Optical properties of gold and silver spherical plasmonic nanoantennas:

size dependent multipolar resonance frequencies and plasmon damping rates

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http://www.ifpan.edu.pl/ON-2/on22/staff/kolwak.html

„Small is different"

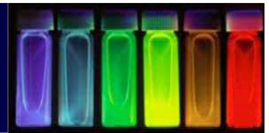
physical and chemical properties of some nanometer size structures

U. Landmann

Example:
gold, the element known as the most noble from all the metals.

When reduced in size to the nanometer range, gold looses its nobleness (and colour)

- striking reactive features
- spectacular optical effects
- unusual electric conductivity
- unusual surface friction properties
- mechanical features (e.g. ductility)
- …



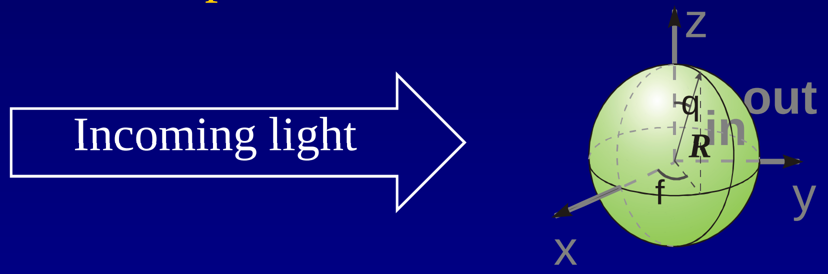
Properties of metal nanoparticles

depend on:

- ✓ **shape**
- ✓ **size**

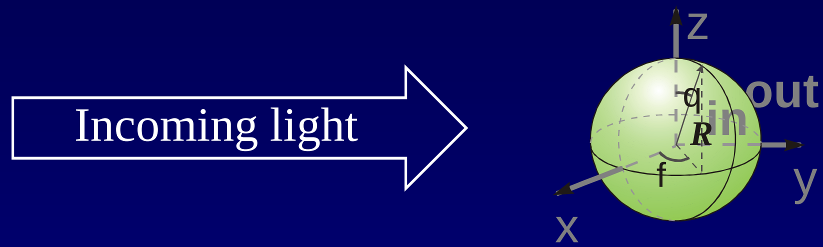
This work:

- optical properties of spherical particles
- the quantitative description of their plasmon-dependent size characteristics.



- striking reactive features
- spectacular optical effects
- unusual electric conductivity
- unusual surface friction properties
- mechanical features (e.g. ductility)
- …

Size and shape dependence:



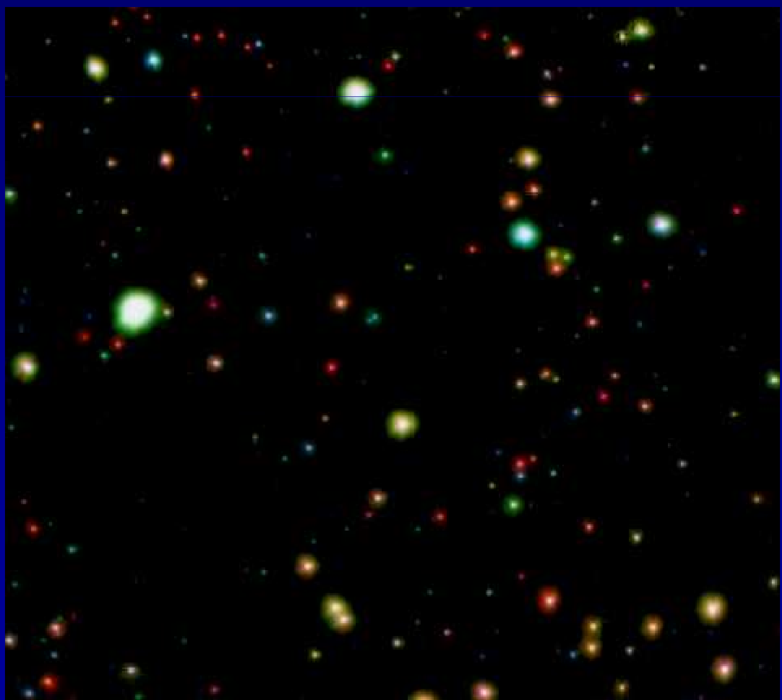


Image: Neil Anderson

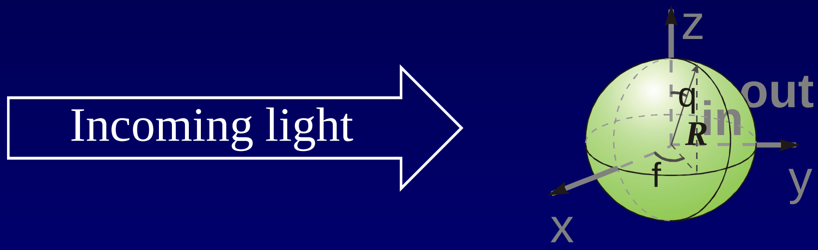
10µm

Scattering of white light by 30nm silver nanoparticles and clusters of nanoparticles of various sizes and shapes

(dark-field microscope image)

M. Beversluis , Ph.D.Thesis, University of Rochester, 2005

Size and shape dependence:



white light illumination:

back :

ϕ = 150, 100, 80, 60, 40, 200 nm

front :

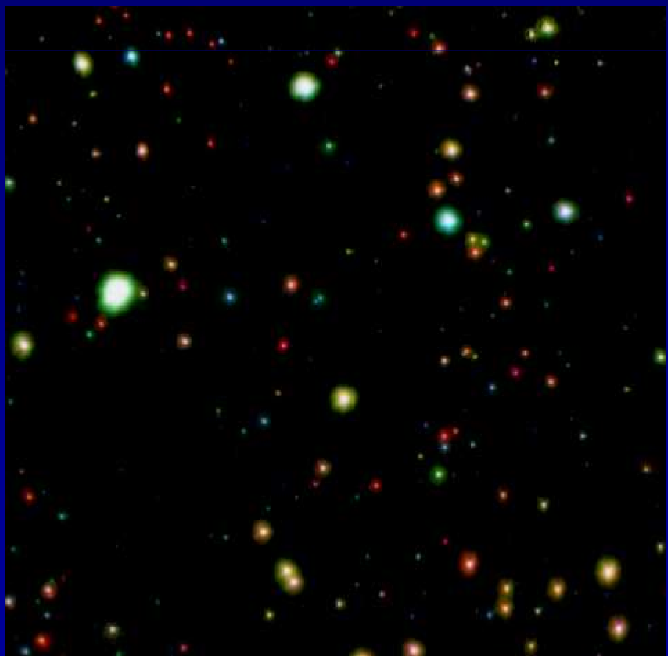
Despite extremely low concentration of gold particles ($< 10^{-2}$ weight %), suspensions show bright colours, which depend on the size of particles.

