Nanophotonics

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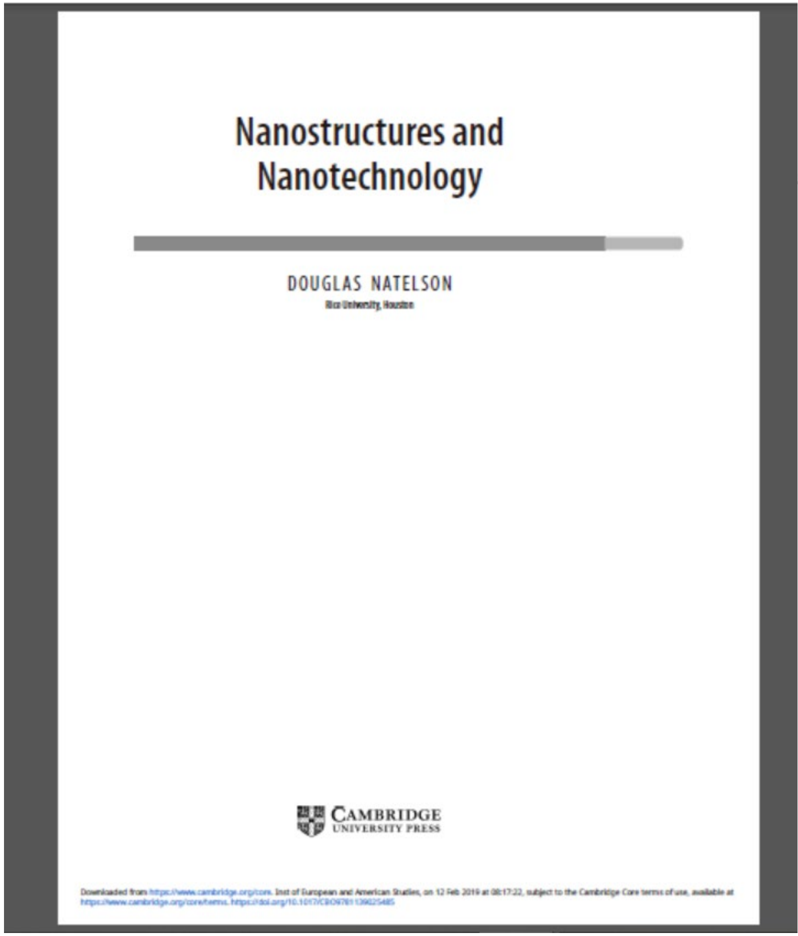
Outline

- Basic concepts of optics
- Optical response of (noble) metals
- Near-field optics and Super-resolution microscopy
- Plasmonics
- Low-dimensional materials
- Surface nonlinear optical spectroscopy



Nanostructures and Nanotechnology

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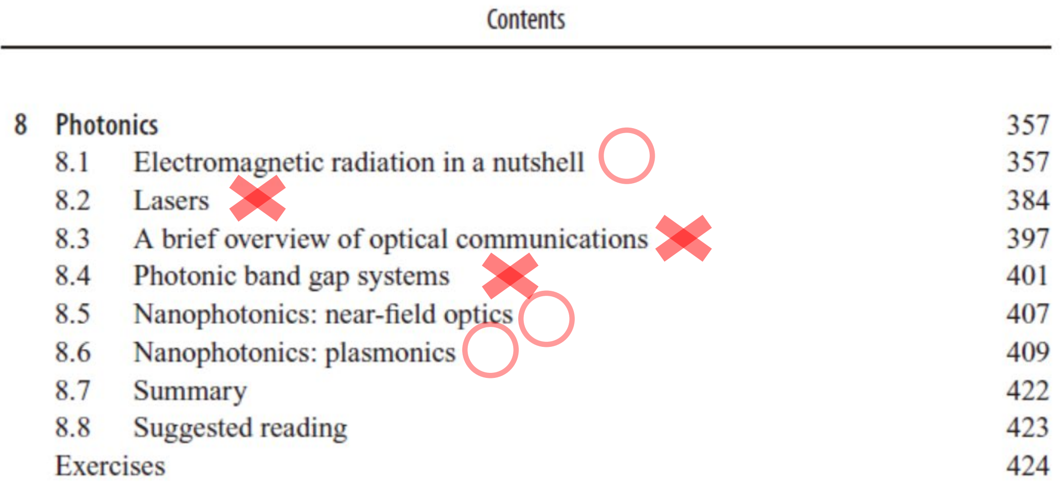


Contents

Basic concepts of optics

What is optics ?

- Optical phenomena
    - Reflection
    - Refraction
    - Absorption
    - Scattering
    - Interference
    - Diffraction

of light

- Optics is not a theory of light
- Optics talks about the interaction between light and matter
- How to describe such an interaction ?

Light ↔ electromagnetic wave

Matter ↔ positive and negative charges

Electromagnetic wave

Maxwell Equations

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

$$\nabla \times \vec{B} = \frac{1}{c}\frac{\partial \vec{E}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

$$\nabla \cdot \vec{E} = 4\pi\rho$$

$$\nabla \cdot \vec{B} = 0$$

Charge conservation law

$$\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0$$

Wave equation

$$[\nabla \times (\nabla\times) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}]\vec{E}(\vec{r}, t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}(\vec{r}, t)$$

, where generalized polarization is defined as $\vec{J} \equiv \frac{d\vec{P}}{dt}$

Light: an electromagnetic wave

- The wave equation writes (<u>in vacuum</u>) :

Plane wave: $|\boldsymbol{E}| = \mathrm{E}(z,t)$

$$\frac{\partial^2 \boldsymbol{E}}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2}$$

- Monochromatic (ω) plane wave solution: $\boldsymbol{E}(x,y,z,t) = \Re e[\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)}]$

  - ➢ $\mathrm{E}_x = \mathrm{E}_{0,x}\cos(\omega t - kz)$ and $\mathrm{E}_y = \mathrm{E}_{0,y}\cos(\omega t - kz - \varphi)$
  - ➢ $\mathrm{E}_z = 0$ (transverse wave)
  - ➢ $k = \omega/c$

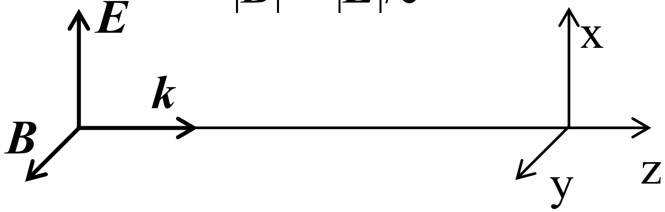
$$\boxed{\begin{aligned}
\frac{\partial}{\partial z}\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)} &= ik\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)}\\
\frac{\partial^2}{\partial z^2}\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)} &= -k^2\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)}\\
\frac{\partial^2}{\partial t^2}\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)} &= -\omega^2\boldsymbol{E}_0\,\mathrm{e}^{i(kz-\omega t)}
\end{aligned}}$$

Electro ➡ Electric field ***E***

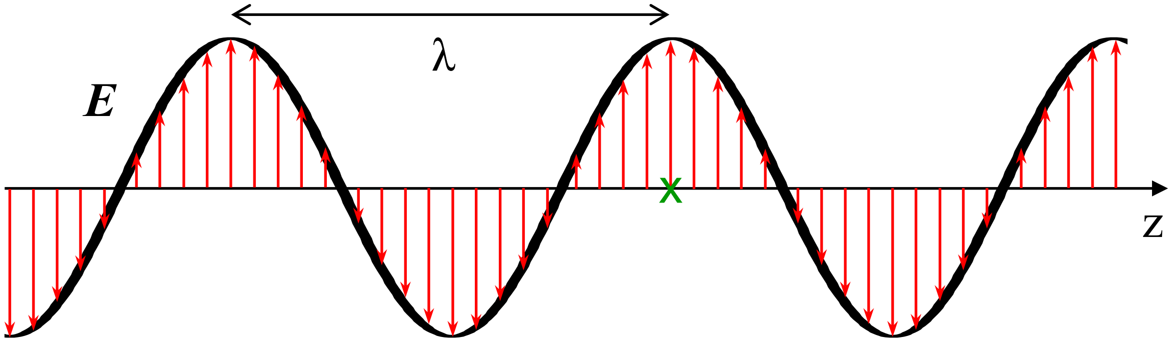
Magnetic ➡ Magnetic field ***B***

Wave ➡ Wave vector ***k***

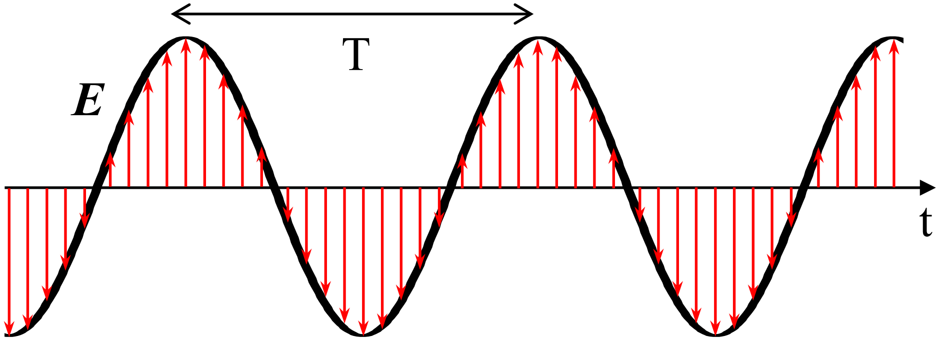
$|\boldsymbol{B}| = |\boldsymbol{E}|/c$



Light: an electromagnetic wave



- Fixed time



- Fixed position (x)

	Time	Space
	➢ $T \rightarrow$ period	➢ $\lambda \rightarrow$ wavelength
Photon energy $E=h\nu=\hbar\omega$	➢ $\omega = 2\pi/T \rightarrow$ angular frequency	➢ $k = 2\pi/\lambda \rightarrow$ wavevector
	➢ $\nu = 1/T \rightarrow$ frequency	➢ $\sigma = 1/\lambda \rightarrow$ wavenumber

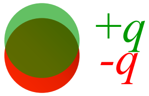
- Relations between space and time quantities in vacuum

$$k = \omega/c = 2\pi/\lambda \qquad \sigma = \nu/c \qquad \lambda = cT$$

When matter comes into play

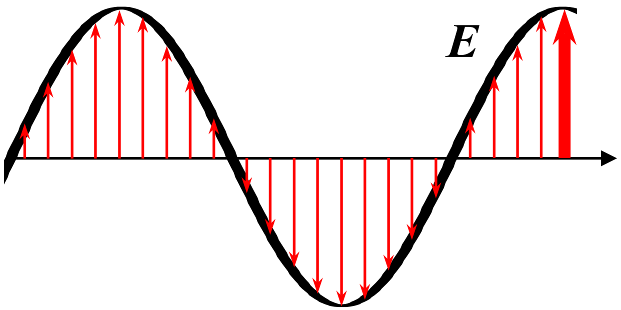
- The electric field of light interacts with bound charges inside matter (nuclei, electrons)
- Electric force: $\boldsymbol{F} = q\,\boldsymbol{E}$ ➡ the charges move

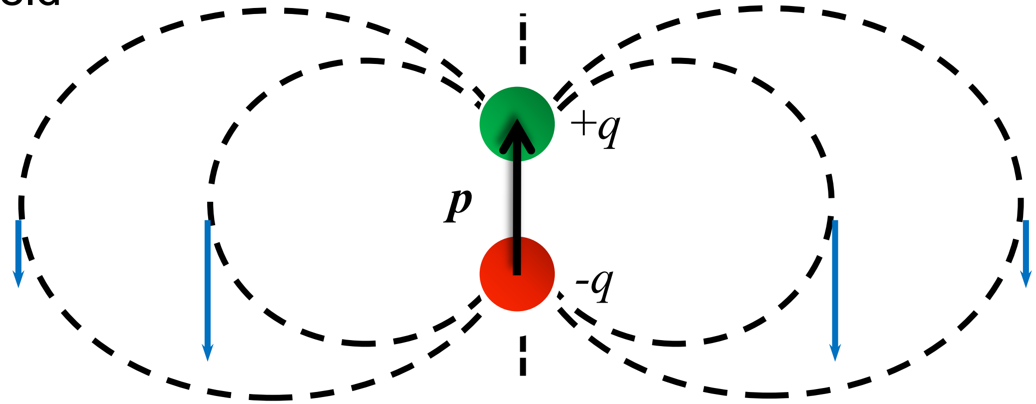
For one (apolar) atom or molecule



When matter comes into play

- The electric field of light interacts with bound charges inside matter (nuclei, electrons)
- Electric force: $\boldsymbol{F} = q\,\boldsymbol{E}$ → Creates oscillating electric dipoles $\boldsymbol{p}$
- Electric dipoles emit electric field





- Linear response

Relative charge displacement

Polarisability

Induced dipolar momentum

$$\mathbf{p} = q\mathbf{r} = \alpha\mathbf{E}_\ell$$

Local field

- Local field $\boldsymbol{E}_\ell$ on one atom/molecule is the sum of incoming and emitted fields

A macroscopic point of view

- Macroscopic point of view: linear, homogeneous, isotropic material

Macroscopic polarisation = volumic density of dipoles

Electric susceptibility

Number of atoms/molecules per unit volume

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

Macroscopic electric field

- Polarisation = new sources of electric field inside the material

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

Refractive index

$$n^2 = \varepsilon_r$$

Dielectric function = *Relative permittivity*

- The dielectric function links the electric displacement to the electric field and <u>implicitly</u> includes all the microscopic polarisation processes
- If local field effects are neglected ($\mathbf{E} \sim \mathbf{E}_\ell$) $N\alpha = \varepsilon_0 \chi$

Linear optical response of the medium is described by susceptibility (χ), dielectric function (ε_r), and refractive index (n)

Light waves in a medium

Interaction of light with medium

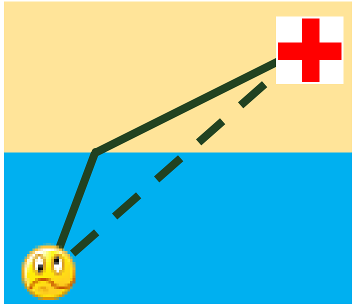
$$\left[\nabla \times (\nabla \times) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\vec{E}(\vec{r}, t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}(\vec{r}, t)$$

- Wave equation

$$\xcancel{\frac{\partial^2 \boldsymbol{E}}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2}} \quad \Rightarrow \quad \frac{\partial^2 \boldsymbol{E}}{\partial z^2} = \frac{\enclose{circle}{n^2}}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2}$$

$v = c/n$: speed of light waves in the medium

- ➢ $E_x = \mathrm{Re}[E_{0,x}\, e^{i(kz-\omega t)}] = E_{0,x}\cos(\omega t - kz)$
- ➢ $k = \frac{\omega}{v} = \frac{n\omega}{c} \quad \neq \quad k(vacuum) = \frac{\omega}{c}$



Lifeguard theorem

Complex optical response

- Complex refractive index $\tilde{n}$ and wavevector $\tilde{k}$

Refractive index

Extinction coefficient

$$\tilde{n} = n + i\kappa$$

$$\tilde{k} = \tilde{n}\frac{\omega}{c} = k + \frac{i\kappa\omega}{c}$$

- Complex dielectric function :

$$\begin{aligned} \varepsilon_r &= \tilde{n}^2 \\ &= \varepsilon_1 + i\varepsilon_2 \end{aligned}$$

- Real and imaginary parts:

