Metal nanoparticles and arrays. Plasmon resonance as a function of size, shape, etc.

PH 673

Nanoscience and nanotechnology

October 22, 2025

Metal nanoparticle plasmons

Nanoparticle resonance can be found from fields in sphere

Recall: electrostatics predicted for particle in external field E_e :

$$\frac{E_i}{E_e} = \frac{3\varepsilon_e}{\varepsilon_i + 2\varepsilon_e}$$

Quasi-electrostatic approximation: oscillatory E_e but $|k \cdot x| << 1$ $\Rightarrow$ use $\varepsilon(\omega)$

$\Rightarrow$ Internal field can become large if $\varepsilon_i + 2\varepsilon_e = 0$ $\Rightarrow$ $\varepsilon_i = -2\varepsilon_e$ (requires ε negative)

This condition indicates a dipolar plasmon resonance

Example: Drude metal nanospheres in air

Drude model: $\varepsilon_r'(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}$

Drude resonance condition in air:

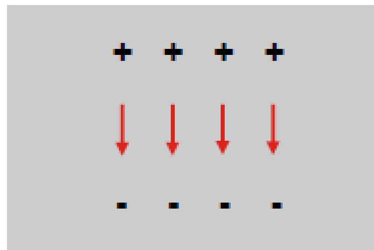
$$\varepsilon_i = -2\varepsilon_e \Rightarrow 1 - \frac{\omega_p^2}{\omega^2} = -2 \Rightarrow \omega = \frac{\omega_p}{\sqrt{3}}$$

This collective dipolar oscillation is called the Fröhlich mode, occurs below ω_p

Many metals: high free-electron densities and large ω_p : resonances in VIS-UV

Plasmon resonance positions in vacuum

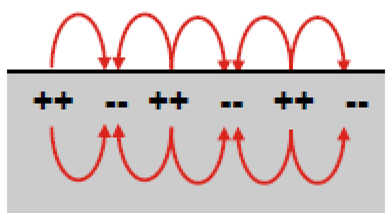
Bulk metal



ω_p

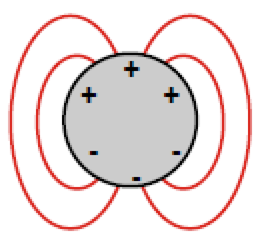
$\varepsilon = 0$

Metal surface



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

Metal sphere
localized SPPs



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

Localized Surface Plasmon

$$\left|\varepsilon(\omega) + 2\varepsilon_d\right| \to 0$$

Complex polarizability enhancement

$$\boxed{\mathrm{Re}\left[\varepsilon(\omega)\right] = -2\varepsilon_d \qquad \textit{if } \mathrm{Im}\left[\varepsilon(\omega)\right] \textit{ is small}}$$

Fröhlic condition

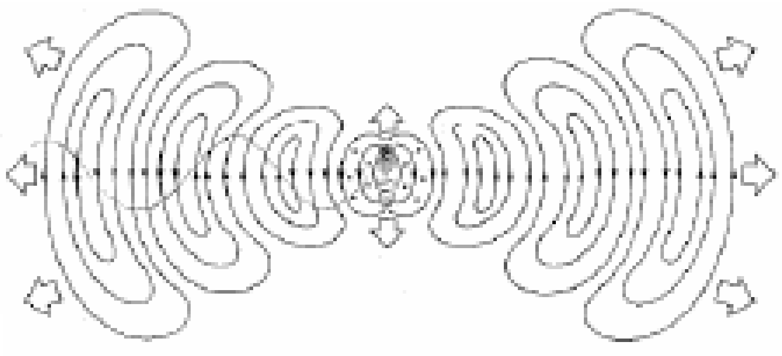
Geometry	*Resonance condition*	*Resonance frequency*
Bulk metal	$\varepsilon_1(\omega) = 0$	$\omega_1 = \omega_p$
Planar surface	$\varepsilon_1(\omega) = -1$	$\omega_1 = \omega_p/\sqrt{2}$
Thin film	$\frac{\varepsilon(\omega)+1}{\varepsilon(\omega)-1} = \pm e^{-k_x d}$	$\omega_1 = \omega_p\sqrt{(1 \pm \exp(-k_x t))/2}$
Sphere (quasi-static)	$\varepsilon_1(\omega) = -2$	$\omega_1 = \omega_p/\sqrt{3}$
Ellipsoid (quasi-static)	$\varepsilon_1(\omega) = -(1-L)/L$	$\omega_1 = \omega_p L$

Consequences of the nanoparticle plasmon resonance

We know :

Illumination of metal nanoparticle can induce collective charge motion

Oscillating charge
- radiates (dipole radiation pattern)
- causes heating due to damping
  (electron scattering)



Predictions:

- Light scattering strong near the nanoparticle plasmon resonance

- Absorption strong near resonance

- Extinction (abs + scat) strong near resonance

- Sharpest resonance for low resistivity / high conductivity materials

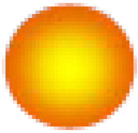
- Resonance broadening if additional damping introduced (e.g. surface scattering)

Question: which metals give the strongest resonances? (low damping needed)

Resonances in ellipsoidal particles

Dipole moment μ of particle given by tensor relation $\vec{\mu}(\omega) = \tilde{\tilde{\alpha}}(\omega)\vec{E}(\omega)$

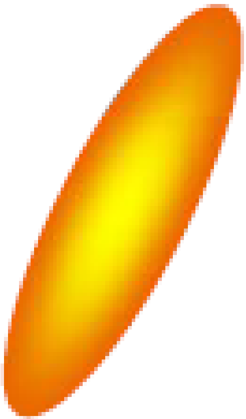
For spherical particle we can use scalar form with $\alpha = 4\pi\varepsilon_0 R^3 \dfrac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$



Here ε is the dielectric constant of the particle, and ε_m that of the surroundings

For ellipsoidal particles under illumination with E along one of the principal axes, the polarizability can be written as

$$\alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L(\varepsilon - \varepsilon_m)}$$



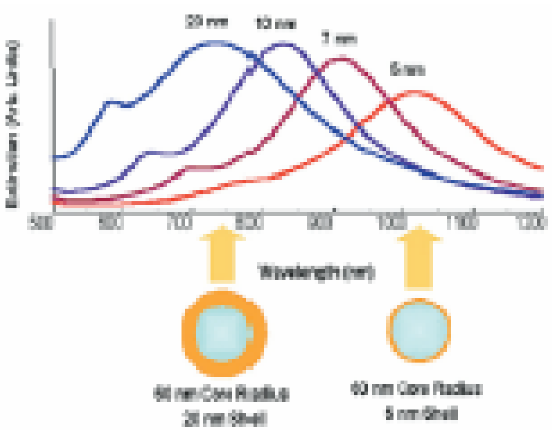
with L a geometry dependent factor between 0 and 1

Resonance when denominator vanishes, or $\varepsilon = \varepsilon_m\left(1 - \dfrac{1}{L}\right)$

Geometrical factor L for sphere : 1/3

Surface plasmons on core-shell particles

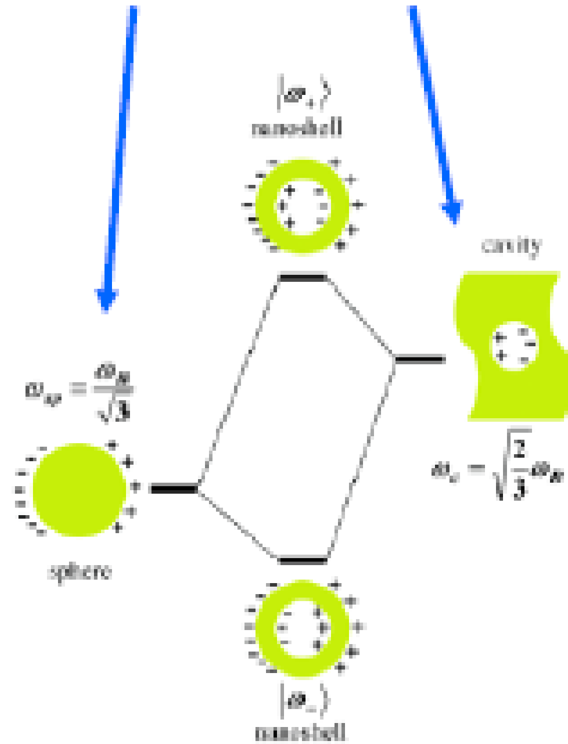
Design of the local environment of particles can also be used to control the resonance



http://www-ece.rice.edu/~halas/pubs.html

Via the Babinet principle:

$$\omega_{struct}^2 + \omega_{inv.struct}^2 = \omega_p^2$$



E. Prodan, C. Radloff, N.J. Halas and P. Nordlander, Science 302(2003)419-422

Localized Surface Plasmon

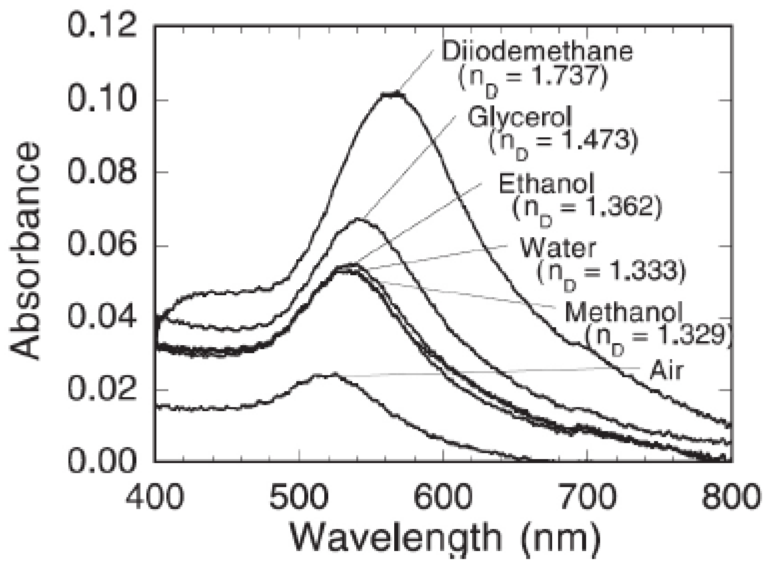
Corresponding absorption & scattering cross sections calculated via the Pointing vector from the full EM field associated with an oscillating dipole

$$\sigma_{sca} = \frac{k^4}{6\pi}\left|\alpha\right|^2 = \frac{8\pi}{3}k^4 a^6 \left|\frac{\varepsilon(\omega)-\varepsilon_d}{\varepsilon(\omega)+2\varepsilon_d}\right|^2$$

$$\sigma_{abs} = k\,\mathrm{Im}(\alpha) = 4\pi k a^3\,\mathrm{Im}\left[\frac{\varepsilon(\omega)-\varepsilon_d}{\varepsilon(\omega)+2\varepsilon_d}\right]$$