Suspensions of nanospheres

Mie scattering theory

G. Mie, Ann. Phys. 25, 377 (1908)

- a plane electromagnetic wave illuminating a homogeneous, perfectly spherical particle embedded in an infinite homogenous host medium
- the solutions of Maxwell equations supplemented by appropriate boundary conditions



10µm

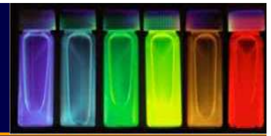
Image: Neil Anderson
M. Beversluis , Ph.D.Thesis, University of Rochester, 2005

Mie theory explains many observed effects, e.g.
diversity of colours of gold particles of diverse sizes.

white light illumination:

ϕ = 150, 100, 80, 60, 40, 200 nm

C. Sönnichsen, Dissertation der Fakultät für Physik der Ludwig-Maximilians-Universität München, 2004



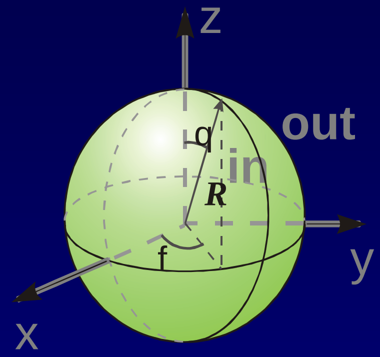
Size dependence

WHY

these effects are so wavelength selective?

What is the origin of spectacular colour effects observed?

Plasmon excitations



The unique optical properties of metal nanostructures are known to be due to surface plasmons.

Surface plasmons: collective oscillations of **free-electrons** at the metal-dielectric interface and electromagnetic fields associated with these oscillations (TM polarization).

Surface plasmon waves can be excited by light at some frequencies of the incoming light field: $\boxed{\omega = \omega_l(R)}$

However:

Mie theory **does not** deal with the notion of **plasmon resonances**.

In spite: maxima in the absorption or scattering resulting from Mie theory are interpreted as due to plasmon resonance positions.

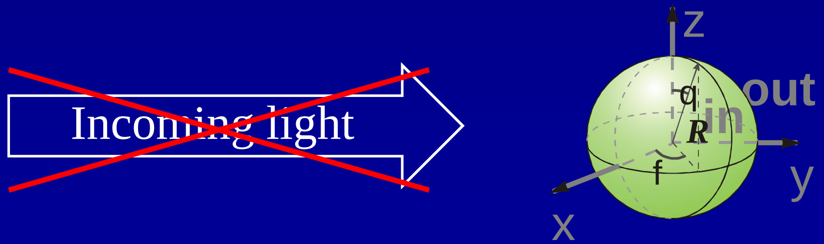
Eigenfrequencies of a metal sphere

Our interest: rigorous description of optical properties of a plasmonic spherical particle **as a function of size:**

$$\boxed{\omega = \omega_l(R), \quad l = 1,2,3,...}$$

Possibility of resonant excitation of the SP oscillations and damping of these oscillations we describe as the inherent property of a conducting sphere,.

The eigenvalue problem is formulated
in absence of external, incoming fields and
is abstracted from the quantity, which can be observed
(analogy to SP at a flat metal–dielectric interface)



central problem: dispersion relation
for the wave at the spherical metal–dielectric interface

K. Kolwas, S. Demianiuk, M. Kolwas, J. Phys. B, **29**, (1996) 4761
K. Kolwas, A. Derkachova, S. Demianiuk, Comp.. Mat. Sc., **35**, (2006) 337
K. Kolwas, A. Derkachova, M. Shopa J.Q.S.R.T. **110** 1490–1501(2009)

Surface plasmons

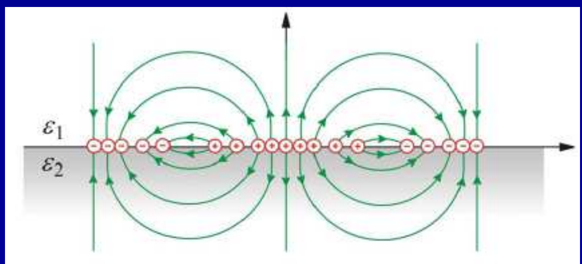
(re-consideration, rigorous size dependent modelling)

Helmholtz equations + continuity relations

Flat boundary:

Dispersion relation:

$$k_{SP}=\frac{\omega}{c}\sqrt{\frac{\omega^2-\omega_p^2}{2\omega^2-\omega_p^2}}$$



Spherical boundary:

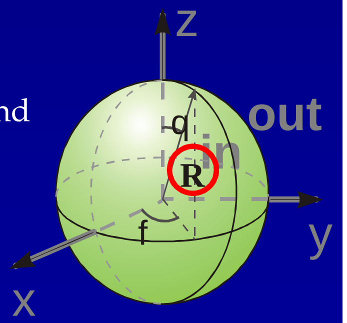
Equation defining dispersion relation (TM mode):

$$\sqrt{\varepsilon_{in}}\,\xi_l(k_{out}(\omega)R)\,\psi_l'(k_{in}(\omega)R)-\sqrt{\varepsilon_{out}}\,\xi_l'(k_{out}(\omega)R)\,\psi_l(k_{in}(\omega)R)=0,$$

$$k_{in}=\frac{\omega}{c}\sqrt{\varepsilon_{in}},\qquad k_{out}=\frac{\omega}{c}\sqrt{\varepsilon_{out}}$$

$\psi_l,\ \chi_l$ - Bessel function of the 1-st and2-nd kind

$\xi_l=\psi_l-i\chi_l$ - Hankel function

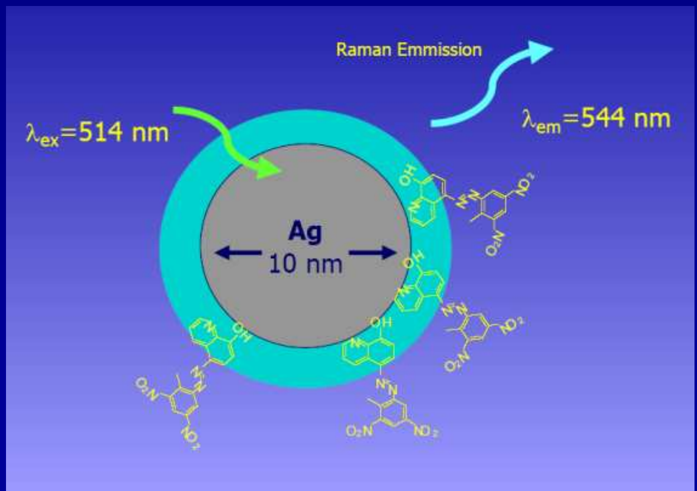


R. Fuchs , P. Halevi, Spatial Dispertion in Solids and Plasmas, ed. P. Halevi, 1992
K. Kolwas, S. Demianiuk, M. Kolwas, J. Phys. B, **29**, (1996) 4761
K. Kolwas, A. Derkachova, S. Demianiuk, Comp.. Mat. Sc., 35, (2006) 337

