Plasmonics: Application-oriented fabrication

Part 1. Introduction

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Alvar Aalto was a famous Finnish architect and designer

Outline

- Three parts of the tutorial
- Plasmonics in our life
- Optical properties of metals
- Surface plasmon polariton
- Localized surface plasmon

Content of the tutorial

- Part I.
  - Introduction to plasmonics
    - SPP
    - LSP
- Part II.
  - Nanofabrication and plasmonic devices
- Part III.
  - Most popular fabrication methods in plasmonics and correstponding applications

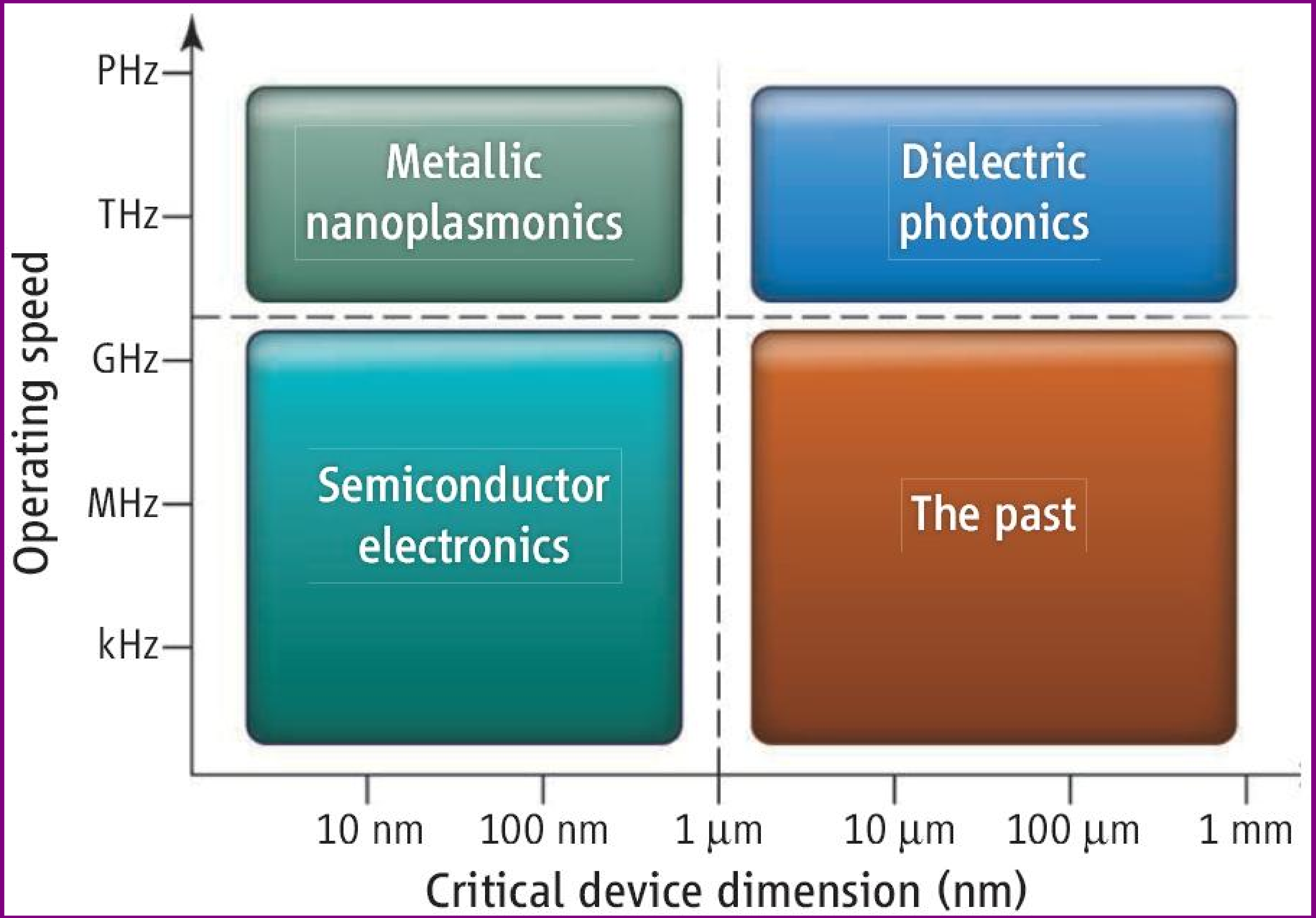
Plasmonics (Plasmon photonics, plasmon optics)

- Near-field optical microscopy
- Biosensing (enhanced fluorescence, SERS)
- Computer chips (plasmonic waveguides)
- Perfect lens (negative index of refraction)
- Light trapping (photovoltaics)
- Heating (welding, thermal cancer treatment)

Reasons of plasmonic boom

- Development of nanofabrication
- Development of optical characterization
- Development of simulation power
- Appearence of applications

Materials:
application domens



M. L. Brongersma, and V. Shalaef, Science,328, 440–441 (2010)

Relative permittivity ε (dielectric function)

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For dielectrics: real numbers $(\varepsilon_d = \varepsilon_1)$

ε_d:

Material	ϵ	E_g (eV)
SiO_2	3.9	9.0
Si_3N_4	7	5.3
Al_2O_3	9	8.8
La_2O_3	30	6.0
Y_2O_3	15	6.0
ZrO_2	25	5.8
Ta_2O_5	22	4.4
HfO_2	25	5.8
$HfSiO_4$	11	6.5

For metals: contains real and imaginary parts

ε_{m2}:

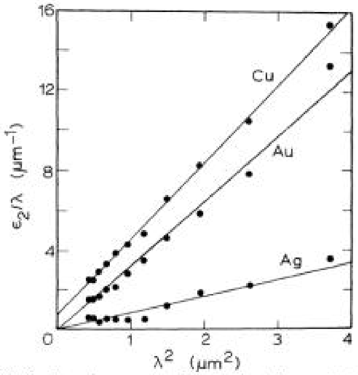


FIG. 6. Imaginary part of the dielectric constants for copper, silver, and gold, divided by wavelength vs the square of the wavelength.

$(\varepsilon_m = \varepsilon_{m1} + i\varepsilon_{m2})$

ε_{m1}:

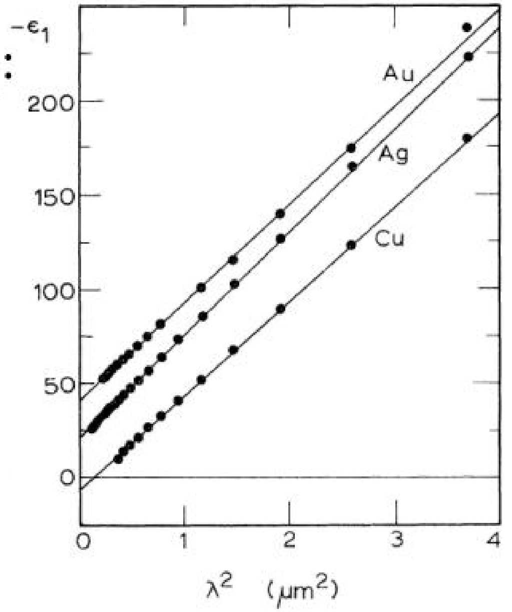
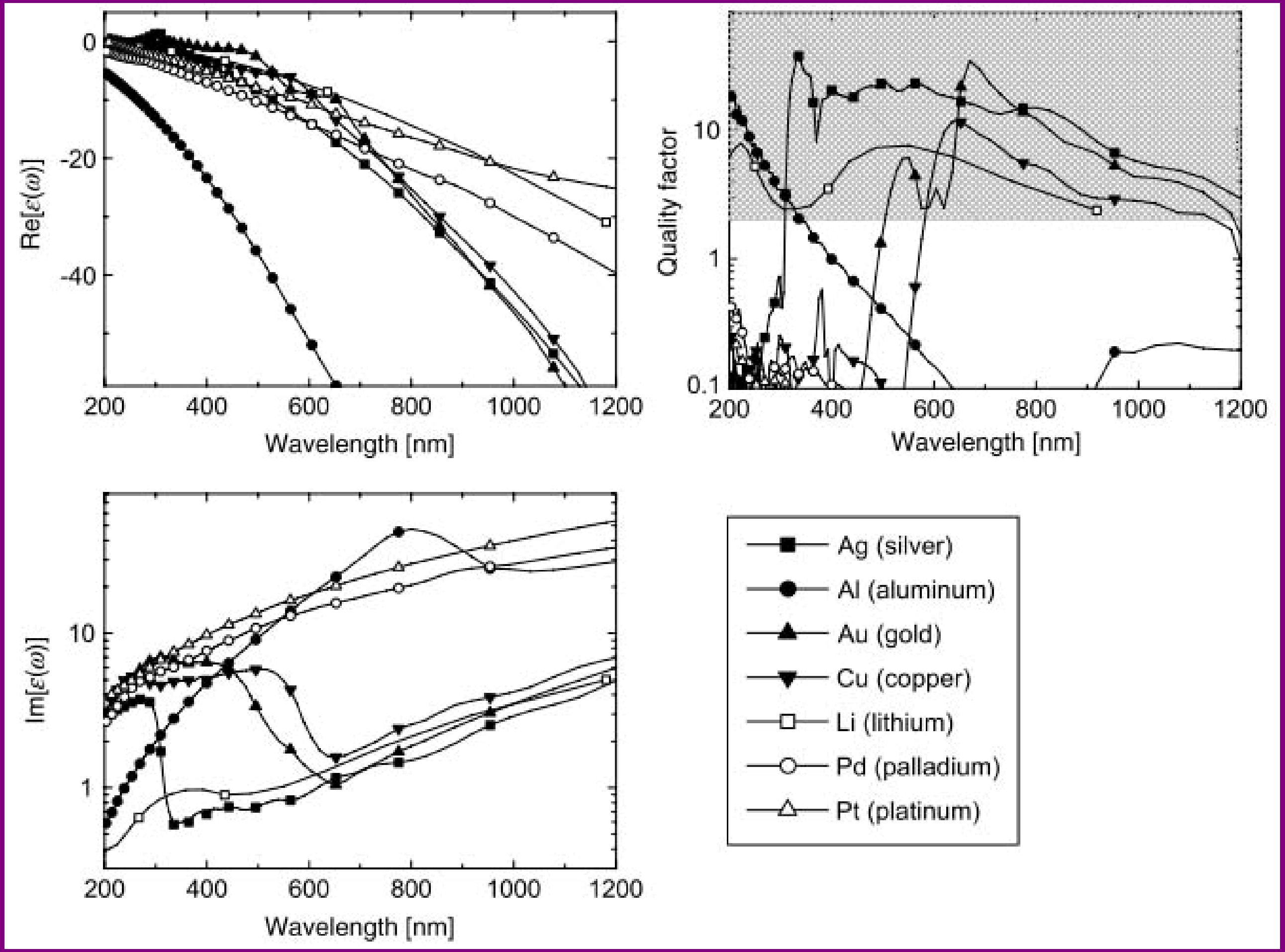


FIG. 5. Negative of the real part of the dielectric constants for copper, silver, and gold vs the square of the wavelength. The zeros in $-\epsilon_1$ for silver and gold are offset by 25 and 50, respectively.

Phys. Rev. B 6, 4370–4379 (1972)

Optical properties of metals



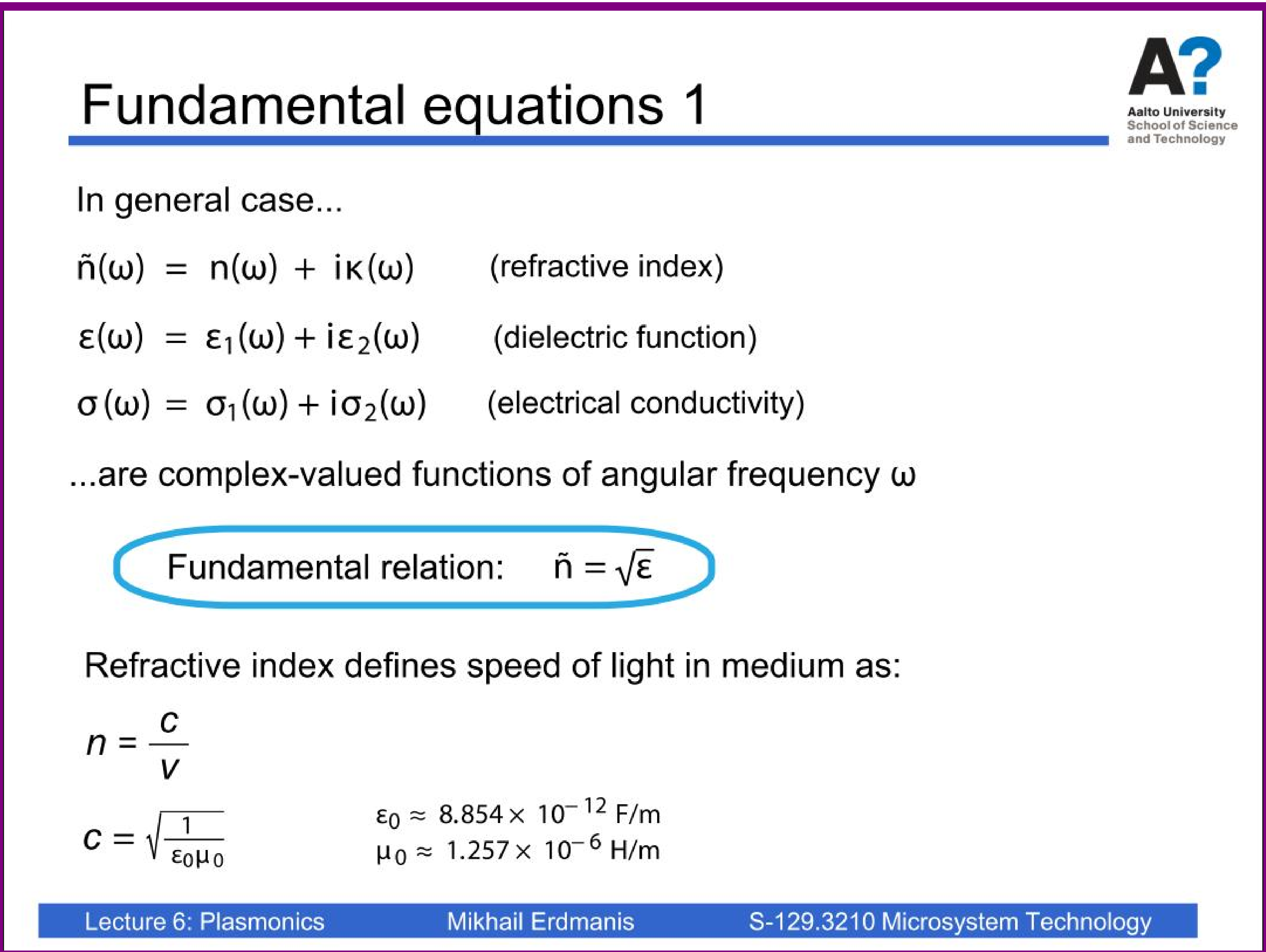
$$Q = \frac{\omega(d\varepsilon'/d\omega)}{2(\varepsilon''(\omega))^2}$$

$\varepsilon' = \mathrm{Re}(\varepsilon)$,
$\varepsilon'' = \mathrm{Im}(\varepsilon)$

$\mathrm{Re}(\varepsilon) = -20...-1$
$\mathrm{Im}(\varepsilon)$ is small
$Q>2$
$\omega < \omega_p$

E. D. Palik, editor. Handbook of optical constants of solids III. Academic Press, New York, 1998.

E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009



Fundamental equations 1

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In general case...

