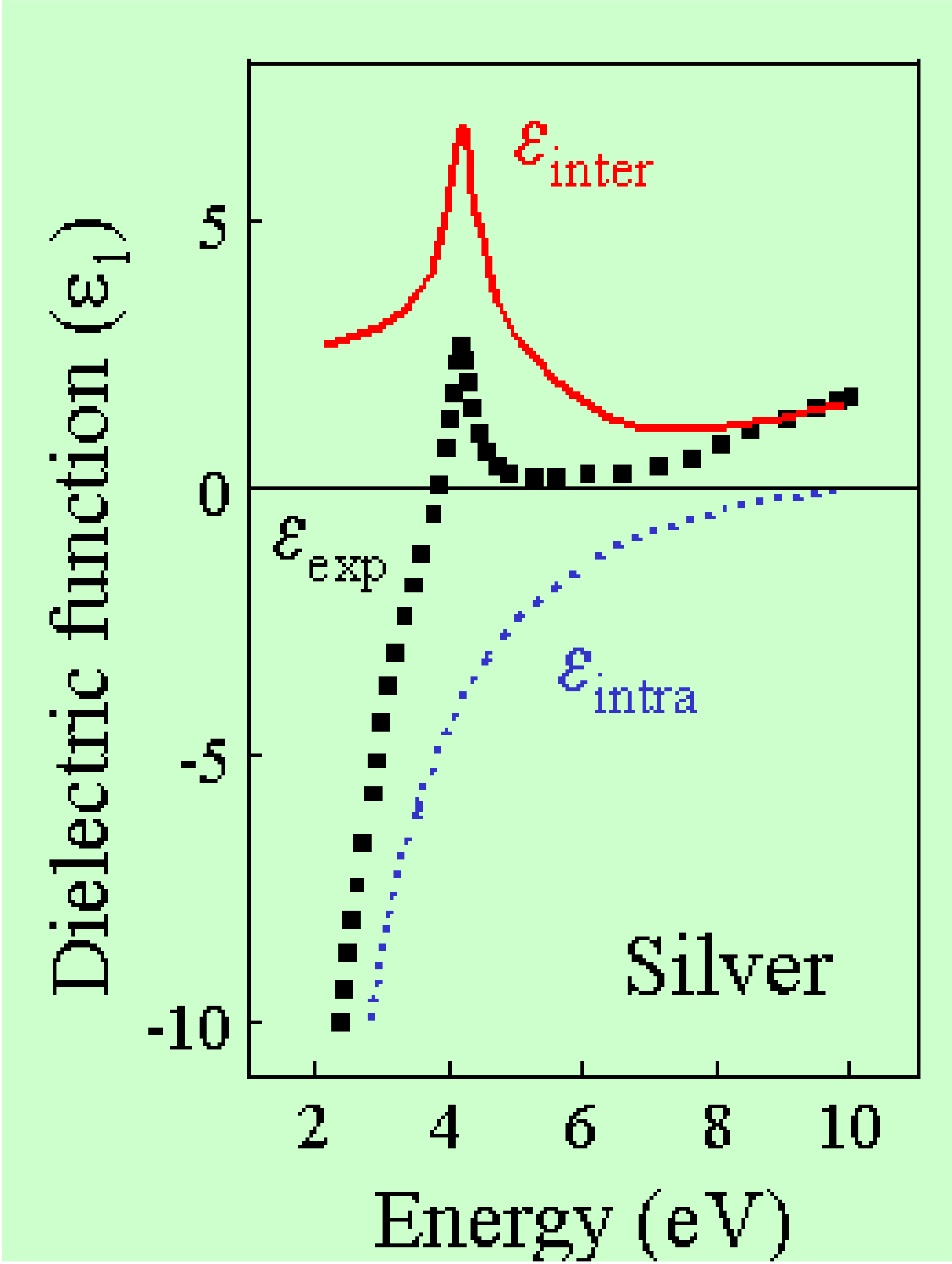
Nanophysics 13

Nanoparticle plasmons

Supplementary materials

Recap

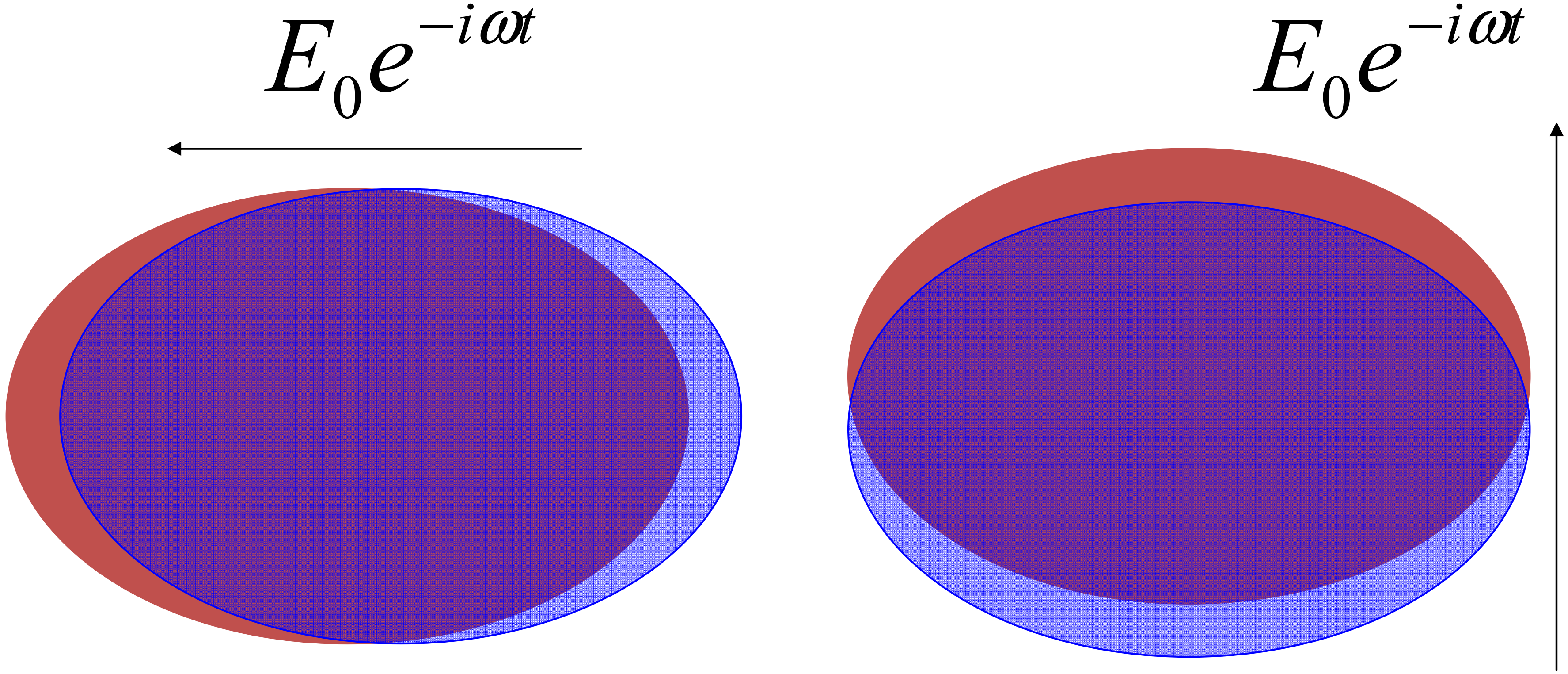
- Plasmon
  - Collective excitation of valence electrons
  - Energy for Volume Plasmon in Drude-like metals
- Dielectric function
  - Definition
  - Relation to optical properties
  - Condition for bulk plasmon excitation in real solids
  - Transparency of metals



Outline

- Condition for plasmon in nanoparticles
- Dipole mode and Mie theory
- Coupling of plasmon in nanoparticles
  - Subwavelength energy transfer of light
- Surface plasmon-polarions (concept only)
- Applications
  - Optical decorations (vie scattering absorption)
  - Refractive index sensor (bio sensor)
  - Plasmonics (energy transport of light in subwavelength dimensions)

Plasmon oscillation in an ellipsoid



$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1$$

Depolarization factors for ellipsoids

- A uniform polarization P produces a uniform depolarization field E_1 and

$$E_{1x} = -N_x P_x$$

- N's are the depolarization factors, whose values are positive and depend on the ratio of the principal axes of the ellipsoids, with the sum rule

$$N_x + N_y + N_z = 1$$

- Specific examples:

  N=1/3 for spheres, 1 for thin slabs at its normal direction

Equation of motion for collective oscillation of valence electrons of density n

- Uniform polarization

$$\mathbf{P} = -ne\mathbf{r}$$

- Depolarization field as the driving force for electron motion

$$m\frac{d^2\mathbf{r}}{dt^2} = -e\mathbf{E}_1 = eN\frac{\mathbf{P}}{\varepsilon_0} \underset{\mathbf{P}=ne\mathbf{r}}{=} \frac{ne^2}{\varepsilon_0}N\mathbf{r}$$

- For oscillation motion of the form

$$\mathbf{r} = \mathbf{r}_0 e^{-i\omega t}$$

- The energy for resonance oscillation is

$$\longrightarrow \boxed{\omega^2 = \frac{ne^2 N}{m\varepsilon_0} = \omega_p^2 N}$$

Examples of plasmons of ellipsoids

- Spheres, single plasmon energy

$$N = N_x = N_y = N_z = \frac{1}{3}$$

$$\boxed{\omega = \frac{\omega_p}{\sqrt{3}}}$$

- Ellipsoids, multiple plasmon energy

$$N_x + N_y + N_z = 1;$$

$$\boxed{\begin{aligned} \omega_x &= \omega_p \sqrt{N_x} \\ \omega_y &= \omega_p \sqrt{N_y} \\ \omega_z &= \omega_p \sqrt{N_z} \end{aligned}}$$

Polarization of a general ellipsoid

$$\mathbf{P} = \chi \mathbf{E}$$

Local response

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - N\mathbf{P}$$

$$\mathbf{P} = \chi \mathbf{E} = \chi\left(\mathbf{E}_\mathbf{0} - N\mathbf{P}\right)$$

$$\boxed{\mathbf{P} = \frac{\chi}{1 + N\chi}\mathbf{E}_0}$$

Net result of collective response

Plasmon excitation corresponds to zero of the denominators
Its excitation energy is shape dependent because of the depolarization factor N

Light-particle interaction in general

- Solving the inhomogeneous Maxwell equation in the presence of nanoparticles

$$\nabla \wedge \left(\nabla \wedge \mathbf{E}(\mathbf{r},\omega)\right) - \frac{\omega^2}{c^2}\varepsilon(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega) = 0$$

- To account for light interacting with nanoparticles
- General solutions, Mie theory, including the magnetic field components
- A simpler case of dipole plasmon mode is presented next

Dipole mode

- Quasi-static approximation
  - Easily satisfied for nanoparticles at visible range (wavelength ¬500nm)
  - field can be considered to be spatially uniform apart from a time varying factor
- Electrostatic can apply