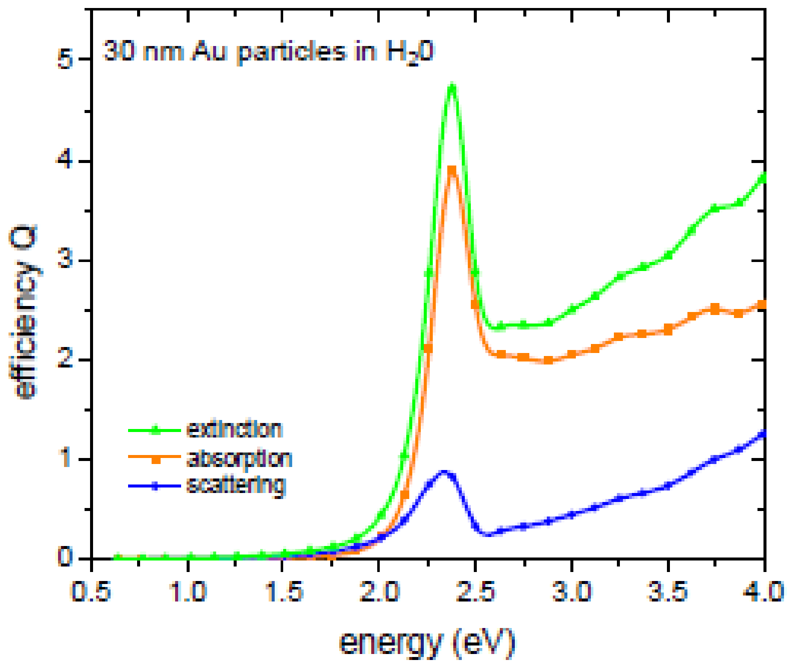
$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs}$$

$$I_{ext}(\omega) = \frac{I_0(\omega)}{S}\sigma_{ext}(\omega)$$



Scattering vs absorption

Define Q = optical cross-section / physical cross-sectional area ($\sigma = Q \times \pi a^2$)



Formulas used:

$$Q_{abs} = 4x\,\mathrm{Im}\left(\frac{\varepsilon_1 + i\varepsilon_2 - \varepsilon_m}{\varepsilon_1 + i\varepsilon_2 + 2\varepsilon_m}\right)$$

$$Q_{sca} = \frac{8}{3}x^4\left|\frac{\varepsilon_1 + i\varepsilon_2 - \varepsilon_m}{\varepsilon_1 + i\varepsilon_2 + 2\varepsilon_m}\right|^2$$

with size parameter

$$x = ka = \frac{2\pi N a}{\lambda}$$

with N the refractive index of the medium

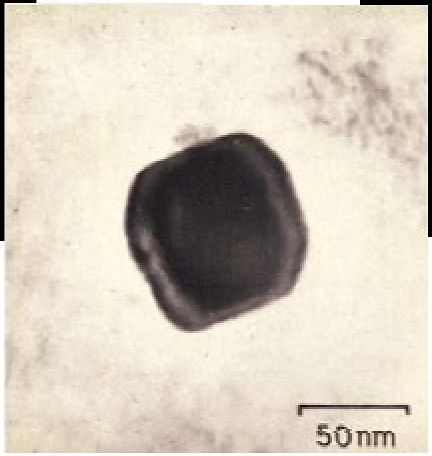
Scattering cross-section $\propto V^2/\lambda^4$: Rayleigh scattering

Absorption cross-section $\propto V/\lambda$ (dominates over scattering for small size)

Localized Surface Plasmon

Overview

Illuminated from inside

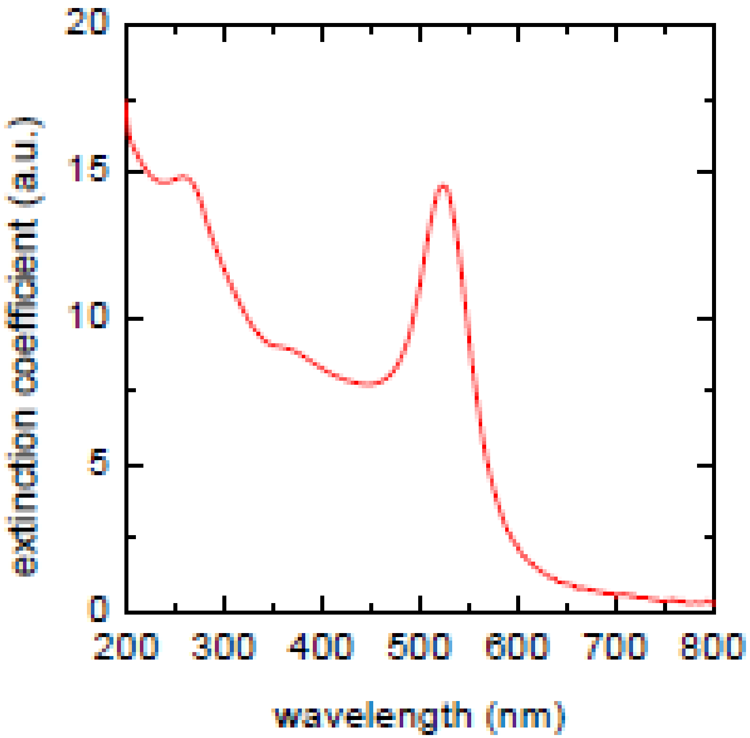


Illuminated from outside

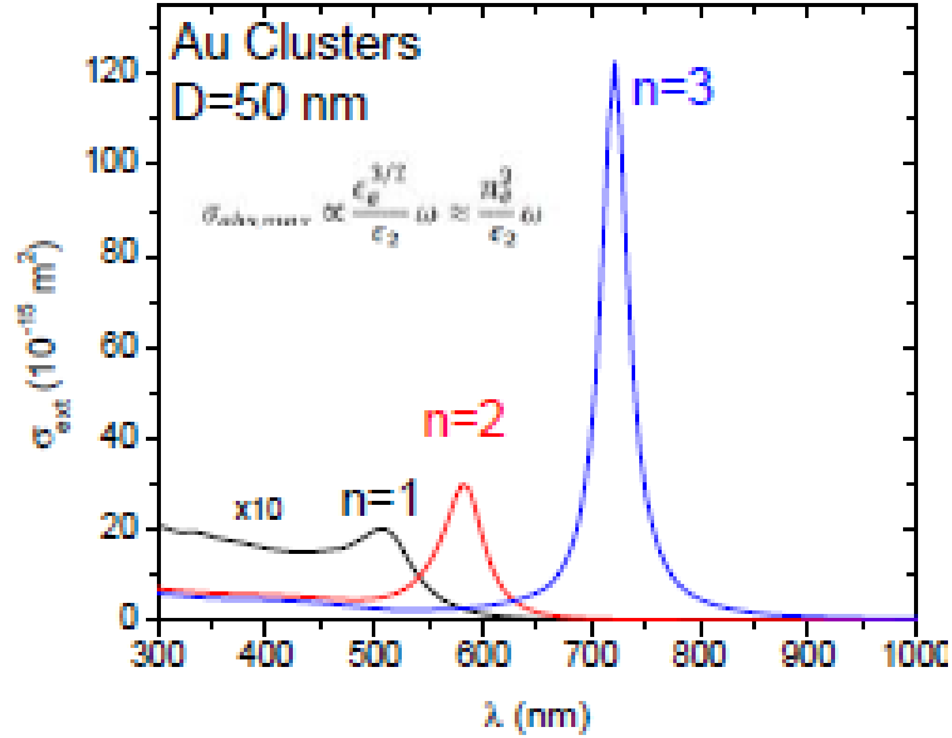
Lycurgus cup

Example: extinction of Au nanoparticles

Au (∅ 30 nm) in solution



Calculated values

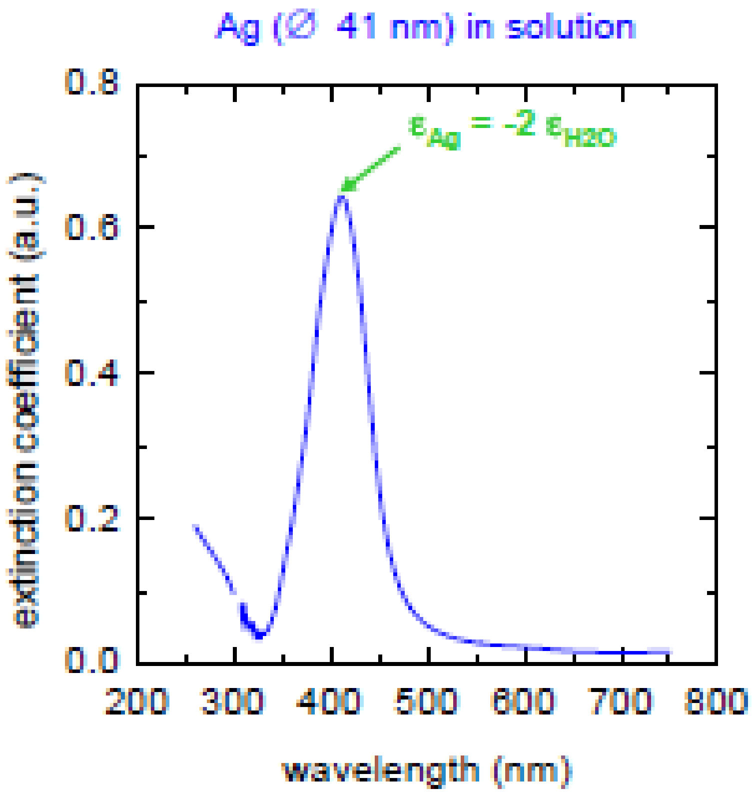


λ_{res}=524 nm τ_{relax} = 4 fs

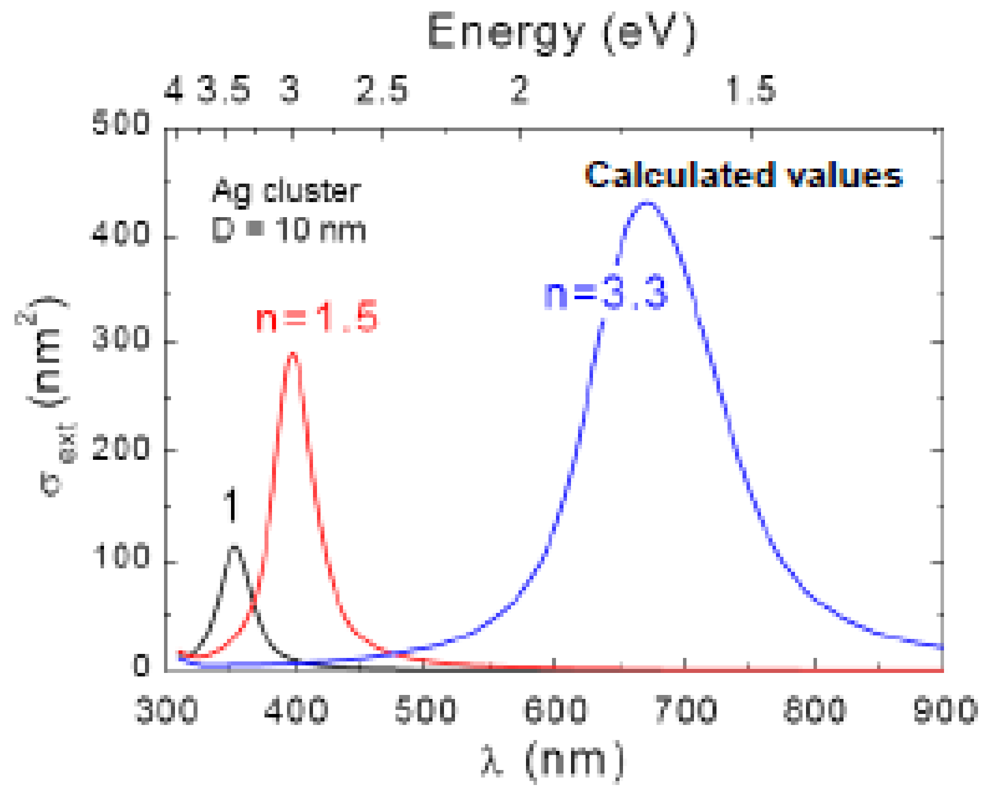
Extinction measurement of gold nanoparticles in water (n=1.33-1.35)