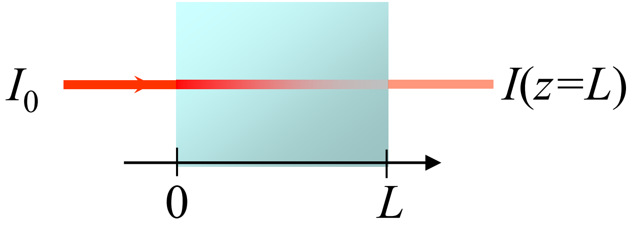
$$\begin{aligned} \varepsilon_1 &= n^2 - \kappa^2 \\ \varepsilon_2 &= 2n\kappa \end{aligned} \quad \Longleftrightarrow \quad \begin{aligned} n &= \frac{1}{\sqrt{2}}\left(\varepsilon_1 + \sqrt{\varepsilon_1{}^2 + \varepsilon_2{}^2}\right)^{1/2} \\ \kappa &= \frac{1}{\sqrt{2}}\left(-\varepsilon_1 + \sqrt{\varepsilon_1{}^2 + \varepsilon_2{}^2}\right)^{1/2} \end{aligned}$$

Absorption

- Electric field wave

$$E_x = E_{0,x}\, \mathrm{e}^{i(\tilde{k}z-\omega t)} = E_{0,x}\, \overbrace{e^{-\kappa\omega z/c}}^{\textit{Attenuation}}\, \overbrace{e^{i(kz-\omega t)}}^{\textit{Propagation}} \qquad \tilde{k} = \tilde{n}\frac{\omega}{c}$$

- Intensity: $I = \frac{1}{2} c\, \varepsilon_0 n \left| \boldsymbol{E_0} \right|^2$



$$\boxed{I(z) = I_0 e^{-\beta z}}$$

Beer-Lambert law

- Absorption coefficient $\boxed{\beta = \frac{2\kappa\omega}{c} = \frac{4\pi\kappa}{\lambda}}$

- Absorbance $\ln \frac{I_0}{I(L)} = \beta L$

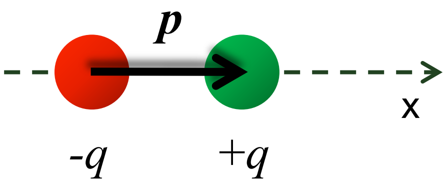
- Penetration depth $\delta = \frac{2}{\beta}$

metal	**δ (nm) @620 nm**
Au	31
Ag	24
Cu	30
Al	13

Optical resonance

- Refractive index n is related to the movement of the charges as a response to the excitation by the electric field of light

n ⟷ $\mathbf{P} = \varepsilon_0 \chi \mathbf{E}$ ⟷



- Charges don't move freely (e.g. along x)
  - Restoring force: $-K\,x$
  - Resisting force: $-m\gamma\,(dx/dt)$ for example collisions
  - Electric force: $q.E_{\ell,x}$

- Fundamental equation of dynamics along x

Electric force

Mass of the moving charge

$$m\frac{d^2x}{dt^2} = -Kx - m\gamma\frac{dx}{dt} + qE_{\ell,x}$$

Acceleration

Restoring force

Resisting force

Optical resonance

- For an oscillating electric field (ω=excitation frequency) $E_{\ell,x} = E_0 e^{-i\omega t}$

- Response of the charge

$$x = \frac{q/m}{\omega_0^2 - \omega^2 - i\gamma\omega} E_0 \qquad \text{with} \qquad \omega_0^2 = \frac{K}{m}$$

Resonance frequency

- When ω ~ ω_0 and γ << ω_0

Polarisability α

$$x \sim \frac{q/2m\omega_0}{\omega_0 - \omega - i\Gamma} E_0 \qquad p_x = qx \sim \frac{q^2/2m\omega_0}{\omega_0 - \omega - i\Gamma} E_0 \qquad (\Gamma = \gamma/2)$$

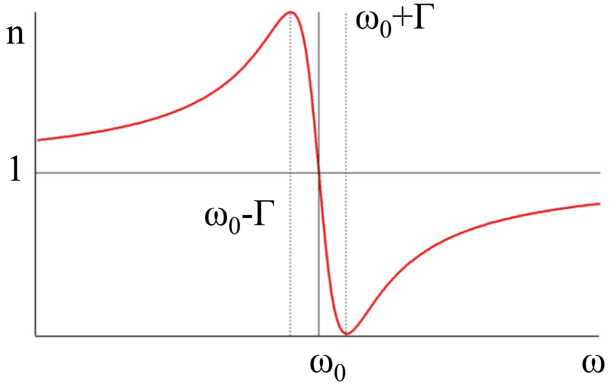
Lorentzian resonance

- Neglecting local field effects

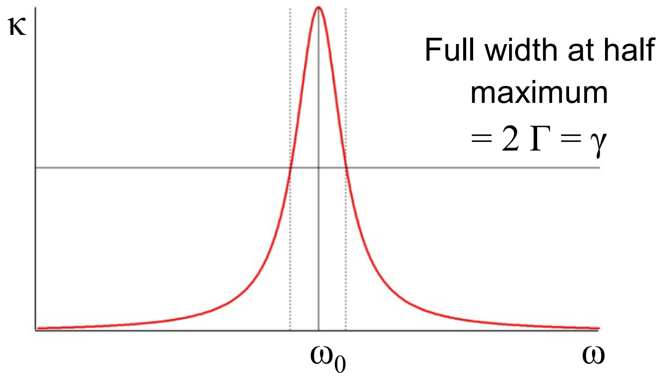
$$\chi = N\alpha/\varepsilon_0 \sim \frac{Nq^2/2\varepsilon_0 m\omega_0}{\omega_0 - \omega \ - i\Gamma} = \boxed{\varepsilon_r - 1}$$

Enhanced near the resonance

- Real part $\varepsilon_1 = n^2 - \kappa^2 \approx n^2$
  - Dispersion of the refractive index near a resonance

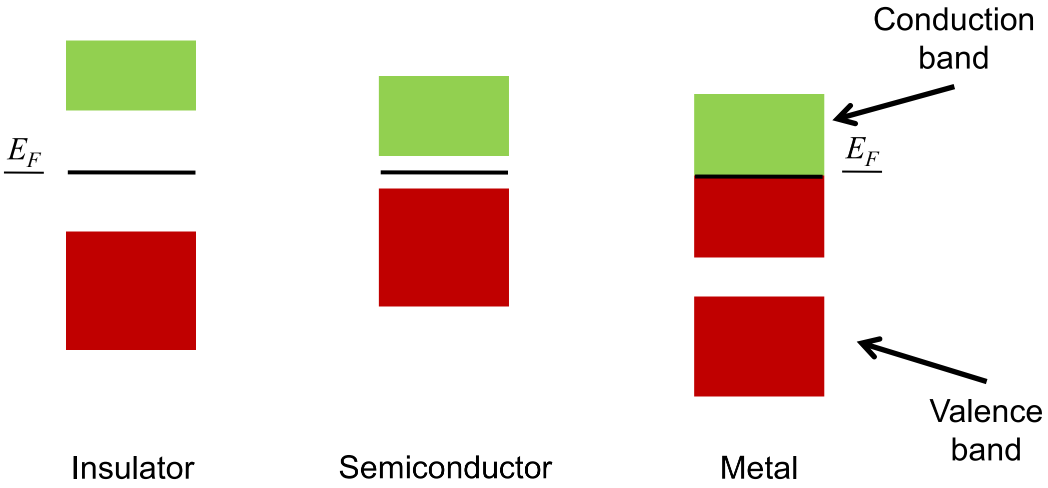


- Imaginary part $\varepsilon_2 = 2n\kappa$
  - Absorption spectroscopy



Full width at half maximum $= 2\,\Gamma = \gamma$

Optical response of (noble) metals

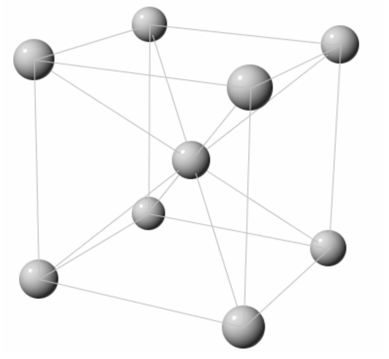


Structure of monovalent metals

Alkali metals

Metal	Atomic structure
Li	$1s^2\,2s^1$
Na	[Ne] $3s^1$
K	[Ar] $4s^1$
Rb	[Kr] $5s^1$
Cs	[Xe] $6s^1$

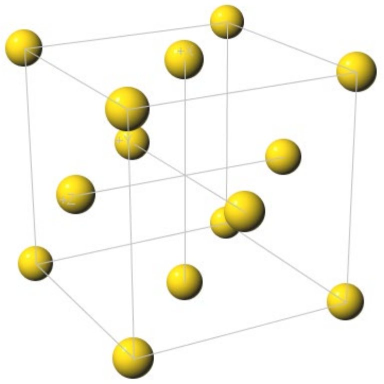
Crystal lattice:
centered cubic (bcc)



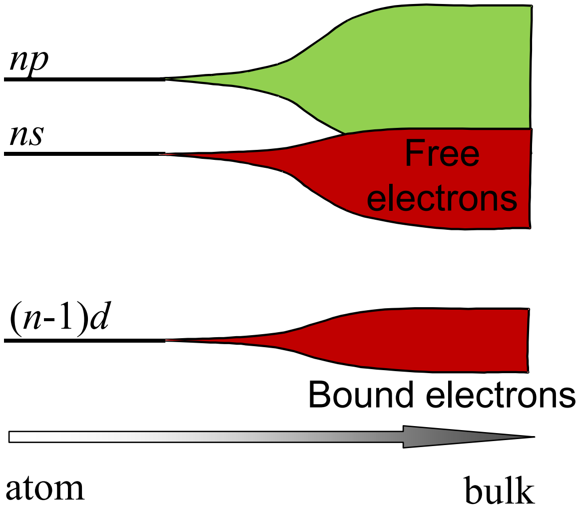
Noble metals

Metal	Atomic structure
Cu	[Ar] $3d^{10}\,4s^1$
Ag	[Kr] $4d^{10}\,5s^1$
Au	[Xe] $5d^{10}\,6s^1$

Crystal lattice:
face-centered cubic (fcc)



Band formation:



Crystal unit cells

Intraband contribution

Elastically bound electron model (Lorentz)

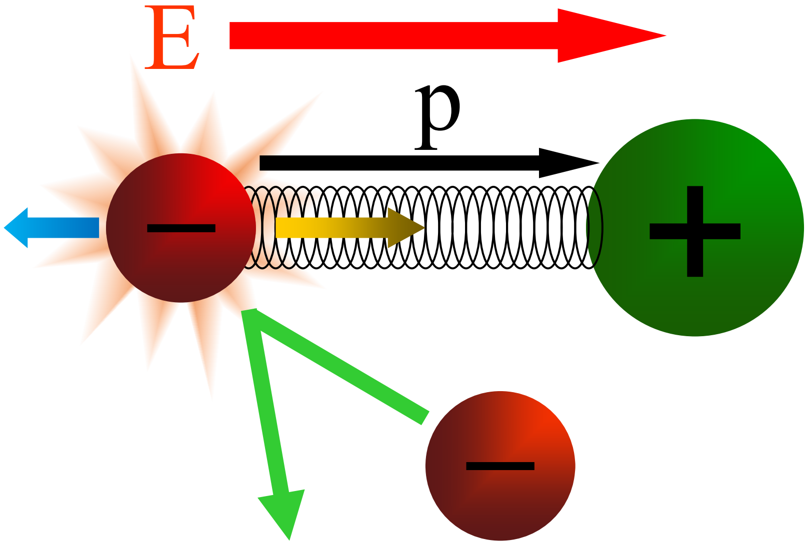
$$m_e \frac{d^2x}{dt^2} + m_e \gamma \frac{dx}{dt} + Kx = -eE_{\ell,x}$$

Acceleration

Restoring force (harmonic potential)

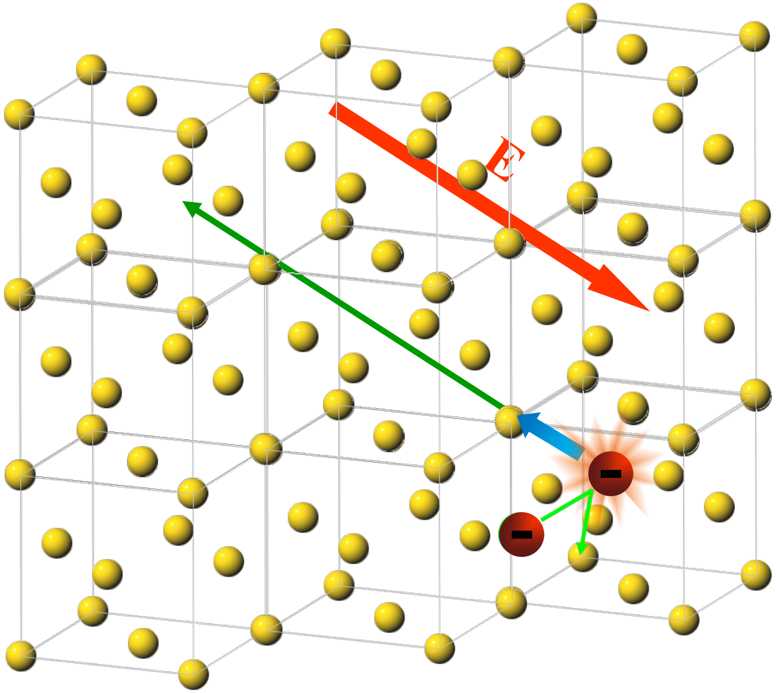
Collisions (dissipation)

Electric force



(Nearly) free electron model (Drude)

$$m_e^* \frac{d^2x}{dt^2} + m_e^* \Gamma \frac{dx}{dt} + \xcancel{Kx} = -eE_x$$



Drude model

- Optical response of free electrons: identical to the optical response of a bound charge, without restoring force (K=0)
- For an oscillating electric field (ω = excitation frequency)

$$E_x = E_0 e^{-i\omega t}$$

- Response of the charge

$$x = \frac{e / m_e^*}{\omega(\omega + i\Gamma)} E_0$$

(ω_0=0)

- Induced dipoles

Polarisability α

$$p_x = -ex = \frac{-e^2 / m_e^*}{\omega(\omega + i\Gamma)} E_0$$

- Induced polarisation

$$P_x = N p_x = \frac{-Ne^2 / m_e^*}{\omega(\omega + i\Gamma)} E_0$$

Drude model

- Finally

$$P_x \equiv \varepsilon_0 \chi^D E_x \quad \text{with} \quad \chi^D = \frac{-Ne^2/\varepsilon_0 m_e^*}{\omega(\omega + i\Gamma)}$$

- Drude electric susceptibility

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

- Plasma angular frequency of bulk metal

$$\omega_p = \sqrt{\frac{Ne^2}{m_e^* \varepsilon_0}}$$

➢ $\hbar\omega_p$ ~ 9 eV (ultraviolet) for Au and Ag

- Drude dielectric function

$$\varepsilon_r^D = 1 + \chi^D \quad \Rightarrow \quad \varepsilon_r^D(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}$$

Intraband contribution

- Real and imaginary parts of conduction electron contribution to dielectric function

