Metallic nanoantennas for Field-Enhanced Spectroscopy and Microscopy: from Visible to TeraHertz

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Summer School on Plasmonics
September 13-17, 2009
Porquerolles Island, Côte d’Azur, France
Outline

• Basics: Localized Plasmons

• Optical antennas for SERS

• Infrared antennas for SEIRA

• Substrate-Enhanced Infrared Near-Field Microscopy

• THz Near-field Nanoscopy
Radio Frequency Antennas

- Half wave dipole antennas
- Monopole antenna
- Yagi-Uda antenna
- Parabolic antenna
- Biconical antenna
- Combilog antenna
- Horn antenna
- Active loop antenna

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Scaling down in size ↔ Scaling down in wavelength

Visible light → Optical antenna → Nanoantenna

\[ \lambda/2 \text{ nanoantenna} \]

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
The simplest optical antenna: a metallic particle

Enhancement of absorption and emission:
Bringing effectively the far-field into the near-field

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Metal particle plasmons

Standard textbooks:
- Kreibig, Vollmer, Optical properties of metal clusters, Springer 1995
- Bohren, Huffmann, Absorption and scattering of light by small particles, Wiley 1983

FIG. 2 (color). True color photograph of a sample of gold nanorods (red) and 60 nm nanospheres (green) in dark-field illumination (inset upper left). Bottom right: TEM images of a dense ensemble of nanorods and a single nanosphere.
Metallic nanorod as a $\lambda/2$ optical antenna

In analogy to a $\lambda/2$ radiowave antenna, we call a nanosized rod-like metallic structure a $\lambda/2$ optical antenna.

YES BUT, it is just similar, and not equal because of plasmons.
Bulk plasmons

A plasmon is a collective oscillation of the conduction electrons.

**Bulk plasmon:**
The rigid displacement of the electrons induces a dipolar moment and an electric field opposing the displacement.

**Newton’s equation for \( \delta(t) \):**

\[
 nm_e \frac{d^2 \delta(t)}{dt^2} = -enE(t) = -4\pi n^2 e^2 \delta(t)
\]

All the electrons are involved in the oscillation. The energy of those oscillations in typical metals might be triggered out by external probes.

\[ \omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}} \]

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
**Surface plasmons**

Electromagnetic surface waves which exist at the interface between 2 media whose $\varepsilon$ have opposite sign.

**Metal** $(\varepsilon_1=\varepsilon_1'+i\varepsilon_1''')$

**Dielectric** $(\varepsilon_2=\varepsilon_2'+i\varepsilon_2''')$

\[
E^{(1)} = E_o^{(1)} e^{i(k_x x - \omega t - a^{(1)} |z|)}
\]

\[
k_x = k_x' + i k_x'' = \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \left( \frac{\omega}{c} \right)
\]

**Dispersion relation**

\[
\omega = c k_x
\]

**Drude model**

\[
\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2}
\]

**Surface plasmons**

\[
\omega_s = \frac{\omega_p}{\sqrt{2}}
\]

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Plasma Losses by Fast Electrons in Thin Films

R. H. Ritchie
Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received February 7, 1957)

The angle-energy distribution of a fast electron losing energy to the conduction electrons in a thick metallic foil has been derived assuming that the conduction electrons constitute a Fermi-Dirac gas and that the fast electron undergoes only small fractional energy and momentum changes. This distribution exhibits both collective interaction characteristics and individual interaction characteristics, and is more general than the result obtained by other workers. Describing the conduction electrons by the hydrodynamical equations of Bloch, it has been shown that for very thin idealized foils energy loss may occur at a value which is less than the plasma energy while as the foil thickness decreases below $\sim \pi/\omega_p$ the loss at the plasma energy becomes less than that predicted by more conventional theories. The net result is an increase in the energy loss per unit thickness as the foil thickness is decreased. It is suggested that the predicted loss at subplasma energies may correspond to some of the low-lying energy losses which have been observed by experimenters using thin foils.