$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$ (refractive index)

$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ (dielectric function)

$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ (electrical conductivity)

...are complex-valued functions of angular frequency ω

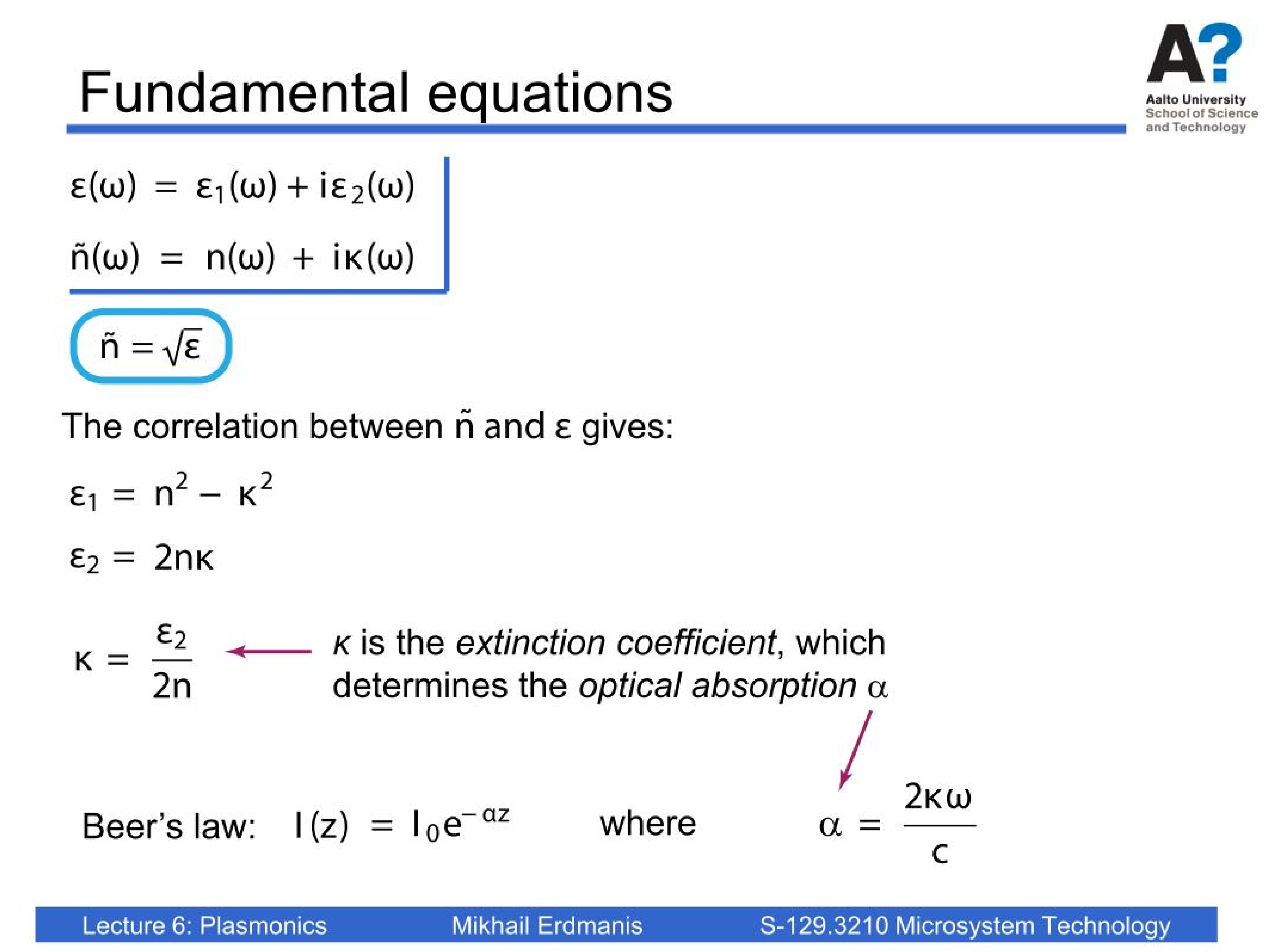
Fundamental relation: $\tilde{n} = \sqrt{\varepsilon}$

Refractive index defines speed of light in medium as:

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

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

$\varepsilon_0 \approx 8.854 \times 10^{-12}$ F/m
$\mu_0 \approx 1.257 \times 10^{-6}$ H/m



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Fundamental equations

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$

$$\boxed{\tilde{n} = \sqrt{\varepsilon}}$$

The correlation between ñ and ε gives:

$$\varepsilon_1 = n^2 - \kappa^2$$

$$\varepsilon_2 = 2n\kappa$$

$$\kappa = \frac{\varepsilon_2}{2n}$$

κ is the *extinction coefficient*, which determines the *optical absorption* α

Beer's law: $I(z) = I_0 e^{-\alpha z}$ where $\alpha = \frac{2\kappa\omega}{c}$

Deilectric function of metals

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{{\omega_p}^2}{\omega^2 + i\gamma_0\omega}\right)$$

Drude model, no inter-band transition

γ_0 - damping term

ε_∞ - optical response of the positive ions

$$\varepsilon_\infty \geq 1$$

ω_p - plasma frequency

$$\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_0\varepsilon_\infty}}$$

n, m - concentration of free electrons

m - effective mass of electron

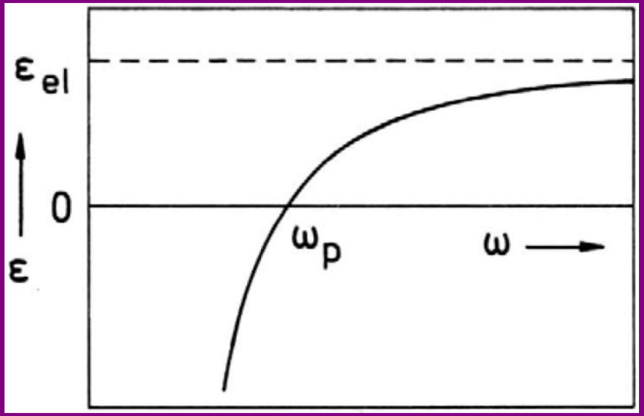
e - charge of electron

ε_0 - vacuum permittivity

γ_0 =1/τ, τ - collision time, γ_0 is about 100 THz

K_0 – free-space wave-vector

L_{2z} = 1/(2Im(k_{2z}) - penetration depth

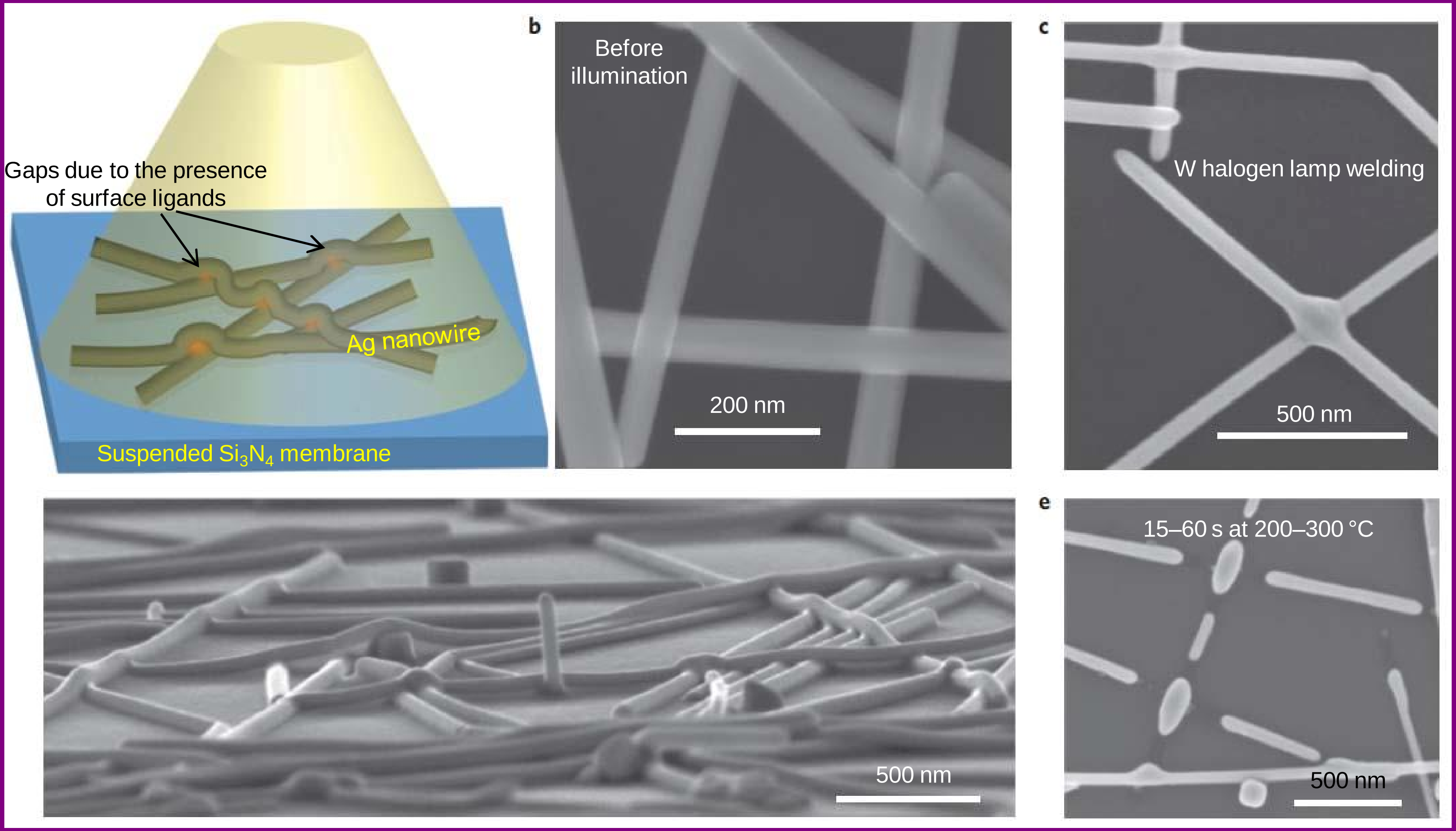


E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009.

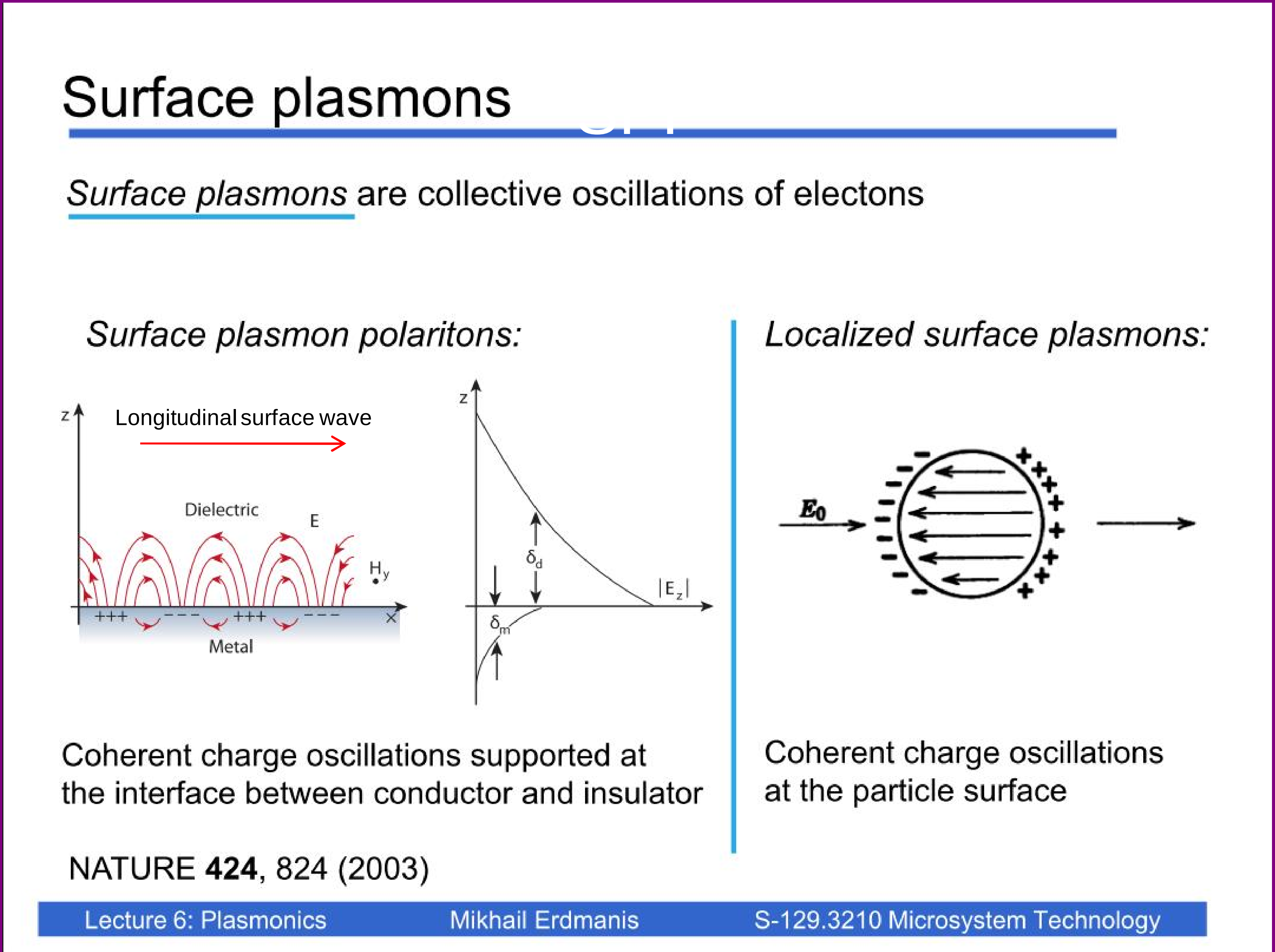
Metals vs. dielectrics

- Metals exhibit absorption of light due to nonzero imaginary part $\varepsilon''(\omega)$
- Electromagnetic fields fall off inside the metal as: $e^{-z/\delta}$, where δ is the skin depth
- Strong frequency dependence of dielectric function $\varepsilon(\omega)$