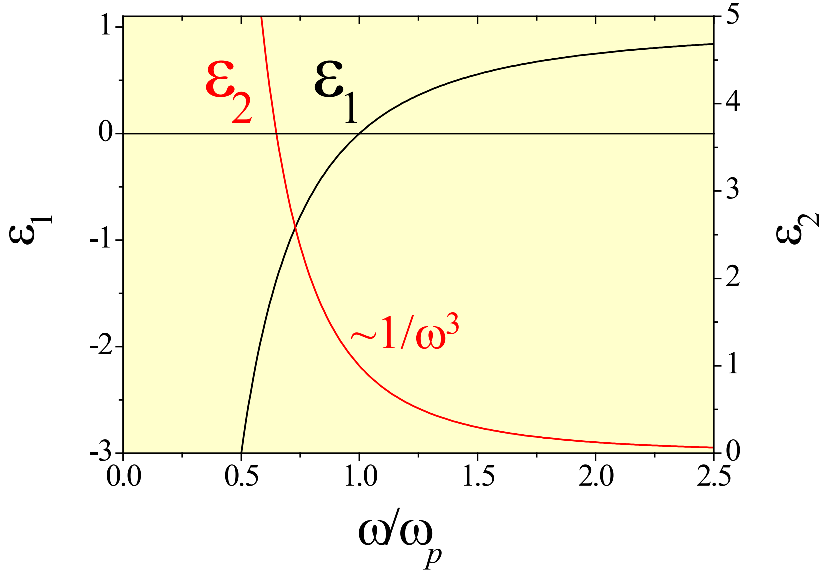
$$\varepsilon_1^D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2}$$

$$\varepsilon_2^D(\omega) = \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)}$$

- For photons in the near IR-visible-UV range, i.e. energies of the order of a few eV, these expressions simplify

- With $\hbar\Gamma$~0.1 eV and $\hbar\omega_p$~10 eV

  - $\Gamma \ll \omega$
  - $\varepsilon_1^D(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}$
  - $\varepsilon_2^D(\omega) \approx \frac{\omega_p^2 \Gamma}{\omega^3}$



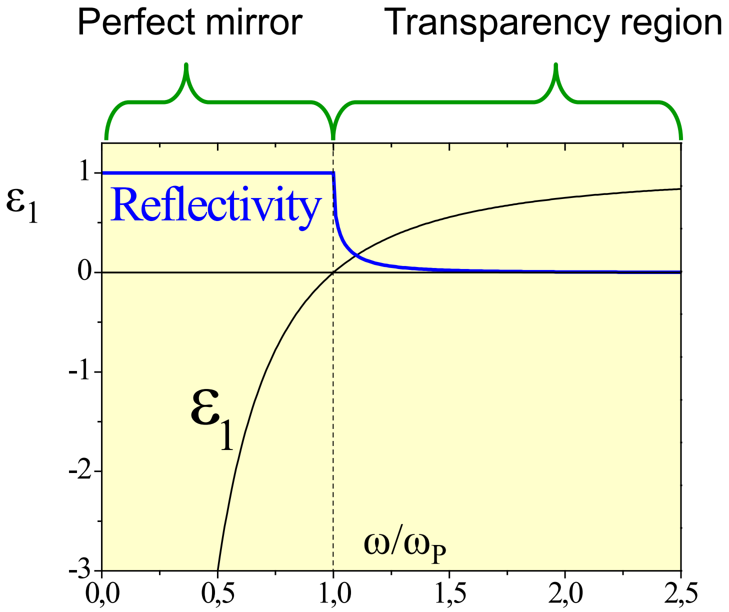
Intraband contribution

- Reminder: dispersion equation

$$\tilde{k}^2 = \varepsilon \frac{\omega^2}{c^2}$$

- Dispersion equation for Drude model

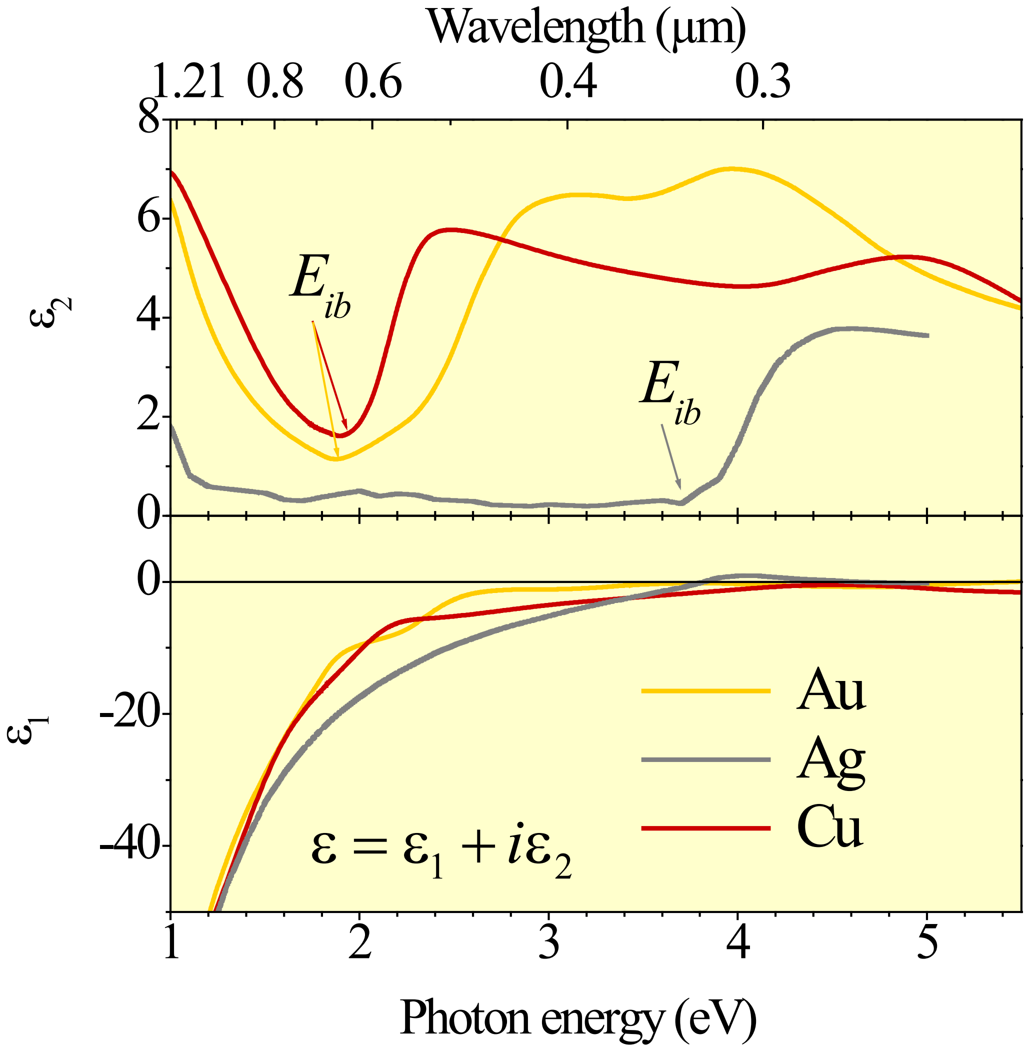
$$\omega \approx \sqrt{\omega_p^2 + c^2 \tilde{k}^2}$$



- $\omega < \omega_P \Rightarrow \tilde{k}^2 < 0 \Rightarrow \tilde{k} = \frac{i\kappa\omega}{c} \Rightarrow E_x = E_{0,x} e^{-\kappa\omega z/c} e^{-i\omega t}$
  - ➢ In the medium, the wave does not propagate and rapidly vanishes
  - ➢ The energy is reflected by the metallic surface
  - ➢ A free electron metal is a perfect mirror below ω_P (i.e. in the visible range)
- $\omega > \omega_P \Rightarrow \tilde{k}^2 > 0 \Rightarrow$ propagative wave

Experimental dielectric function

- The dielectric function is the sum of the intraband and interband contributions



$$\varepsilon = 1 + \chi^D + \chi^{ib} = \chi^D + \varepsilon^{ib}$$

- E_{ib} = threshold for interband contribution
    - Au ~2.0 eV
    - Ag 3.9 eV
    - Cu 2.1 eV

- Experimental determination and analysis of the noble metal dielectric function:

E. D. Palik, *Handbook of Optical Constants of Solids*
Johnson & Christy, PRB **6**, 4370 (1972)
Thèye, PRB **2**, 3060 (1970)
Ehrenreich & Philips, PRB **128**, 1622 (1962)
Innes & Sambles, J. Phys. F **17**, 277 (1987)

The various contributions

- The contributions clearly show up on the imaginary part

① Free electron behaviour

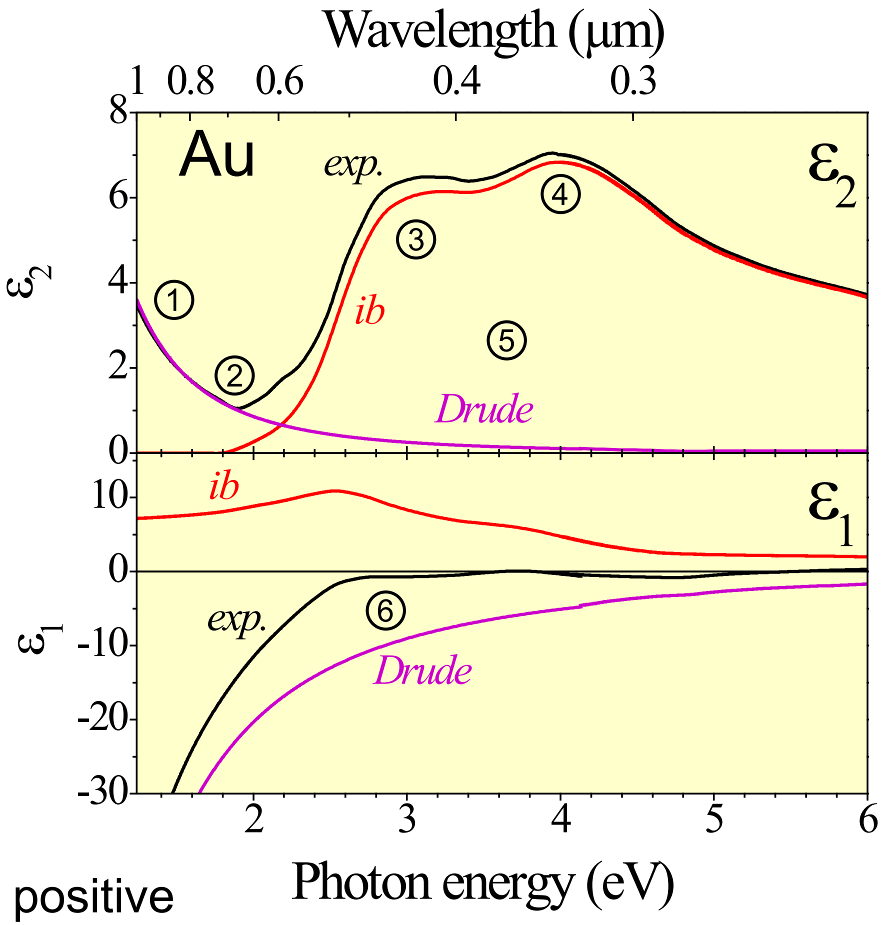
② Interband threshold

③ First maximum: transitions from d to s-p band at L point

④ Second maximum: transitions from d to s-p band at X point + transition between low energy s-p and higher energy s-p bands at L point

⑤ d bands are flat and s-p steeper,
➡ the maxima are broad

⑥ Real part of interband contribution is positive
➡ shift of the Drude contribution towards lower energies
➡ ω_P (real) < ω_P (theory)



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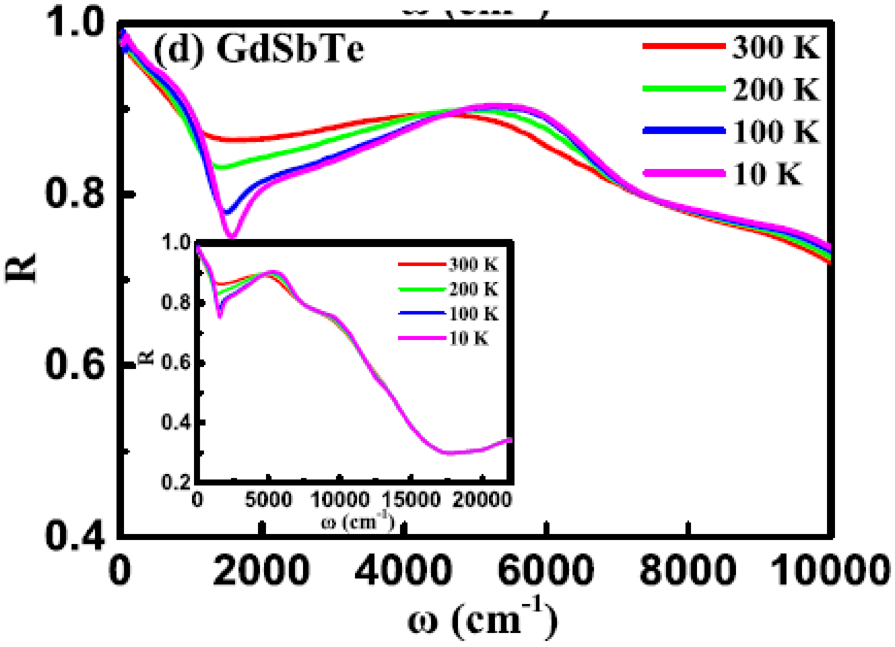
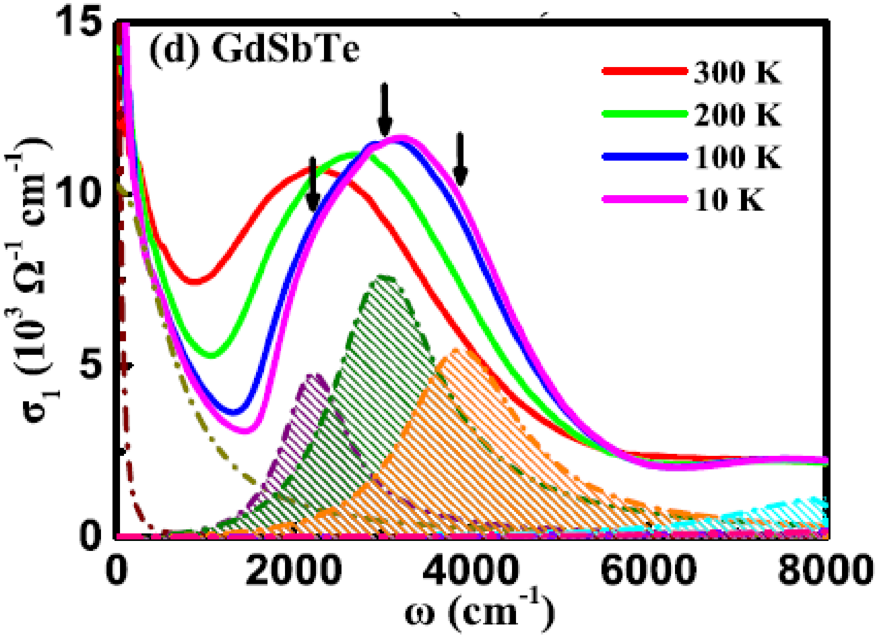
Optical study of the topological materials *Ln*SbTe (*Ln* = La, Ce, Sm, Gd)

$$\sigma(\omega) = \sum_i \frac{\omega_{Pi}^2}{4\pi} \frac{1}{\gamma_{Di} - i\omega} + \sum_j \frac{S_j^2}{4\pi} \frac{\omega}{i(\omega_j^2 - \omega^2) + \omega\gamma_j}.$$





Near Field optics & Super-resolution microscopy

Diffraction (far-field approximation)