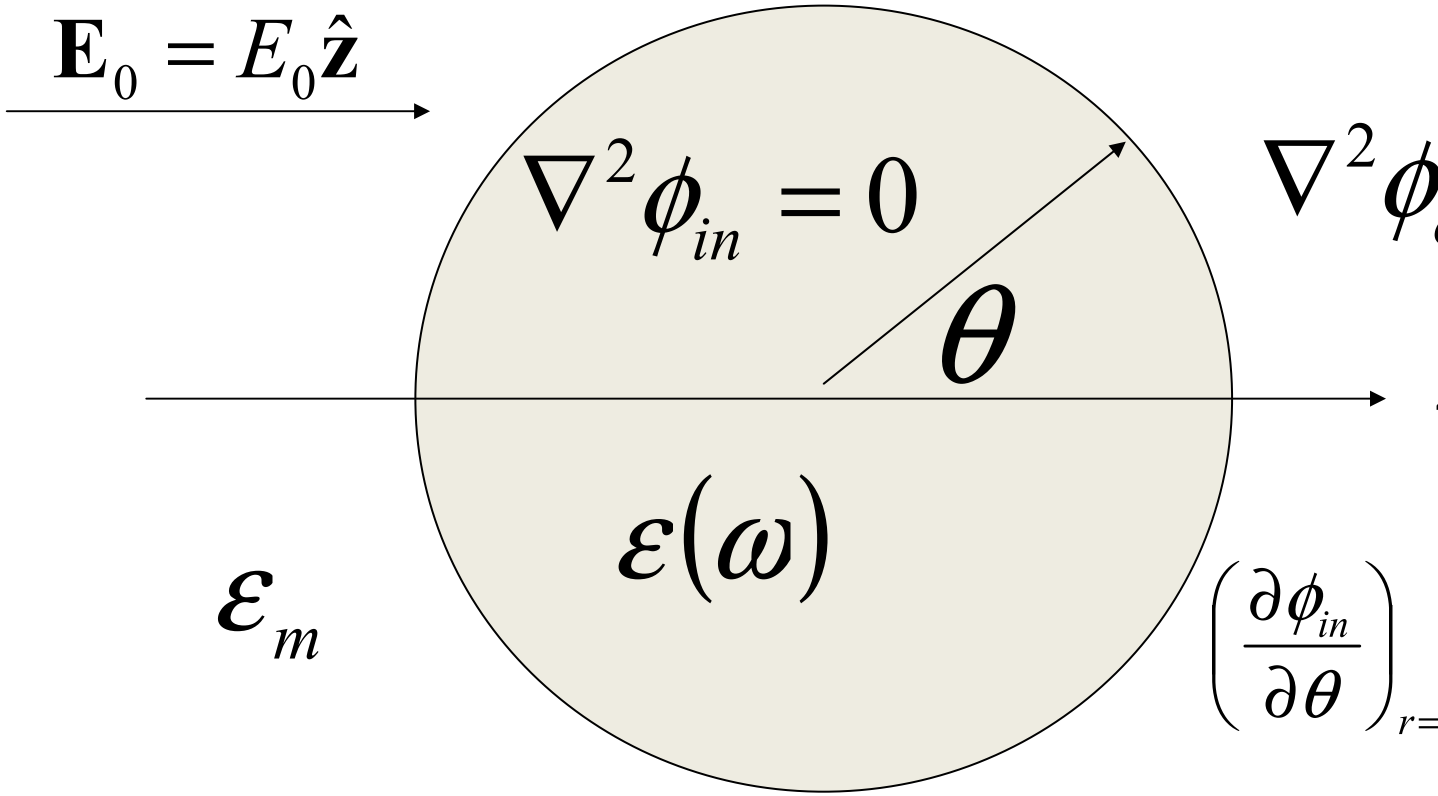
$$\mathbf{k}\cdot\mathbf{r}\le 1 \qquad \frac{2\pi a}{\lambda}\le 1$$

$$\mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}-\mathbf{i}\varpi\mathbf{t}} \approx \mathbf{E}_0 e^{-\mathbf{i}\varpi\mathbf{t}}$$

$$\nabla\cdot\mathbf{D}=\nabla\cdot\left(\varepsilon\mathbf{E}\right)=0$$

Electrostatic

$$\nabla \cdot \mathbf{D} = \nabla \cdot \left(\varepsilon \mathbf{E} \right) = 0$$



$$\nabla^2 \phi_{out} = 0$$

$$\varepsilon_m$$

$$\left(\frac{\partial \phi_{in}}{\partial \theta} \right)_{r=a} = \left(\frac{\partial \phi_{out}}{\partial \theta} \right)_{r=a}$$

Boundary conditions:

$$\varepsilon(\omega) \left(\frac{\partial \phi_{in}}{\partial \theta} \right)_{r=a} = \varepsilon_m \left(\frac{\partial \phi_{out}}{\partial \theta} \right)_{r=a}$$

Solutions in spherical coordinates

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

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

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

light field

$$\mathbf{p} = \varepsilon_0 \varepsilon_m \alpha \mathbf{E}_0$$

Induced dipole

Enhanced polarizability
at dipole plasmon resonance

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

- Enhancement at Fröhlich condition

$$\varepsilon = -2\varepsilon_m$$

- For Drude metal, corresponding to nanoparticle plasmon excitation (dipole mode)

$$\omega = \frac{\omega_p}{\sqrt{3}}$$

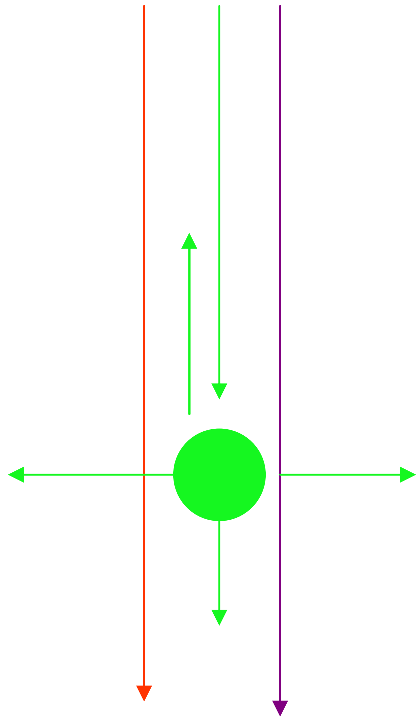
Size dependence

- Not implicitly
- Explicitly
  - Size-dependent change in dielectric function of materials
    - Reduced valence electron density
    - Enhanced absorption due to Increased surface inelastic scattering