Now let us define

$$P(k_1, \omega) = \frac{e^2 \alpha}{\hbar c \pi^2 \hbar^2} \frac{\text{Im}(1/\epsilon)}{(k_1^2 + \omega^2/\epsilon^2)} - \frac{2k_1}{a(k_1^2 + \omega^2/\epsilon^2)} \text{Im} \left( \frac{1-\epsilon}{\epsilon(1+\epsilon)} \right)$$

Now let us define

$$P(k_1, \omega) = \{ aP'_{\omega}(k_1, \omega) + P_b(k_1, \omega) \},$$

where $P'_{\omega}$ is the transition probability per unit foil thickness in an infinite foil and $P_b$ is the term introduced by the boundary effect. Then one may write, inserting the expression for $\epsilon$,

$$P_b = \frac{e^2}{\pi^2 \hbar^2 (k_1^2 + \omega^2/\epsilon^2)^2} \frac{g \omega_p^4}{\omega} \left\{ \frac{1}{\omega^2} + \frac{\omega_p^2}{(\omega^2 - \frac{1}{2} \omega_p^2)^2 + g \omega_p^2} \right\} \left( \omega^2 - \omega_p^2 \right)^2 + g \omega_p^2.$$

One notes that the effect of the boundary is to cause a decrease in loss at the plasma frequency and an additional loss at $\omega = \omega_p / \sqrt{2}$. Call the probabilities for these
Surface plasmons

Electromagnetic surface waves which exist at the interface between 2 media whose \( \varepsilon \) have opposite sign.

Metal (\( \varepsilon_1 = \varepsilon_1' + i\varepsilon_1'' \))

Dielectric (\( \varepsilon_2 = \varepsilon_2' + i\varepsilon_2'' \))

\[
E^{(1)} = E_0^{(1)} e^{i(k_x x - \omega t) - a^{(1)}|z|}
\]

\[
k_x = k_x' + i k_x'' = \sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \left( \frac{\omega}{c} \right)
\]

Dispersion relation

\( \omega = c k_x \)

Drude model

\[
\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2}
\]

Surface plasmons

\[
\omega_s = \frac{\omega_p}{\sqrt{2}}
\]

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Methods of SPP excitation

SPP excitation configurations: (a) Kretschmann geometry, (b) two-layer Kretschmann geometry, (c) Otto geometry, (d) excitation with an SNOM probe, (e) diffraction on a grating, and (f) diffraction on surface features.

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Nano-optics with localised plasmons

Characteristics

- Confined fields:  
  - Nanooptics

- Enhanced field:  
  - Lighting rod effect

- Tunability:  
  - Geometry

- Coupling:

- Wavelength range:  
  - Visible \( \rightarrow \) Infrared

Resonances dependence

- with size
- with shape
- with material
- with coupling

Plasmon polariton

\[ \omega(k) \]

\[ \omega_p \]

\[ \omega_s \]

\[ \omega = ck \]

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**Light-particle interaction**

### General case: $\lambda \leq a$

- $E(t = t_0)$
- Phase shifts in the particles: retardation, multipole excitations

### Quasi-static case: $\lambda >> a$

- Homogeneous polarization: All points of an object respond simultaneously to the incoming (exciting) field.
- Helmholtz eq. reduces to Laplace equation:
  \[ \nabla^2 \Phi = 0 \]
- El. field:
  \[ E = -\nabla \Phi \]
The electric fields inside \( (E_1) \) and outside \( (E_2) \) the sphere can be obtained from the scalar potentials \( \Phi = \Phi(r, \theta, \varphi) \):

\[
\begin{align*}
E_1 &= -\nabla \Phi_1 & \text{with} & \nabla^2 \Phi_1 = 0 \\
E_2 &= -\nabla \Phi_2 & \text{with} & \nabla^2 \Phi_2 = 0 \\
\Phi_2 &= \Phi_{\text{scatter}} + \Phi_0
\end{align*}
\]

Solve Laplace equation in spherical coordinates:

\[
\frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \varphi^2} \right] \Phi(r, \theta, \varphi) = 0
\]

Boundary conditions:

\[
\begin{align*}
\frac{\partial \Phi_1}{\partial \theta} &= \frac{\partial \Phi_1}{\partial \theta} \quad (r = a) & \text{continuity of the tangential} \\
\varepsilon_1 \frac{\partial \Phi_1}{\partial r} &= \varepsilon_2 \frac{\partial \Phi_2}{\partial r} \quad (r = a) & \text{continuity of the normal} \\
\end{align*}
\]

continuity of the electric fields

continuity of the normal component of the electric displacement
Homogeneous electric field along x-direction: \( \Phi_0 = -E_0 x = -E_0 r \cos \theta \)