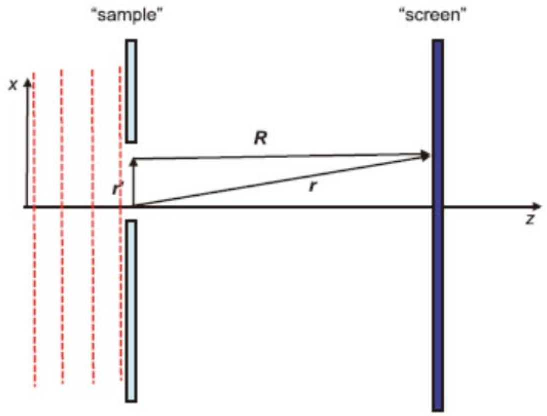


Fig. 8.6 Geometry considered for generic scalar diffraction. A plane wave is incident on an opaque screen at $z = 0$ containing a hole. Of interest is the field at some position $\mathbf{r}$ with $z > 0$. A point on the screen has position $\mathbf{r}'$, and $\mathbf{R} \equiv \mathbf{r} - \mathbf{r}'$.

$$\psi_\mathrm{d}(\mathbf{r}) \approx -\frac{\mathrm{i}k}{4\pi}\frac{\mathrm{e}^{\mathrm{i}kr}}{r}(\cos\theta_\mathrm{i} + \cos\theta_\mathrm{d})\int_S da'\,\psi_\mathrm{i}(\mathbf{r}')\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}'}. \tag{8.72}$$

$$I = I_0\frac{k^2(1+\cos\theta_\mathrm{d})^2}{\pi^2 r^2}\frac{\sin^2 k_x a \sin^2 k_y b}{k_x^2 k_y^2}. \tag{8.74}$$

$$I = I_0\frac{k^2 a^4}{4r^2}\left(\frac{2J_1(ka\sin\theta_\mathrm{d})}{ka\sin\theta_\mathrm{d}}\right). \tag{8.75}$$

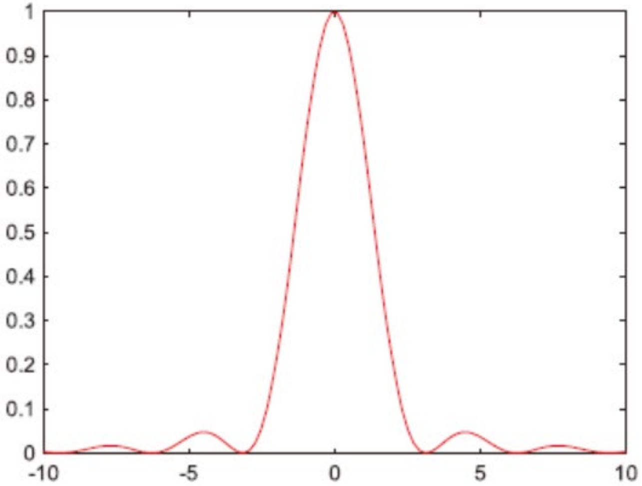
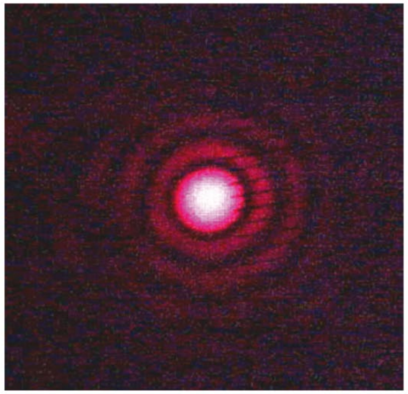


Fig. 8.7 Diffraction pattern in the far field from a single slit at normal incidence.

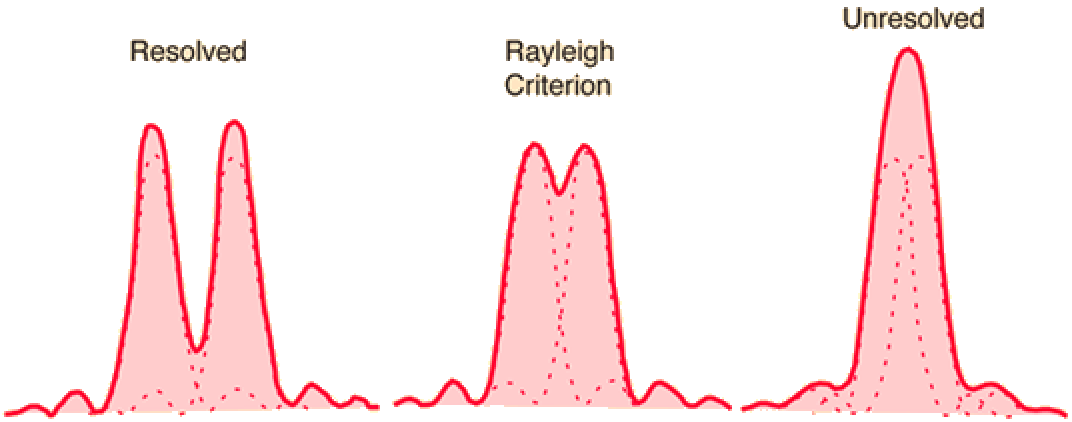


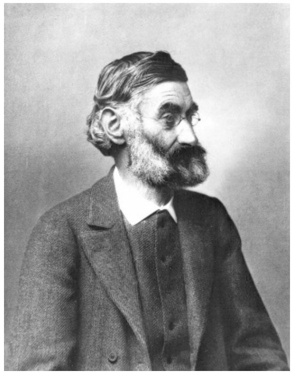
Far field "Airy" diffraction pattern from a circular aperture, as described by Eq. (8.75); image from Indiana University. **Fig. 8.8**

Diffraction limitation

- Resolution is diffraction limited.
- Abbe (1873) reported that smallest resolvable distance between two points (d) using a conventional microscope may never be smaller than half the wavelength of the imaging light (~200 nm)

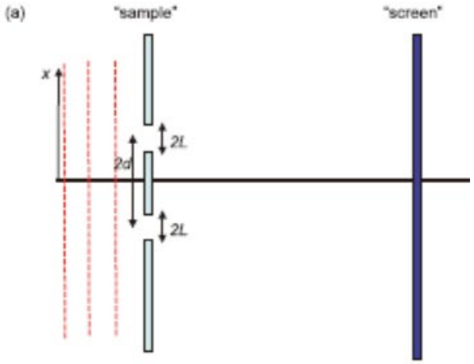
$$d = \frac{\lambda}{2n\sin\theta} = \frac{\lambda}{2\mathrm{NA}}$$



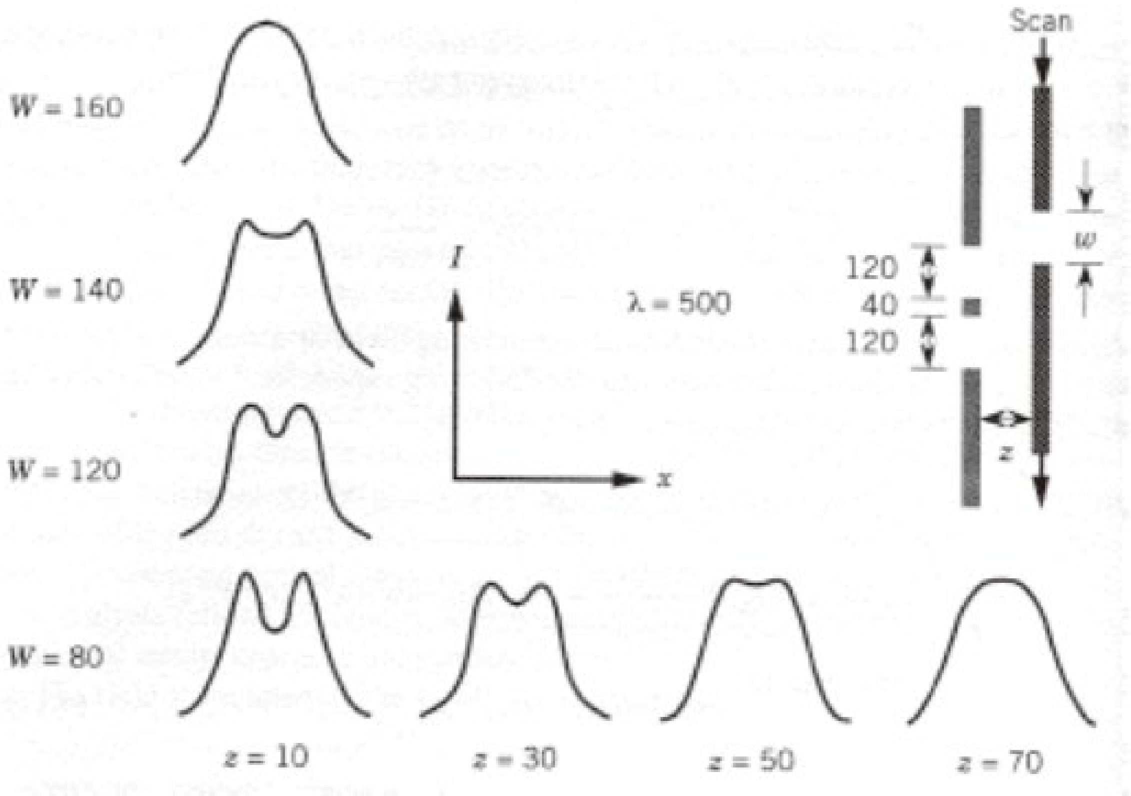


Ernst Abbe (1840-1905)

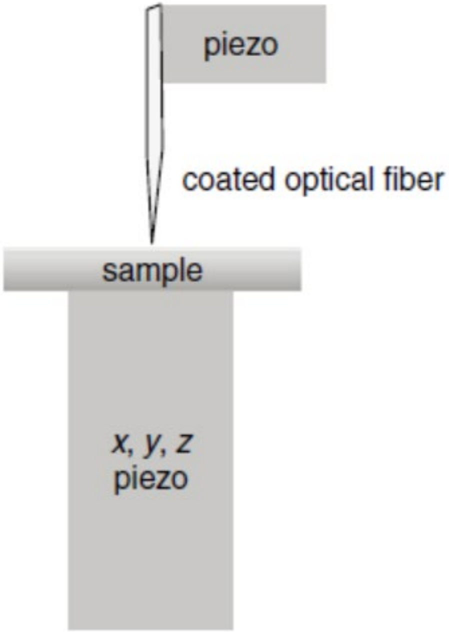
Near field regime

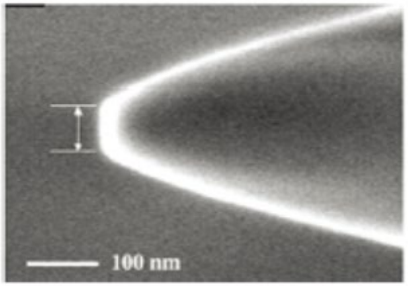


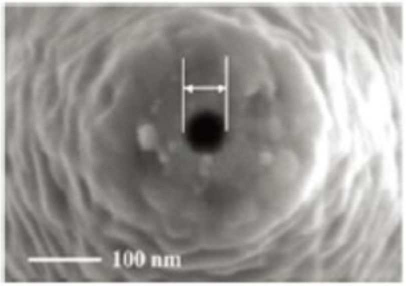
A near-fie
the "samp

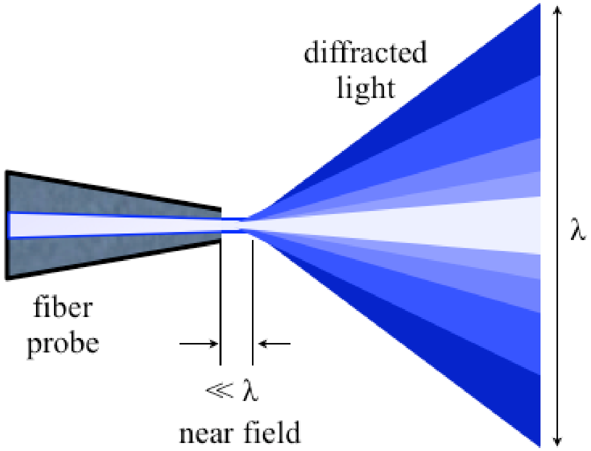


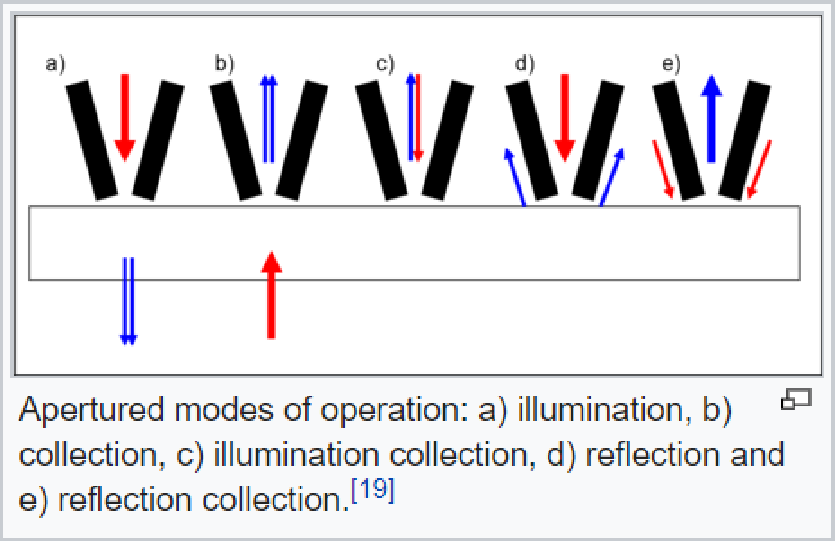
Near-Field Scanning Optical Microscopy (NSOM)









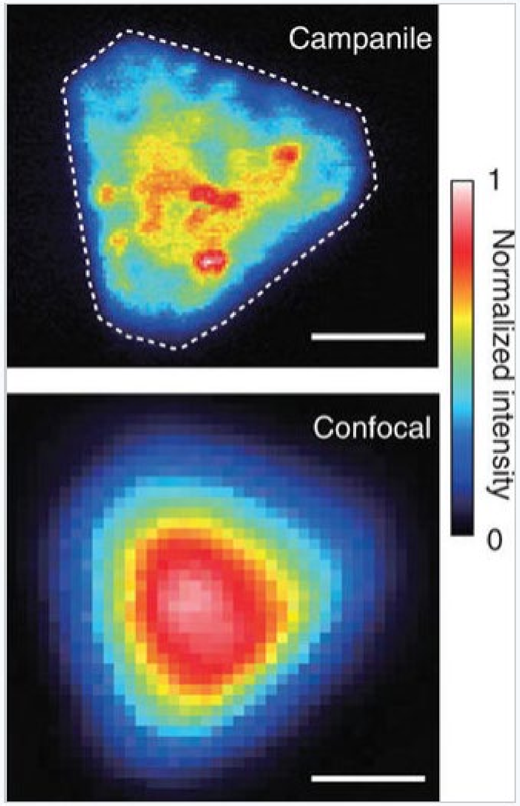


Apertured modes of operation: a) illumination, b) collection, c) illumination collection, d) reflection and e) reflection collection.[19]

Near-Field Scanning Optical Microscopy (NSOM)

- Scanning Near-Field Optical Microscopy (SNOM)
- But only for superficial structures
- A form of Scanning Probe Microscopy (SPM)

- Aperture diameter less than the wavelength of light
- In 1993 Eric Betzig and Robert Chichester used NSOM for *repetitive* single molecule imaging



Comparison of photoluminescence maps recorded from a molybdenum disulfide flake using NSOM with a campanile probe (top) and conventional confocal microscopy (bottom). Scale bars: 1 μm.[2]