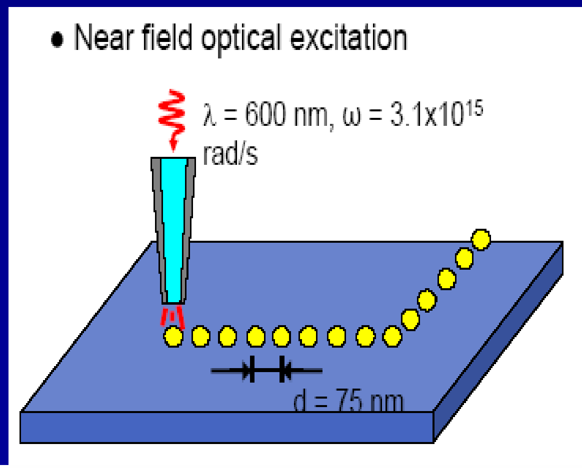
The explicit size dependence of plasmon resonance frequencies

- would be very useful in the numerous plasmon applications that involve e.g. **plasmon near field enhancement**.

SERS spectroscopic techniques



Guiding the light along the array of nanoparticles



R.M. Dickson et al., J. Phys. Chem. B **104**, 6095-6098 (2000)

Eigenfrequencies of a metal sphere

(rigorous size dependent modelling)

$$\varepsilon_D(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

relaxation rate of free electron movement

contribution of the bound electrons to the polarizability

Effective parameters for gold:
ε_∞ = 9,84eV
ω_p = 9,09eV
γ = 0,072eV

Self-consistent (divergent free) Maxwell eq. (no external fields)

+

Continuity relations for tangent component of **E** i **H** at frequency ω

Conditions for existence of solutions (TM in character) define:
$\Omega_l(R) = \omega'_l(R) + i\omega''_l(R)$

Frequencies of plasmon oscillations

Damping rates (radiation and heat)

The explicit plasmon size characteristics

$$\Omega_l(R) = \omega'_l(R) + i\omega''_l(R)$$

$\omega'_l(R)$ – resonace frequencies of plasmon oscillations of multipolar modes l =1,2,3,…,

$0 \neq |\omega''_l(R)|$ - plasmon damping rates (radiation and heat)

When plasmon is excited, a sphere acts as

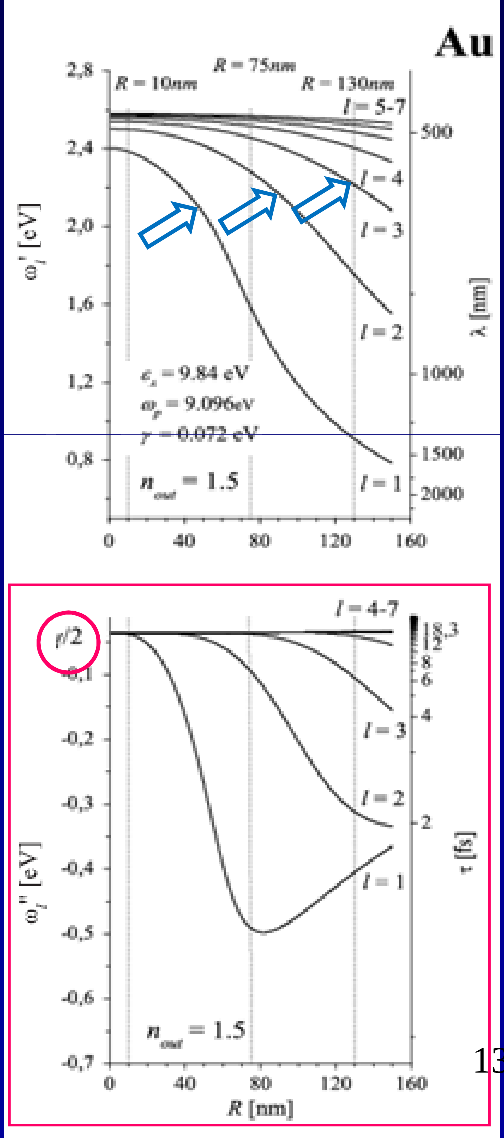
a ***reciving*** or ***radiating antenna,***

depending on the relative contribution of

- radiative damping rate $\gamma_l^{rad}(R)$ and
- nonradiative damping rate $\gamma/2$

to the **total plasmon damping rate**:

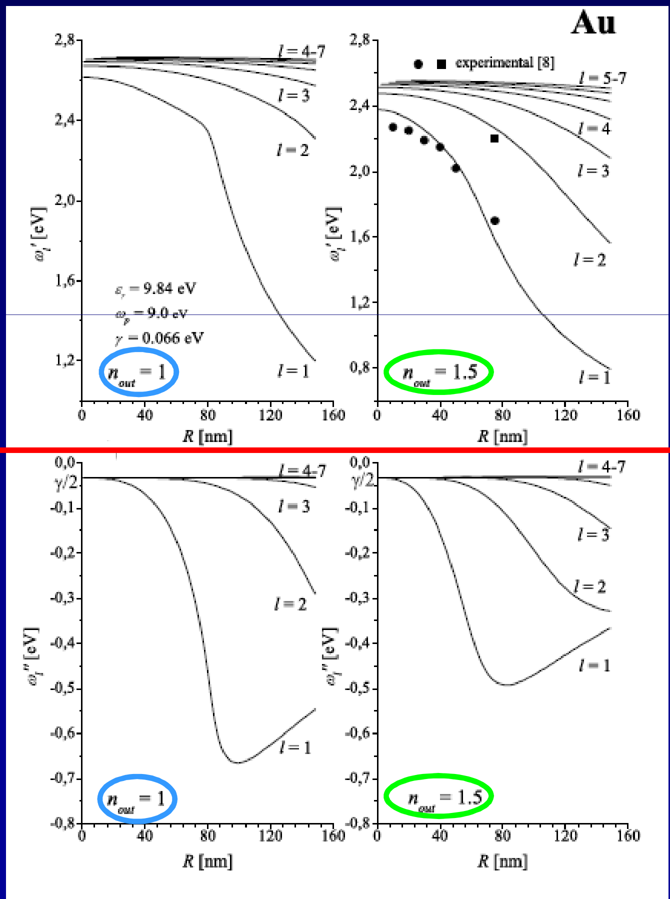
$$|\omega''_l(R)| = \gamma_l^{rad}(R) + \gamma/2$$