Nanoplasmon-polarions

- Coupling of electromagnetic waves at far field to nanoparticle excitation at near field
- Solving the Maxwell's equation for both E and B-fields
- Absorption and radiation of light in nanoparticles

The dichroic effect of the Lycurgus Cup
(Novel pigments)

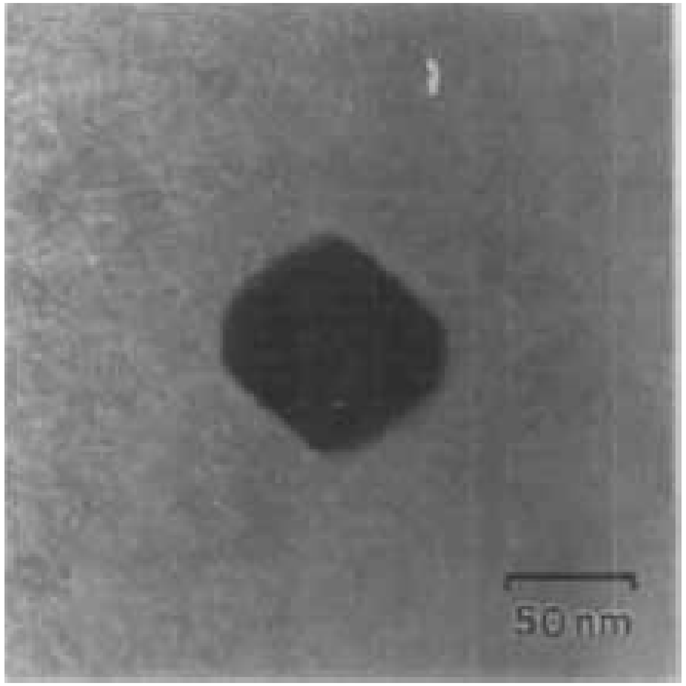


Lycurgus Cup

- Roman glasswork (4^{th} century AD) called ‘*Cage Cups*’ or *diatreta*
- A mythological frieze depicts King Lycurgus of Thrace being dragged to the underworld at the hands of Dionysus and his followers in the form of vine (sixth book of Homer’s Lliad)
- Purchased from Rothschild for 2000 pounds in 1958 by the art fund for British Museum

Science

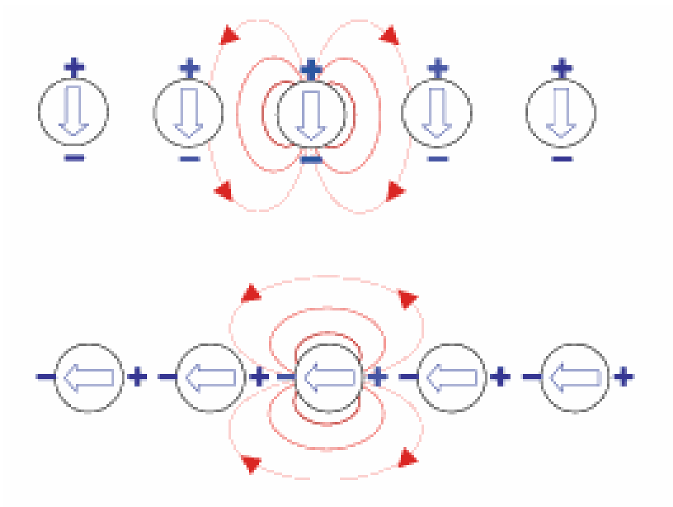
- Electron microscopy reveals (silver alloyed) gold nanoparticles 70 nm in diameter
- Colour response different to that of gold in bulk
- Particles resonantly reflect green light (520-570nm)