The following potentials satisfy the Laplace equation and boundary conditions:

\[
\begin{align*}
\Phi_1 &= -E_0 \frac{3 \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2} r \cos \theta \\
\Phi_2 &= -E_0 r \cos \theta + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2} \frac{a^3 \cos \theta}{r^2}
\end{align*}
\]

From \( \mathbf{E} = -\nabla \Phi \) we obtain

\[
\begin{align*}
\mathbf{E}_1 &= E_0 \frac{3 \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2} (\cos \theta \mathbf{e}_r - \sin \theta \mathbf{e}_\theta) = E_0 \frac{3 \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2} \mathbf{e}_x \\
\mathbf{E}_2 &= E_0 (\cos \theta \mathbf{e}_r - \sin \theta \mathbf{e}_\theta) + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2} \frac{a^3}{r^3} F_0 \left( 2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta \right)
\end{align*}
\]

The field is independent of the azimuth angle \( \varphi \) which is a result of the symmetry implied by the direction of the applied electric field.
Small sphere

Small sphere: \[ \Phi_2 = -E_0 r \cos \theta + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 \frac{\cos \theta}{r^2} \]

Dipole: \[ \Phi_{\text{dipole}} = \frac{p}{4\pi \varepsilon_2} \frac{\cos \theta}{r^2} \]

The field outside the sphere is the superposition of the applied field and the field of an ideal dipole at the sphere origin.

The dipole moment is given by

\[ p = 4\pi \varepsilon_0 \varepsilon_2 a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} E_0 \]

Generally the dipole moment is defined by \[ p = \varepsilon_0 \varepsilon_2 \alpha E_0 \]

Polarizability of the sphere: \[ \alpha = 4\pi a^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \]

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Small sphere

We can describe the light scattering of a small sphere by plane wave scattering at an ideal point dipole with dipole moment derived on the previous slides. The dipole field is given by:

\[
E(r) = \frac{1}{4\pi\varepsilon_0} \frac{e^{ikr}}{r} \left\{ k^2[(n \times p) \times n] + \frac{1}{r}\left(\frac{1}{r} - ik\right)[3n(n \cdot p) - p] \right\} e^{i\omega t}
\]

with \( n = \frac{r}{r} \)

**Near-field zone:**

\( kr \ll 1 \quad (r \ll \lambda) \)

Electrostatic dipole field

Harmonic time dependency

**Radiation zone:**

\( kr \gg 1 \quad (r \gg \lambda) \)

Propagating wave

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Far- and near-field calculations for a sphere $a << \lambda$

**Far-field scattering**
(transverse fields)

- Pointing vector always radial!

**Near-field scattering**

$$I = \left| E_{in} + E_{particle} \right|^2$$

- Pointing vector is not always radial

---

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Optical cross sections of small spheres

Integrating the Poynting vector $\mathbf{S}_{\text{sca}} (\mathbf{S}_{\text{abs}})$ over a close spherical surface we obtain the totally scattered (absorbed) power $P_{\text{sca}} (P_{\text{abs}})$ from which we can calculate the scattering (absorption) cross section $C_{\text{sca}} = P_{\text{sca}}/I_i$ ($C_{\text{abs}} = P_{\text{abs}}/I_i$):

**Scattering cross section:**

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

$$\Rightarrow C_{\text{sca}} \propto \frac{a^6}{\lambda^4}$$

**Absorption cross section:**

$$C_{\text{abs}} = 4\pi k a^3 \text{Im} \left\{ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right\} = k \text{Im} \{\alpha\}$$

$$\Rightarrow C_{\text{abs}} \propto \frac{a^3}{\lambda}$$

- stronger scattering at shorter wavelength (Rayleigh scattering, blue sky)

- for large particle extinction is dominated by scattering whereas for small particles it is associated with absorption

- scattering of single particles $<10\text{nm}$ is difficult to measure (low signal/noise and low signal/background)
Dielectric function of metals and polar crystals

**Metal**
- collective free electron oscillations (*plasmons*)
- plasma frequency (longitudinal oscillation)

**Polar crystal**
- strong lattice vibrations (*phonons*)
- transversal optical phonon frequency, TO
- longitudinal optical phonon frequency, LO