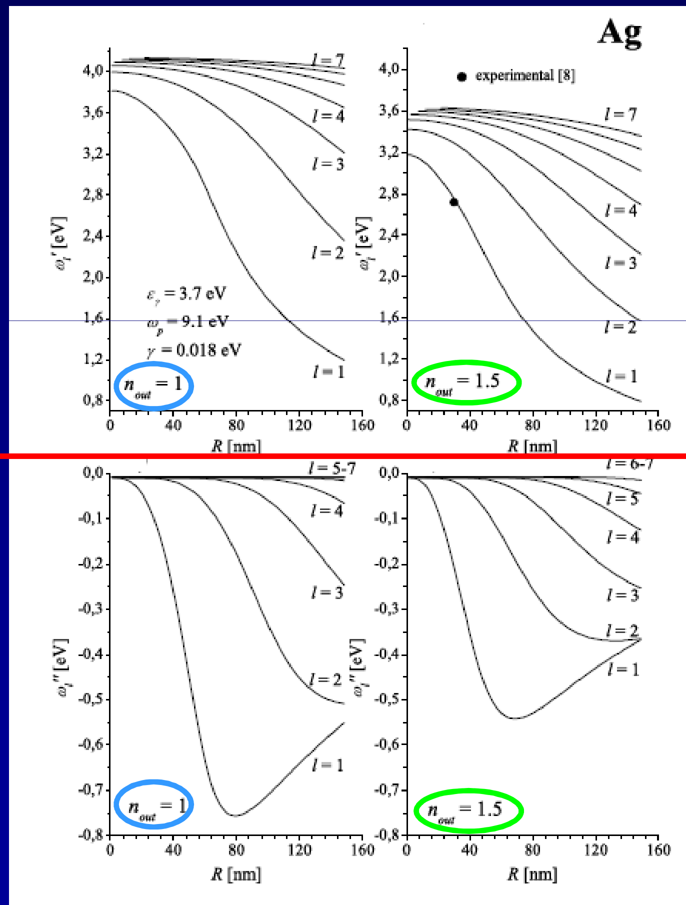


Plasmon size characteristics for noble metal nanospheres

Plasmon resonance frequencies

Plasmon damping rates
(dominated by radiative damping)





Resulting plasmon size characteristics: ready-to-use data allowing to optimize surface plasmon features in practical applications by choosing:
- appropriate particle size for choosen application
- nanosphere material and its environment.

K. Kolwas, A. Derkachova, *accepted in* Opto-Electr. Rev. (2010)

Plasmon size characteristics for noble metal nanospheres

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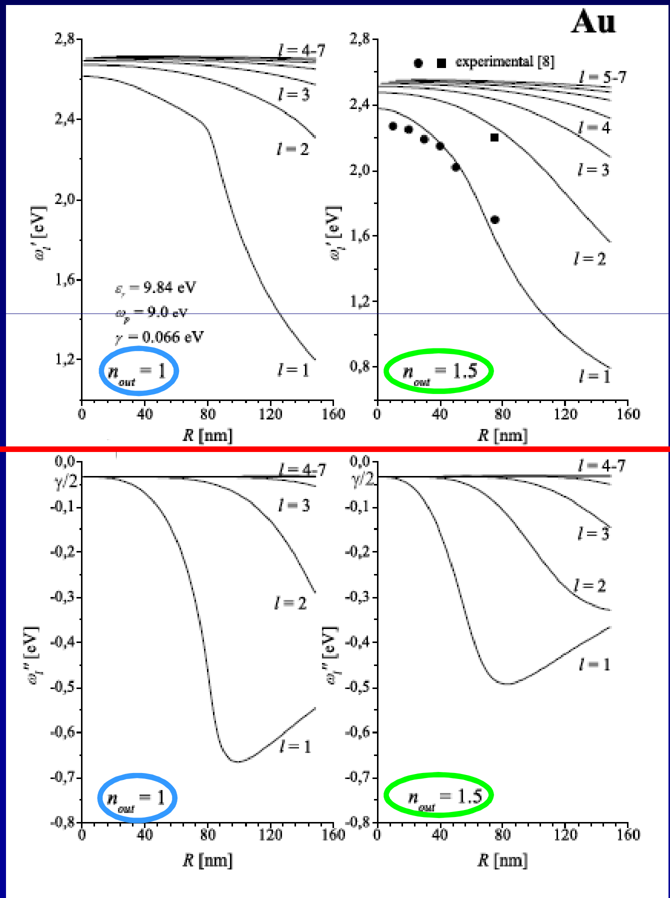
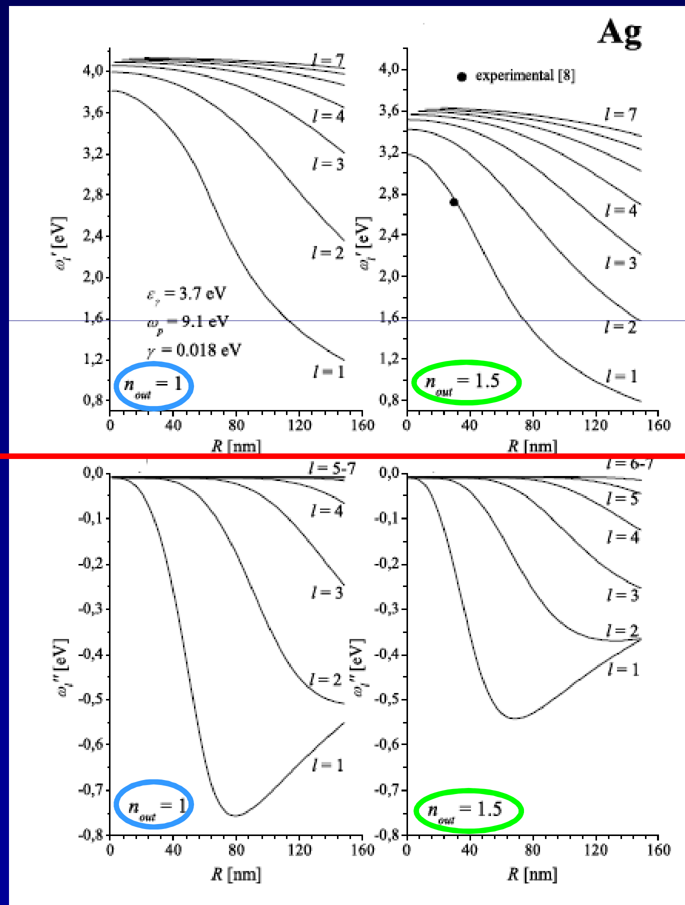