Note that a large refractive index can move the resonance away from the interband transitions in gold

Example: extinction of Ag nanoparticles



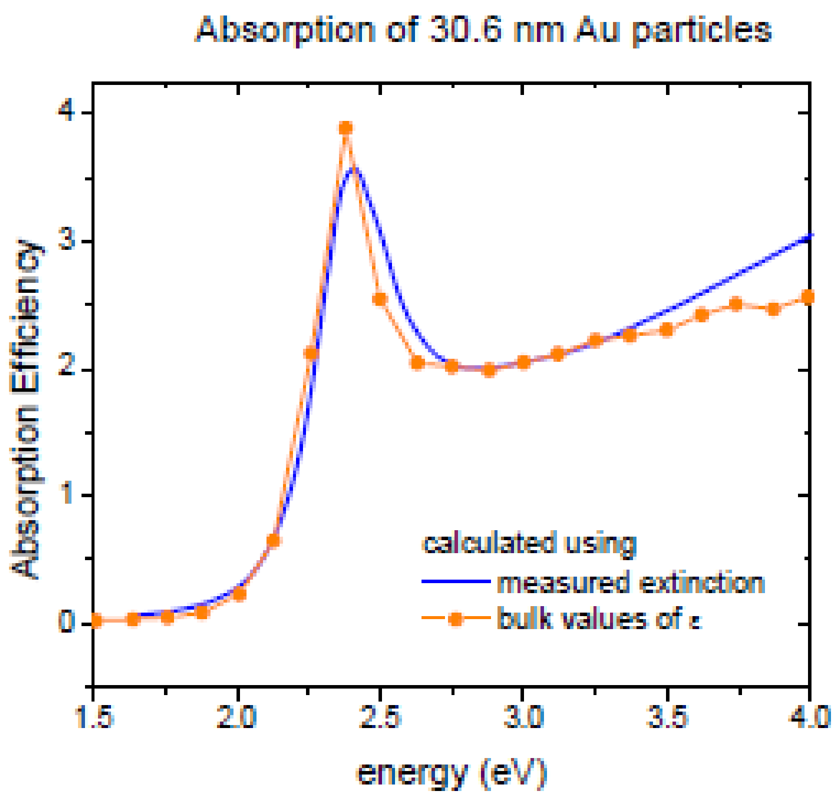
λ_{res}=410 nm τ_{relax} = 2 fs



$$\sigma_{abs,max} \propto \frac{\varepsilon_e^{3/2}}{\varepsilon_2}\omega \approx \frac{n_e^3}{\varepsilon_2}\omega$$

Extinction measurement of silver nanoparticles in water (n=1.33-1.35)

How small is still bulk?



For 'large' (but < λ) particles, optical properties nanoparticles near resonance well described by electrostatic formula with **bulk dielectric functions**.

Damping in very small particles

Very small particles (d<10nm): electrons start to interact significantly with the particle surface, leading to additional damping due to *surface scattering*

Effect becomes significant if particle diameter << mean free path

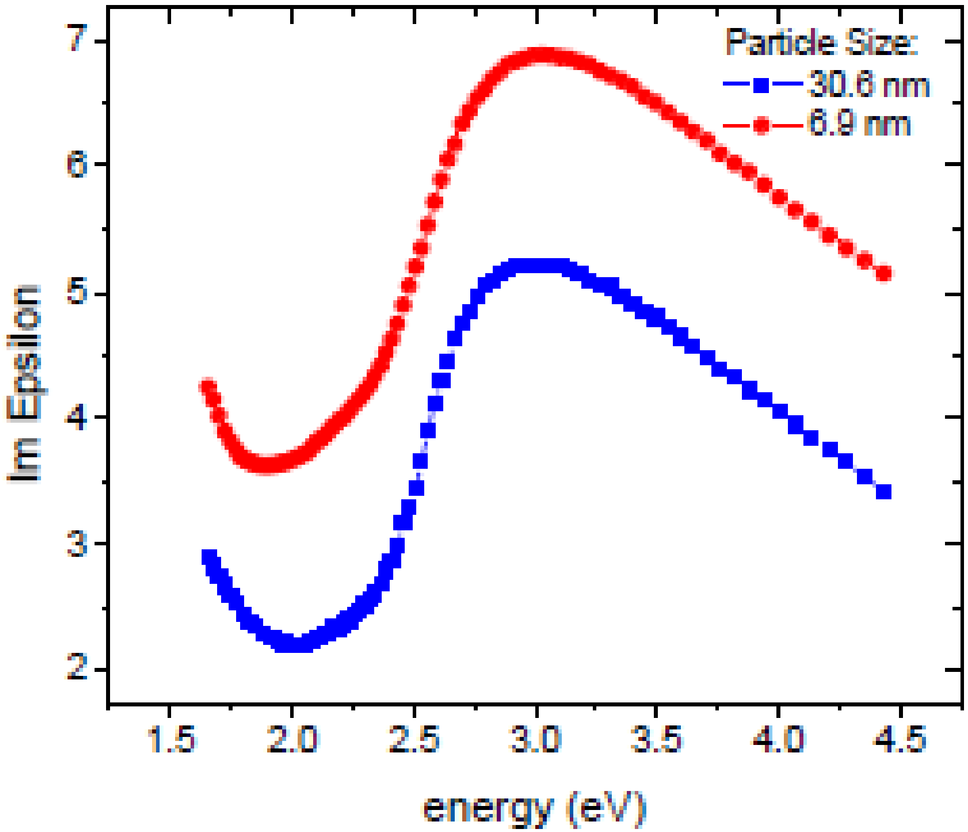
$$\gamma = \gamma_{bulk} + A\frac{v_F}{a}$$

total damping   surface component

Here described in terms of Fermi velocity v_f, diameter a, and electron scattering coefficient A

Value for gold: $v_f \approx 1.4\cdot10^6$ m/s

Diameter of 14 nm: $v_f/a = 10^{14}\ s^{-1}$
Frequency of red light: $5\cdot10^{14}\ s^{-1}$



⇒ Dielectric function of the metal particle is size dependent for small diameter

Size-dependence of extinction of Al nanoparticles (calculations)

C. Bohren and D. Huffman, “Absorption and scattering of light by small particles”, Wiley, 1983
(later on referred to as “B&H”)

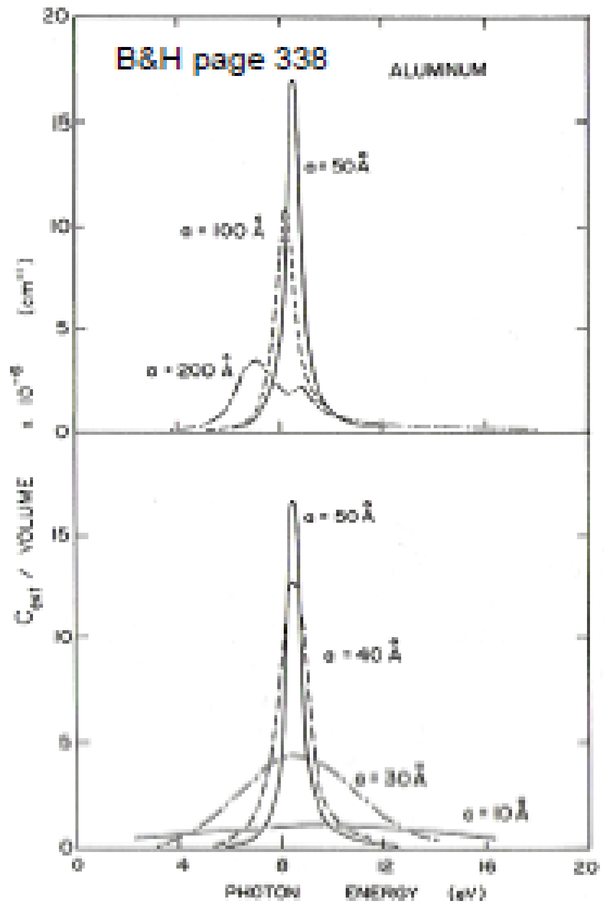


Figure 12.3 Calculated extinction per unit volume of aluminum spheres.

Large particles : electrostatic limit no longer a good approximation

⇒ finite phase delay between front and back of particle leads to excitation of multipolar modes

General broadening and red-shift of resonance for larger size

Small particles : electrostatic limit OK, bulk dielectric function no longer accurate