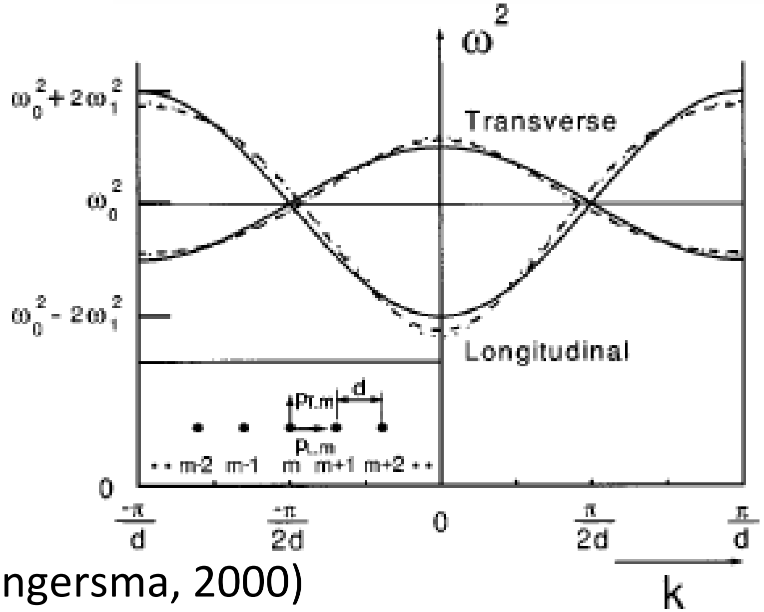


Barber (1990) TEM images of the gold-silver alloyed nanoparticles embedded in the glass

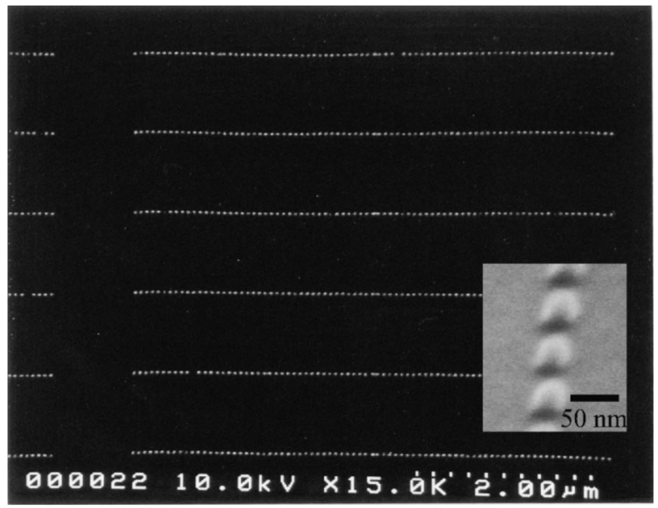
Plasmonic waveguide

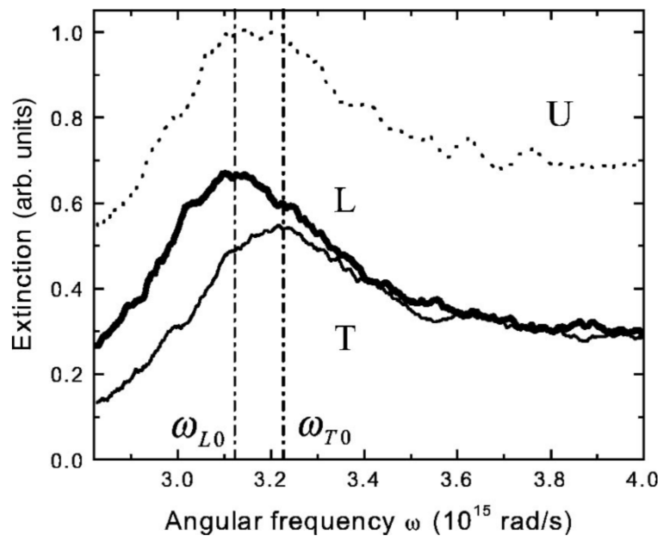
(Theory vs. experiments)





(Brongersma, 2000)