Plasmonic welding



E. C. Garnett, Nature Materials 11, 241–249 (2012)



Surface plasmons

Surface plasmons are collective oscillations of electons

Surface plasmon polaritons:

Localized surface plasmons:

Coherent charge oscillations supported at the interface between conductor and insulator

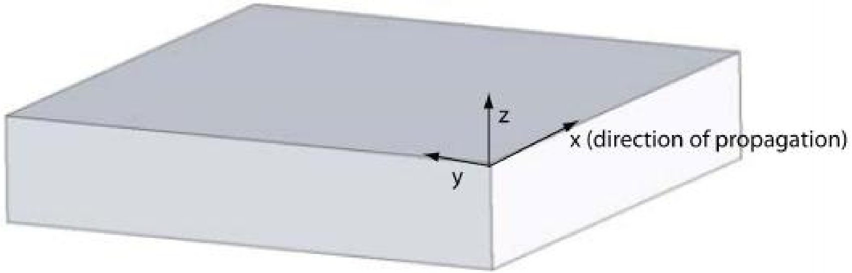
Coherent charge oscillations at the particle surface

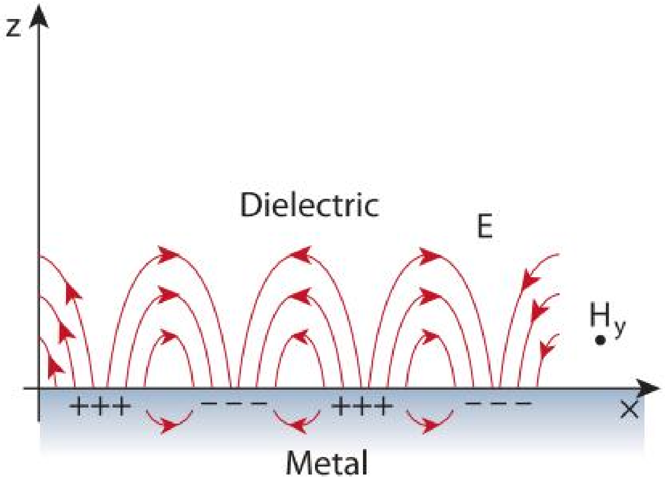
NATURE **424**, 824 (2003)

Lecture 6: Plasmonics Mikhail Erdmanis S-129.3210 Microsystem Technology

Surface plasmon polaritons

Surface plasmon polaritons exist at the interface between metal and insulator only for TM polarization (Electric field vector being perpendicular to the surface)

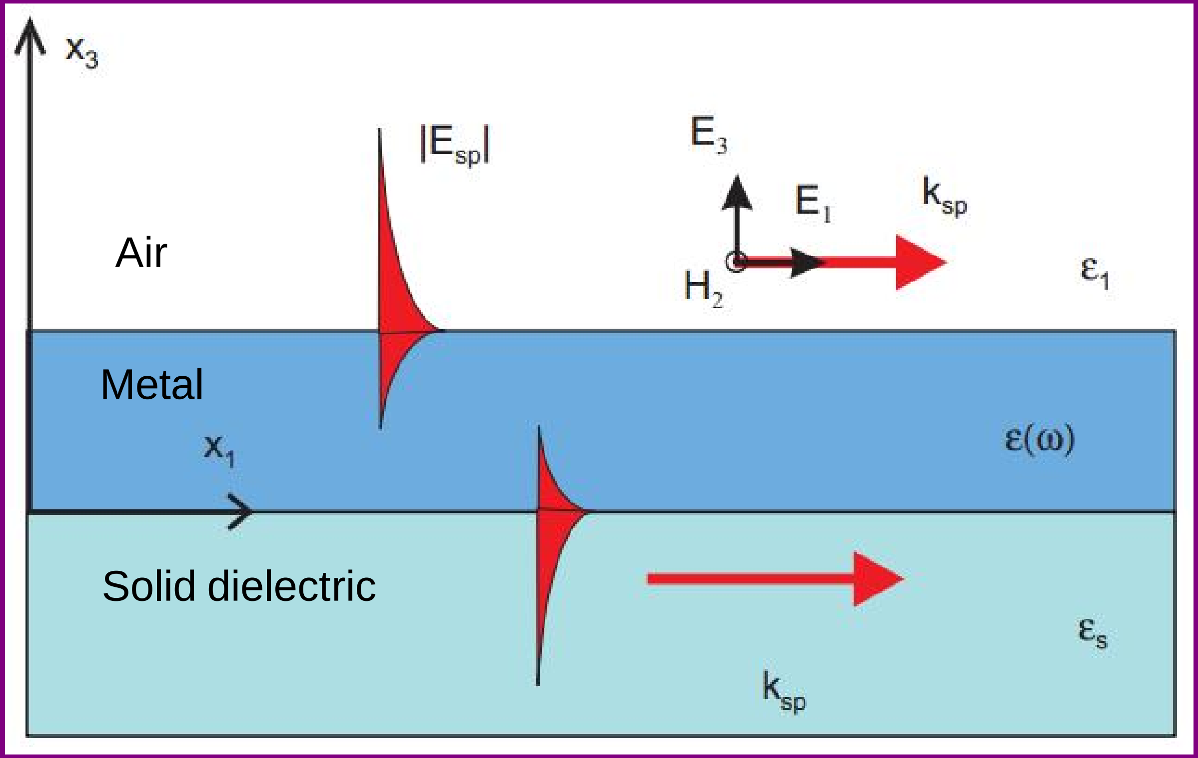




Only E_z and E_x field components, but not E_y!

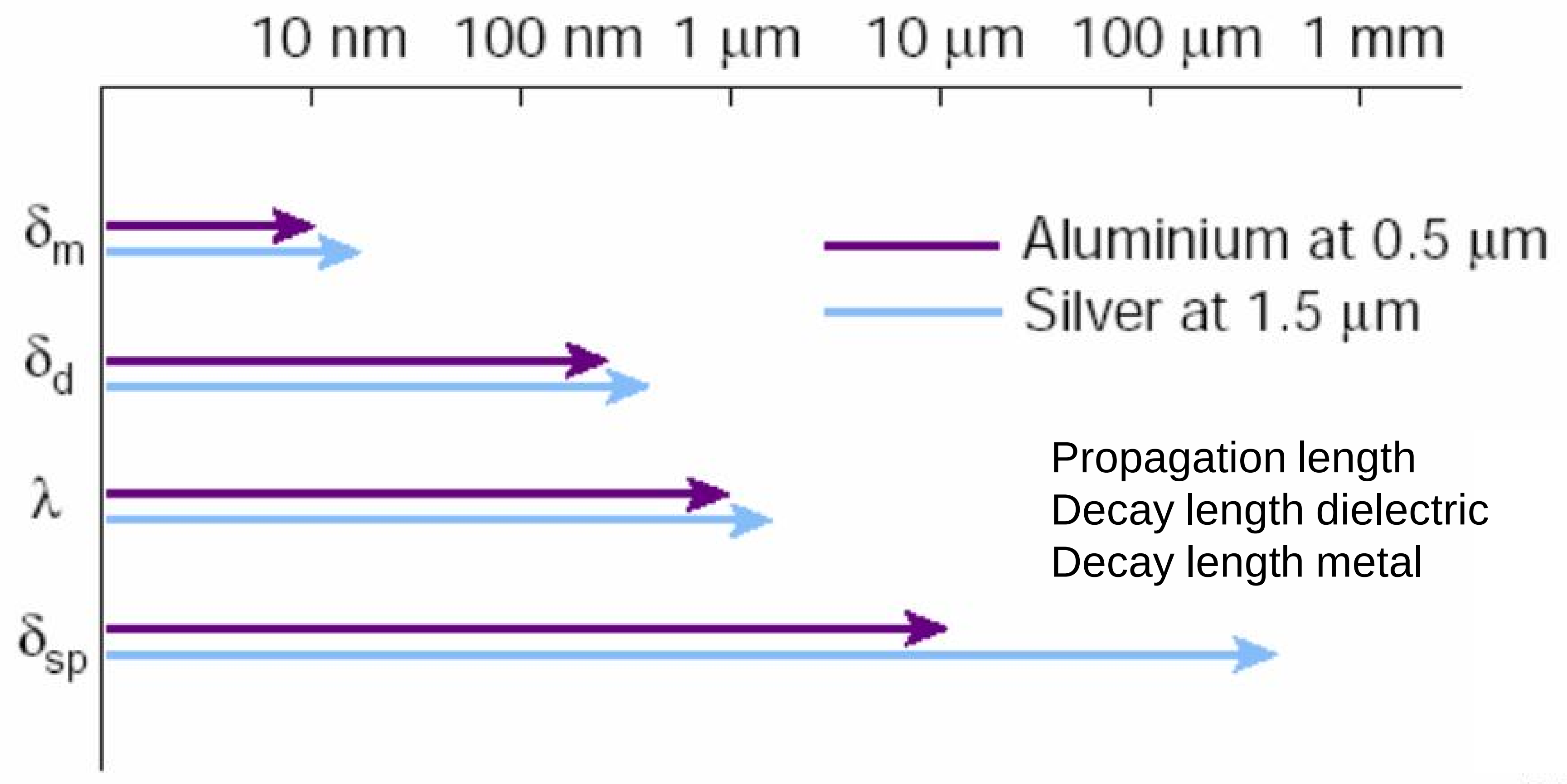
S.A. Maier, Plasmonics: Fundamentals and Applications (2007)

Propagation of SPP



- Propagation length
- Skin depth
- Examples

SPP length scales



Propagation length
Decay length dielectric
Decay length metal

W.L.Barnes et. al., Nature 424, 825 (2003)

Plasmon and polariton

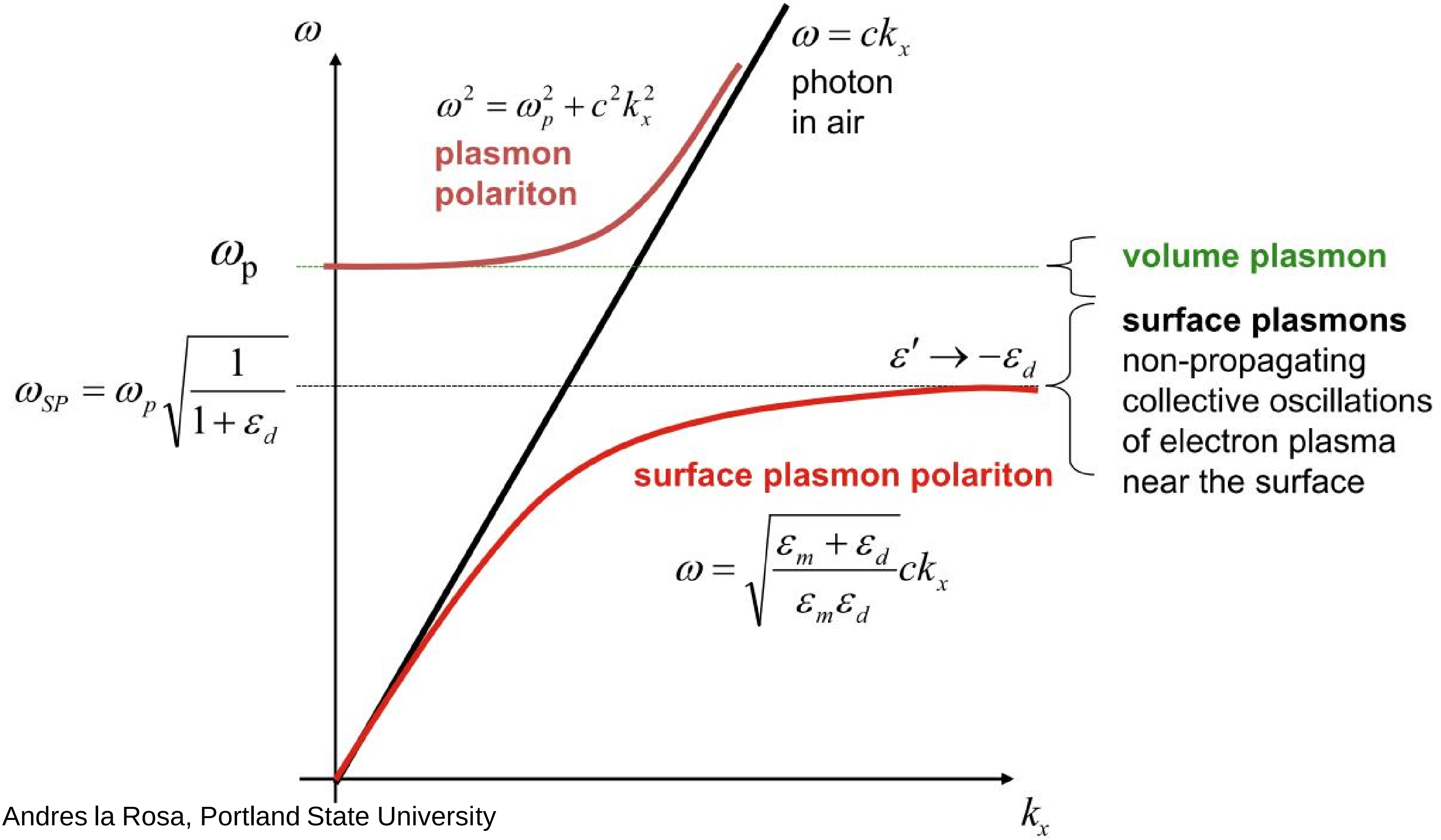
Plasmon is a quantum quasi-particle (γ >0) repersenting the elementary excitations, or modes of charge density oscillations in a plasma

The optical response of a metal is dominated by the interaction of light with free electron plasma and the resulted electromagnetic wave is called plasmon-polariton (mixed photon-plasmon mode)

Radiative (outgoing wave is propagating) vs. non-radiative (the outgoing wave is evanescent)