⇒ significant surface scattering increases ε” and damping, resulting in

General broadening for decreasing size

$$\gamma = \gamma_{bulk} + A\frac{v_F}{a}$$

Size-dependence of absorption of Au nanoparticles

B&H page 370

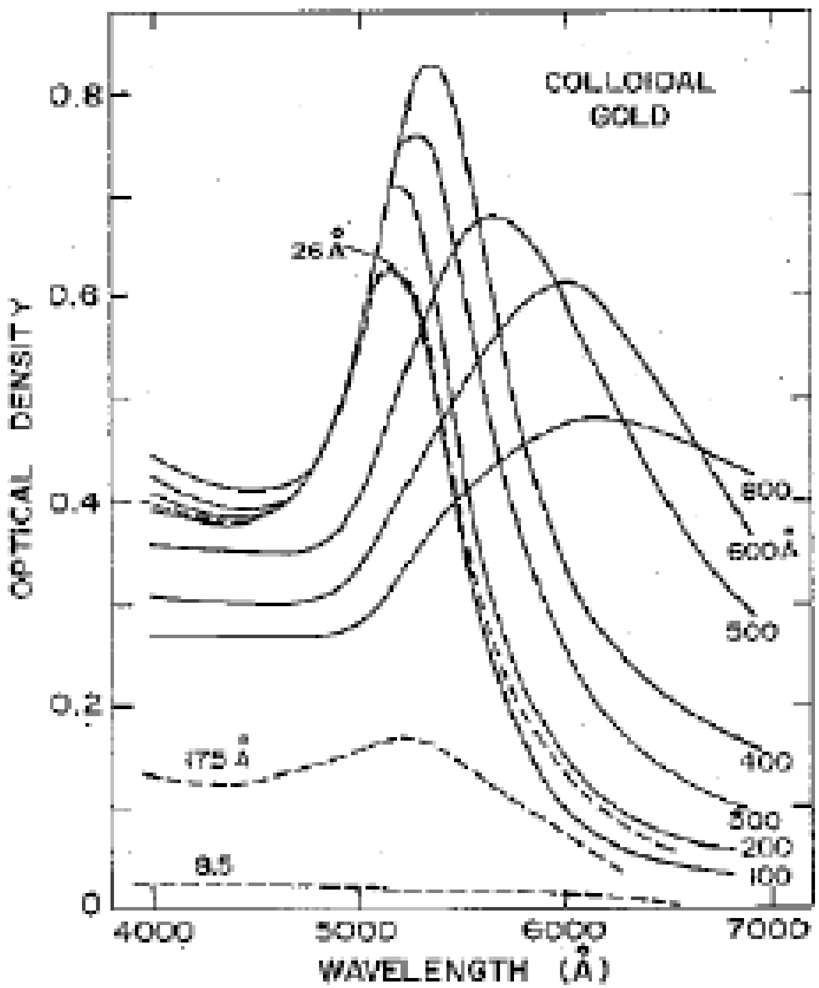
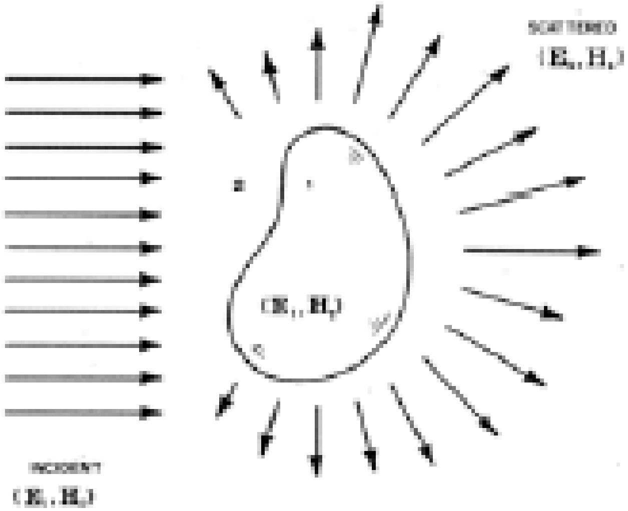


Figure 12.17 Absorption by gold particles of different radii. The solid curves are from Turkevich et al. (1954); the dashed curves are from Doremus (1964).

Fields around finite size particle - beyond quasi electrostatic limit

Irradiation of a small object results in polarization and resulting scattering as well as absorption. General solution quite complicated.

Total field given by $\mathbf{E}_2 = \mathbf{E}_i + \mathbf{E}_s$



Maxwell equations for time harmonic fields:

$$\nabla \cdot \epsilon E = 0 \qquad \nabla \times \mathbf{E} = i\omega\mu\mathbf{H}$$
$$\nabla \cdot H = 0 \qquad \nabla \times \mathbf{H} = -i\omega\varepsilon\mathbf{E}$$

Vector wave equation:

$$\nabla^2\mathbf{E} + k^2\mathbf{E} = 0 \qquad \nabla^2\mathbf{H} + k^2\mathbf{H} = 0$$

where $k^2 = \omega^2\varepsilon\mu$

Boundary conditions at the particle surface:

$$[\mathbf{E}_2(\mathbf{x}) - \mathbf{E}_1(\mathbf{x})] \times \hat{\mathbf{n}} = 0$$
$$[\mathbf{H}_2(\mathbf{x}) - \mathbf{H}_1(\mathbf{x})] \times \hat{\mathbf{n}} = 0$$

From the solutions, we can find the total energy flow outside the particle:

$$\mathbf{S} = \mathbf{S}_i + \mathbf{S}_s + \mathbf{S}_{ext} = \tfrac{1}{2}\mathrm{Re}\{\mathbf{E}_i \times \mathbf{H}_i^*\} + \tfrac{1}{2}\mathrm{Re}\{\mathbf{E}_s \times \mathbf{H}_s^*\} + \tfrac{1}{2}\mathrm{Re}\{\mathbf{E}_i \times \mathbf{H}_s^* + \mathbf{E}_s \times \mathbf{H}_i^*\}$$

This problem has been solved analytically for spherical objects by Gustav Mie

Extinction by a sphere - Mie Theory

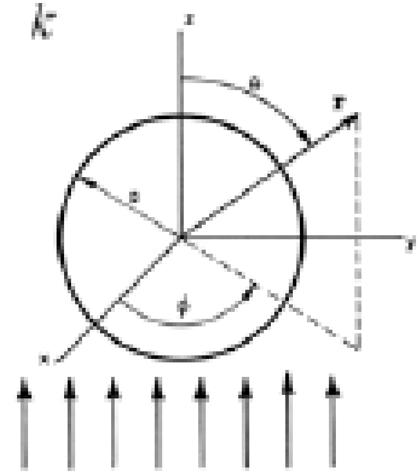
Solution makes use of the fact that one can construct functions that satisfy the *vector wave equation* based on a function ψ that satisfies the *scalar wave equation*

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin\theta}\frac{\partial^2\psi}{\partial\phi^2}+k^2\psi=0.$$

These 'vector harmonic' solutions are constructed from ψ according to : $\mathbf{M}=\nabla\times(\mathbf{r}\psi)$ $\mathbf{N}=\dfrac{\nabla\times\mathbf{M}}{k}$

First: solve the scalar wave equation

Next: construct solutions to vector wave equation



Scalar solutions:

$$\psi_{emn}=\cos(m\phi)P_n^m(\cos\theta)z_n(kr)$$

$$\psi_{omn}=\sin(m\phi)P_n^m(\cos\theta)z_n(kr)$$

where P_n^m are Legendre polynomials and
z_n are Bessel functions (see e.g. B&H Ch. 4)

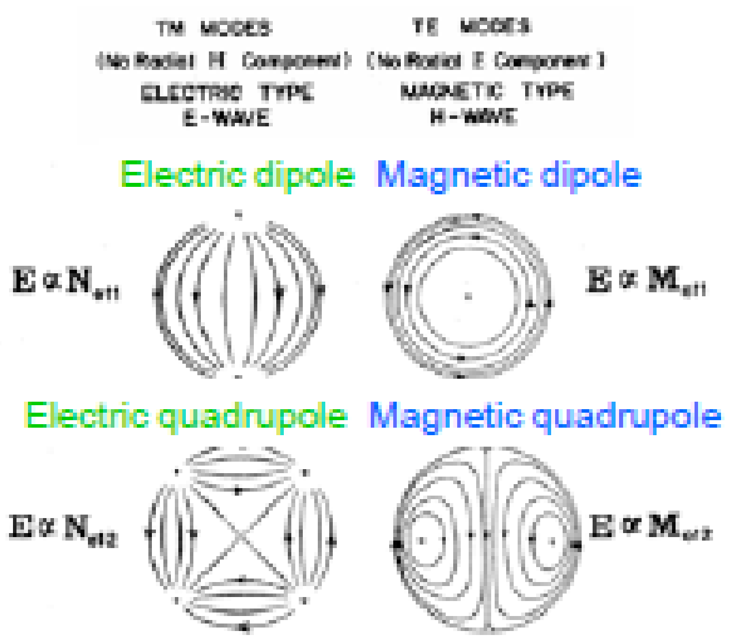
Obtained vector functions form a complete *basis set*

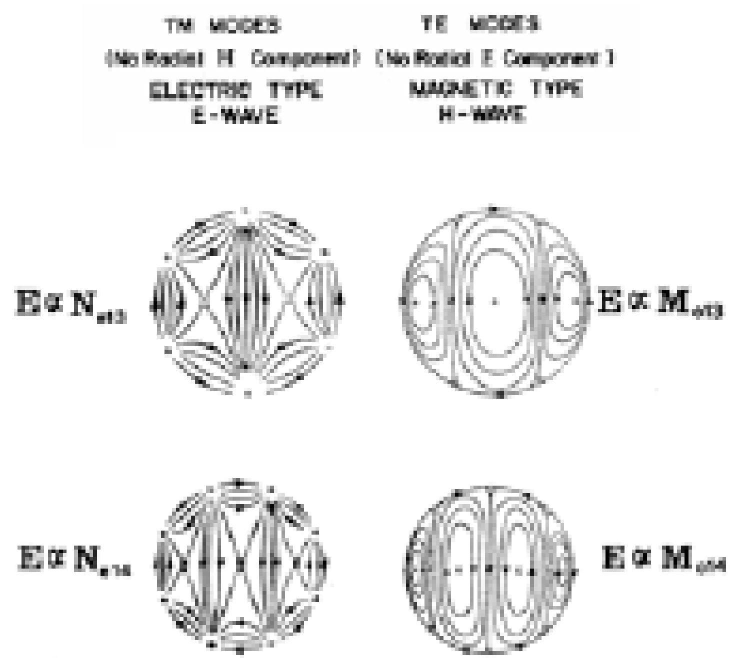
We can solve the scattering problem by describing the incident field, the internal field, and the scattered field in terms of N and M, and satisfying the boundary conditions

Even solutions ψ_e lead to allowed $E \propto N$, odd solutions ψ_o lead to allowed $E \propto M$

Electromagnetic Normal Modes of a Sphere

M and **N** represent a collection of allowed field distributions inside the particle





a_n and b_n are the corresponding scattering coefficients resulting from satisfying the boundary conditions under plane wave illumination

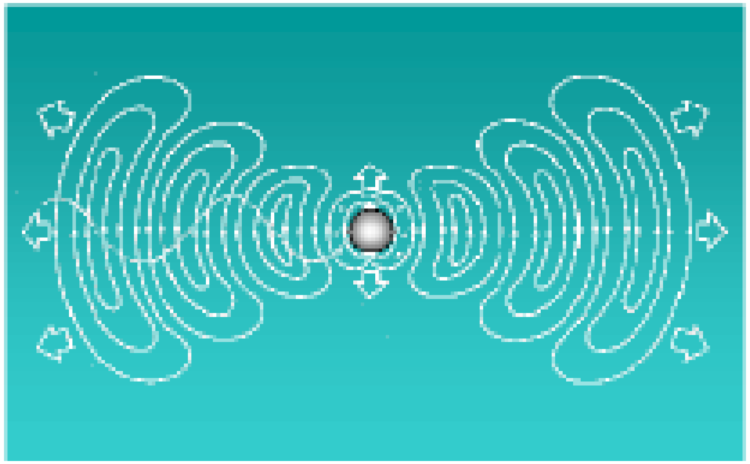
Note: lines correspond to field lines on the sphere surface (!), not the field lines inside the sphere volume. Hence the curvature in the dipolar mode

Any field in the particle can now be described in terms of a superposition of excited normal modes of the sphere

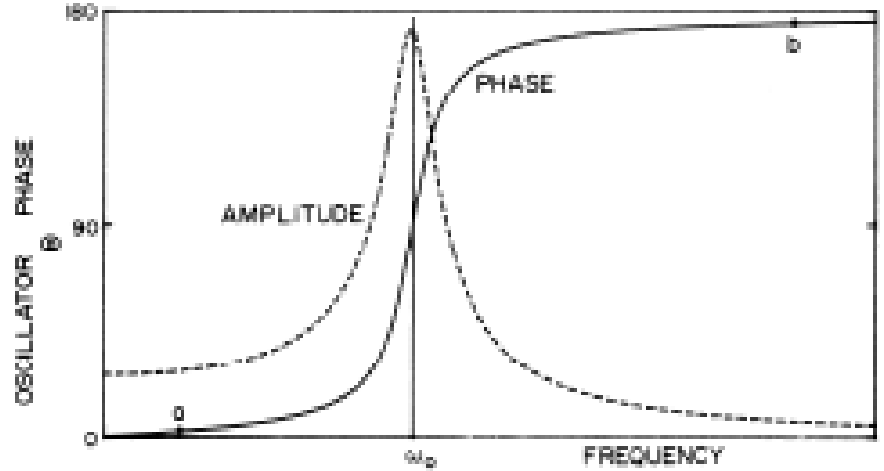
Polarization of particles is not just dipolar, but superposition of multipolar modes