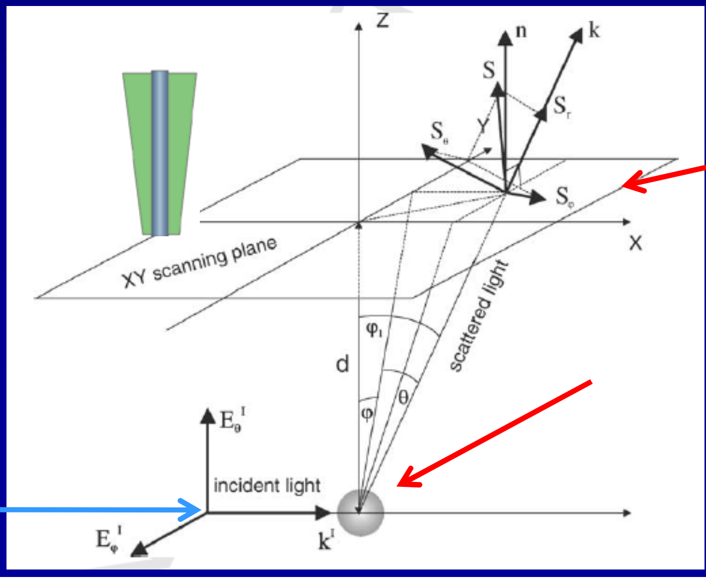
Plasmons contribute to the particle near field distribution and to the particle images formatted in the particle surface proximity and cause:

- **enhancement of the near field intensity**,
- but also important modification of the spatial field and intensity distribution.

Near field images of a plasmonic nanosphere (Mie theory)

Our aim is to reconstruct :

1. The image of the particle in the XY detection plane as a function of scanning field frequency (*close to* and *equal to* the **plasmon dipole** and **quadrupole** resonance frequencies)
2. The particle image and distribution of E_r and its modification with changing distance *d* to the detection plane *at* the **plasmon dipole** and **quadrupole** resonance frequencies:



$\omega = \omega'_{l=1,2}(R)$

W. Bazhan, K. Kolwas, Comp. Phys. Comm., **165** 191 (2005)

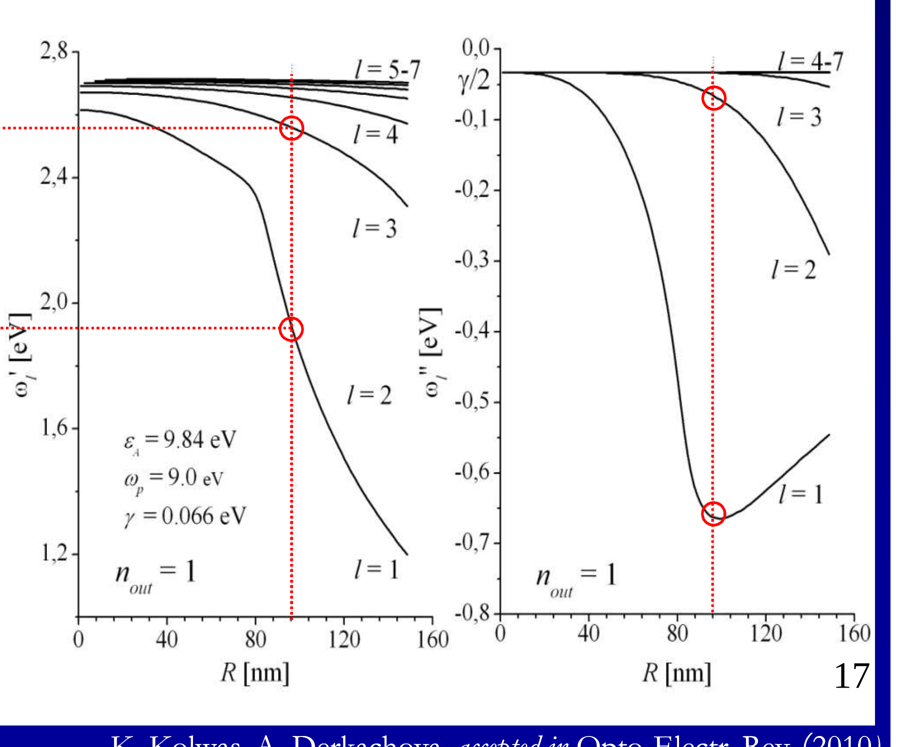
Near field images of a plasmonic nanosphere (Mie theory)

A plasmonic scattering object: Au sphere of radius 95nm:

- Significant plasmon radiative rates
- **Dipole** and **quadrupole** plasmon resonance frequencies in the visible range:

$\omega_{l=2}(95nm)$=2,57eV

$\omega_{l=1}(95nm)$=1,96eV



K. Kolwas, A. Derkachova, *accepted in* Opto-Electr. Rev. (2010)

Near field images of a plasmonic nanosphere (Mie theory)

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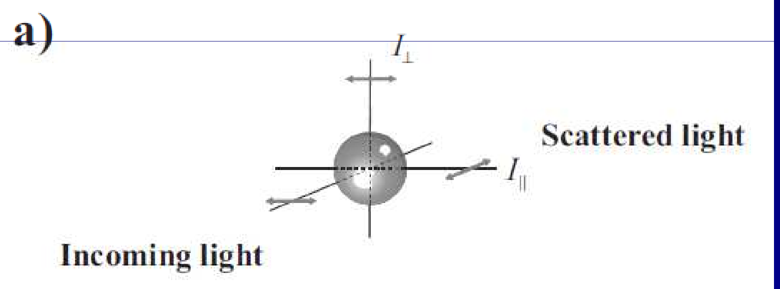
Orthogonal scattering geometry:

polarization of the incident and scattered field:

- perpendicular
- parallel

to the observation plane



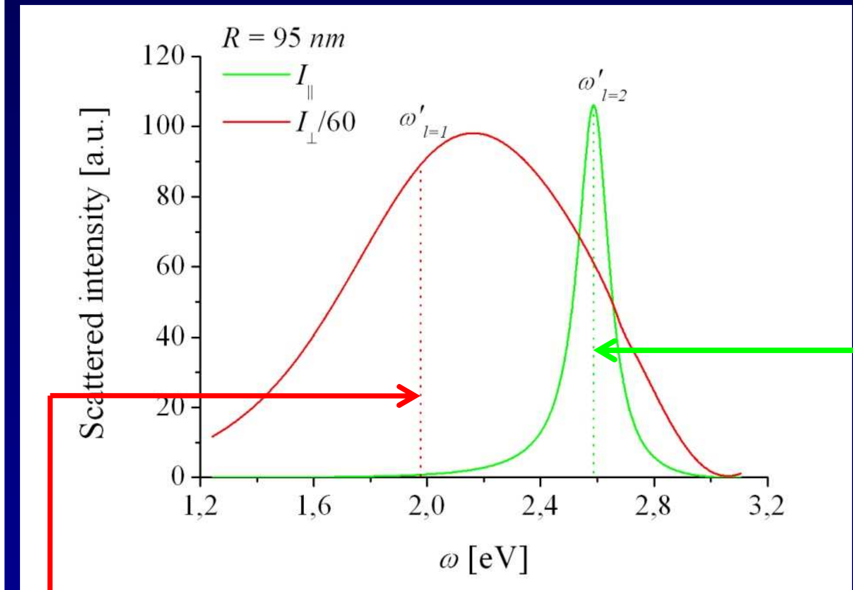
K. Kolwas, A. Derkachova, J.Q.S.R.T. 110 1490–1501(2009)

”Clinical” orthogonal scattering geometries that enable to expose:

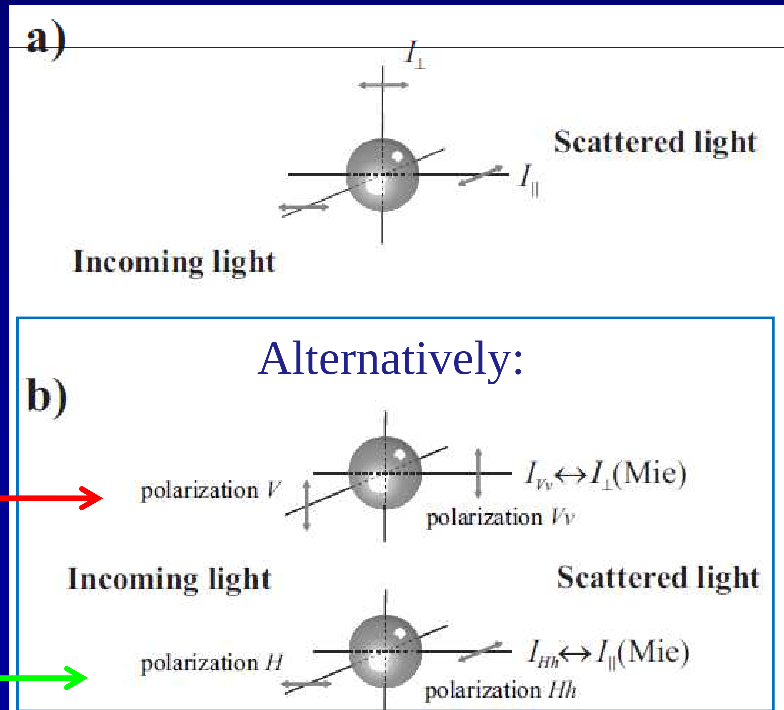
- a single dipole (l = 1) plasmon contribution,
- a single quadrupole (l = 2) plasmon contribution

and to separate these contributions spatially from $l < 2$ contributions by observing $I_\perp(\omega,R)$ and $I_\parallel(\omega,R)$ scattered intensities (Mie theory)

Near field images of a plasmonic nanosphere (Mie theory)



K. Kolwas, A. Derkachova, M. Shopa J.Q.S.R.T. **110** 1490–1501(2009
S. Demianiuk, K. Kolwas., J. Phys. B, **34** 1651 (2001)



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Near field imaging

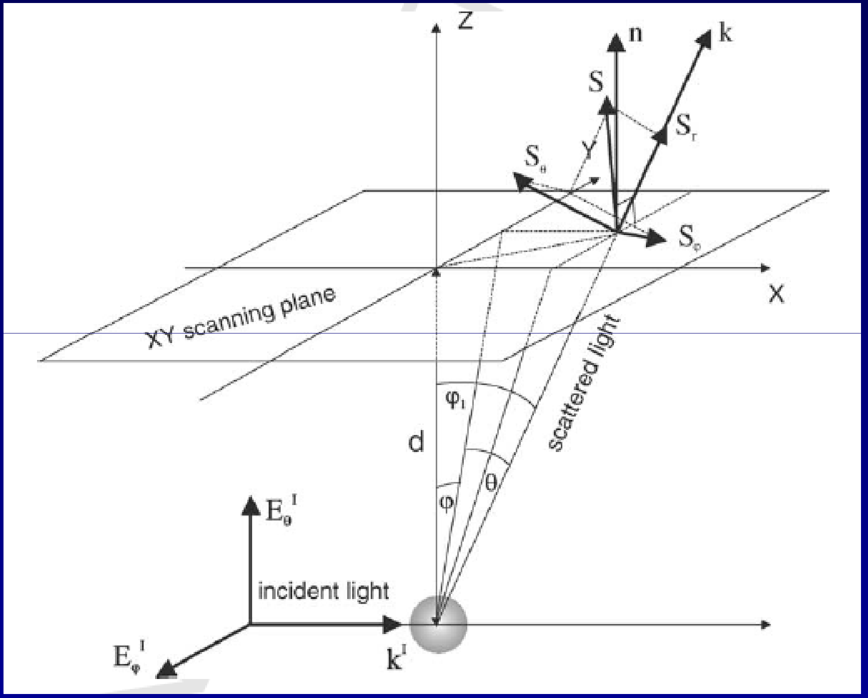
$I(x,y) \sim S_n(x,y)$ *as a function of a distance* d *between the particle and the scanning plane*

The Poynting vector $\mathbf{S}(\theta, \phi, r)$ for scattered fields:

$$\mathbf{S}(\theta,\varphi,r) \sim \frac{1}{2}\mathrm{Re}\begin{vmatrix} \hat{\mathbf{r}} & \hat{\theta} & \hat{\varphi} \\ E_r & E_\theta & E_\varphi \\ H_r & H_\theta & H_\varphi \end{vmatrix}$$