Propagating (k is real) vs localized (all modes are evanescent)

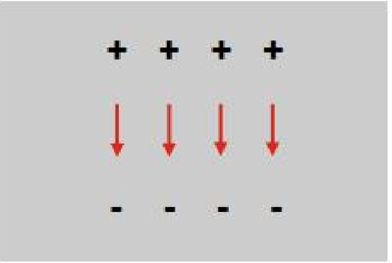
Dispersion relation of SPPs



Andres la Rosa, Portland State University

Plasmon resonance positions in vacuum

Bulk metal



ω_p

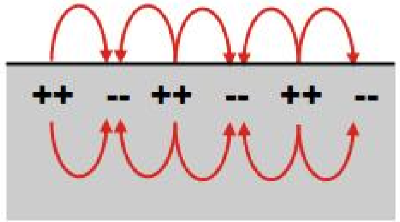
$\varepsilon = 0$

Drude model

$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2}$$

ω_p- highest frequency for plasmonic applications

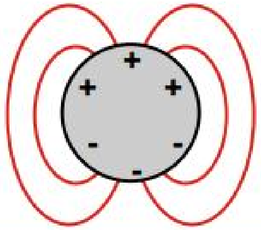
Metal surface



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

drude model

Metal sphere
localized SPPs

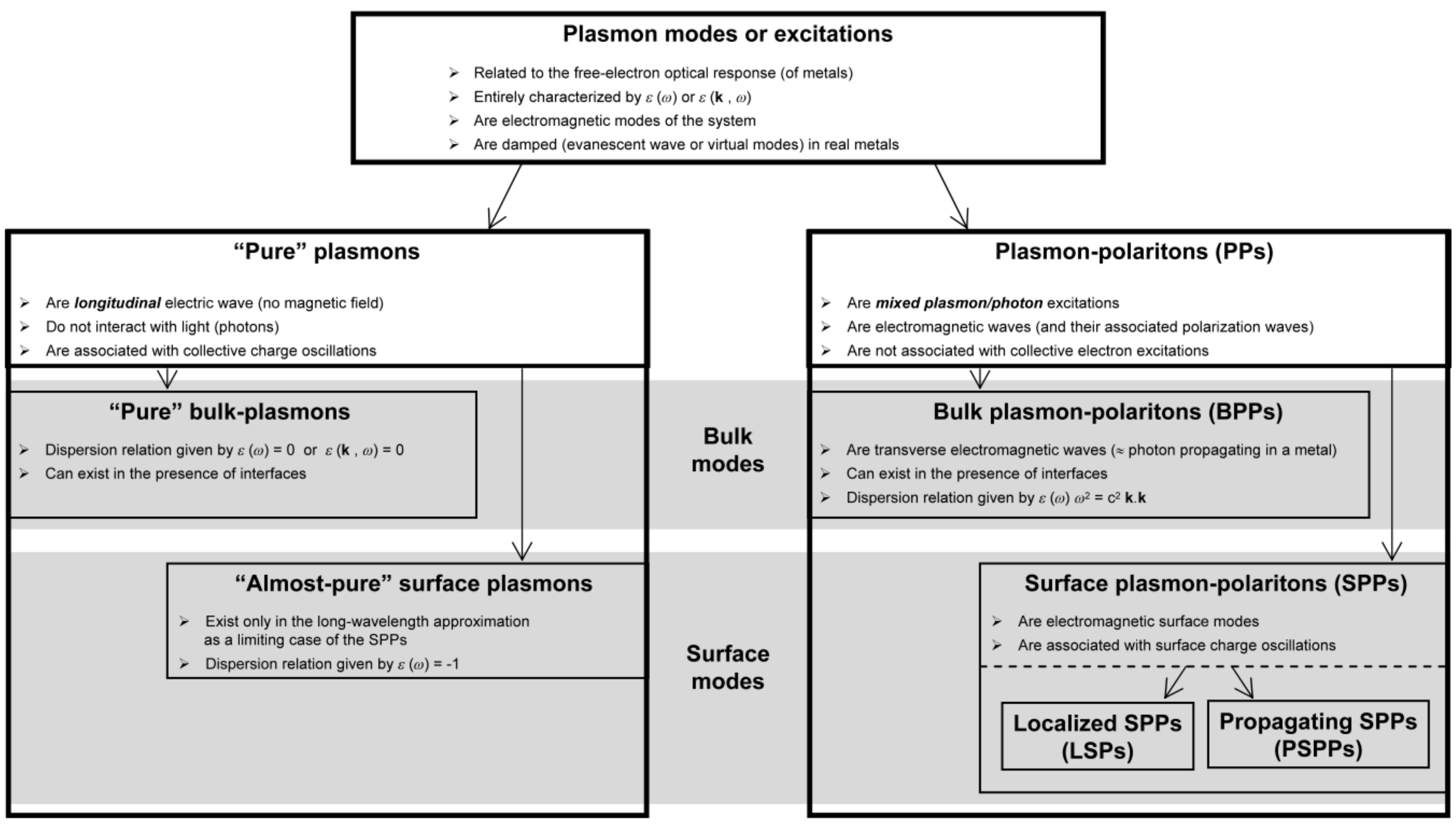


$\varepsilon = -2 \xrightarrow{} \omega_p / \sqrt{3}$

drude model

Plasmon types and properties

E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009



Plasmon modes or excitations

- Related to the free-electron optical response (of metals)
- Entirely characterized by $\varepsilon(\omega)$ or $\varepsilon(\mathbf{k},\omega)$
- Are electromagnetic modes of the system
- Are damped (evanescent wave or virtual modes) in real metals

"Pure" plasmons

- Are ***longitudinal*** electric wave (no magnetic field)
- Do not interact with light (photons)
- Are associated with collective charge oscillations

Plasmon-polaritons (PPs)

- Are ***mixed plasmon/photon*** excitations
- Are electromagnetic waves (and their associated polarization waves)
- Are not associated with collective electron excitations

Bulk modes

"Pure" bulk-plasmons

- Dispersion relation given by $\varepsilon(\omega) = 0$ or $\varepsilon(\mathbf{k},\omega) = 0$
- Can exist in the presence of interfaces

Bulk plasmon-polaritons (BPPs)

- Are transverse electromagnetic waves (≈ photon propagating in a metal)
- Can exist in the presence of interfaces
- Dispersion relation given by $\varepsilon(\omega)\,\omega^2 = c^2\,\mathbf{k}.\mathbf{k}$

Surface modes

"Almost-pure" surface plasmons

- Exist only in the long-wavelength approximation as a limiting case of the SPPs
- Dispersion relation given by $\varepsilon(\omega) = -1$

Surface plasmon-polaritons (SPPs)

- Are electromagnetic surface modes
- Are associated with surface charge oscillations

Localized SPPs (LSPs)

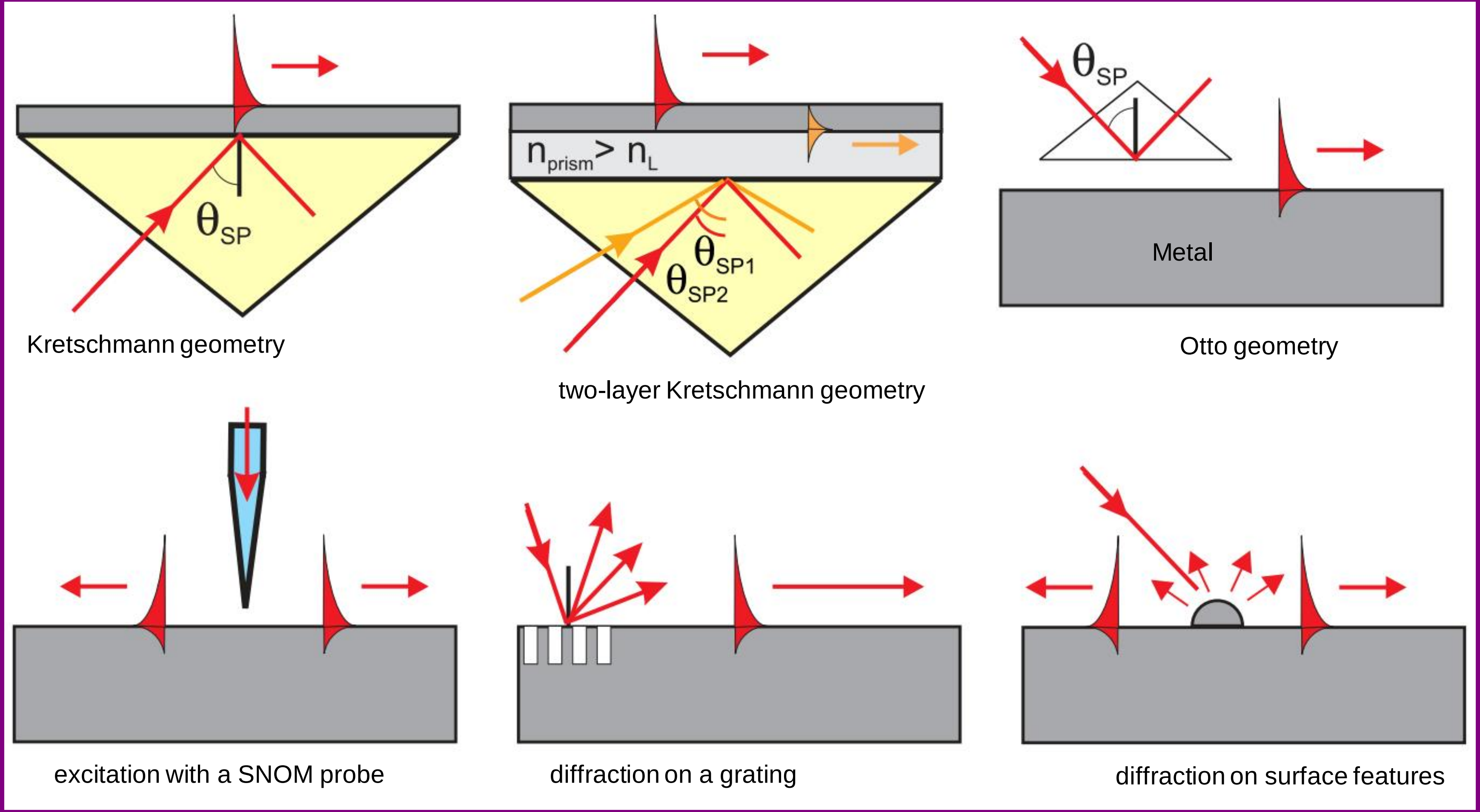
Propagating SPPs (PSPPs)

Excitation of SPP

- Optical prism
- Coupling gratings
- Optical fiber or cantilever tip
- High energy electron beam
- Highly focused optical beams

SPP excitation configurations

A.V. Zayats et al. / Physics Reports 408 (2005) 131–314



Kretschmann geometry

two-layer Kretschmann geometry

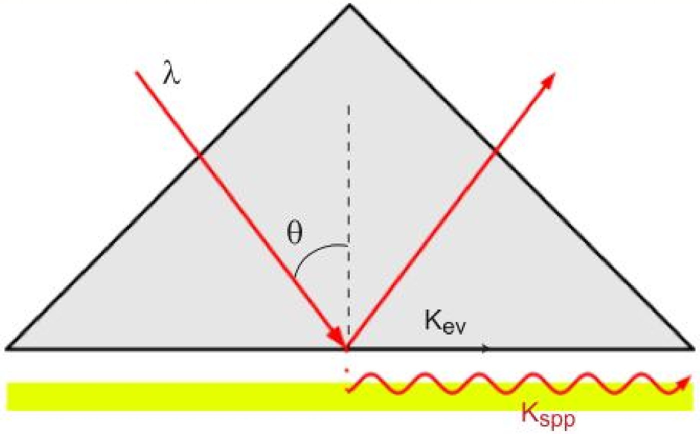
Otto geometry

excitation with a SNOM probe

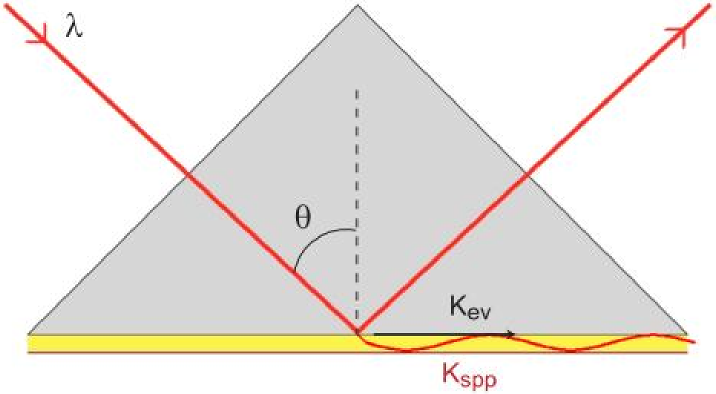
diffraction on a grating

diffraction on surface features

Excitation via optical prism



Otto configuration



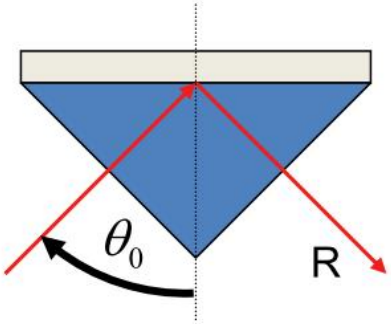
Kretschmann configuration

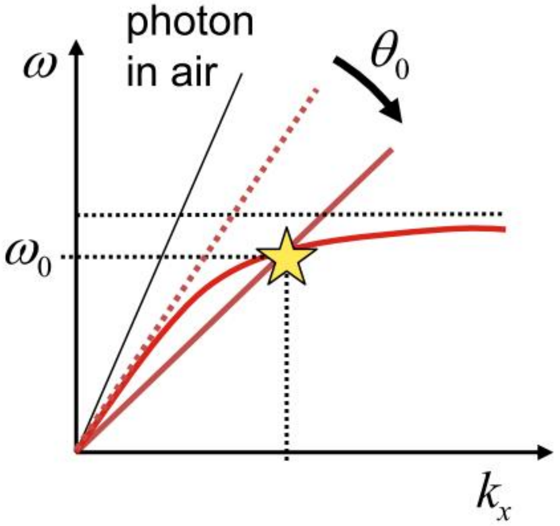
For both schemes factors affecting the excitation are:

- Dielectric functions of metal and prism
- Wavelength of incoming light (dispersion of ε)
- Angle of incidence