Summary: metal nanoparticle plasmons

Metal nanoparticles support collective charge oscillations



Absorption and scattering of light by small particles, Bohren & Huffman



- Electron oscillation amplitude strong near the nanoparticle plasmon resonance
- Absorption (electronic collisions) strong near resonance
- Optical scattering (dipole radiation) strong near resonance
- Sharpest resonance for high AC conductivity materials
- Sharpest resonance for particles with d > ~5nm (prevents surface damping) and d << λ (prevents multipolar excitations)
- Resonance frequency depends on shape and dielectric environment

Surface Plasmon Photonics

Optical technology using
- propagating surface plasmon polaritons
- localized plasmon polaritons

Also called:
- Plasmonics
- Plasmon photonics
- Plasmon optics

Topics include:

Localized resonances/ local field enhancement	- nanoscopic particles - near-field tips
Propagation and guiding	- photonic devices - near-field probes
Enhanced transmission	- aperture probes - filters
Negative index of refraction and metamaterials	- perfect lens
SERS/TERS	- surface/tip enhanced Raman scattering
Molecules and quantum dots	- enhanced fluoresence

Surface Plasmon-assisted Spectroscopy

Technique	*Largest enhancement factor*
Surface enhanced raman SERS	10^{14} Nie and Emery, *Science*, 1997, *275*, 1102.
Surface enhanced IR SEIRA	10^{4} Tsang, et.al., *Phys. Rev. Lett.*, 1980, *45*, 201.
Sum frequency generation SESFG	10^{4} Baldelli, et.al., *J. Chem.Phys.*, 2000, *113*, 5432.
Second harmonic generation SESHG	10^{4} Chen, et.al., *Phys. Rev. Lett.*, 1981, *46*, 145.
Surface enhanced fluorescence	~100

Nanoparticles for detection

Several properties make resonant nanoparticles unique for detection:

- **bright** (large scattering cross section) : easy to detect
- **small** : can diffuse through biological tissue
- **can be modified** : can be linked to many organic molecules
- can be made **stable** in solution (low spontaneous degradation)
- **low photobleaching** : long illumination times possible
- can **enhance local fields** : enhanced Raman scattering near nanoparticle
- resonance can be **'tuned'** (multilayers/core-shell) : 'parallel detection'

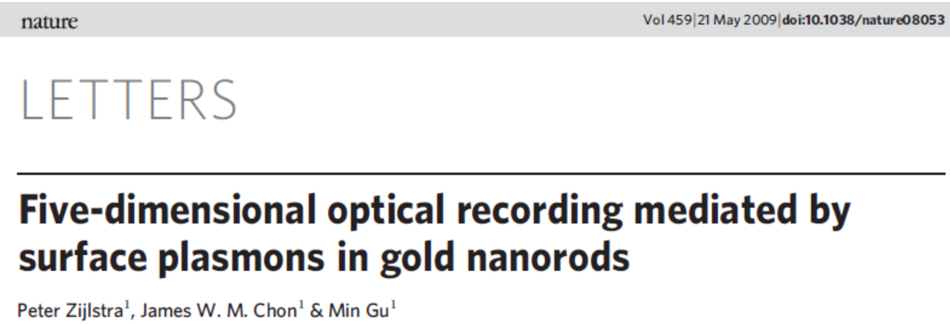
Nanoparticle plasmon-based approaches in biology and medicine

Biodetection techniques

- use surface enhanced Raman to identify molecules
- use resonance shift due to binding (local epsilon change)
- use nanoparticles as tracers
- use nanoparticle-DNA hybridization for gene detection
- use nanoparticle aggregation to detect cross-linking
- use fluorophore quenching as indication of DNA binding

Nanoparticles in medicine

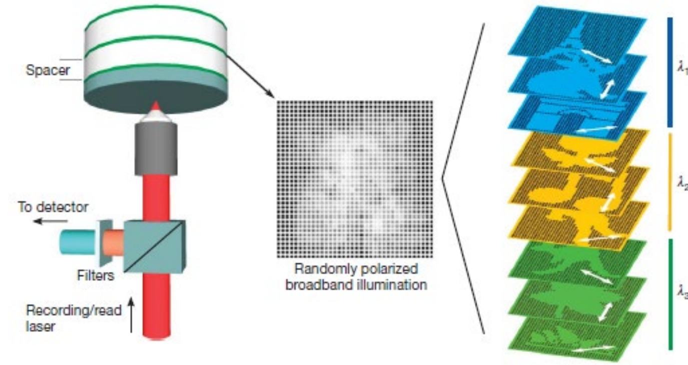
- use nanoparticles as local heat source
- use nanoparticles as drug release agent

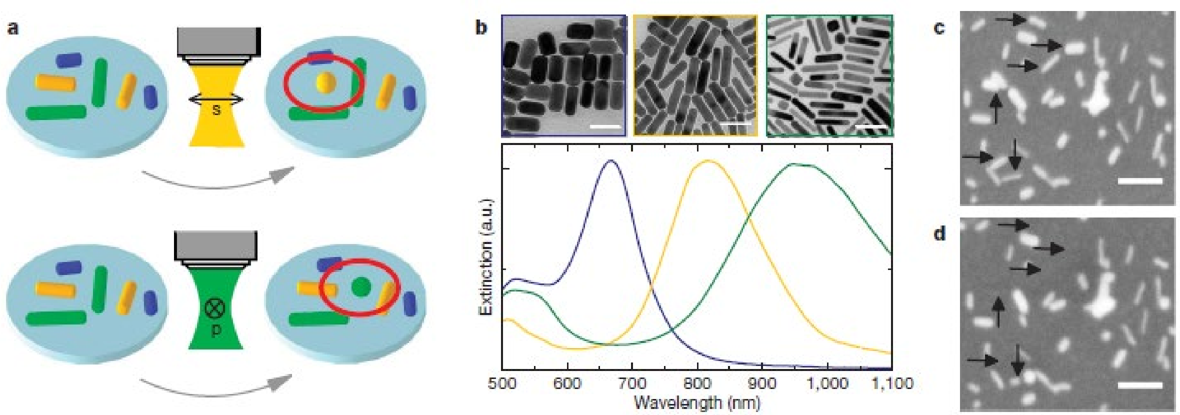

nature Vol 459|21 May 2009|doi:10.1038/nature08053

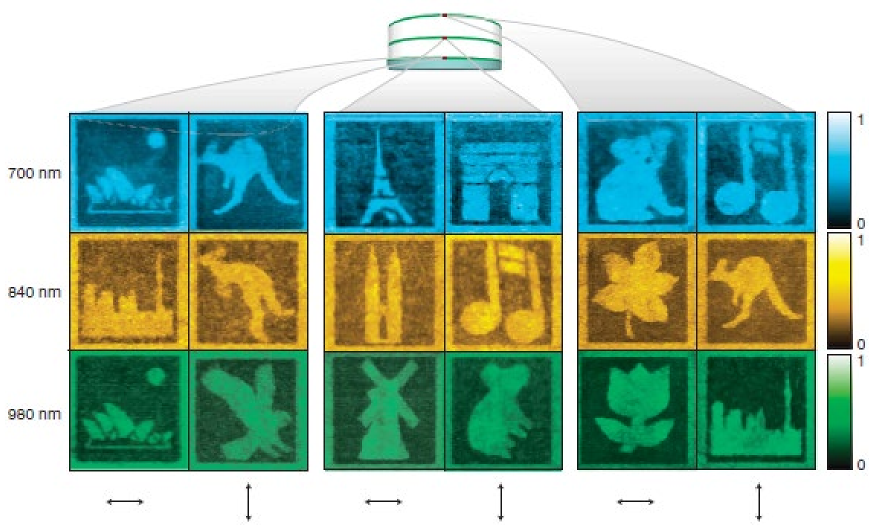
LETTERS

Five-dimensional optical recording mediated by surface plasmons in gold nanorods

Peter Zijlstra[1], James W. M. Chon[1] & Min Gu[1]





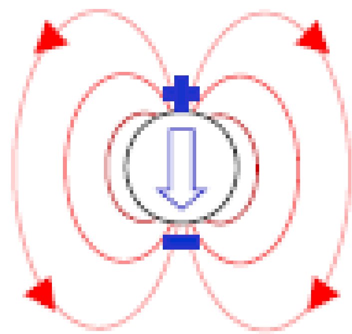


- Recording medium: thin polymer film with Au nanorods
- Recording: utilize enhanced absorption due to plasmon resonance to selectively reshape nanorods (at which point the resonant wavelength shifts)
- Use wavelength and polarization multiplexing (3 + 2)
- Readout with 2-photon PL

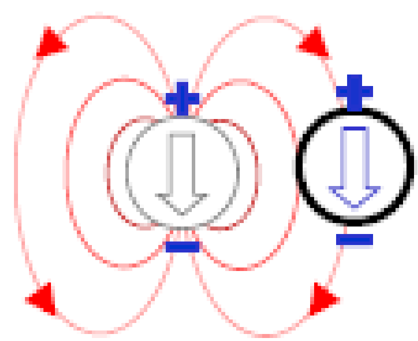
Inter-particle coupling

Individual particle :
resonance determined by size, shape, dielectric, metal
charge displacements leads to surface charge ⇒ restoring force ⇒ resonance

Excitation by plane wave,
vertically polarized,
moving into page



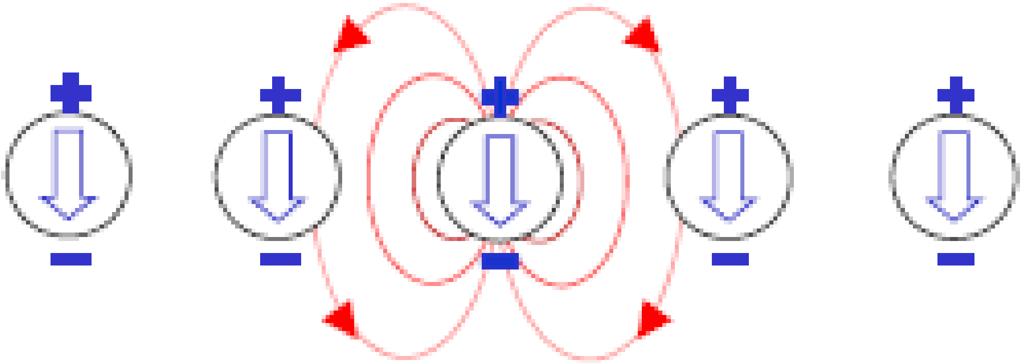
Multiple particles :
neighboring particles introduce additional field components
⇒ modified restoring force ⇒ modified resonance



