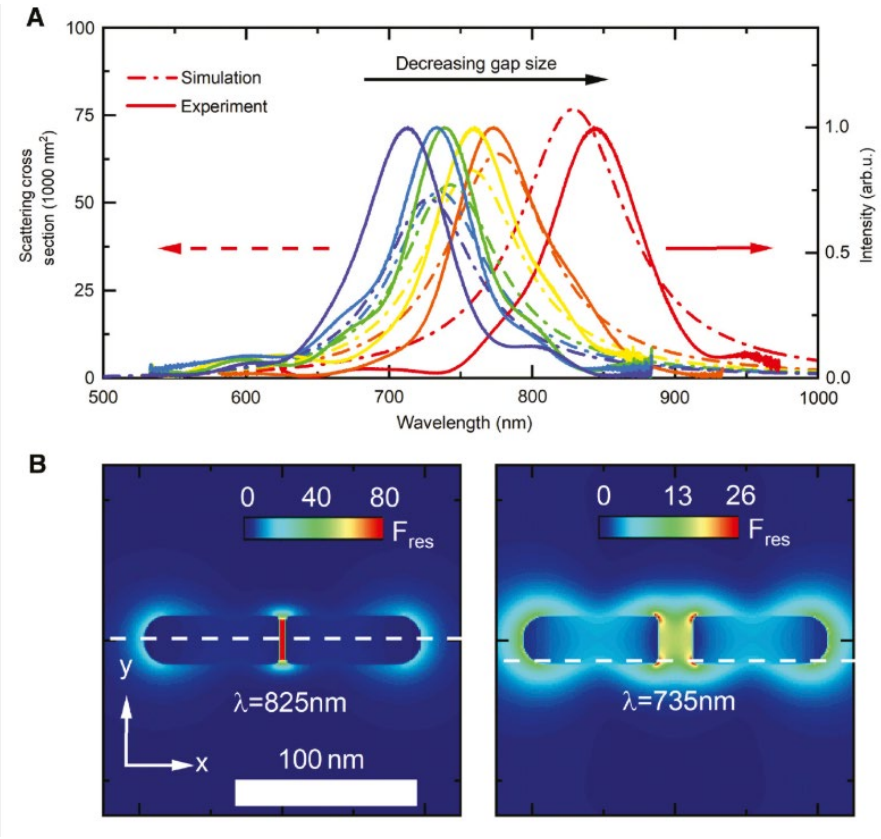
The polarizability is very sensitive to the size, shape, materials of the nanostructure as well as its coupling with other resonators.