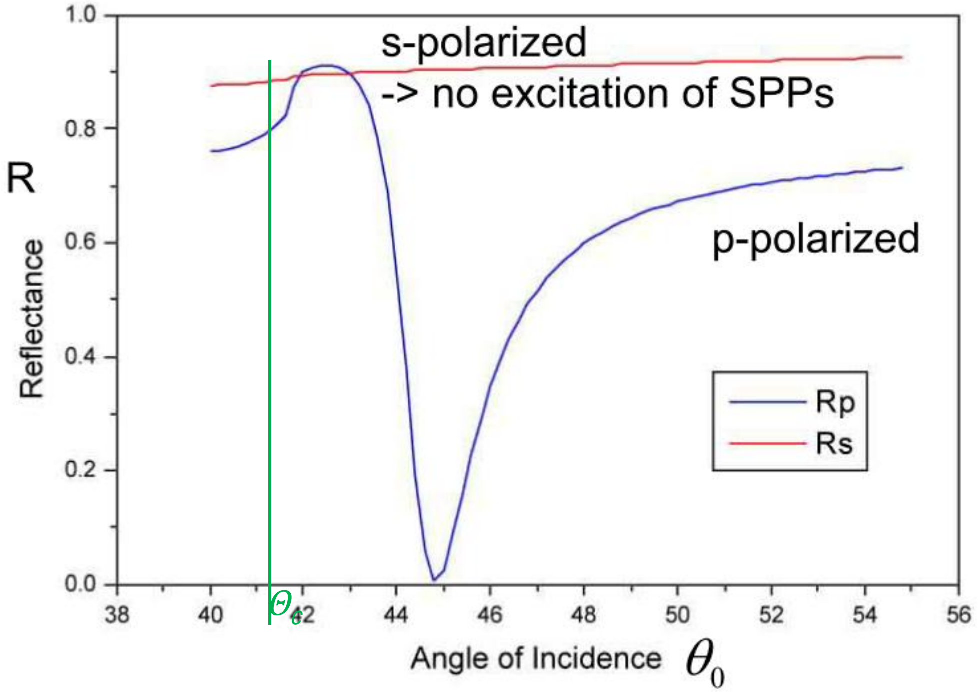
Excitation condition: $K_{spp} = K_{ev} \longrightarrow \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_a}{\varepsilon_m + \varepsilon_a}} = \frac{\omega}{c}\sqrt{\varepsilon_p}\sin\theta$

Kretschmann configuration – angle scan





ω_0 = const.



s-polarized
-> no excitation of SPPs

p-polarized

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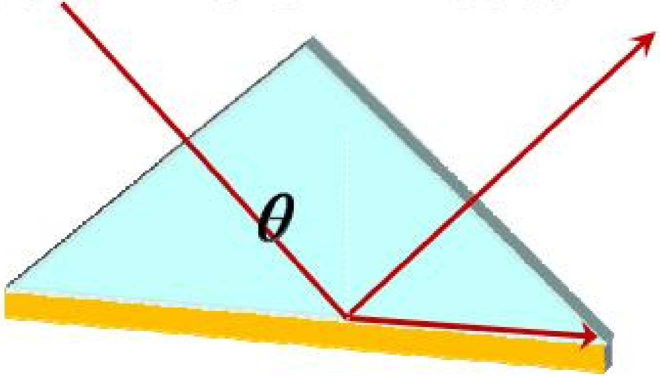
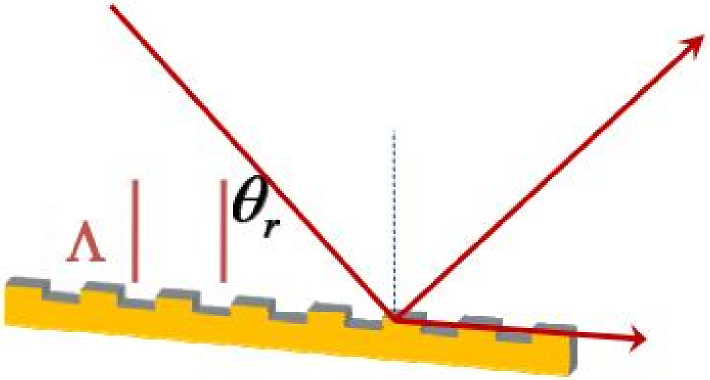
From prism to gratings

Radiation into SPP modes



$$k_{spp} = k_0 \sqrt{\varepsilon_p} \sin\theta$$

Kretschmann
configuration

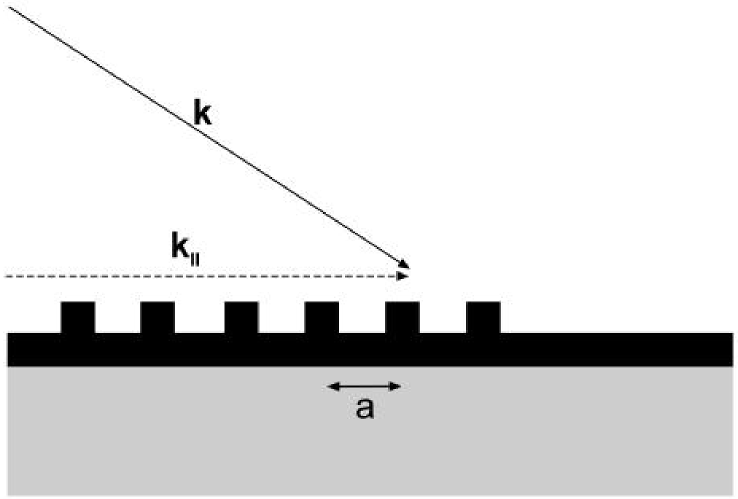


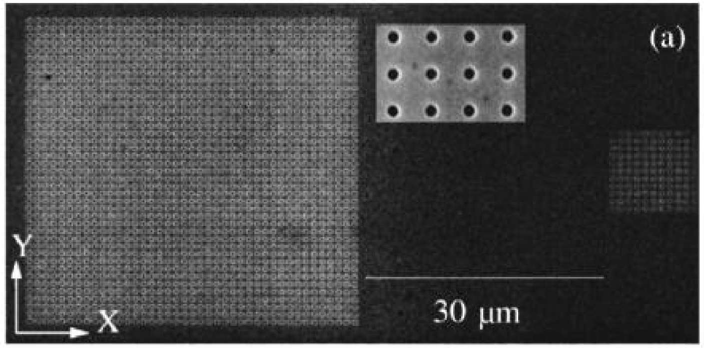
$$k_0 \sin\theta_r = k_{spp} - qK$$

$K = 2\pi / \Lambda$

grating
„Wood´s anomaly“

Coupling gratings

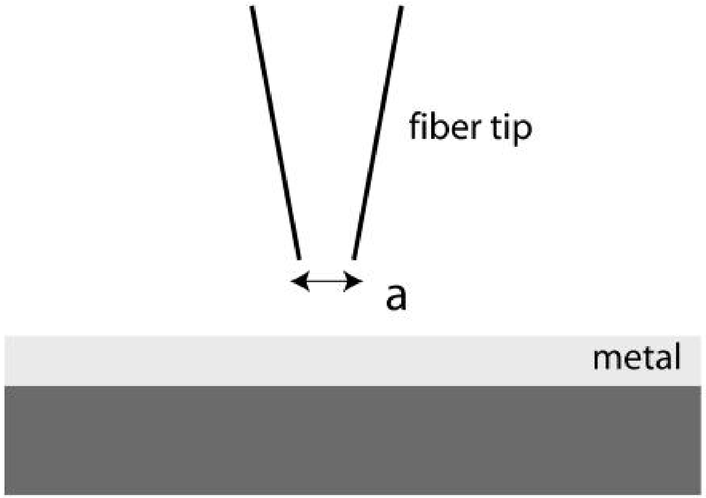


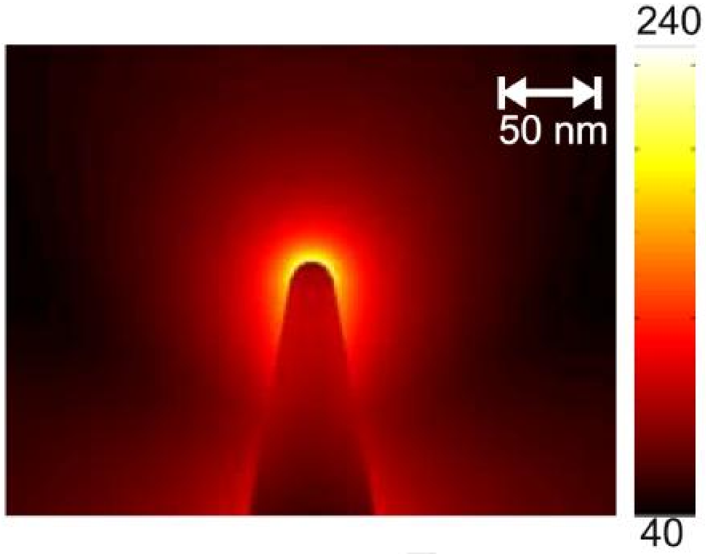


Under certain conditions gratings and hole arrays transform direct light into propagating SPP

Appl. Phys. Lett. **83**, 4936 (2003)

Optical fiber or cantilever tip





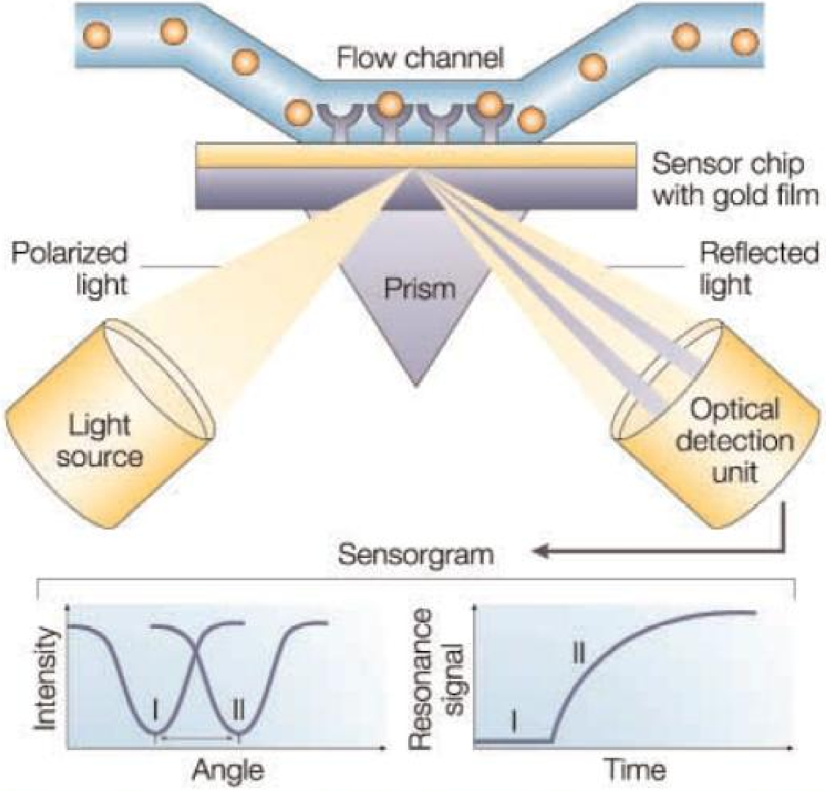
- The excitation is based on optical near-field
- While passing the fiber tip light squeezes and transforms from propagaing form into the near-field

Plasmonics **4** 51 (2009)

SPP-based sensors

Advantages: high sensitivity and posibility to use standard optical signal for sensing

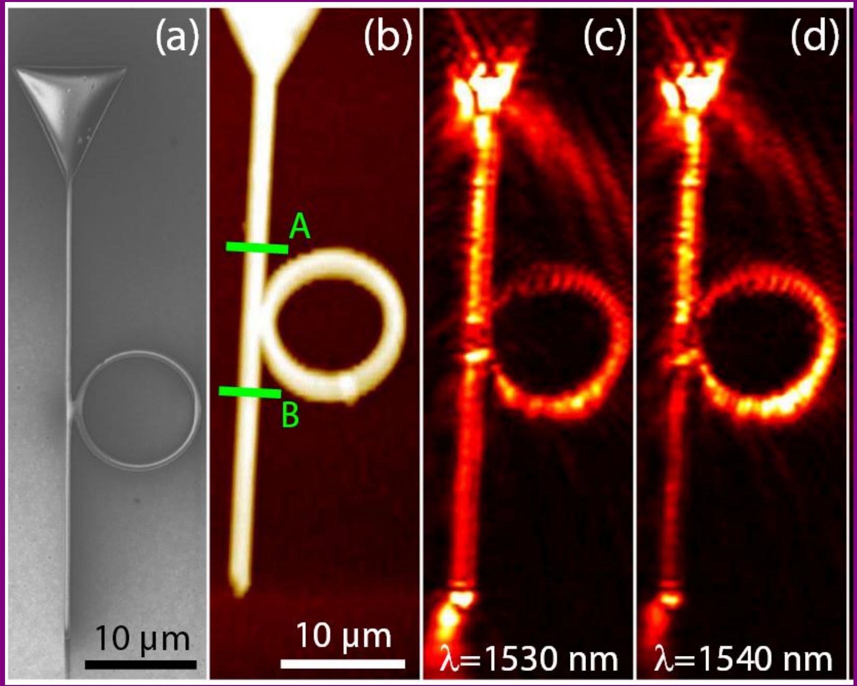
Disadvantages: difficult fabrication and narrow operation range