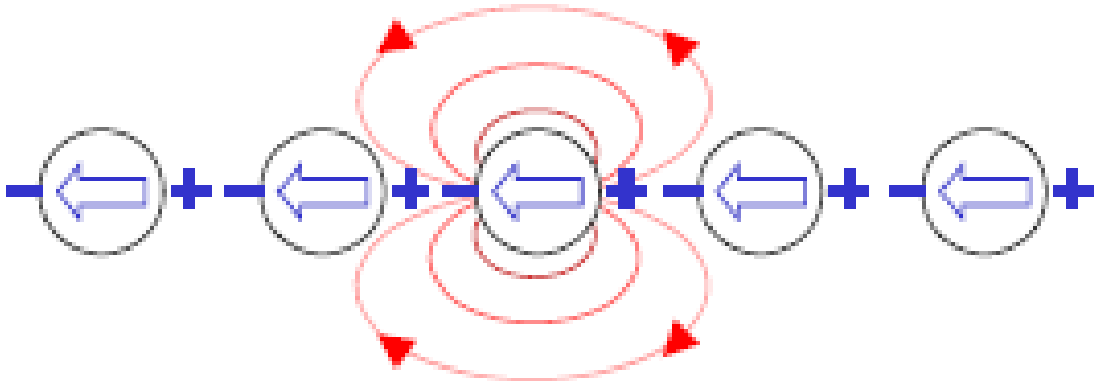
This situation: neighbor
in-phase and laterally displaced ⇒
increased restoring force for same dz
⇒ increased resonance frequency

Inter-particle coupling – collective modes, dipole picture

Transverse oscillation ⇒ blue-shifted resonance

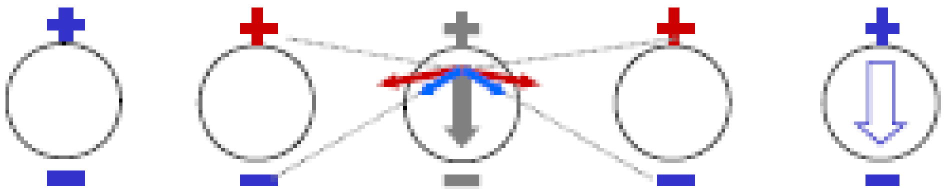


Longitudinal oscillation ⇒ red-shifted resonance



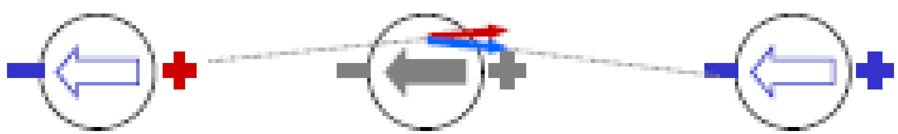
Inter-particle coupling – collective modes, Coulomb force interpretation

Transverse oscillation ⇒ Coulomb forces **add**: blue-shifted resonance
Note, at center of particle, neighbor-induced forces perfectly vertical
Forces stronger near particle edges (closer to neighbor), and
field lines not exactly vertical (see also previous slide)



Question: do you expect multipolar particle modes for diameter << λ_{exc}?

Longitudinal oscillation ⇒ Coulomb forces **subtract**: red-shifted resonance

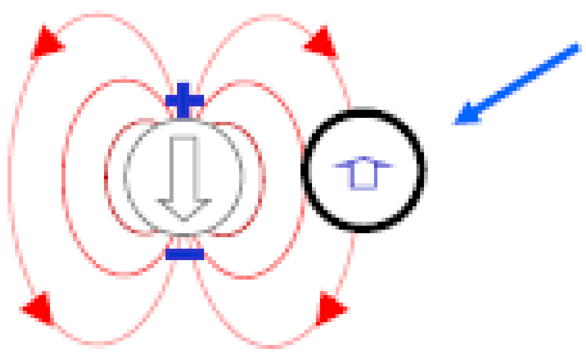


Important realization: for *large*, *closely spaced* particles, neighbor fields not homogeneous over particle volume ⇒ higher order modes can be excited

Inter-particle coupling

Driven particles

If particle 1 is somehow excited at a frequency near the nanoparticle resonance then particle 2 experiences a rapidly oscillating driving field $\Rightarrow$ phase lag!



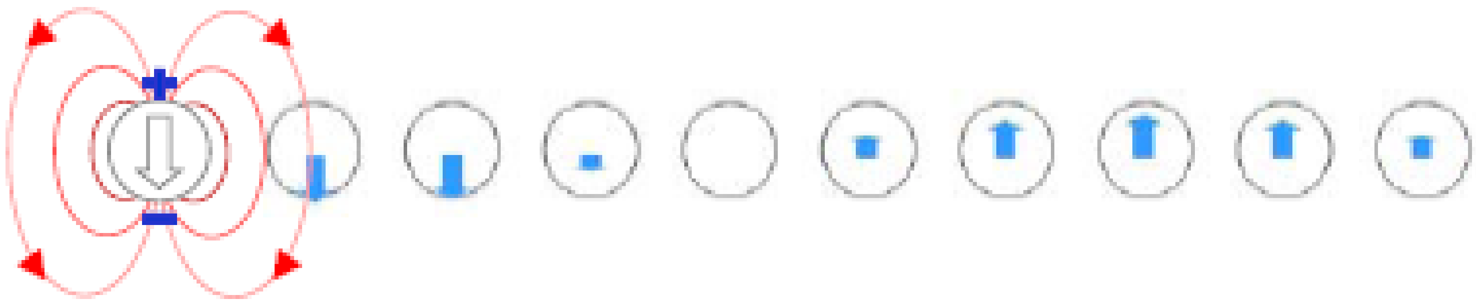
This case: low frequency: particle tends to cancel the applied field, but phase lag allows finite oscillating response field

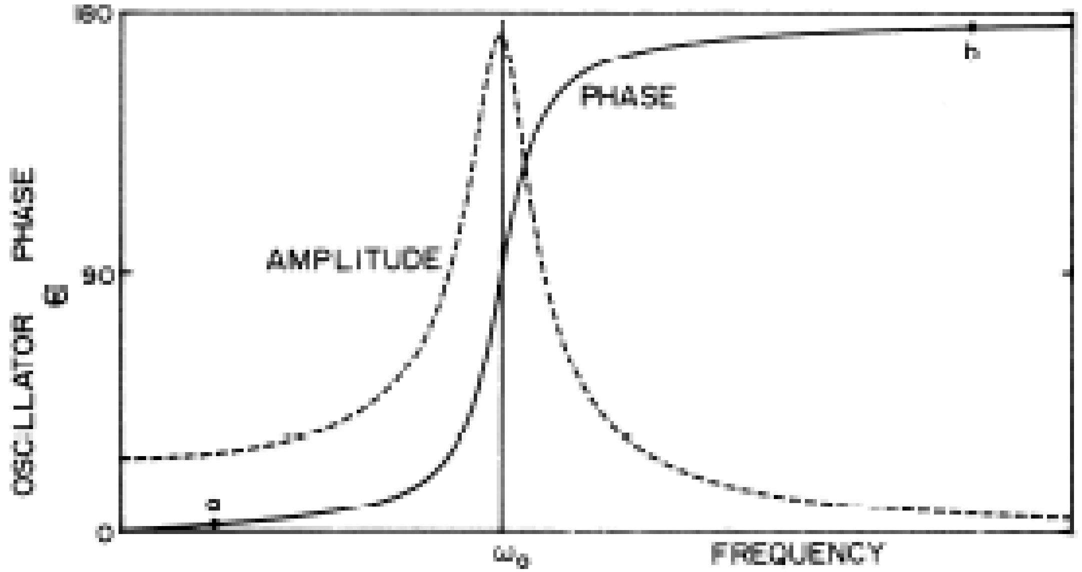
$\Rightarrow$ excitation of single particle can set up response in neighboring particles with a relative phase that is frequency dependent

This effect can be used to build nanoscale waveguides

The dipole model

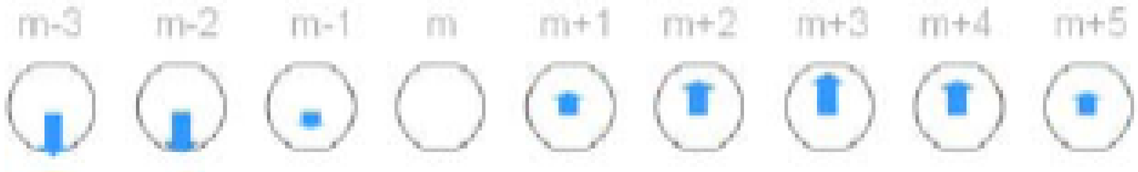
Excitation frequencies near single particle resonance ⇒ propagating waves





Wavelength depends on particle-particle phase lag

Mode propagation



Mathematical approach

Describe nanoparticle array as collection of interacting dipole oscillators with p=q·x the dipole moment (previously x was 'dz')

Assume each nanoparticle has individual resonance frequency ω_0 and a damping time constant given by $1/\Gamma$

Dipole field drops off rapidly with distance: assume only nearest neighbor interactions (only particle m-1 and m+1 affect restoring force)

Equation of motion for p:

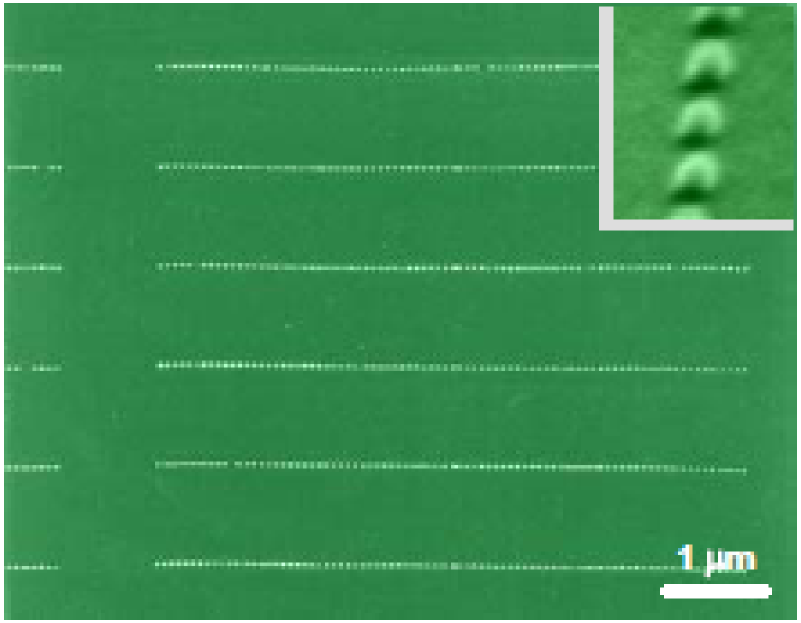
$$\ddot{p}_{I,m} = -\omega_0^2 p_{I,m} - \Gamma_I \dot{p}_{I,m} - \gamma_I \omega_1^2 \left(p_{I,m-1} + p_{I,m+1} \right)$$