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# Plasmon vs. Phonon

<table>
<thead>
<tr>
<th>Plasmon polaritons:</th>
<th>Phonon polaritons:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light - electron coupling in</td>
<td>Light - optical phonon coupling in polar crystals</td>
</tr>
<tr>
<td>• metals</td>
<td>• SiC, SiO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>• semiconductors</td>
<td>• III-V, II-VI-semiconductors</td>
</tr>
<tr>
<td>typically visible <em>(metals)</em></td>
<td>mid-infrared to terahertz</td>
</tr>
<tr>
<td>typically IR and terahertz <em>(doped SC)</em></td>
<td></td>
</tr>
<tr>
<td>resonant excitation of collective electron oscillation</td>
<td>resonant excitation of optical lattice vibrations</td>
</tr>
</tbody>
</table>

**surface polariton resonances @ ε ≈-1**
Optical cross sections of small spheres

Drude model

\[ \varepsilon = 1 - \frac{\omega_p^2}{\omega^2 + 0.2i\omega} \]

Optical phase of scattered light

\[ \text{Arg}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \sim \text{opt. field amplitude} \]

Absorption and scattering cross sections

\[ \frac{\varepsilon - 1}{\varepsilon + 2} \propto C_{\text{sca}} \]

\[ \text{Im}\left[\frac{\varepsilon - 1}{\varepsilon + 2}\right] \propto C_{\text{abs}} \]

J. Aizpurua, Lecture given at SSOP, Porquerolles, Sept. 2009
Small particle resonances

\[ E_0 = 2 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_{in} \]

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

polarizability:

\[ \varepsilon = -2\varepsilon_m \]

\[ E_0 / E_{in} \]

wavelength \( \lambda \) (\( \mu \)m)

Plasmon polariton resonance

Au

Ag

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Nanotechnology with plasmonics: before the nanorevolution

Lycurgus Cup
(British Museum; 4th century AD)

Illumination: from outside
(from inside)

(strong absorption at and below 520 nm)

J. Aizpurua, Lecture given at SSOP
Porquerolles, Sept. 2009
Ancient roman Lycurgus cup illuminated by a light source from behind. Light absorption by the embedded gold particles leads to a red color of the transmitted light whereas scattering at the particles yields a greenish color. From http://www.thebritishmuseum.ac.uk/science/lycurguscup/sr-lycugus-p1.html.
Higher multipole resonances in quasistatic limit

In the quasistatic limit the Mie theory yields the resonance positions of the higher multipoles at

\[ \varepsilon_L = -\varepsilon_{medium} \frac{l + 1}{l} \]

Drude

\[ \omega_L = \omega_p \frac{1}{\sqrt{1 + \frac{l + 1}{l} \varepsilon_{medium}}} \]

\[ \frac{1}{\omega} \begin{array}{c} \omega_1 \\ \omega_{L \to \infty} \\ \omega_p \end{array} \]

However, higher multipoles in the quasistatic limit are negligible compared to the dipole contribution (l=1)

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An alternative to excite high order modes in a sphere

EELS in nanoparticles

\[ \alpha_l(\omega) = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + (l+1)/l} a^3 \]

\[ P_\omega(a, b, \nu) = \frac{4q^2}{\pi v^2 a^2} \sum_{l=0}^{\infty} \sum_{m=0}^{l} A_{lm} \left( \frac{\omega a}{v} \right)^{2l} K_m^2 \left( \frac{\omega b}{v} \right) \text{Im}[\alpha_l(\omega)] \]

Ferrell and Echenique, PRL 55, 1526 (1985)

Probability of losing energy \( h\omega \) for a 50-keV electron moving at grazing incidence on an aluminum sphere of radius \( a = 10\text{nm} \)

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Mie-theory

2.1.3 Exact Electrodynamical Calculation of Spherical Metal Clusters (Mie Theory)

Kreibig/Vollmer

Mie-theory is an electrodynamic theory for optical properties of spherical particles. The solution is divided into two parts: the electromagnetic one which is treated from first principles (Maxwell equations) and the material problem with is solved by using phenomenological dielectric functions taken from experiments or model calculations.

\begin{align*}
\Delta \Pi + |k|^2 \Pi &= 0 \\
\text{in spherical coordinates:} & \quad \Pi^{\text{inc}}_{e,m} \text{ of the incident plane wave} \\
& \quad \Pi^{\text{in}}_{e,m} \text{ of the wave inside the cluster} \\
& \quad \Pi^{\text{esc}}_{e,m} \text{ of the outgoing scattered wave} \\
\end{align*}

The indices e and m indicate the sets of electrical and magnetic partial waves, respectively. The solutions can be separated in spherical coordinates

\begin{equation}
\Pi = R(r)\Theta(\theta)\Phi(\phi)
\end{equation}

and have the form

\begin{equation}
\Pi = \{\text{cylindrical fct.}\} \cdot \{\text{Legendre spherical fct.}\} \cdot \{\text{trigonometric fct.}\}
\end{equation}

The relevant parameter in all formulas is the size parameter \(x = |k|R\) which distinguishes the regime of geometrical optics \((x \gg 1)\) from the one important for clusters \((x \ll 1)\) (a compressed description is given in \([2.9]\)).