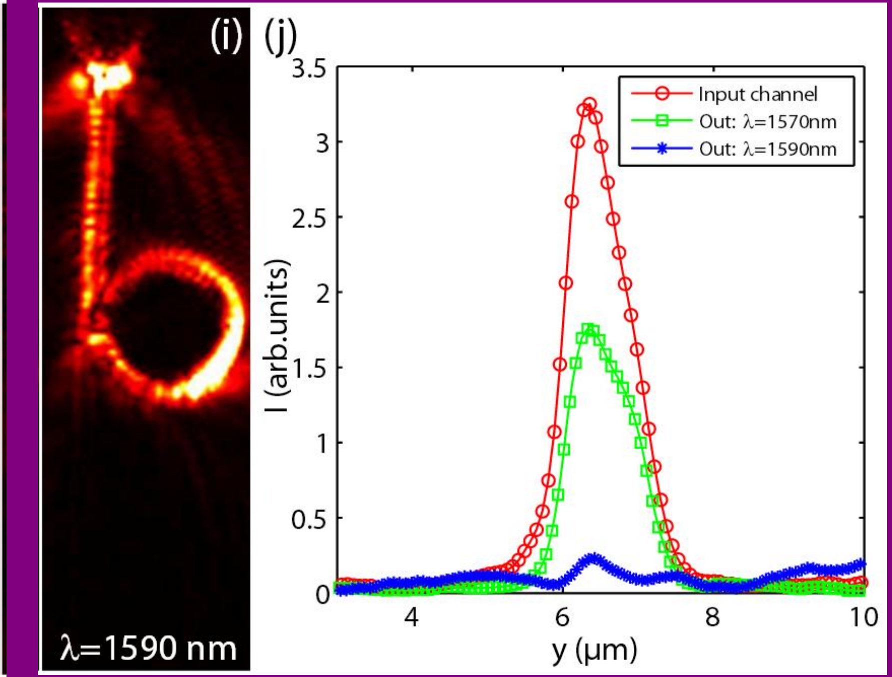


Waveguide-ring resonator

SEM Topography Near-field images

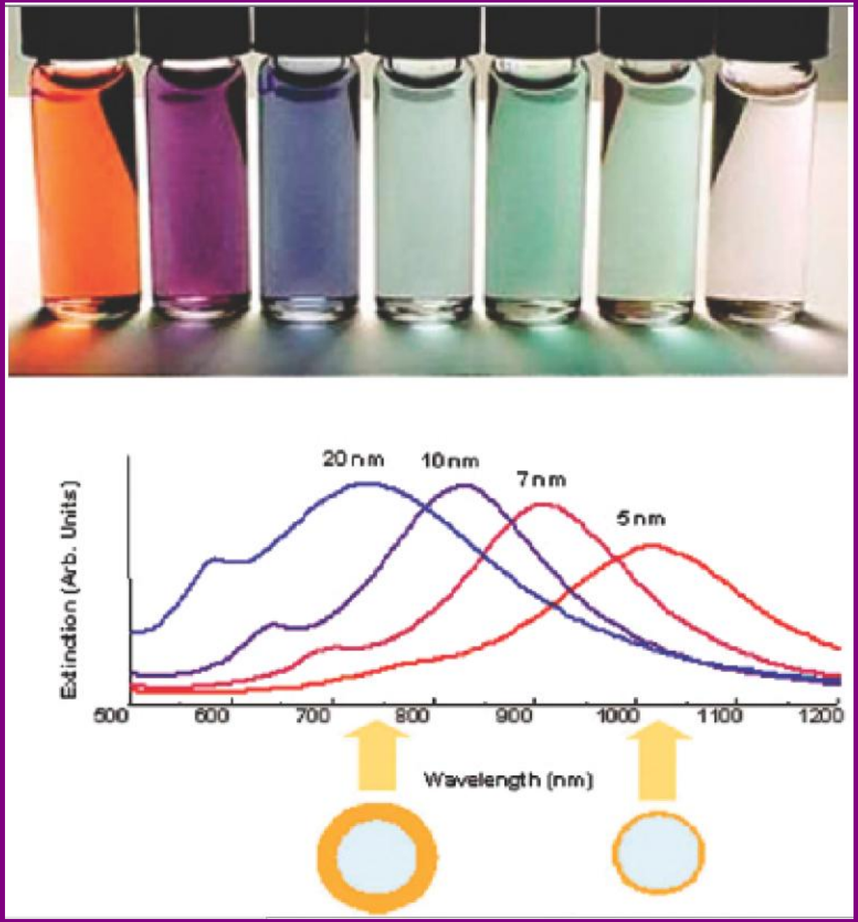
Intensity in A and B

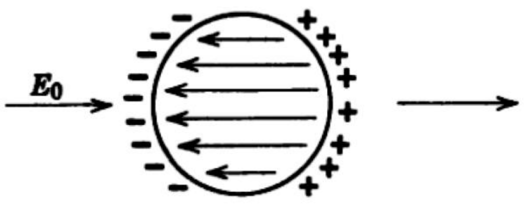




Opt. Express 17, 2968 (2009)

Localized surface plasmon polariton (LSPP)

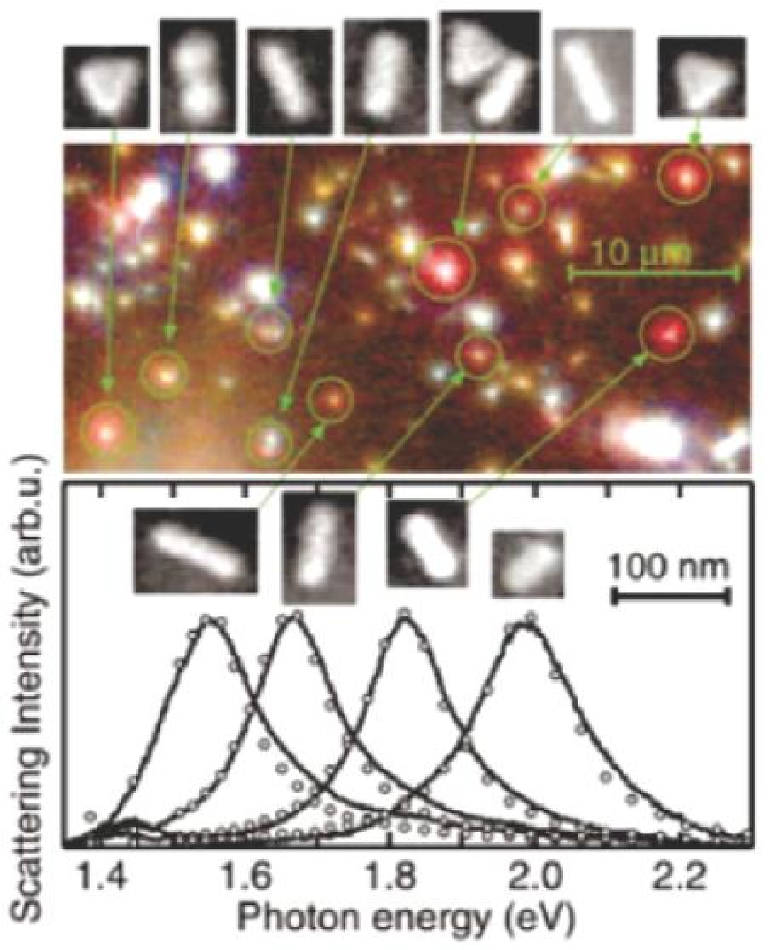




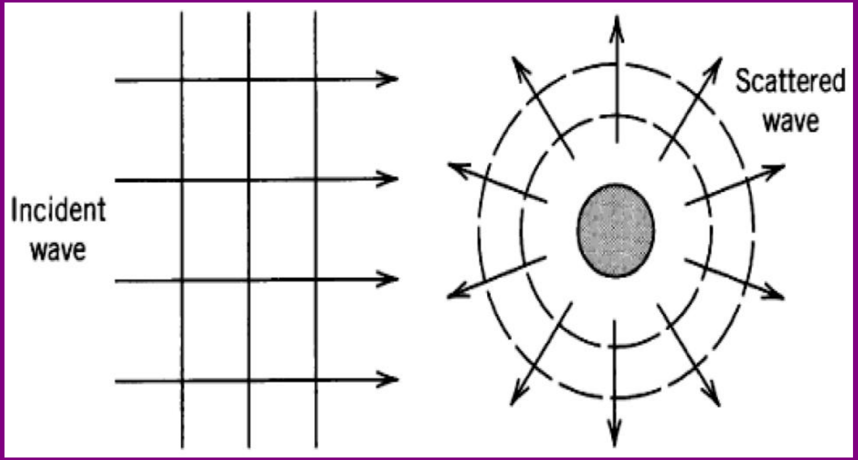
- Do not require special techniques for excitation
- Scattering and absorption of incident light depending on the particular shape and geometry of the particle

LSP and particle geometry

Chemical Reviews, 2008, Vol. 108, No. 2 497



Manipulating the geometry is an effective tuning tool: it affects both the resonance position and the overall frequency response profile.



Extinction = Absorption + Scattering

Localized surface plasmon (LSP)

- They would not exist without the presence of the interfaces
- Their properties depend on the optical properties of the outside medium.

- The frequency of the dipolar LSP mode of the sphere depends on several parameters:
- Obviously, the metal (through its frequency-dependent optical properties characterized by $\varepsilon(\omega)$).
- The environment, through its dielectric constant ε_M .
- The size of the sphere (i.e. its radius a).
- For spheres with radius a<10nm
- $\mathrm{Re}(\varepsilon(\omega\ \mathrm{LSP})) = -2\varepsilon_{\mathrm{M}}$

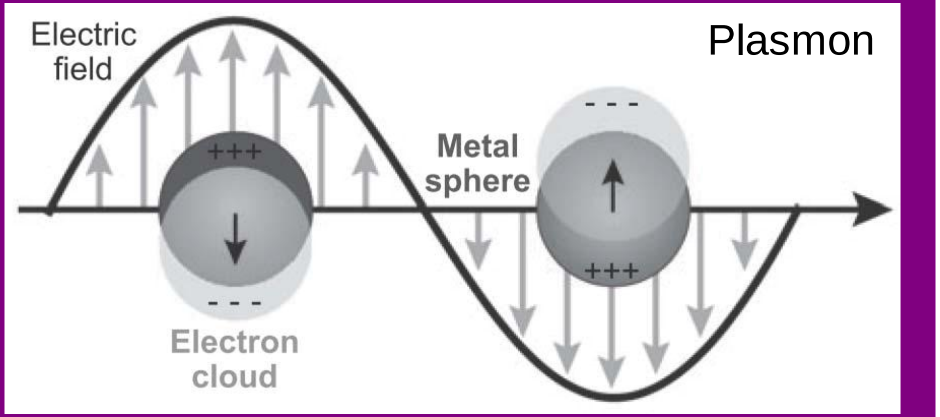
Lolcalized surface plazmon resonance (SPR) in metal sphere

The (complex) electric field inside the sphere is constant

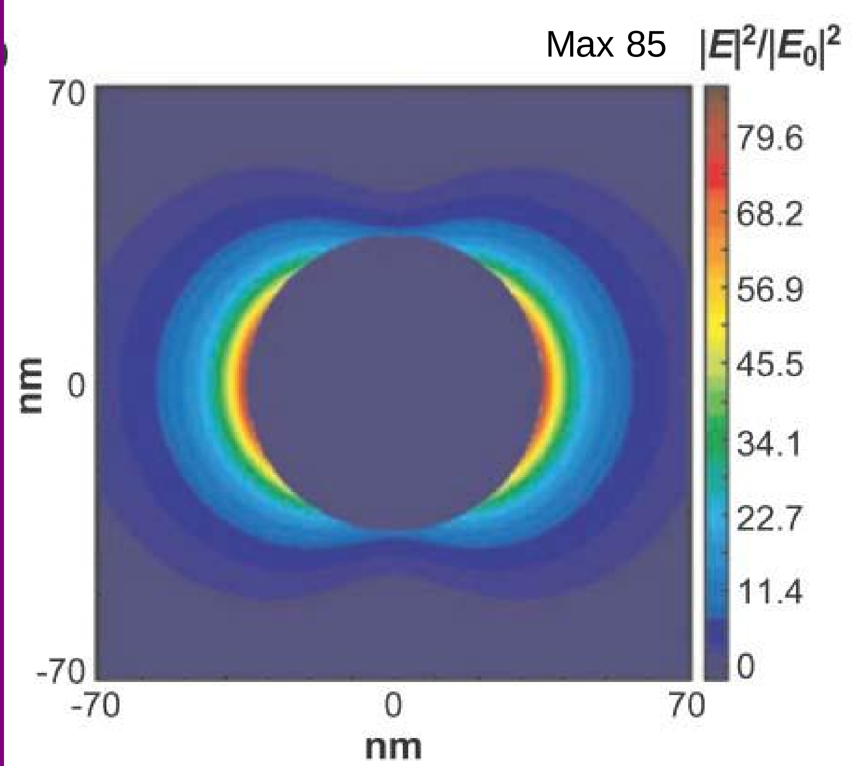
$$E_{in} = \frac{3\varepsilon_M}{\varepsilon(\omega) + 2\varepsilon_M} E_0$$

ε_M - relative dielectric constant of medium

$\mathrm{Re}(\varepsilon(\omega)) \approx -2\varepsilon_M$ resonance condition



Ag sphere (35nm) in vacuum,
at resonance wavelength 370 nm



E.C. Le Ru and P. G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects, Elsevier , 2009.
Stiles P.L. *et all*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

Electric field outside of metal sphere

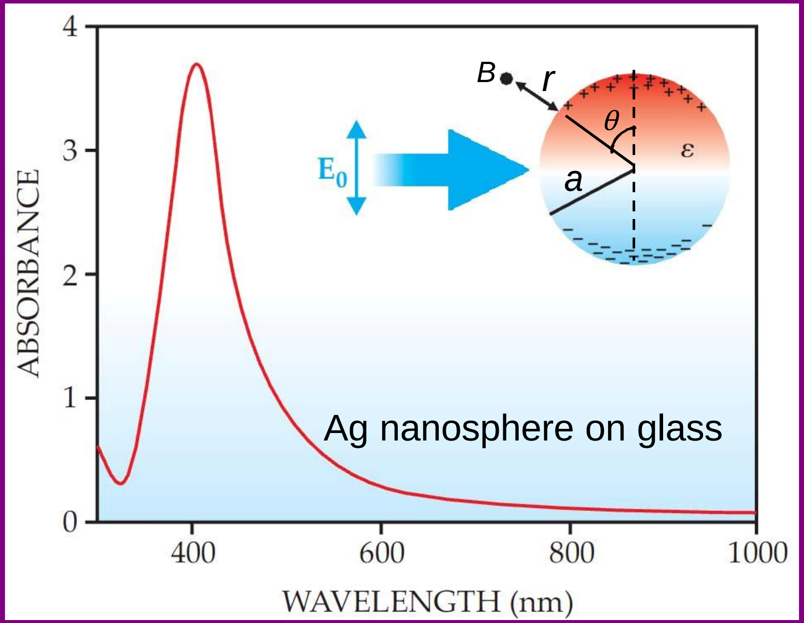
$$\mathbf{E}_{out}(x,y,z) = E_0\hat{\mathbf{z}} - \alpha E_0\left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5}(x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}})\right]$$

x, y, z – Cartesian coordinates,
r – radial distanse from sphere to the point $B(x,y,z)$
$\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ – Cartesian unit vectors

$$\alpha = ga^3$$

a– radius of the sphere

$$g = \frac{\varepsilon(\omega) - \varepsilon_M}{\varepsilon(\omega) + 2\varepsilon_M}$$



K. Kneipp, Physic Tody, **60**(11), 2007, p. 40-46
Stiles P.L. *et all*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