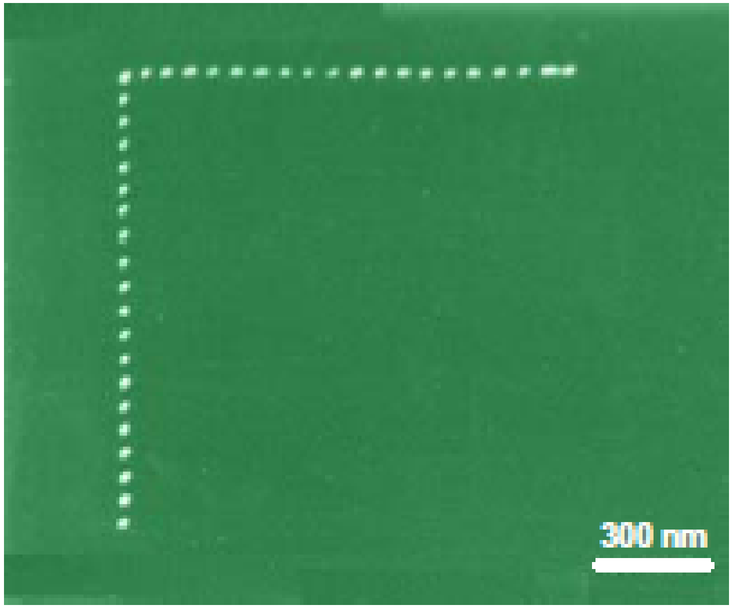
resonance damping coupling; $\gamma\omega_1^2 \propto d^{-3}$

M.L. Brongersma et al., Physical Review B 62, R16356 (2000)

Metal nanoparticle arrays made by e-beam lithography

50 nm Au particles on ITO coated glass



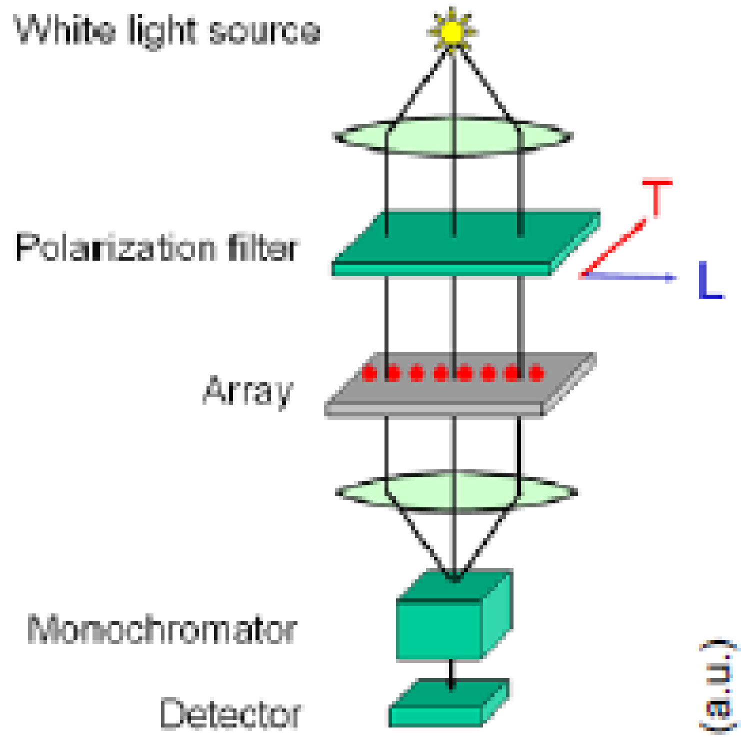


Dense array of particle lines, so 'large' fraction of surface area covered

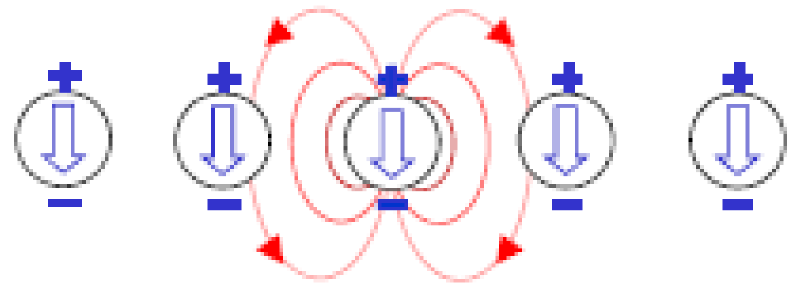
$\Rightarrow$ extinction measurements possible

Do polarization dependent extinction measurements, and look for resonantly enhanced extinction peaks

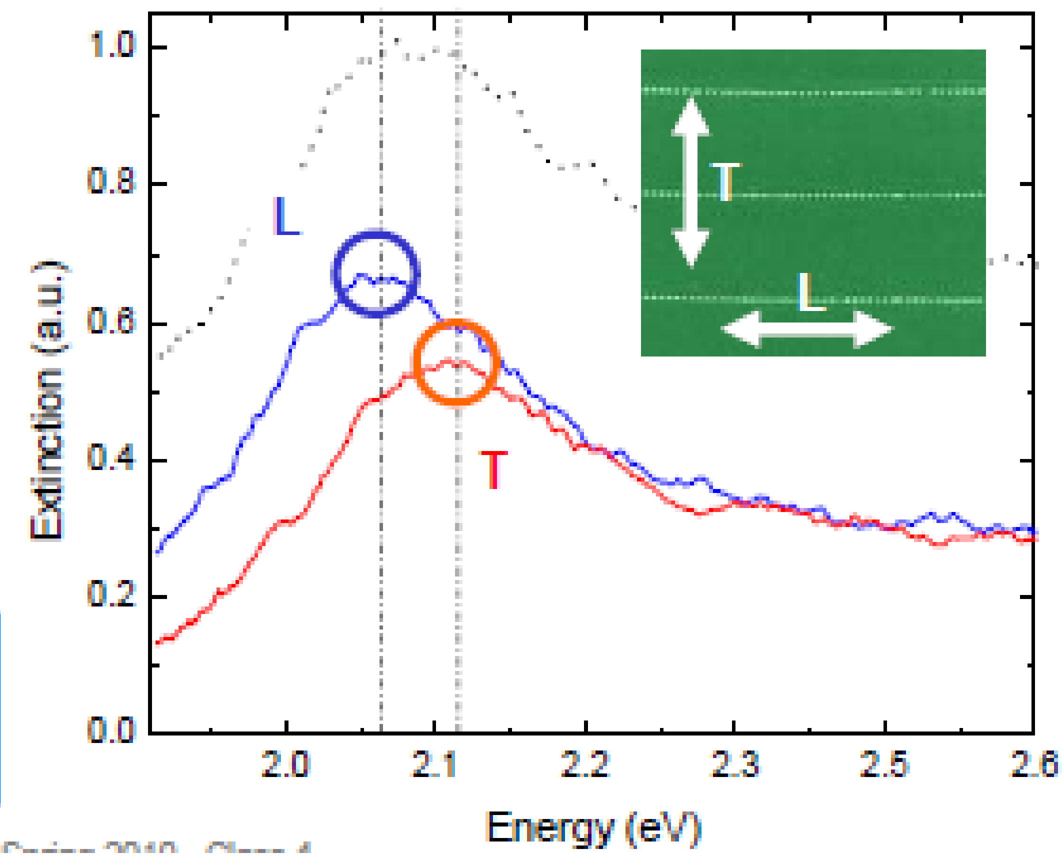
Experimental observation of collective modes



transverse polarization

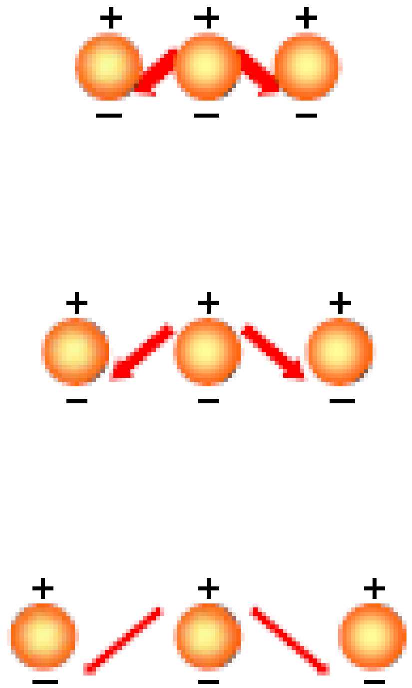


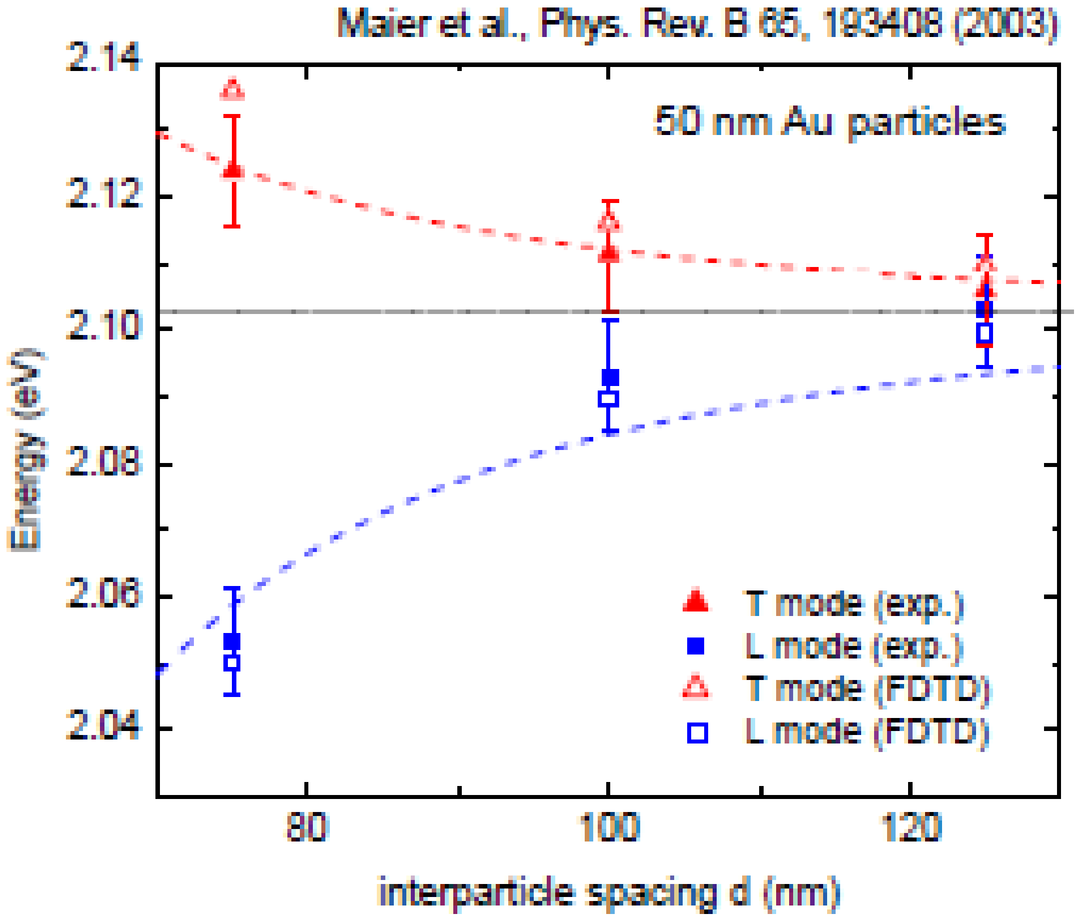
Maier et al., Phys. Rev. B 65, 193408 (2003)