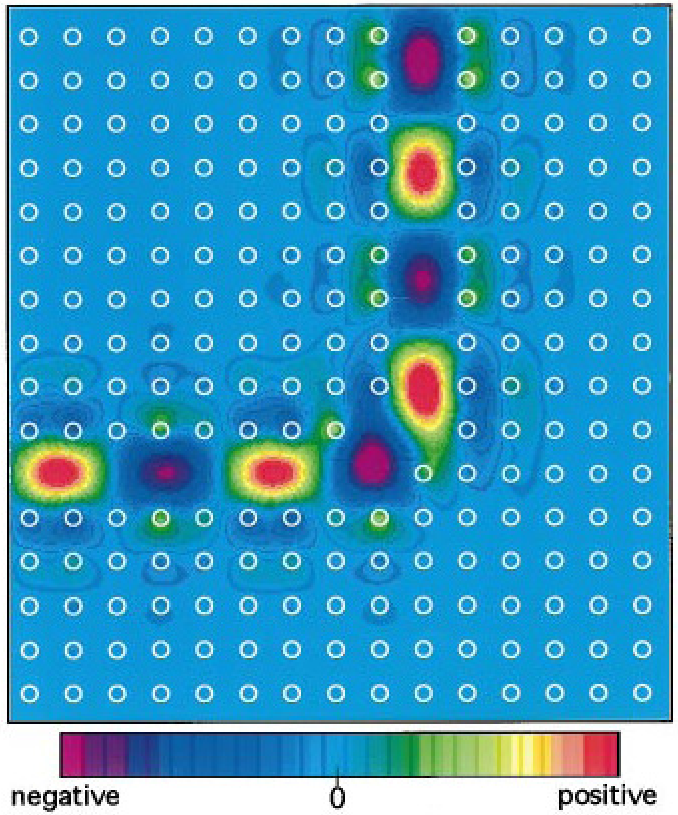




(Maier 2002)

Light Bending

Comparison of Photonics and Plasmonics



(Mekis, 1996)

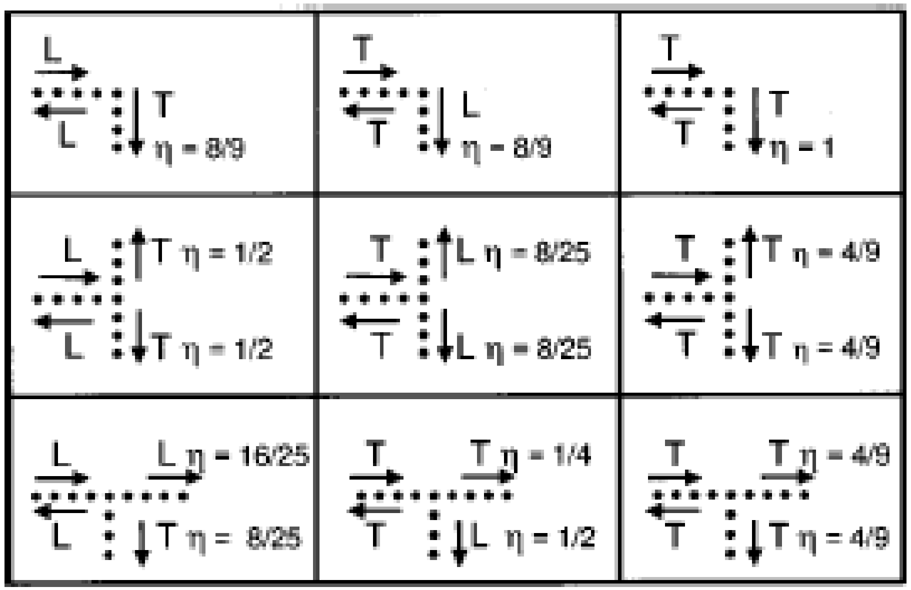


FIG. 2. Calculated power transmission coefficient η for nanoparticle chain-array corner and tee structures with 90° corners. The arrows indicate the direction of the power flow of longitudinal waves (L) and transverse waves (T). An η value of 1 corresponds to 100% transmission.

(Brongersma, 2000)

Summary

- Particles Plasmons:
  - Collective excitation of valence electrons in a nanoparticles
  - Dipole plasmon conditions:
- Resonance energy depends on
  - Materials (valence electron density, in metals, spill out effect)
  - Shape and size
  - Surrounding media
- Nanoparticles can sustains dipole-like plasmon motion
  - Strong scatter of light (decorative windows and glasses)
  - Coupled plasmons of nanoparticles
    - Change of frequency (plasmon hybridization)
    - Sub-wavelength energy transfer of electromagnetic waves at optical frequency (plasmonics)

Further readings

- Maier *et al*, ‘Plasmonics- aroute to nanoscale optical devices’ Advanced Materials, Vol. 13, p1501-1505