E^4 enchancement of outside field

Electric field at the surface of nanosphere

$$|\mathbf{E}_{out}|^2 = {E_0}^2[|1-g|^2 + 3\cos^2\theta(2\mathrm{Re}(g) + |g|^2)]$$

Maximum $\mathbf{E}_{out}$ at θ=0°

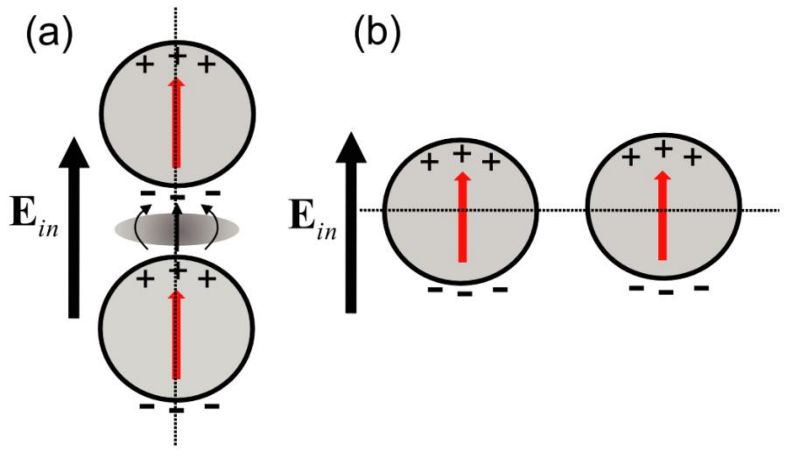
$$|\mathbf{E}_{out}|^2 = 4{E_0}^2|g|^2$$

Enhancement factor

$$EF = \frac{|\mathbf{E}_{out}|^2|\mathbf{E}'_{out}|^2}{|\mathbf{E}_0|^4} = 4|g|^2|g'|^2$$

Stiles P.L. *et all*, Annual Review of Analytical Chemistry, 1, 2008, p.601-26

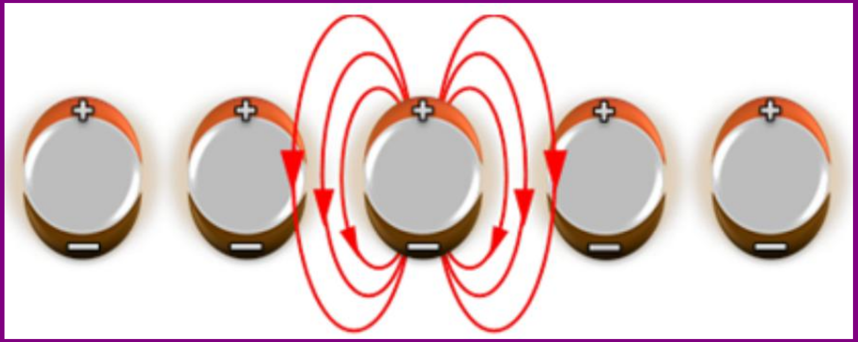
Dimer, coupling



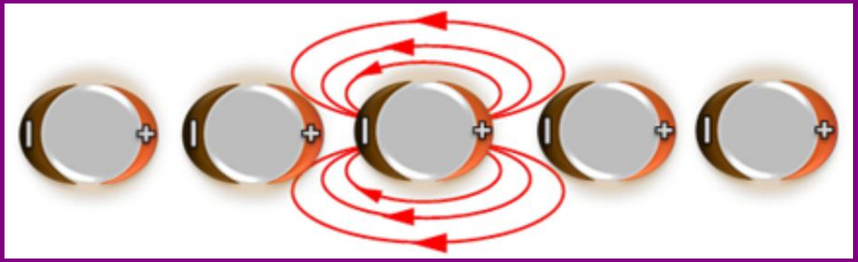
- Longitudinal (a) and transverse (b) modes for a dimer of particles. When the longitudinal mode is excited, the gap between the particles becomes a hot spot.

2012 Rivera et al., licensee InTech, chapter 11
http://dx.doi.org/10.5772/50753

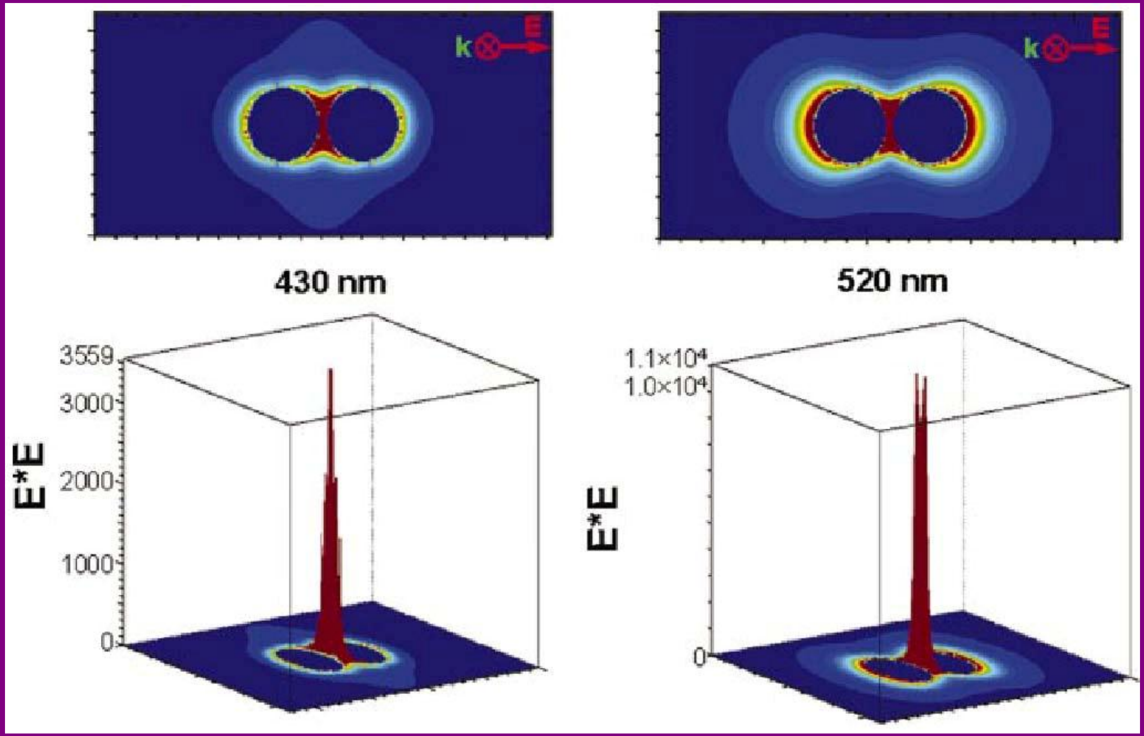
Transverse, blue-shift



Longitudinal, red-shift

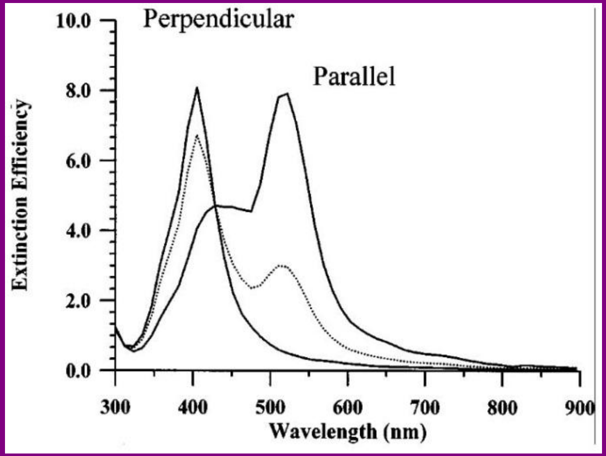


Ag dimer enhancement



36 nm spheres with 2 nm gap
For sphere is EF= 85 (slide 32)

Splitting of SPR

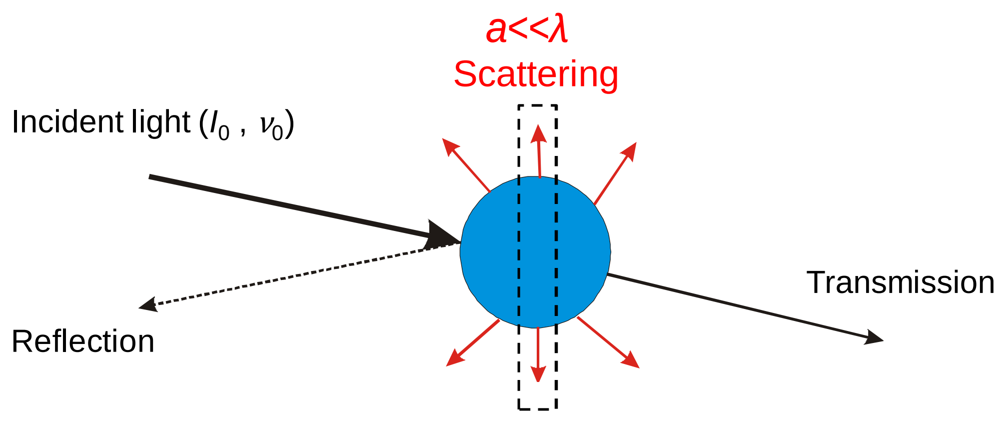


E. Hao and G. C. Schatz, J. Chem. Phys., Vol. 120, No. 1, 1 January 2004

Applications of LSPP

- Coloured materials
- Sensing and chemical imaging
- Surface Enhanced Raman Spectroscopy (SERS)
- Metamaterials
- Sub-difraction limit imaging
- Enhancement of Molecular Fluorescence
- Solar cells

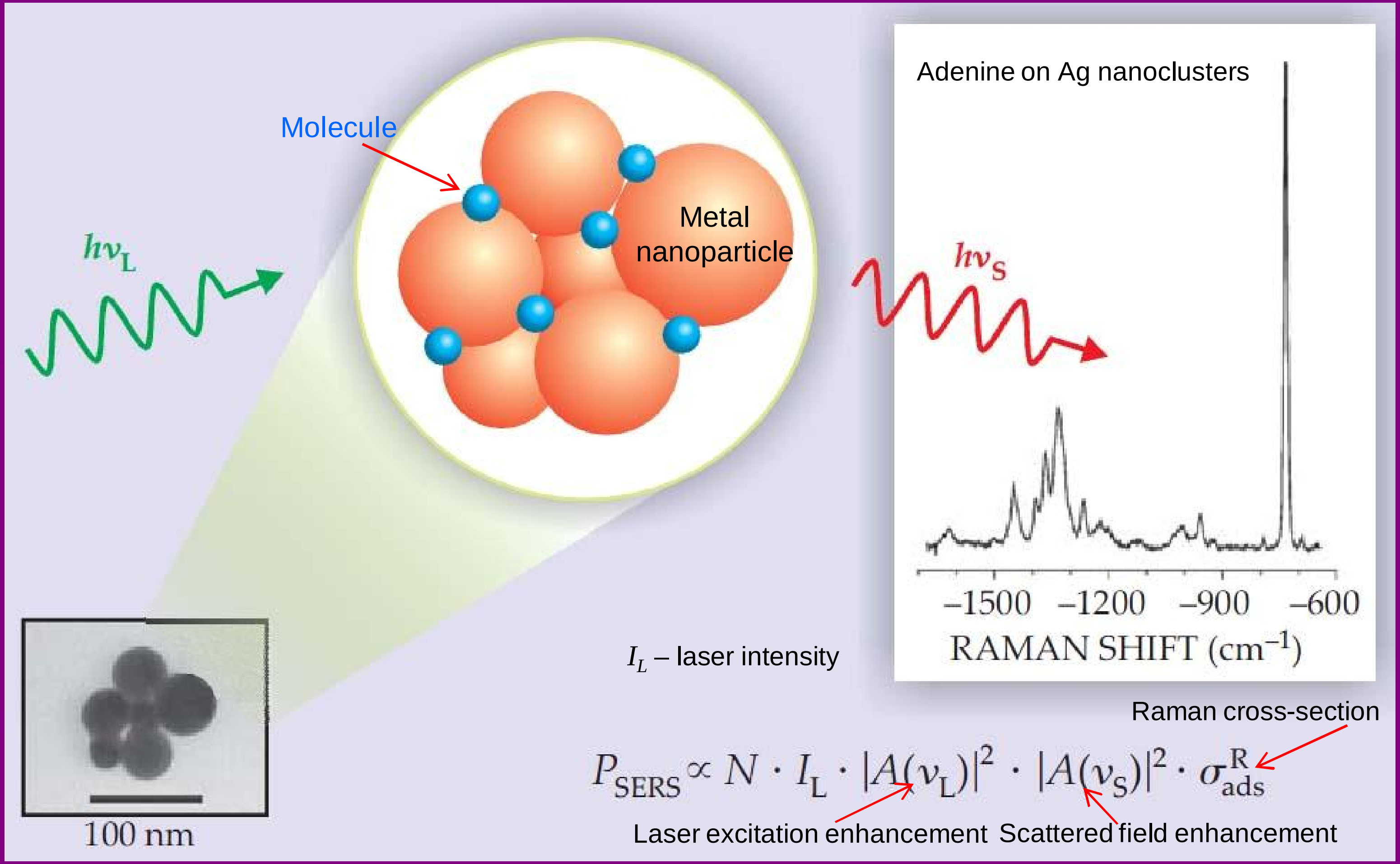
Scattered radiation



Scattering processes

Rayleigh	Raman
ν_0	$\nu_0 \pm \nu$
particles	molecular vibrations
$I_s \sim 10^{-3}\, I_0$	$I_s \sim (10^{-6} – 10^{-9})\, I_0$
	$\nu < 10^4$ cm^{-1}

Electromagnetic enhancement in near-field



I_L – laser intensity

Raman cross-section

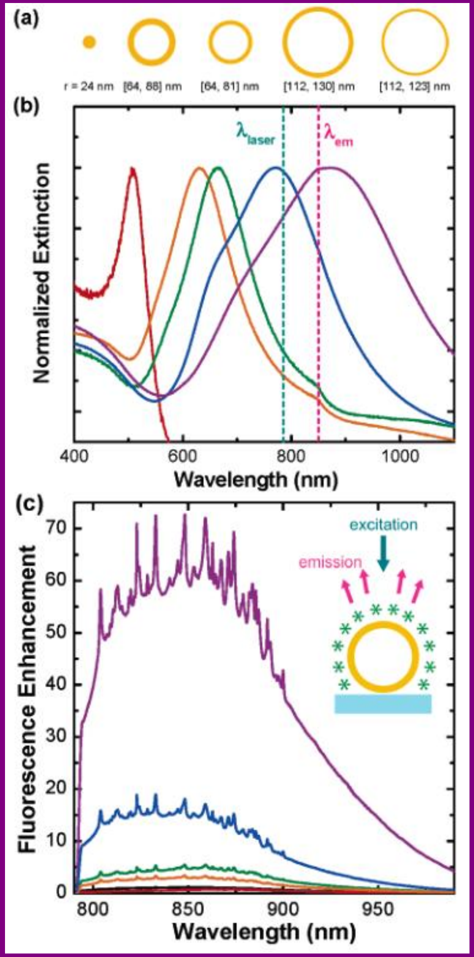
$$P_{SERS} \propto N \cdot I_L \cdot |A(\nu_L)|^2 \cdot |A(\nu_S)|^2 \cdot \sigma_{ads}^{R}$$