Knight et al. Science 332, 2014

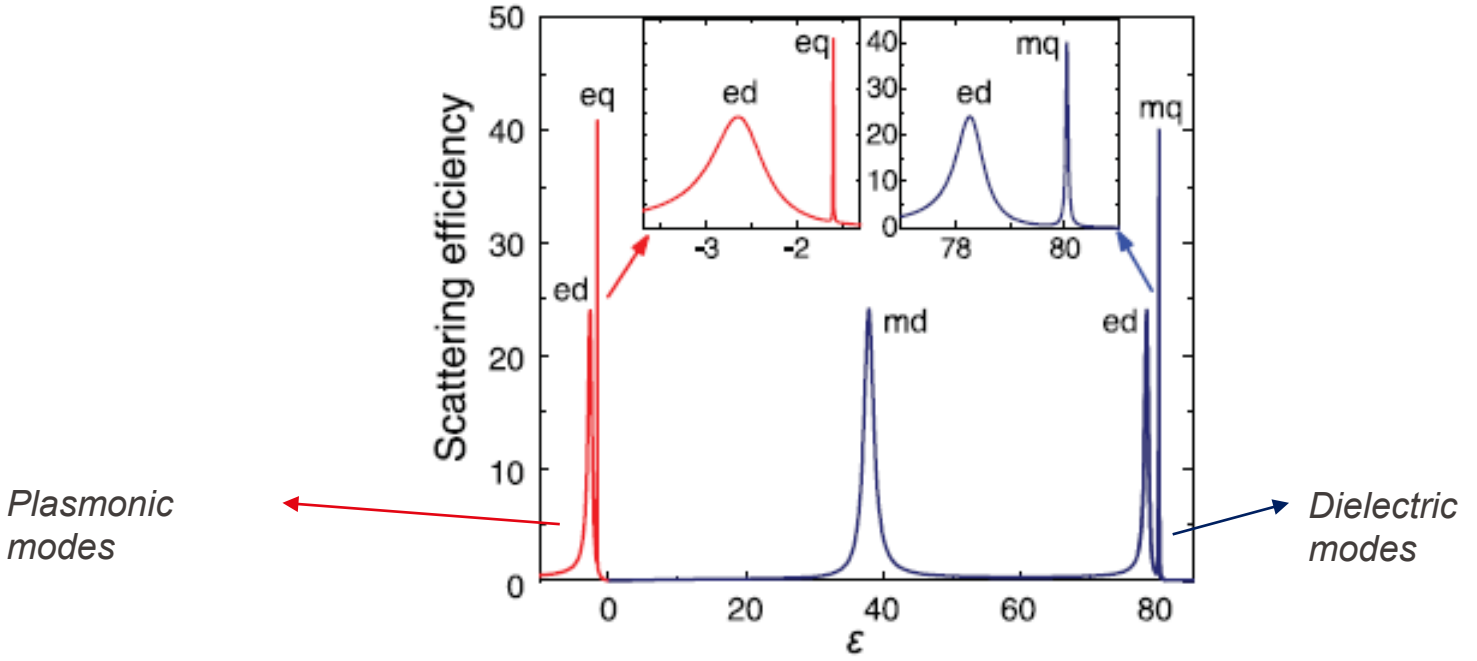


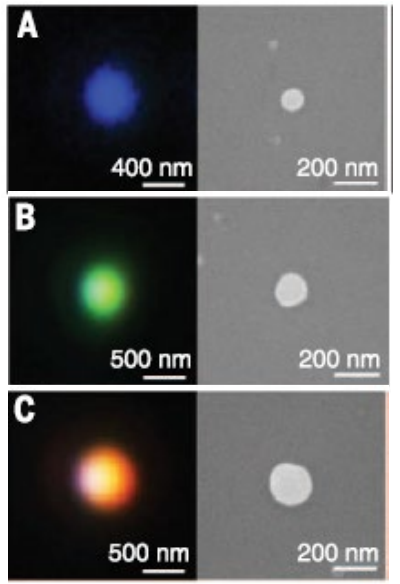
Maier, Fundamentals of Plasmonics

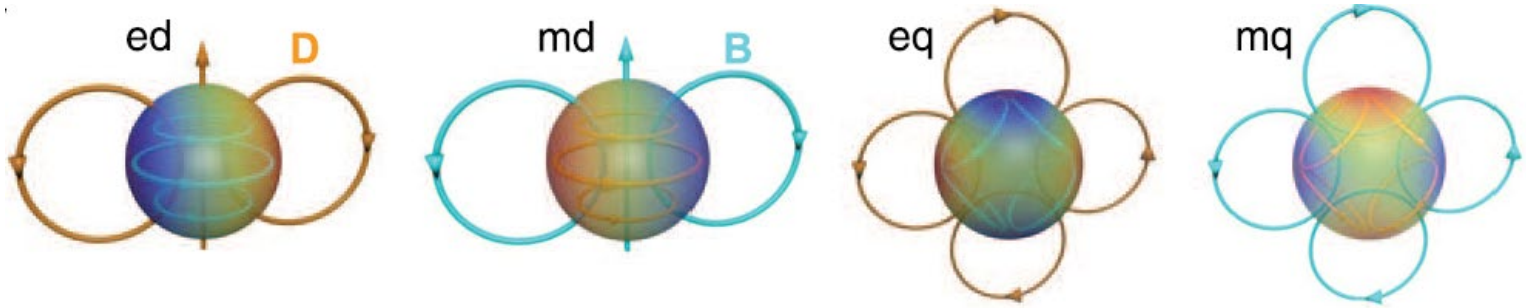


Nanophotonics, 9(2), 401-412, 2020