Extinction measurements show presence of frequency-shifted collective resonances

Energy of the collective plasmon modes vs. spacing



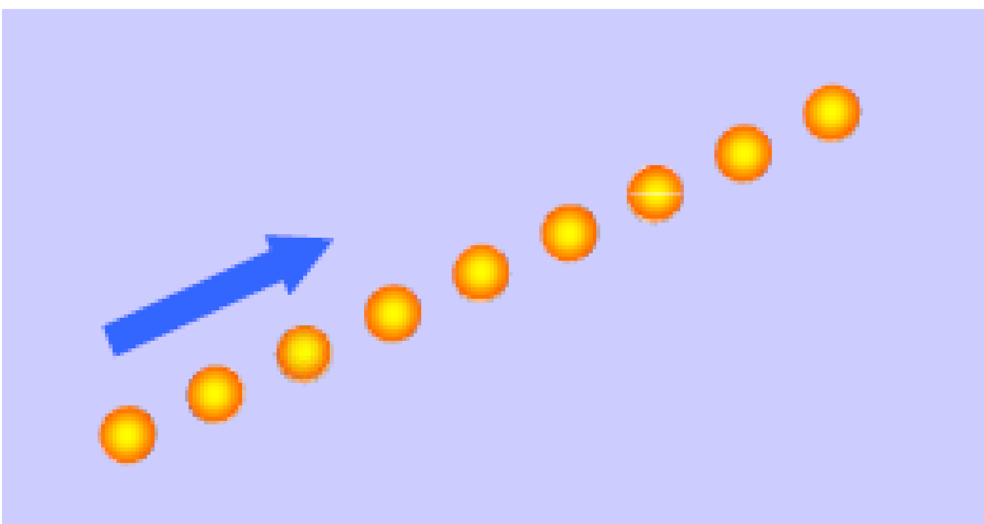


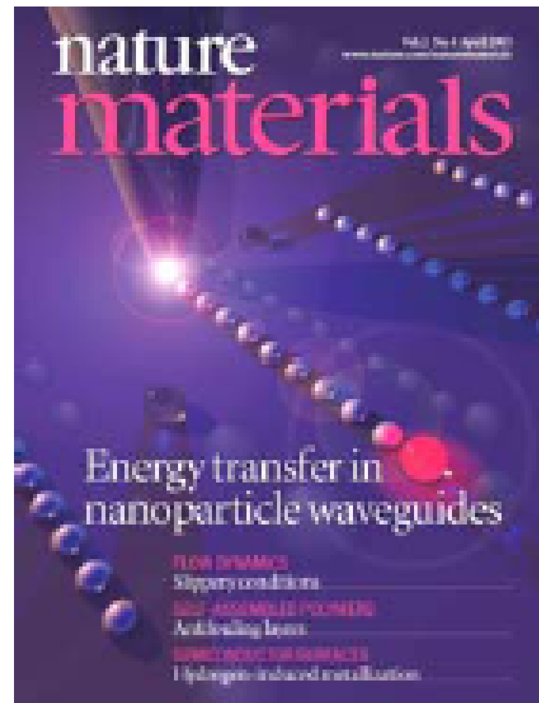
Spacing 3R $\Rightarrow$ group velocity for energy transport: 4×10^6 m/s

Coupled resonances in nanoparticle arrays

Nanoparticle arrays:

- individual particles have specific resonance frequency
- closely spaced particles show coupled oscillation modes
- light propagation through 'coupled resonators'
- optical waveguides with mode confinement << λ
- propagation length up to ~um length scale





Interacting nanoparticles for waveguiding

Summary - nanoparticle waveguides:

- individual particles have specific resonance frequency
- closely spaced particles show coupled oscillation modes
- light propagation can occur through coupled resonators
- propagating modes have frequencies that are near particle resonance
- particle center frequency tunable by material, shape, size
- group velocity tunable by shape, spacing

PRL 94, 017402 (2005) PHYSICAL REVIEW LETTERS week ending 14 JANUARY 2005

Improving the Mismatch between Light and Nanoscale Objects with Gold Bowtie Nanoantennas

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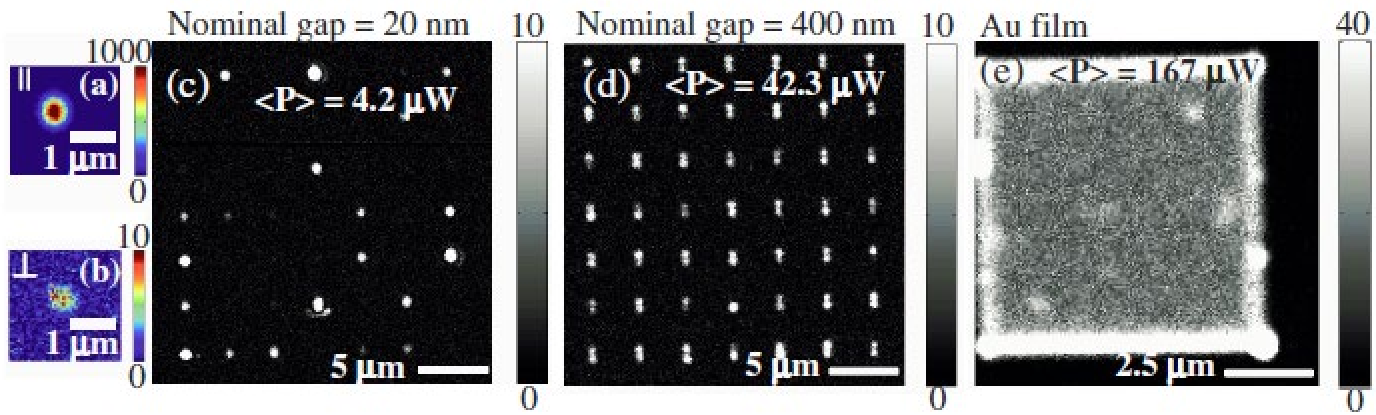
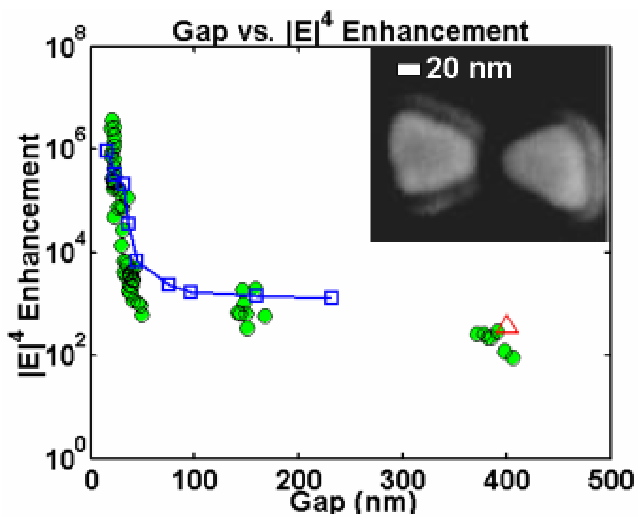
(Received 16 September 2004; published 13 January 2005)





- Au bowtie “nanoantenna” arrays: get enhancement in 2-photon PL due to enhanced E-field due to plasmon coupling
- to see large effects, need the spacings of <50 nm

REVIEWS

Light in tiny holes

C. Genet[1] & T. W. Ebbesen[1]

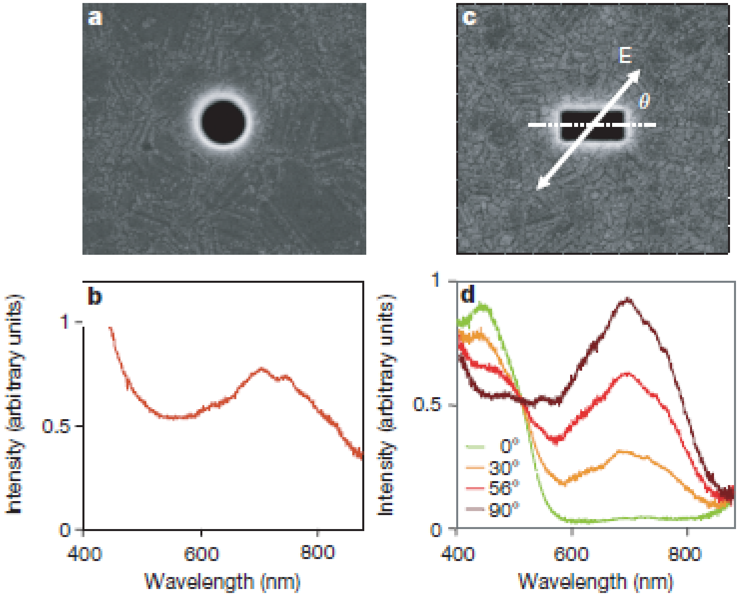


Figure 1 | Optical transmission properties of single holes in metal films. The holes were milled in suspended optically thick Ag films illuminated with white light. **a**, A circular aperture and **b**, its transmission spectrum for a 270 nm diameter in a 200-nm-thick film. **c**, A rectangular aperture and **d**, its transmission spectrum as a function of the polarization angle θ for the following geometrical parameters: 210 nm $\times$ 310 nm, film thickness 700 nm.

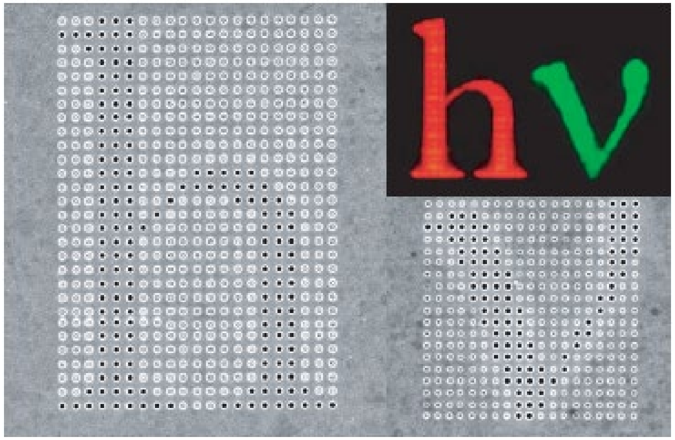


Figure 6 | Holes in a dimple array generating the letters 'hv' in transmission. An array of dimples is prepared by focused-ion-beam milling an Ag film. Some of the dimples are milled through to the other side so that light can be transmitted. When this structure is illuminated with white light, the transmitted colour is determined by the period of the array. In this case the periods were chosen to be 550 and 450 nm respectively to achieve the red and green colours.

The presence of tiny holes in an opaque metal film, with sizes smaller than the wavelength of incident light, leads to a wide variety of unexpected optical properties such as strongly enhanced transmission of light through the holes and wavelength filtering. These intriguing effects are now known to be due to the interaction of the light with electronic resonances in the surface of the metal film, and they can be controlled by adjusting the size and geometry of the holes. This knowledge is opening up exciting new opportunities in applications ranging from subwavelength optics and optoelectronics to chemical sensing and biophysics.