Super-Resolution Microscopy

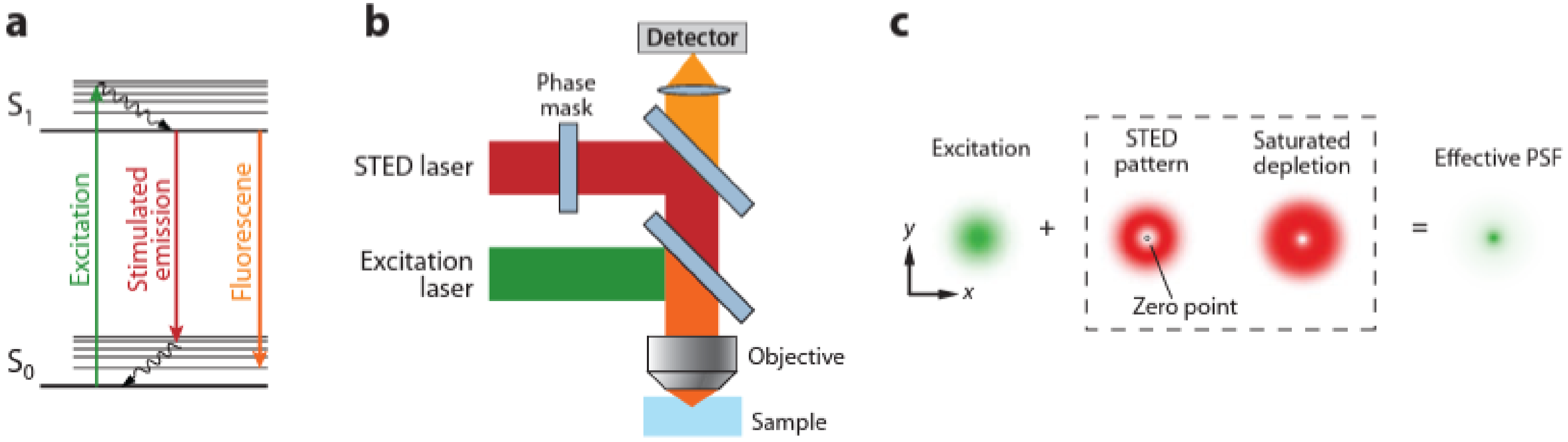
2014 Nobel Prize in Chemistry

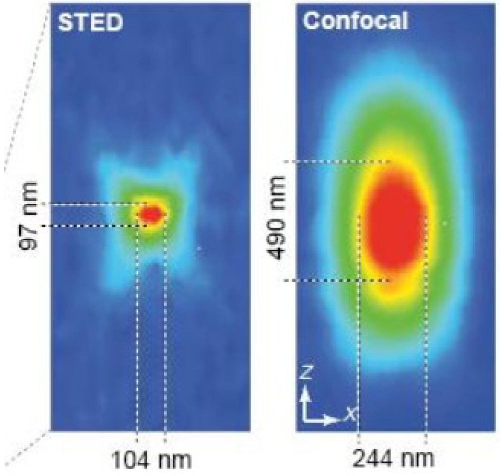
STED (Stimulated Emission Depletion)
Stefan Hell

PLAM (PhotActivated Localization Microscopy)
Eric Betzig

STORM (STOchastic Optical Reconstruction Microscopy)
Xiaowei Zhuang

Stimulated Emission Depletion (STED) Microscopy (Hell)

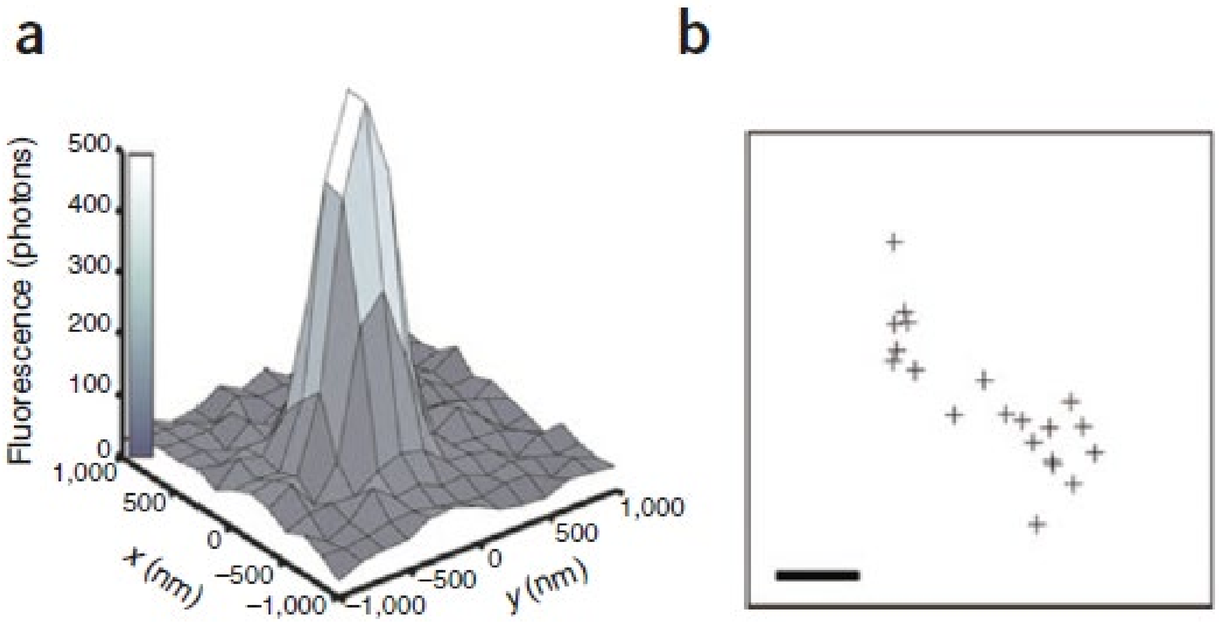




Basic Principle of PLAM or STORM

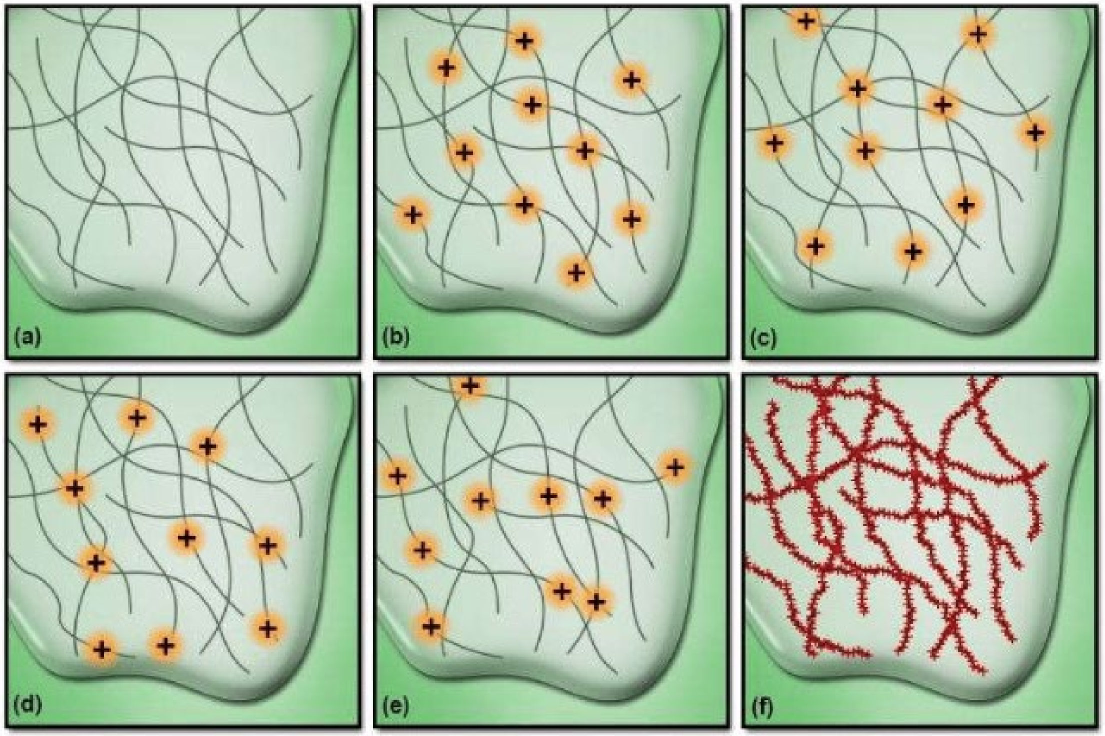
E. Betzig

- Position of a point source can be determined to < 10 nm.
- Point sources separated at ~10 nm apart can be distinguished in imaging if they do not light up at the same time.



Basic Principle of PLAM or STORM

Different random sets of photoswitchable dye molecules can be lighted up at different times



Plasmonics

Bulk plasmon

- Electron plasma effects are most pronounced in free-electron-like metals. The dielectric constant of such materials can be expressed as

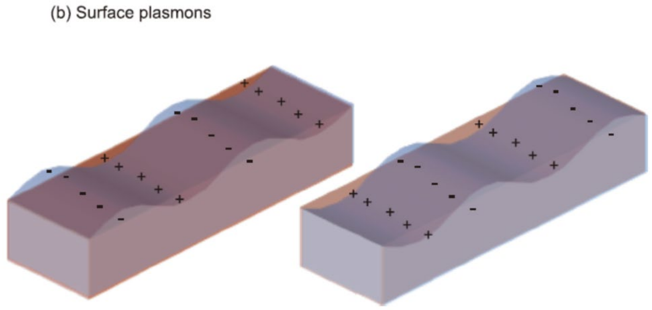
$$\varepsilon_1^D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2}$$

$$\varepsilon_2^D(\omega) = \frac{\omega_p^2 \Gamma}{\omega\,(\omega^2 + \Gamma^2)}$$

- A plasmon is the quantum of the collective excitation of free electrons in solids.

Surface plasmon

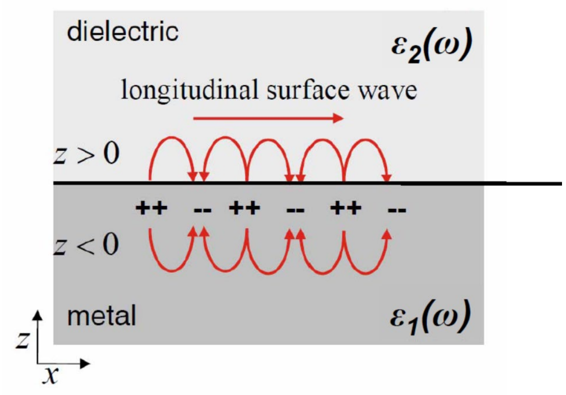
- (2D-confined) surface mode of plasmon



Surface plasmon polariton

- Polariton – any coupled oscillation of photons and dipoles in a medium

TM or p modes



$$E_{x,n}(x,y,z,t) = E_0 e^{ik_x x + ik_{z,n}|z| - i\omega t}$$

$$E_{z,n}(x,y,z,t) = \pm E_0 \frac{k_x}{k_{z,n}} e^{ik_x x + ik_{z,n}|z| - i\omega t}$$

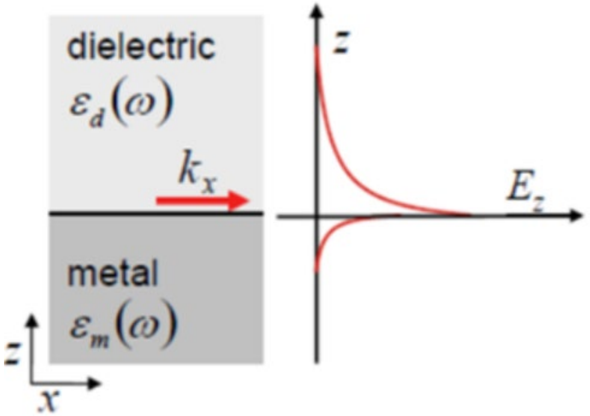
$$H_{y,n}(x,y,z,t) = H_0 e^{ik_x x + ik_{z,n}|z| - i\omega t}$$

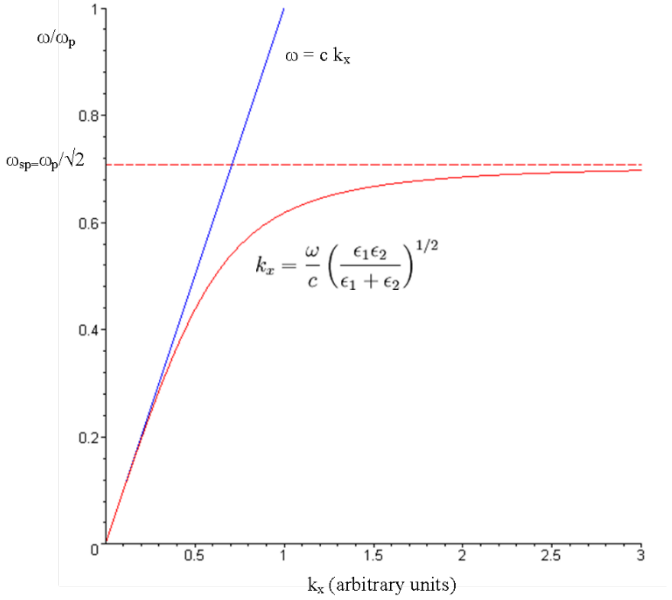
$$\frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0$$

and

$$k_x^2 + k_{zn}^2 = \varepsilon_n \left(\frac{\omega}{c}\right)^2 \qquad n = 1, 2$$

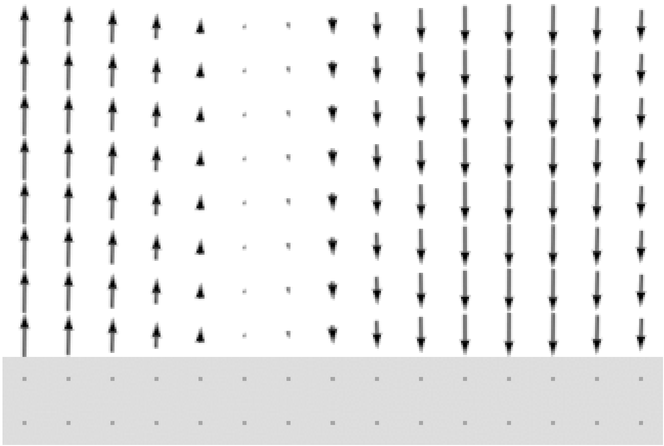
$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}.$$