Mie Resonances

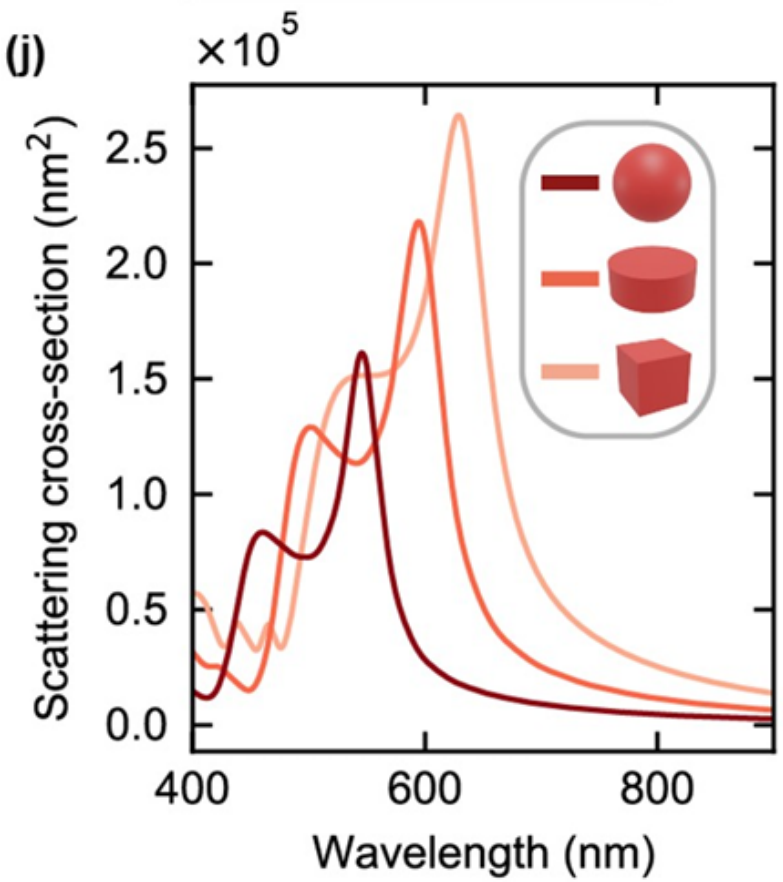


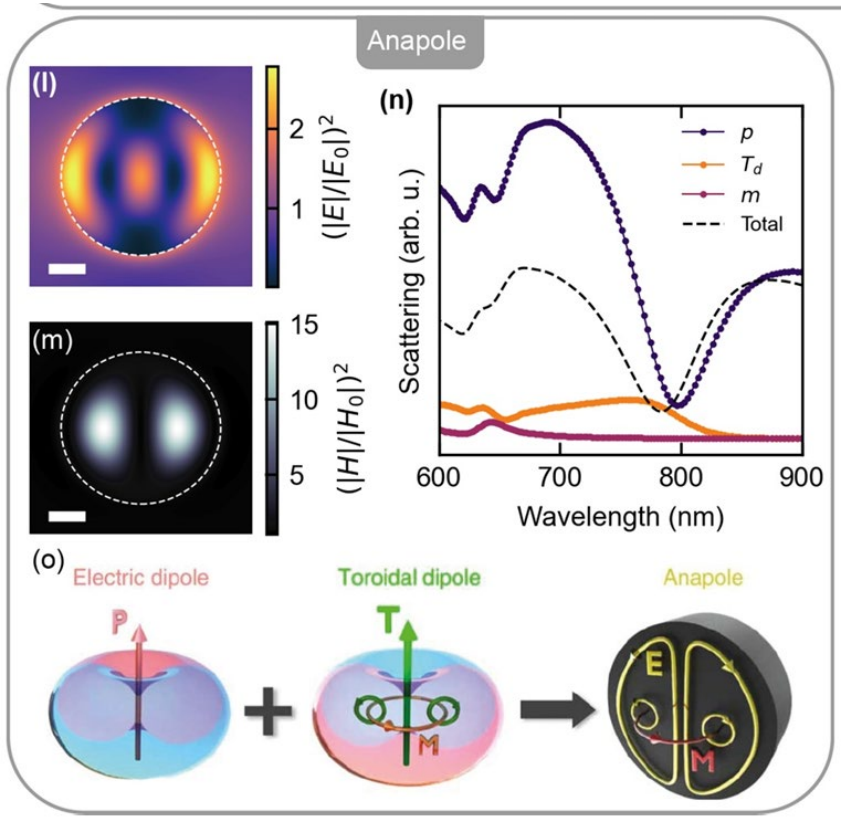




- In dielectric materials magnetic effects are stronger and there is a larger variety of resonance modes.