The numerical image of the particle
in the XY scanning plane:
the distribution of $S_n(\theta, \phi, r)$ over this plane:

$$S_n(\theta,\varphi,r) = \hat{\mathbf{n}}\mathbf{S}(\theta,\varphi,r),$$



Institute of Physics,
Polish Academy of Sciences, Warsaw

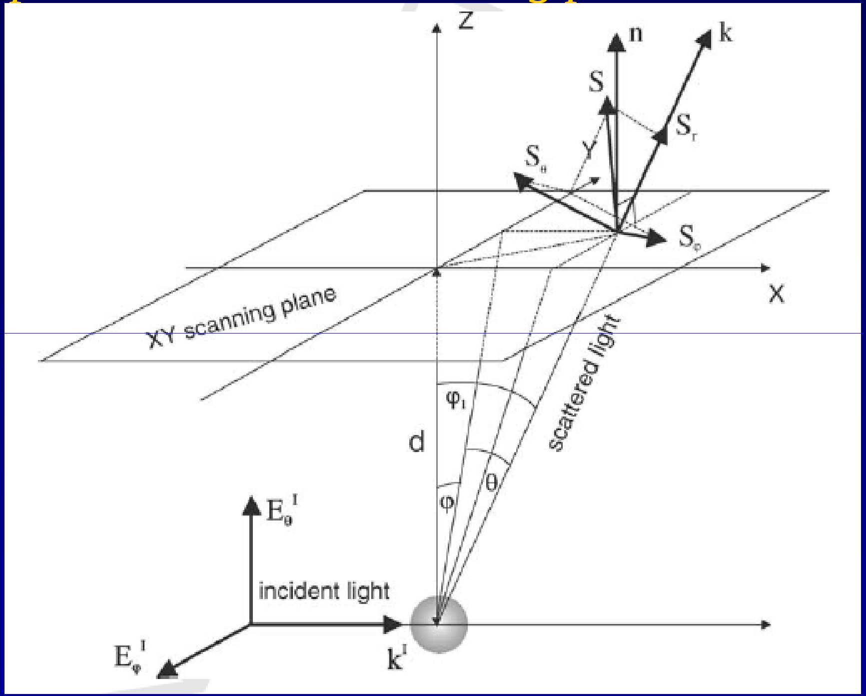
Near field imaging

The role of the distribution of the E_r component

with increasing distance d between the particle and the scanning plane

$$E_r, H_r \sim \frac{1}{r^2},$$

$$E_{\theta,\varphi}, H_{\theta,\varphi} \sim \frac{1}{r}$$

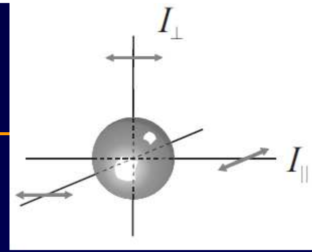


The numerical image of the particle
in the XY scattering plane:
the distribution of $S_n(\theta,\phi, r)$ over this plane:

$$S_n(\theta,\varphi,r) = \hat{\mathbf{n}}\mathbf{S}(\theta,\varphi,r),$$

E_r and H_r play a remarkable role in building the near-field image of a plasmonic particle:

$$S_n \sim (E_\theta H_\varphi - E_\varphi H_\theta)\cos\varphi_1 + (\boxed{-E_r} H_\varphi + E_\varphi \boxed{H_r})\sin\theta\cos\varphi + (\boxed{E_r} H_\theta - E_\theta \boxed{H_r})\sin\varphi$$



Near field distribution

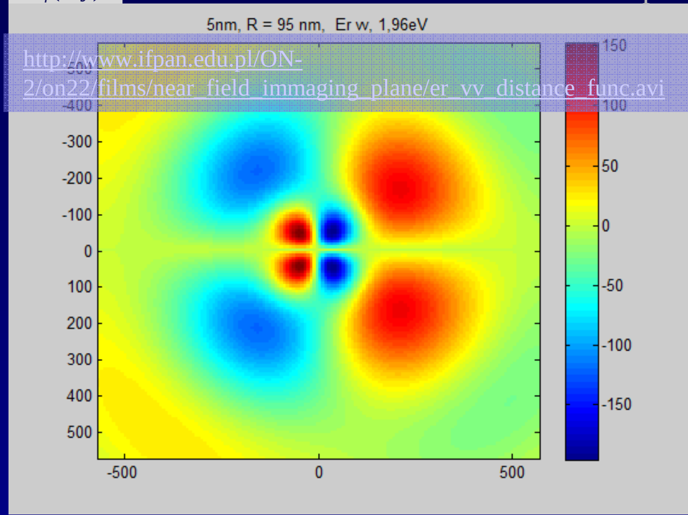
$E_r(x,y)$ as a function of a distance d between the particle and the scanning plane

at the dipole plasmon resonance frequency
$\omega_{l=1}(95nm)$ =1,96eV (*Vv* (⊥) observation geometry)

$\omega_{l=1}(95nm)$=1,96eV

E_r distribution is directly connected to the pattern of the plasma waves induced at the particle surface.

$E_r(x,y)$ M. Shopa...

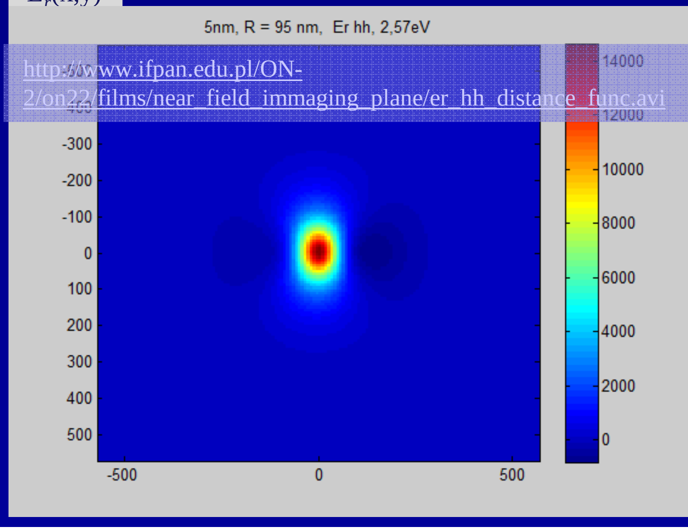


http://www.ifpan.edu.pl/ON-2/on22/films/near_field_immaging_plane/er_vv_distance_func.avi

at the quadrupole plasmon resonance frequency
$\omega_{l=2}(R=95\text{nm})$ =2,57eV (*Hh* (||) observation geometry)