Laser excitation enhancement Scattered field enhancement

K. Kneipp, Physic Tody, **60**(11), 2007, p. 40-46

Enhancement of molecular fluorescence

Nano Lett. 7, 496 (2007)

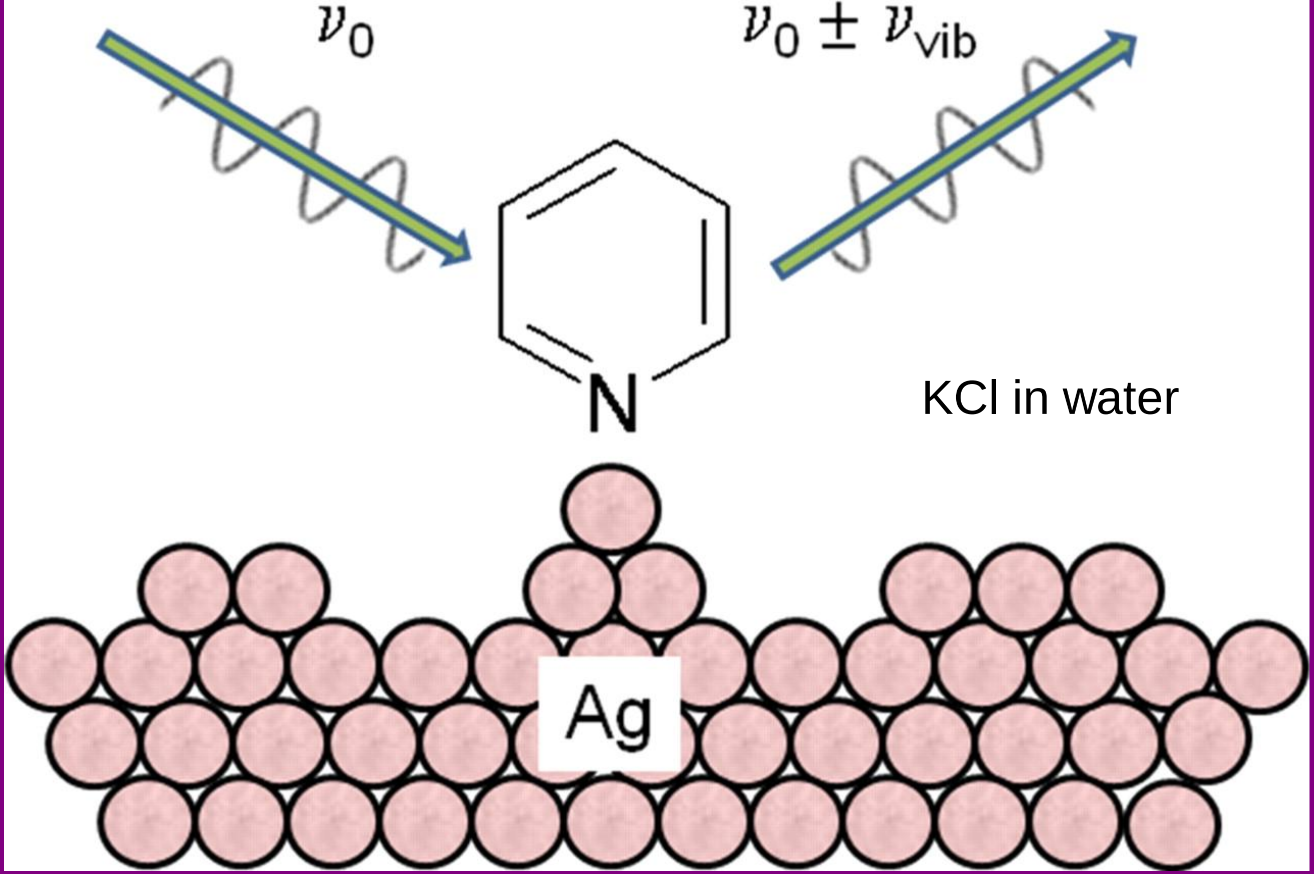


Metallic nanoparticles can strongly modify spontaneous emission of fluorescent molecules and materials:

- increase in optical intensity of incident field by near field enhancement
- modification of the molecule radiative decay rate
- better coupling efficiency of the fluorescence emission to the far field radiation through nanoparticle scattering
- $\lambda_{\text{LSP}} = \lambda_{\text{em}}$

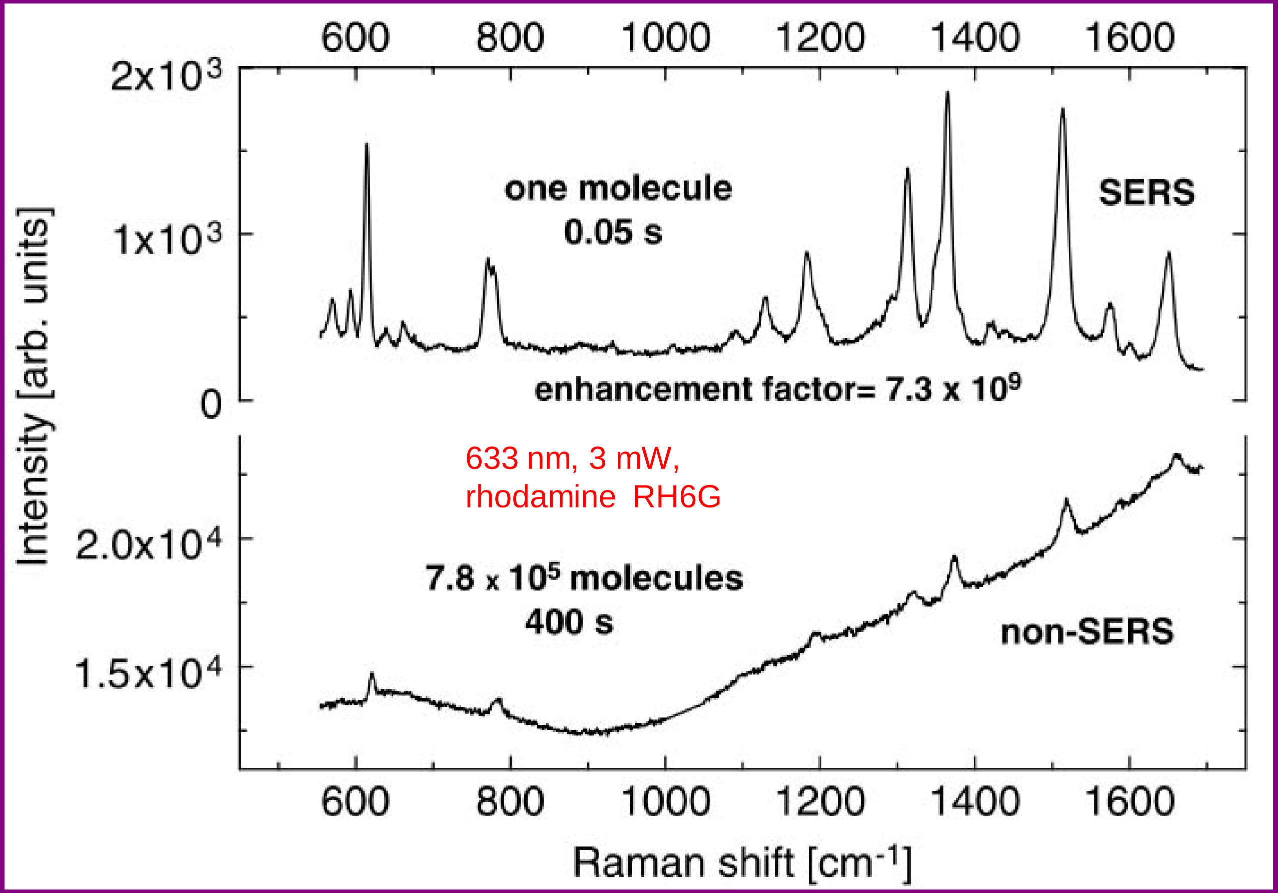
Indocyanine green (ICG) in the vicinity of Au nanospheres and Au - silica nanoshells

SERS experiment with pyridine adsorbed on silver



McQuillan A J Notes Rec. R. Soc. 2009;63:105-109

Bulk Raman versus SERS

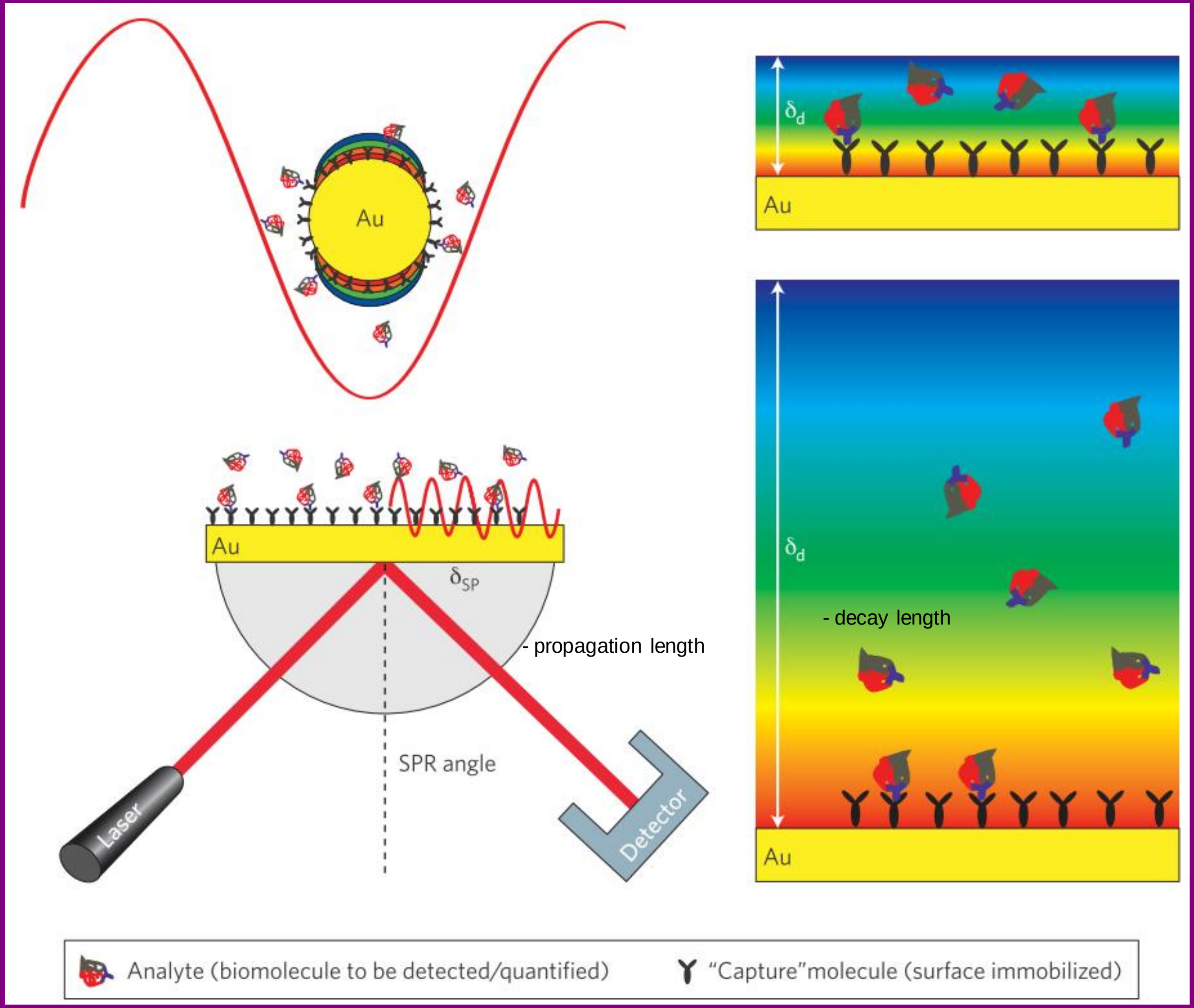


Surface selectrion rules

Bottom spectrum: 100 µM solution in a 13 μm^3 scattering volume, × 100 immersion objective with 400 s integration time. Top: signal from a single molecule under the same experimental conditions, but with 0.05 s integration time.

E. C. Le Ru et al., J. Phys. Chem. C, 111, 2007, p.13794–803

LSPP vs PSPP



- propagation length

- decay length

G. Brolo, NATURE PHOTONICS | VOL 6 | NOVEMBER 2012 | p.709

LSP vs SPP

- SPP is non-radiative mode, resonance response appears in absorption
- LSP is radiative mode (with an absorptive component because of optical absorption in the metal). The resonant response appears in absorption and scattering
- The SPP condition requires conservation of both k_x and ω. This is more difficult to fulfill than only ω conservation for LSP.
- SPPs offer more liberty in the implementation, either in terms of angle-modulation or wavelength-modulation, whereas only wavelength-modulation can be used for LSPs.
- SPPs are typically much sharper resonances compared to LSPs. For SERS, resonances must be broad enough to encompass both the exciting laser and the Stokes frequencies, and SPPs are typically too sharp to fulfill that condition.
- The active surface for SPPs is a single planar interface, while for LSPs it is the nano-particle surface (which can therefore be spread in a 3D volume, for example by dispersing the particles in water).
- There are more degrees of freedom to tailor or engineer the LSPs (shape, size, etc.) as opposed to the SPPs

Intermediate conclusion I

- There are two types of surface plasmons
  - Propagating at planar metal-dielectric interface (SPP)
  - Localized at metal nanostructures (LSP)
- Upon excitation of SPPs or LSP, optical electric fields are generated, enhanced and localized in the nanometer scale regions, in the vicinity of metallic surfaces
- SPP and LSP properties are very sensitive to environment and can be used in sensor applications
- Fabrication of metal nanoengineered structures requires simulations and nanotechnology