- Magnetic hotspots can be created in addition to electric hot spots

Mie Resonances





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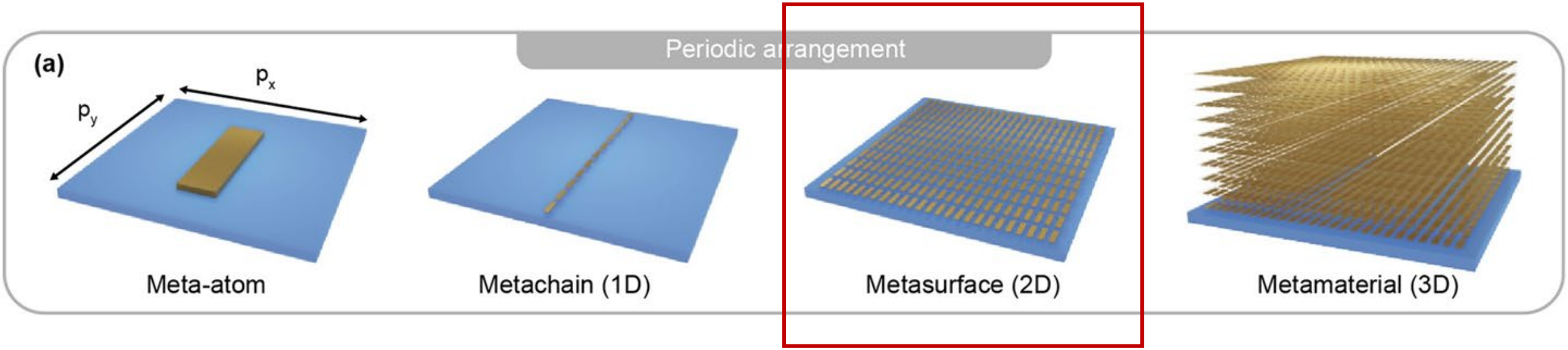
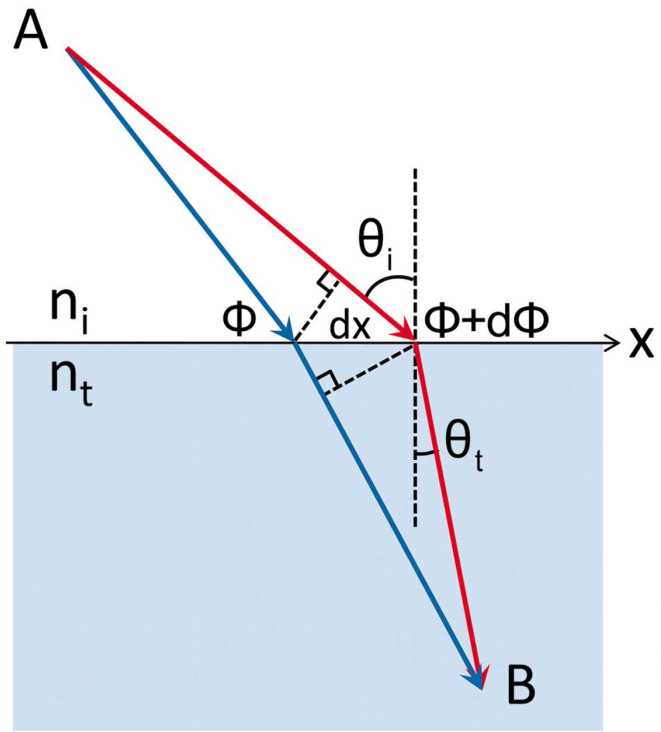
From Nanoresonators to Metamaterials