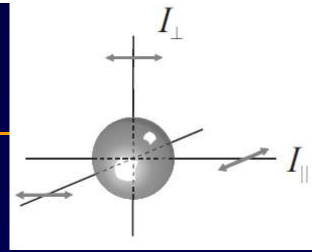
$\omega_{l=2}(95nm)$=2,57eV

$E_r(x,y)$



http://www.ifpan.edu.pl/ON-2/on22/films/near_field_immaging_plane/er_hh_distance_func.avi

d : (R=75) ÷ 1000nm



Near field imaging

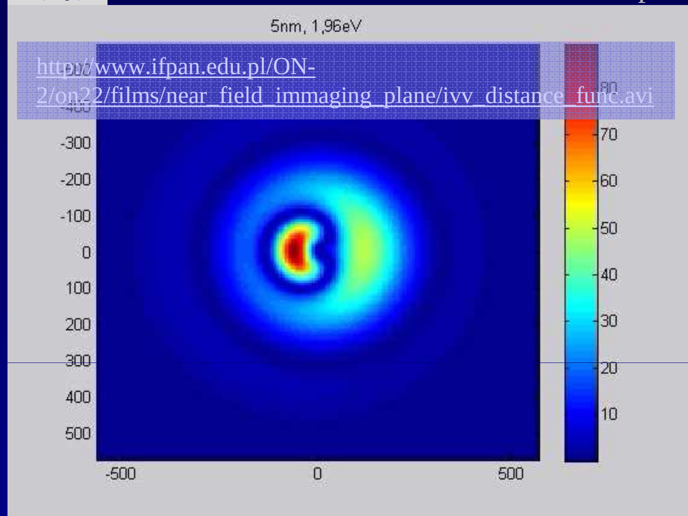
$I(x,y) \sim S_n(x,y)$ *as a function of a distance d between the particle and the scanning plane*

M. Shopa...

at the dipole plasmon resonance frequency
(Vv ($\perp$) observation geometry)

$\omega_{l=1}(95nm)$=1,96eV

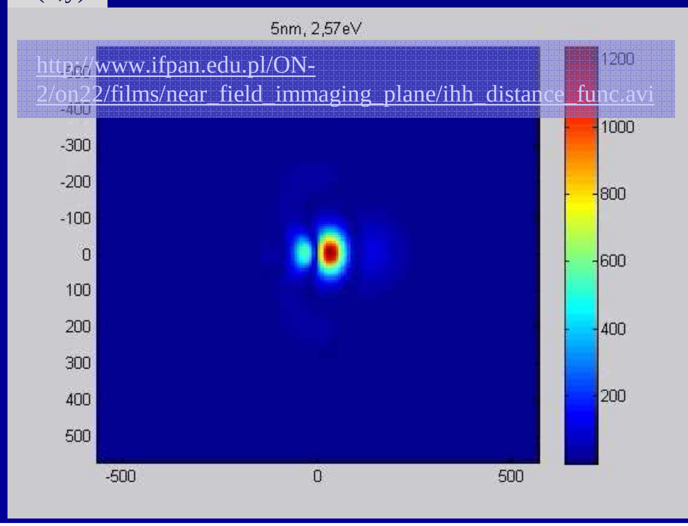
$I(x,y)$



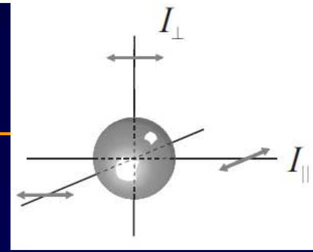
at the quadrupole plasmon resonance frequency
(Hh (||) observation geometry)

$\omega_{l=2}(95nm)$=2,57eV

$I(x,y)$



$d: \; (R=75) \div 1000nm$



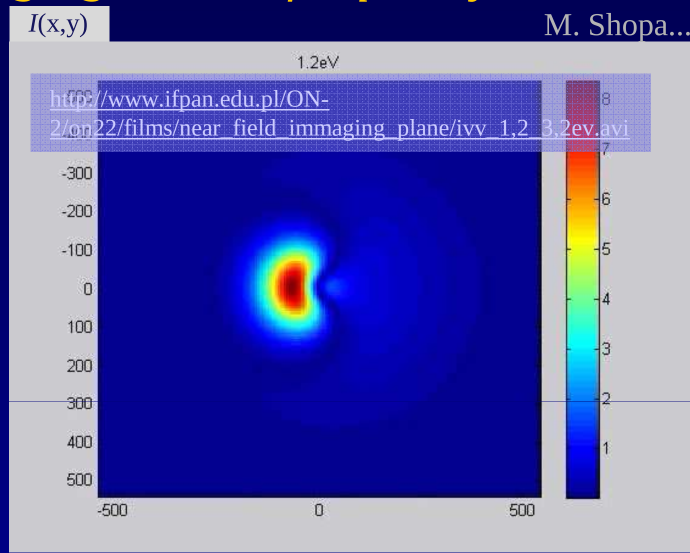
Near field imaging

$I(x,y) \sim S_n(x,y)$ as a function of the incoming light wave frequency ω

M. Shopa...

Vv (⊥) observation geometry

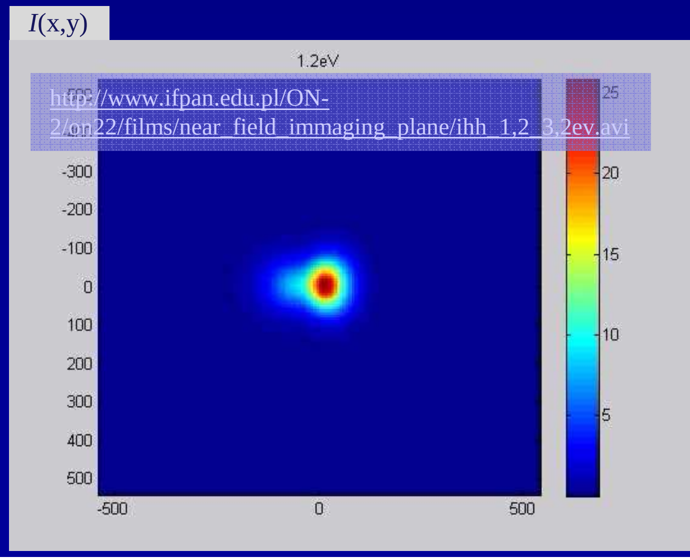
$\omega_{l=1}(95nm)$=1,96eV



ω scanned: $1{,}2eV \div 3{,}2eV$

Hh (||) observation geometry

$\omega_{l=2}(95nm)$=2,57eV



d = 95nm=R

at once

Summary

1. Eigenvalue problem for plasmonic particle:

find the explicit multipolar plasmon size characteristics

- within rigorous size dependent modelling
- for realistic, frequency dependent dielectric function of a metal $\varepsilon_{in}(\omega)$

2. Imaging of a plasmonic particle:

- classify (and understand) diverse near-field images of a plasmonic spherical particle
- at frequencies close to and equal to the frequency of dipole and quadrupole plasmon and
- understand, what localization of the surface plasmon means.

Thank you for your attention

Krystyna Kolwas