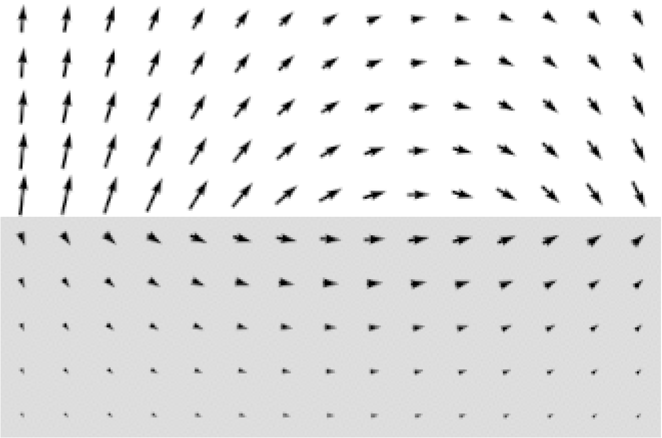


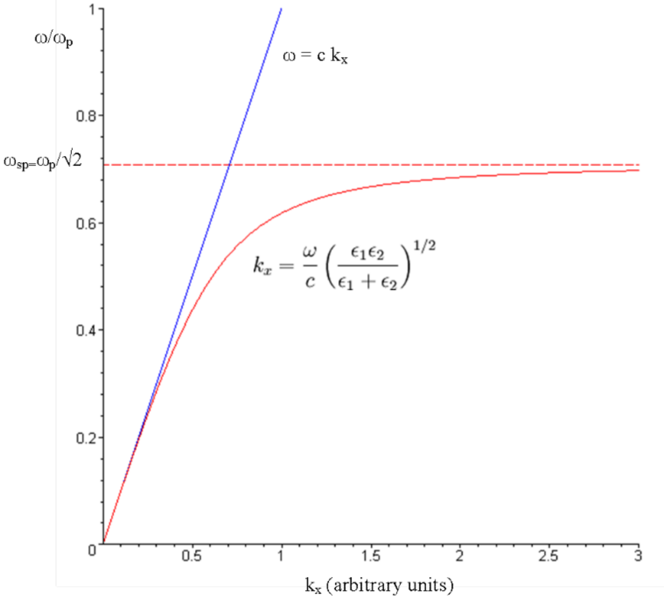
Surface plasmon polariton

E-field of an SPP at the silver-air interface, at wavelength of 10 μm



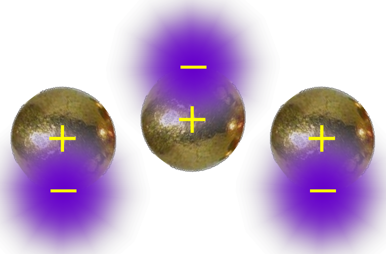
E-field of an SPP at the silver-air interface, at wavelength of 370 nm

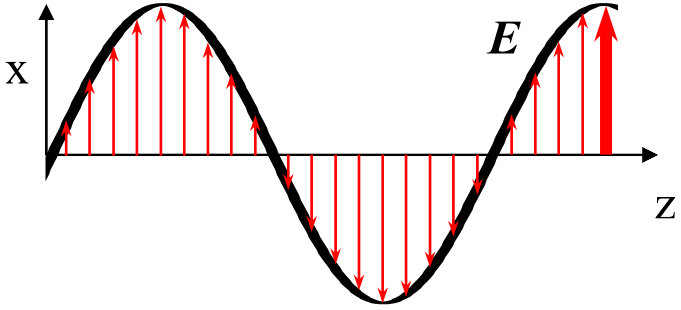




Optical response of a sphere

- The electrons oscillate in time around the fixed nuclei





$$E_x = E_0 \, \mathrm{e}^{-i\omega t}$$

- The particle behaves like an oscillating dipole, a polarisation appears

$$P_x = P_0 \, \mathrm{e}^{-i\omega t} \Longrightarrow P_0 = \varepsilon_0(\varepsilon - 1)E_{\mathrm{int}}$$

- E_{int} is the field inside the particle $E_{\mathrm{int}} = \frac{3}{\varepsilon + 2}E_0$ (constant in the quasi-static limit)

- Equivalent dipole $p = P_0 V_{sph\text{鎱}e} = 4\pi R^3 \varepsilon_0 \frac{\varepsilon - 1}{\varepsilon + 2} E_0 = \alpha E_0$ $\Longrightarrow$ $\alpha = 4\pi R^3 \varepsilon_0 \frac{\varepsilon - 1}{\varepsilon + 2}$

polarisability of the sphere

Metallic sphere (free electrons)

$$\alpha = 4\pi R^3 \varepsilon_0 \frac{\varepsilon - 1}{\varepsilon + 2}$$

- Drude dielectric function for a free electron gas in the visible range

$$\varepsilon^D(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \qquad (\Gamma << \omega)$$

- When $\omega_{SPR} = \frac{\omega_p}{\sqrt{3}}$, $\varepsilon^D(\omega_{SPR}) \approx -2$

→ Giant enhancement of $E_{\text{int}} = \frac{3}{\varepsilon + 2} E_0$

- The electric field inside the particle is more intense than the exciting field E_0
- Explanation: due to the small size of the object (dielectric confinement), the free electrons may oscillate in a coherent way over the whole particle
- The field enhancement at ω_{SPR} corresponds to the resonant and coherent excitation of all the conduction electrons
- By analogy with the plasma wave, considering that the excess charges are present at the surface only, such a phenomenon is called:

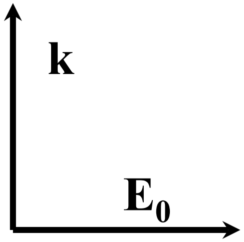
Local surface plasmon resonance

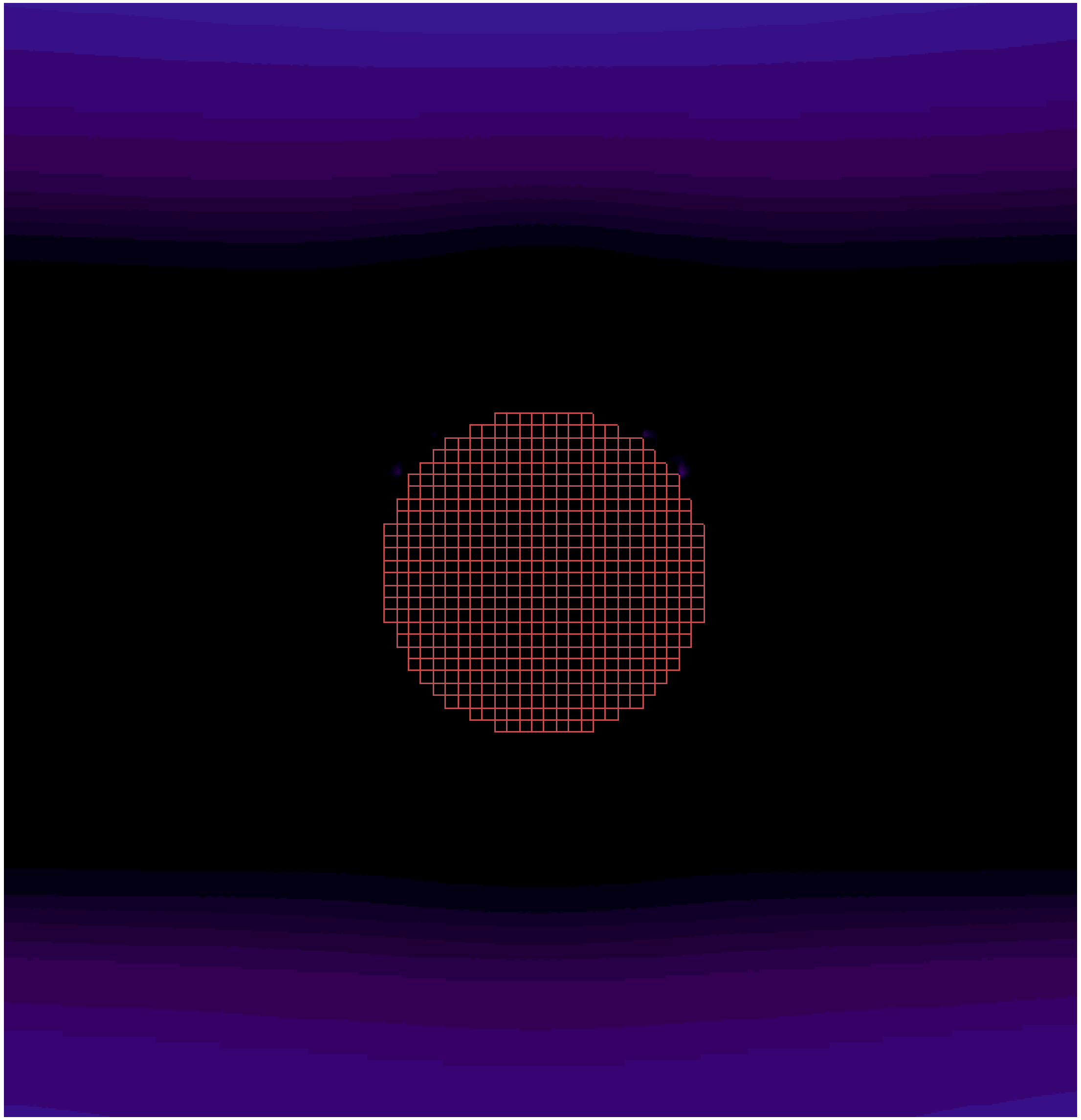
Simulation

Au

R=39 nm

Calculation: Finite Difference Time Domaine (FDTD)

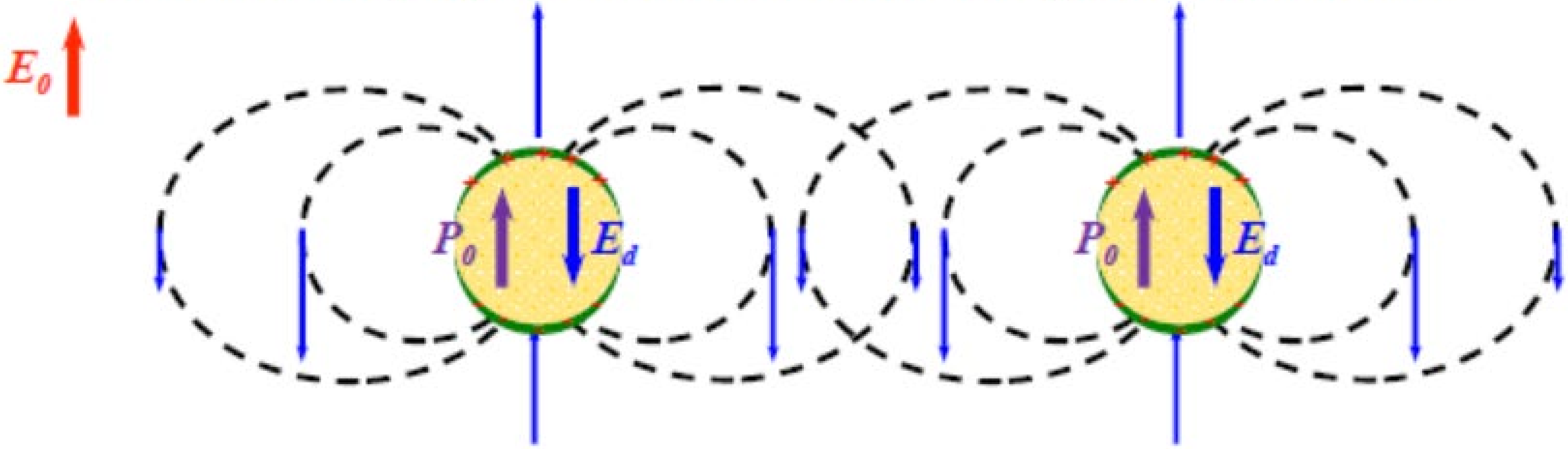




Intensity of light outside the Au sphere

Coupling between nanoparticles

- Transverse coupling when the distance between particles decreases



- The field created by one particle adds constructively to depolarization field inside the other particle
  - Added field remains weak as it is far from the surface charges
  - Restoring force increases (not much)
  - Oscillation frequency increases (not much)
  - Blueshift of the plasmon (small)
- The electric field between the particles increases (not much) when distance decreases
- Multipolar effects appear: the amplitude of SPR decreases (damping)

Reminder: quadrupole resonance is blueshifted

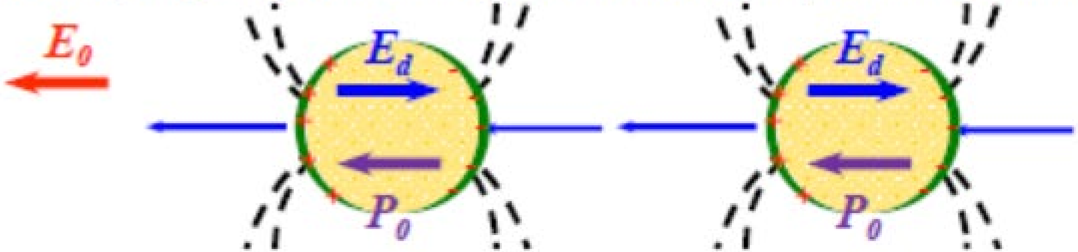
Reminder $\boxed{\omega_{SPR}^2 = \frac{K}{m}}$

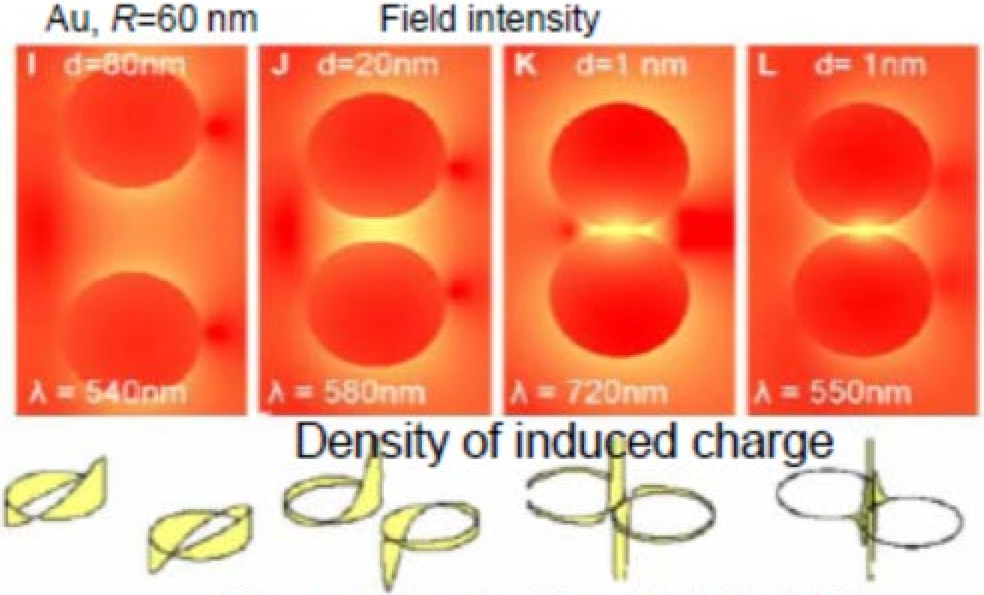
Force constant

Oscillation frequency

Coupling between nanoparticles

- Longitudinal coupling when the distance between particles decreases





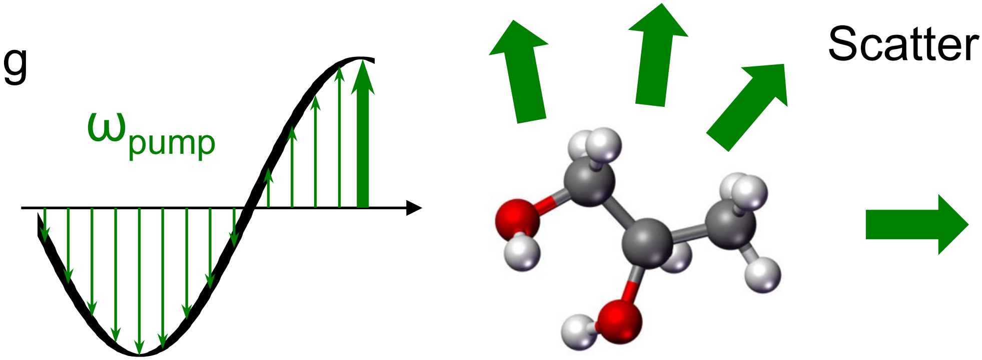
I. Romero *et al.*, *Opt. Expr.* **14**, 9994 (2006)