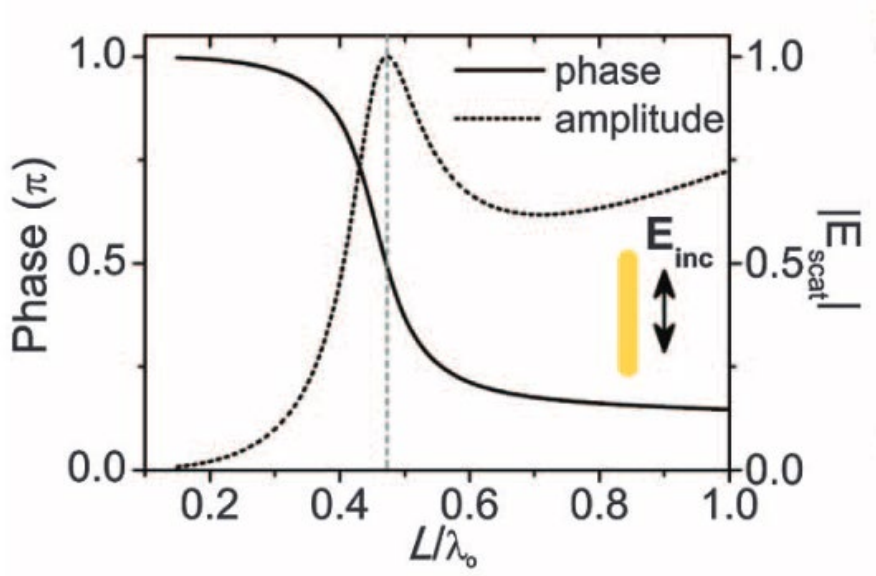
Chem. Rev. 2022, 122, 15082−15176

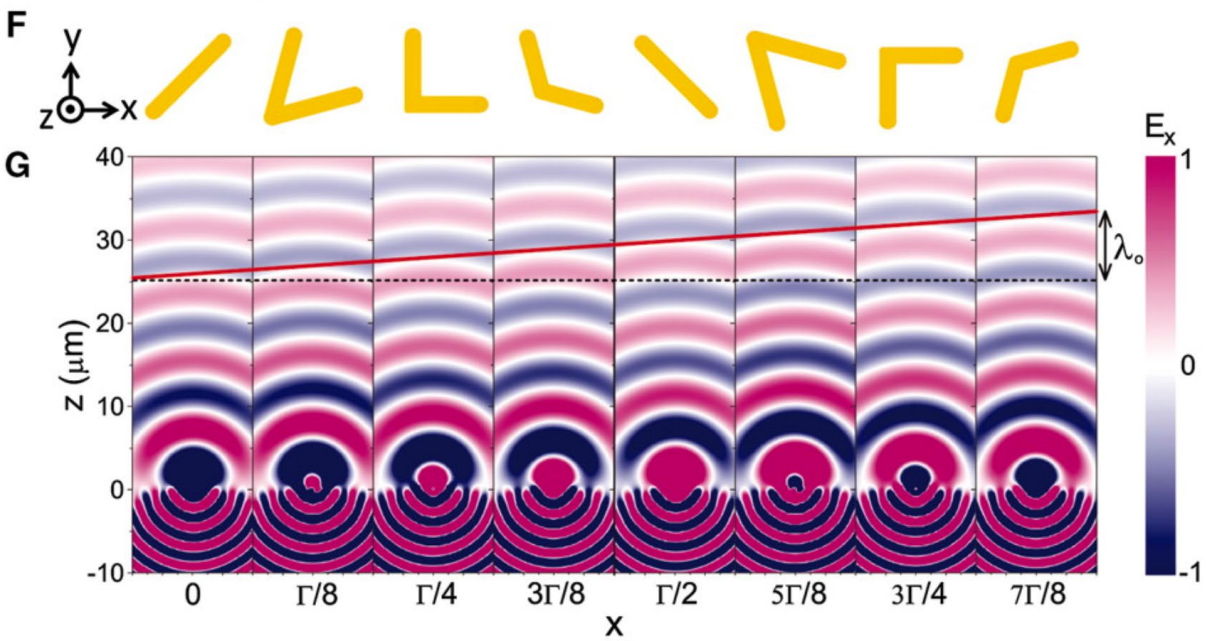
Optical Metasurfaces



$$\sin(\theta_t)n_t - \sin(\theta_i)n_i = \frac{\lambda_o}{2\pi}\frac{d\Phi}{dx}$$