- The added field is opposite to the depolarization field
  - ➢ Force constant decreases ➡ redshift of the plasmon
  - ➢ Amplitude of charge oscillations increases ➡ enhancement of the plasmon resonance
  - ➢ Electric field between the particles increases for small distances ➡ electromagnetic hot spot

- Hot spots are the right place for enhanced molecular phenomena (SERS)

Surface enhanced Raman

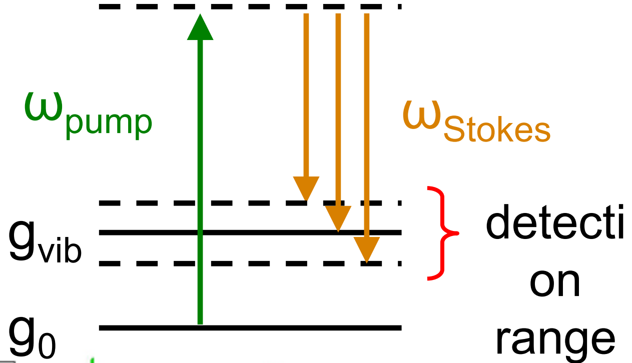
- Scattering



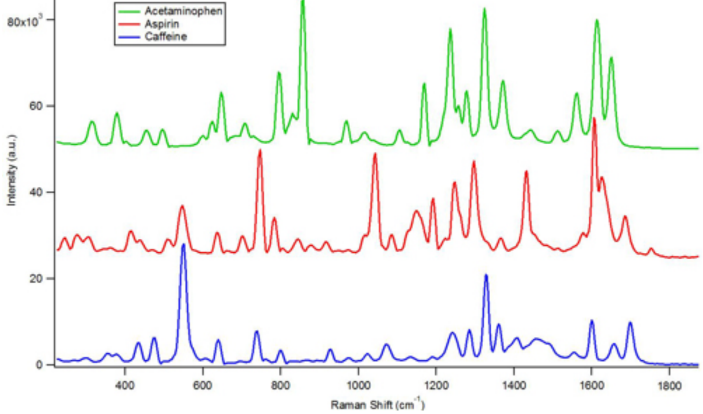
Scattering

Transmission (absorption)

- may be elastic (Rayleigh scattering)
- or inelastic (Stokes scattering)
  - ➡ some energy is kept by the molecule
- if this energy matches that of a vibration mode
  - ➡ the phenomenon is enhanced
  - ➡ Raman scattering



detection range



- Raman spectroscopy
  - one pump beam in the visible range
  - tuneable detection in the visible
  - vibrational spectrum
    - ➡ chemical identification

Examples of applications: SERS

- Raman intensity: $I_{Raman} \propto I_{pump}$

- Molecule near a plasmonic source (nano-object, rough surface)

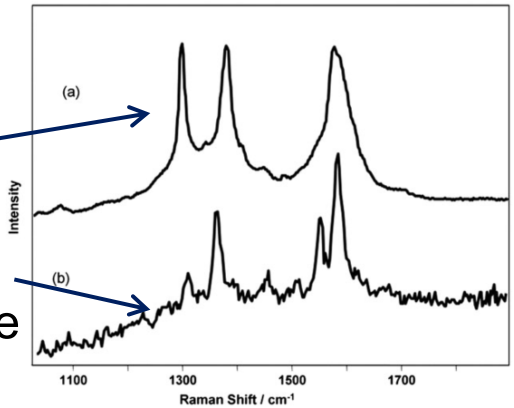
$$f(\omega) = \frac{E_{loc}}{E_{pump}} = \frac{local\ \ field}{applied\ \ field}$$ at frequency ω

$$E_{SERS} \propto f(\omega_{Stokes}) f(\omega_{pump}) E_{pump} \quad \Longrightarrow \quad I_{SERS} \propto f^2(\omega_{Stokes}) f^2(\omega_{pump}) I_{pump}$$

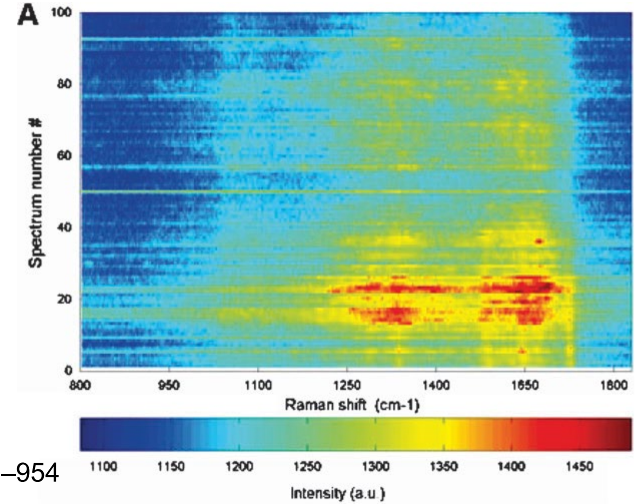
SERS enhancement factor ≈ f^4 ➡ For $f = 100$, $f^4 = 10^8$

- Reduction of detection threshold ➡ single molecule spectroscopy

Usual Raman spectrum differs from single molecule spectrum



N.P.W. Pieczonka, R.F. Aroca *Chem. Soc. Rev.* 37 (2008) 946–954



time

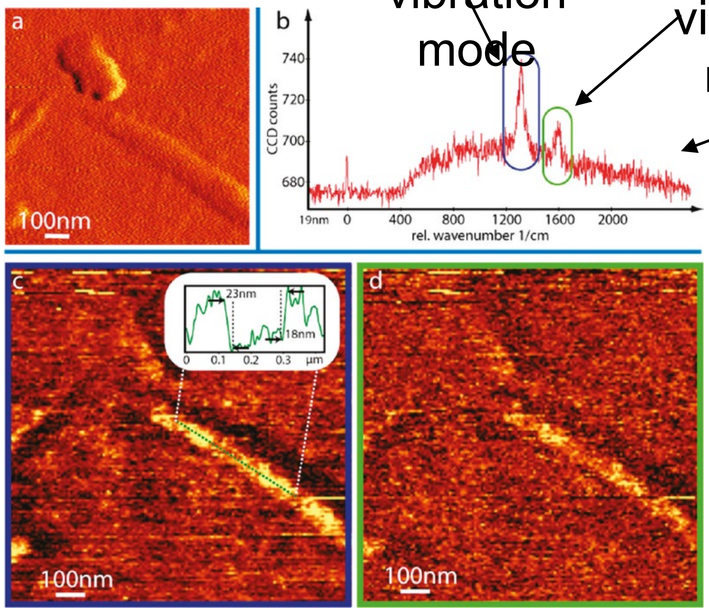
the molecule moves or even goes away

AR Bizzarri, S. Cannistraro *PCCP* 9 (2007) 5315–5319

Examples of applications: TERS

- Tip enhanced Raman scattering (TERS)
  - ➢ same as SERS, but molecules located between a sharp tip and a surface ➡ plasmonic effect
  - ➢ chemical imaging is possible
  - ➢ as with atomic force microscopy (AFM)

➡ TERS imaging of single carbon nanotubes



AFM image

D vibration mode

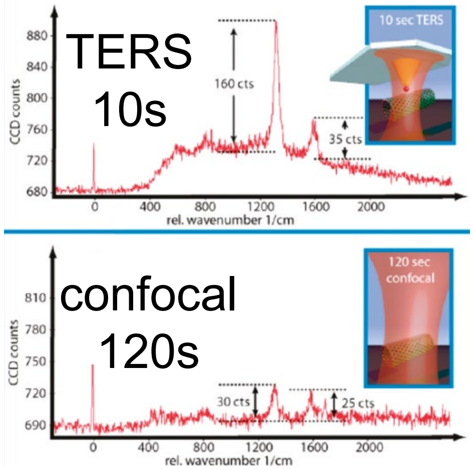
G vibration mode

one Raman spectrum per pixel

mapping of D-mode

mapping of G-mode

Enhancement factors



TERS 10s

confocal 120s

D-mode : 64
G-mode : 17

A.Weber-Bargioni et al.; *NanoLetters* 11 (2011) 1201-1207

Other examples of applications

- Surface-enhanced fluorescence
- Tip-enhanced fluorescence (TEF)

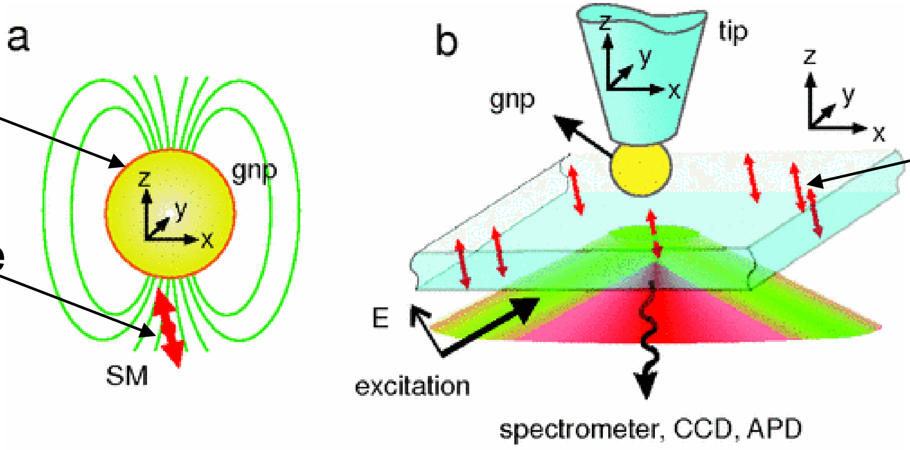
} sensitivity to single fluorescent molecule

- Sensing: molecular recognition ➡ plasmon shift
- Plasmon enhanced catalysis: chemical reactions driven by light

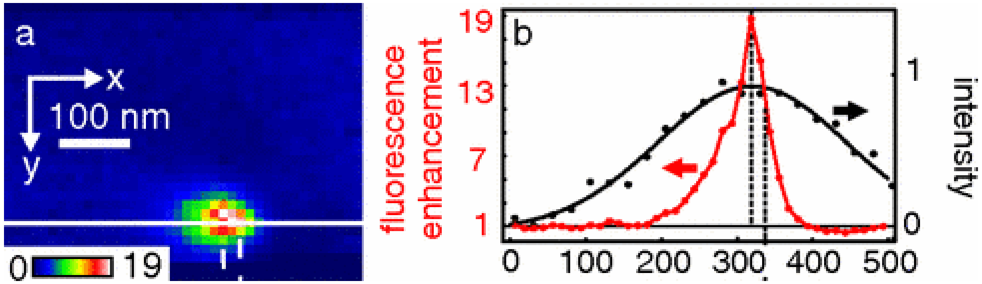
➡ TEF imaging of single fluorescent molecules

gold nanoparticle diameter 100nm

single molecule



single molecule



fluorescence image lateral displacement (nm)

🟥 tip-enhanced fluorescenc

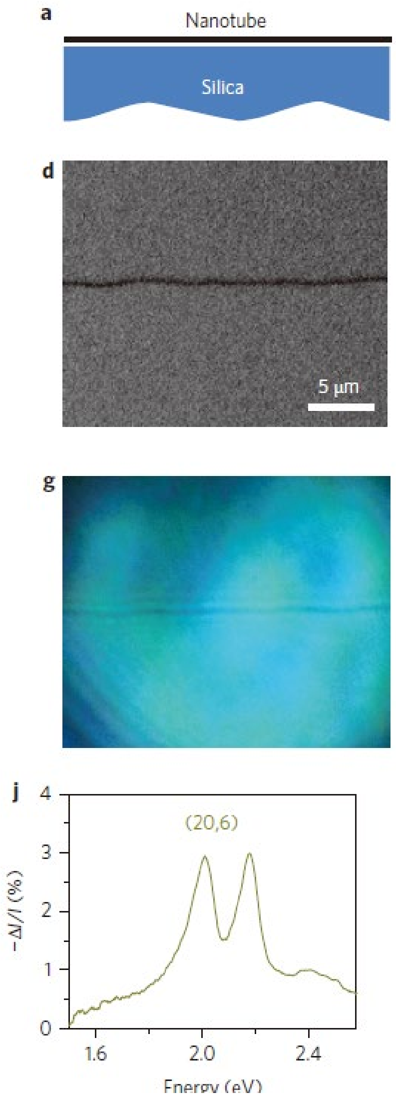
■ confocal fluorescence

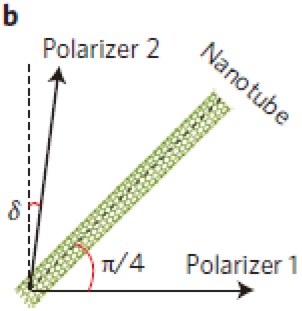
Enhancement factor: 19

S. Kühn et al.; *Phys. Rev. Lett.* 97 (2006) 017402

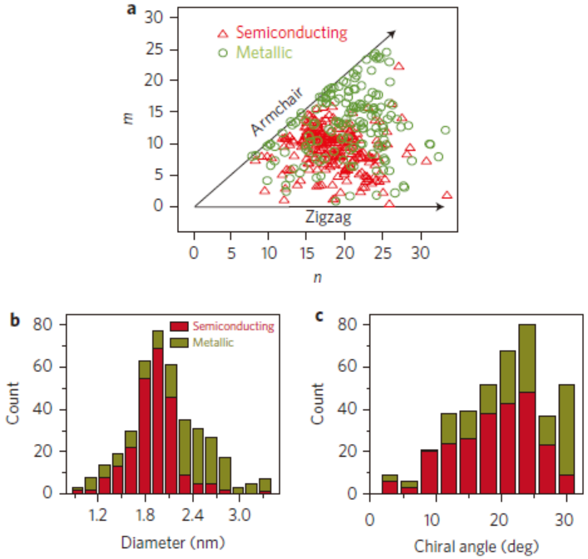
Low-dimensional Materials

Absorption-Reflection Spectrum of Single Carbon Nanotubes on a Substrate



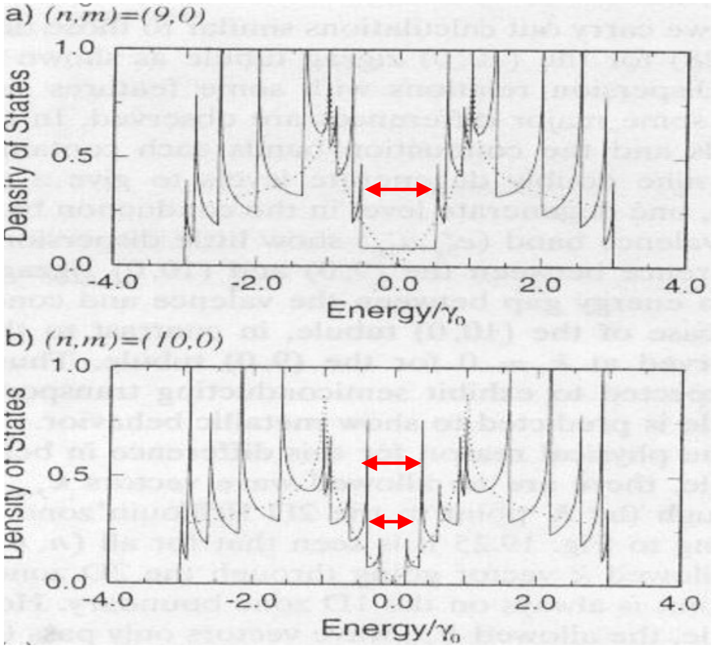


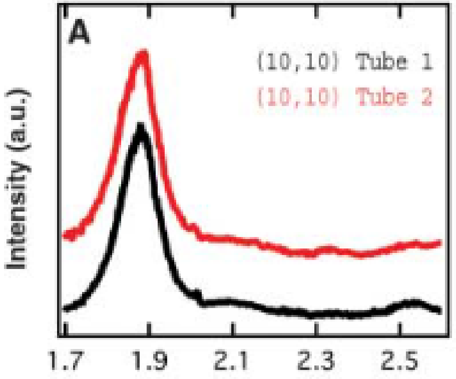
$$\frac{\Delta I}{I}=\frac{\left|E_{NT}+E_r\right|^2-\left|E_r\right|^2}{\left|E_r\right|^2}=\frac{2\,\mathrm{Re}(E_r E_{NT}^{\ *})}{\left|E_r\right|^2}$$



Nat. Nanotech. 8, 917 (2013)

Excitation Spectrum of Rayleigh Scattering of Suspended Single Carbon Nanotubes



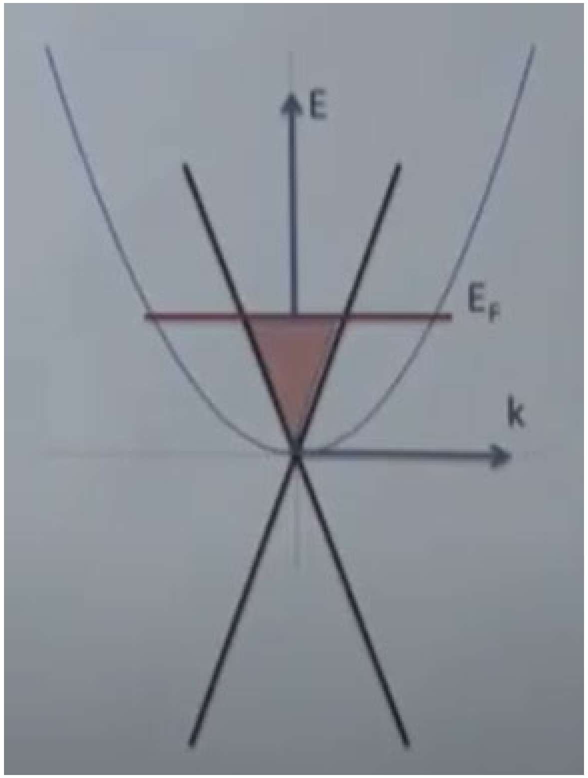


M. Y. Sfeir et. al., Science 306, 1540 (2004)

2D Plasmons in Graphene

Carrier density

$$n = \pm \frac{1}{\pi}\left(\frac{E_F}{\hbar v_F}\right)^2$$



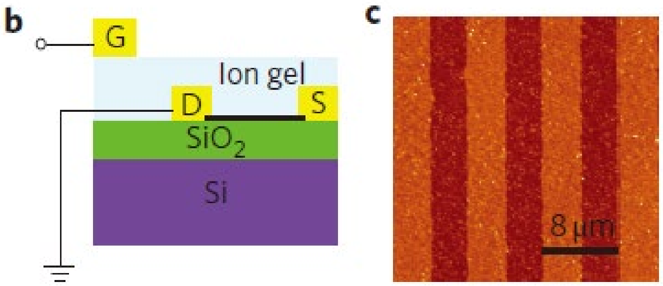
Drude conductivity

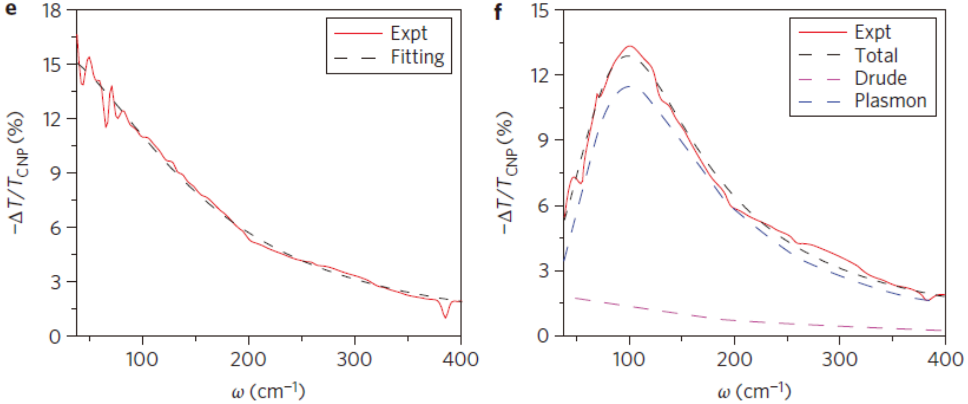
$$\sigma(\omega) = \frac{iD}{\omega + i\Gamma}, \qquad D = \frac{v_F e^2}{\sqrt{\pi} h}\sqrt{n}$$

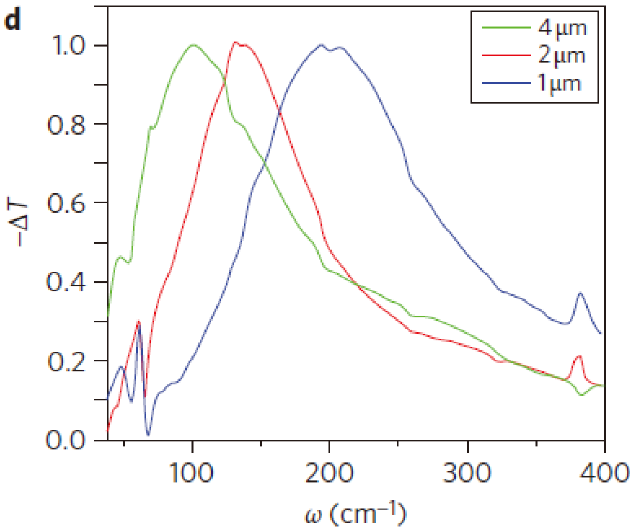
Plasma frequency

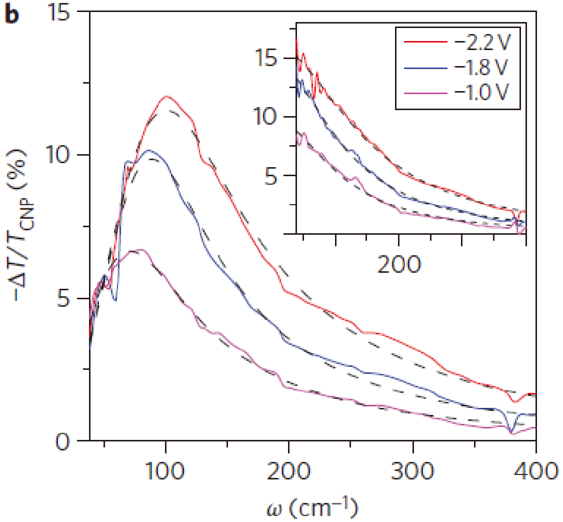
$$\omega_p^2(k) = \left(\frac{e^2}{h v_F}\right)\left(v_F^2 \sqrt{g\pi |n|}\right)k$$

2D Plasmons in Graphene





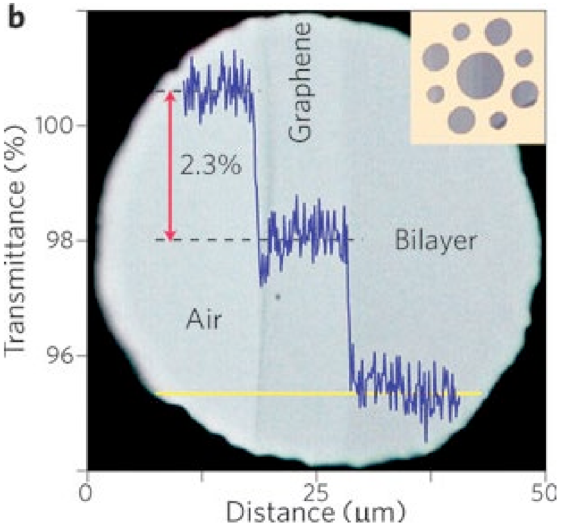




Nat. Nanotech. 6, 630 (2011)

Graphene as transparent conductor

Nature Photonics 4, 611 - 622 (2010)



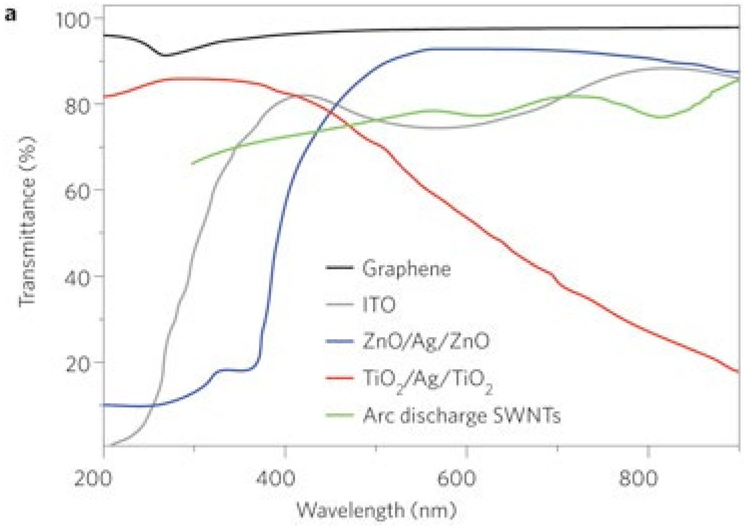
transmittance of a freestanding SLG

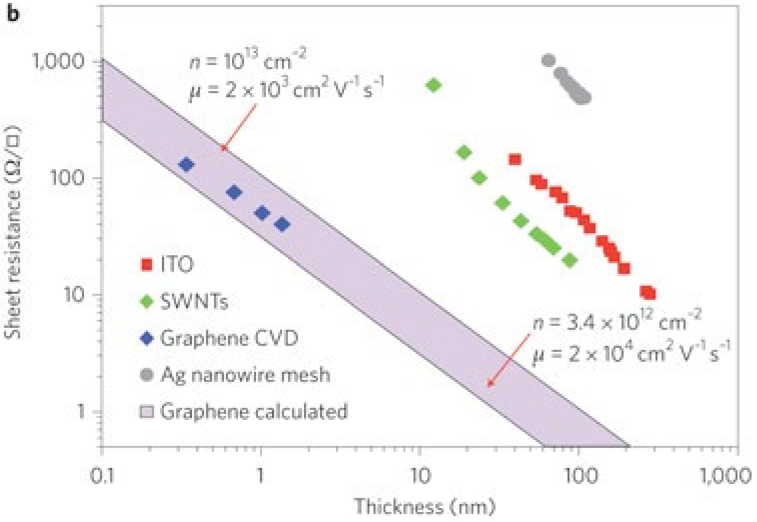
Fresnel equations in the thin-film limit

$$T = (1 + 0.5\pi\alpha)^{-2} \approx 1 - \pi\alpha \approx 97.7\%$$

$\alpha = e^2/(4\pi\varepsilon_0\hbar) \approx 1/137$ is the fine-structure constant

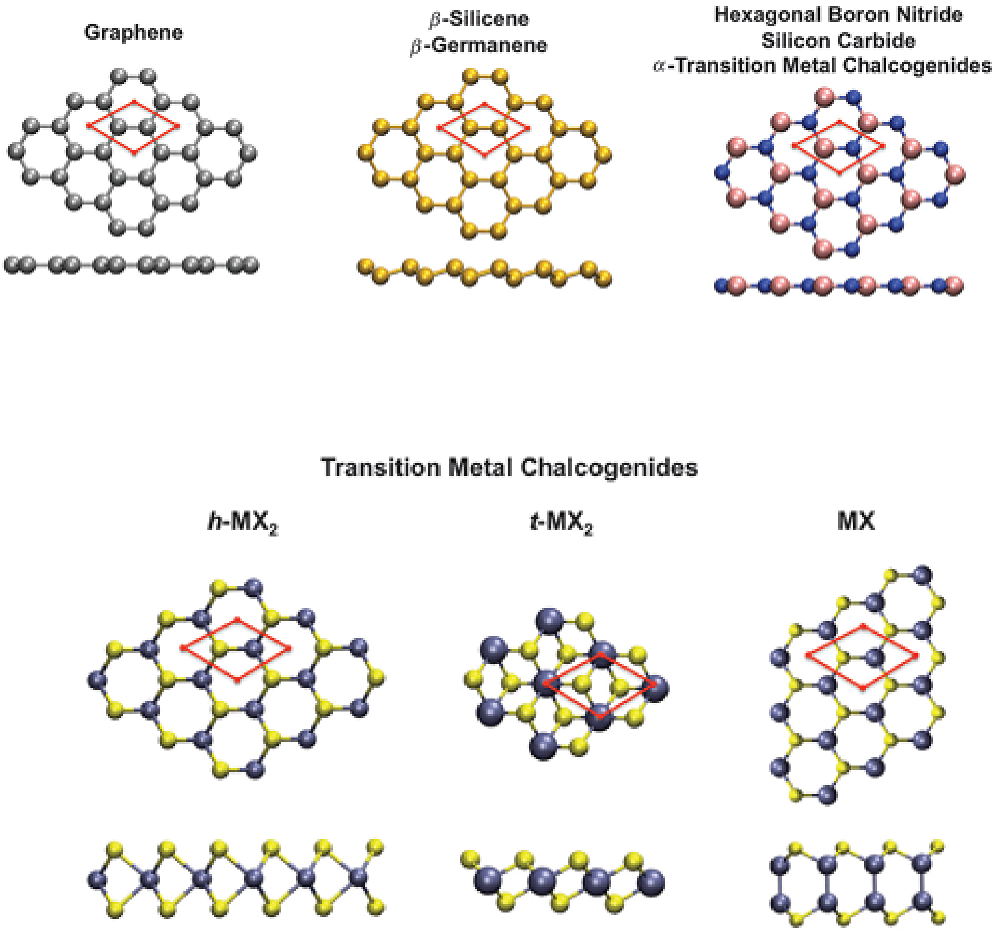
Science 320, 1308–1308

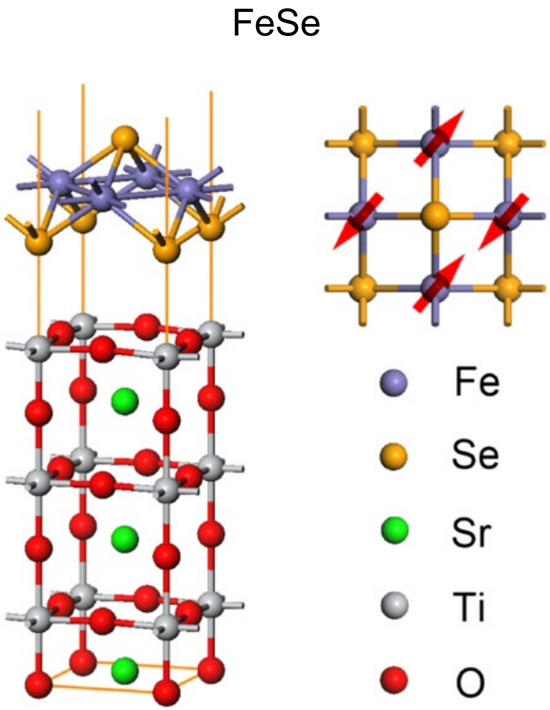




Possible applications: solar cells and light-emitting devices to touch screens, photodetectors and ultrafast lasers

2D Materials beyond Graphene





Electron-Electron and Electron-Hole Interactions in Quasi 1D or 2D systems

- Enhanced Coulomb interaction – reduced dimensionality/phase space
- Strange/strong spatial screening dependence.
- Subsrtate/environmental screening are important