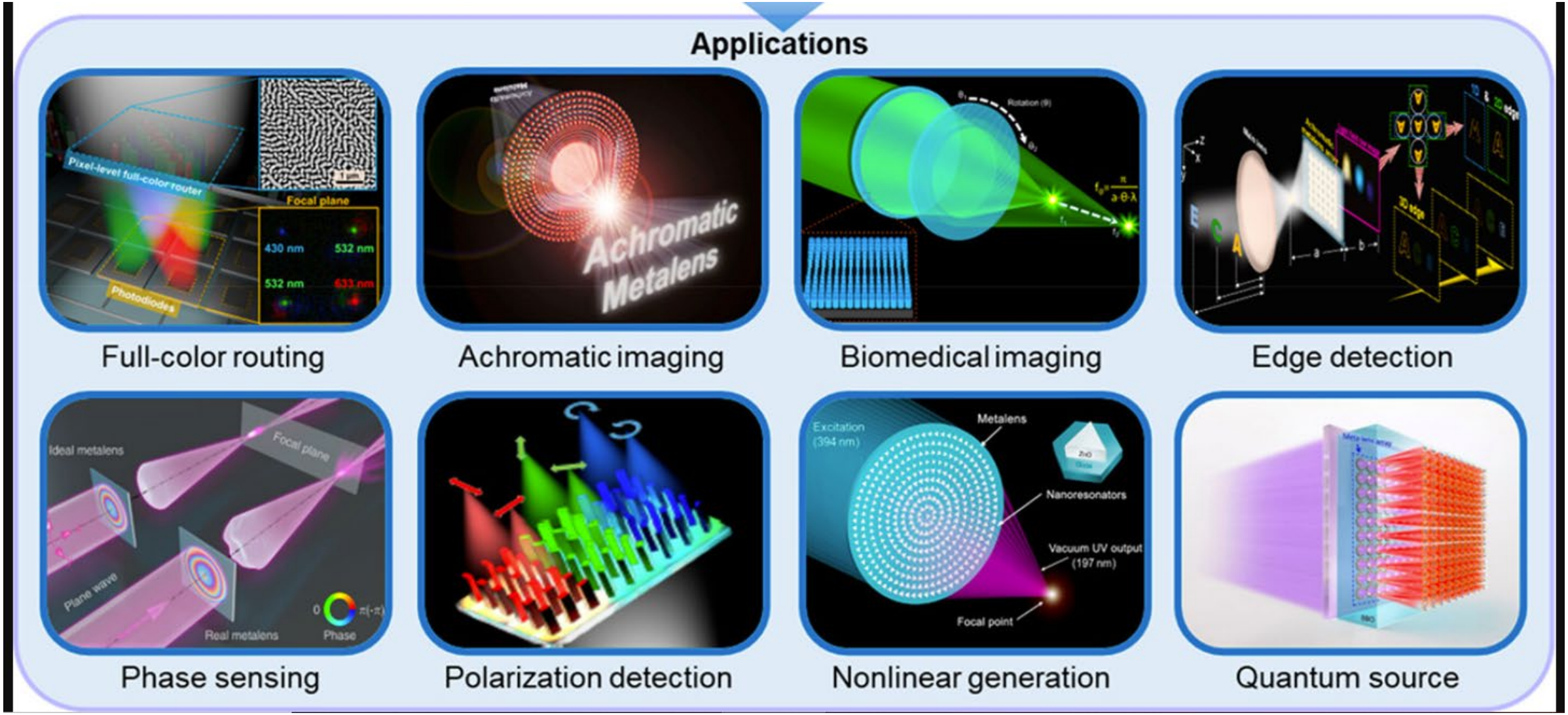
Generalized Snell's law





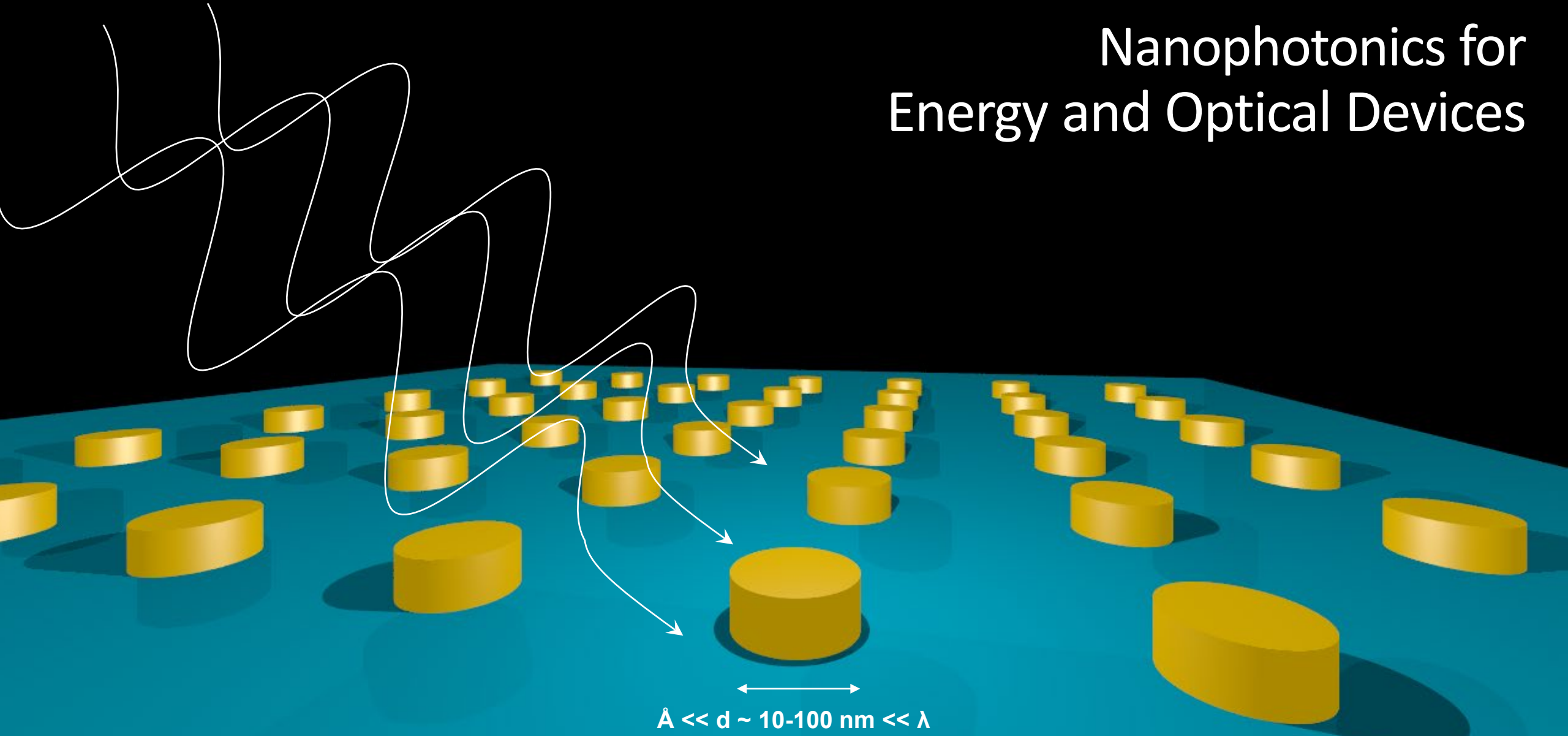
https://doi.org/10.1126/science.1210713

Optical Metasurfaces - Applications



https://doi.org/10.1021/acsphotonics.3c00457

Nanophotonics for Energy and Optical Devices



Nanophotonic structures open new pathways for light-energy conversion and storage.