See also Bohren/Huffman
Mie theory - results

**Fig. 2.5.** Scheme for decomposing the total Mie extinction spectra in dipolar, quadrupolar and higher modes of electronic excitations. Each multipole contributes by electric and magnetic modes, i.e. plasmons and eddy currents which each consist of absorption and scattering losses.

**Fig. 2.6.** Electric and magnetic fields far away from the clusters, of the $L = 1, 2,$ and $3$ electric partial wave, i.e. the electric dipole, quadrupole, and octupole mode. The same field distributions hold for the magnetic partial waves, if electric and magnetic fields are interchanged (after [2.19]).

Fig. 2.6 shows farfield distribution at the surface of a large sphere centered at the small cluster.

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Kreibig/Vollmer
Scattering characteristics (far-field)

Small particle

Large particle (Mie calculation)

Figure 4.9 Scattering by a sphere with $x = 3$ and $m = 1.33 + i 10^{-8}$.

→ Strong forward scattering

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Porquerolles, Sept. 2009
Spherical plasmons:
Mie modes derived from Maxwell’s equations

\[ \omega_l = \sqrt{\frac{l}{2l+1}} \omega_p \]

\[ \varepsilon = 1 - \frac{\omega_p^2}{\omega^2} \]

Drude-like metal

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Effect of finite size on the resonant frequency

same shape, different size
redshift due to higher multipoles

Jin et. al., Science 294, 1901 (2001)

J. Aizpurua, Lecture given at SSOP
Porquerolles, Sept. 2009
Shape: Polarizability of small ellipsoids

\[
\alpha_{xyz} = \frac{4}{3} \pi abc \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L_{xyz}(\varepsilon - \varepsilon_m)}
\]

geometrical factors

sphere: \( L_x = L_y = L_z = \frac{1}{3} \)

generally: \( L_x \neq L_y \neq L_z \)

→ 3 resonances at \( \varepsilon = \varepsilon_m \left(1 - \frac{1}{L_{xyz}}\right) \)
Silver ellipsoid illuminated by a plane wave

size shifts dipole resonance for $E_0 \parallel$ long axis

Calculation by J. Renger, TU Dresden

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Plasmon resonances: dependence on the geometry

Figure 12.5 Effect of shape on the position of the lowest-order surface mode of small spheroids. Arrows next to the various shapes show the direction of the electric field.

Figure 12.11 Surface mode frequencies for insulating and metallic particles of various shapes.
More complex geometries

Control over the plasmon frequencies by playing with particle \textit{shapes} and \textit{coupling}

Nanorods, nanoshells, nanorings, dimers,.....

Coupled systems

Apertureless NSOM

Nanometrology, sensing, spectroscopy

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Boundary Element Method

\[ E(r) = i \frac{\omega}{c} A(r) - \nabla \phi(r) \]

\[ A(r) = A^{\text{ext}}(r) + \int_{S_j} ds \ G_j(r-s) \ h_j(s) \]

\[ \phi(r) = \phi^{\text{ext}}(r) + \int_{S_j} ds \ G_j(r-s) \ \sigma_j(s) \]

The boundary conditions lead to a set of surface integral equations with the interface currents \( h_j \) and charges \( \sigma_j \) as variables. For example, the continuity of \( \phi \) leads to

\[ \int_{S_j} ds' \left[ G_1(s-s') \ \sigma_1(s') - G_2(s-s') \ \sigma_2(s') \right] = \phi_2^{\text{ext}}(s) - \phi_1^{\text{ext}}(s), \]

(1 and 2 refer to the interface sides). The surface integrals are now discretized using \( N \) representative points \( s_i \). This leads to a system of \( 8N \) linear equations with \( h_1(s_i), h_2(s_i), \sigma_1(s_i), \) and \( \sigma_2(s_i) \) as unknowns.

García de Abajo and Aizpurua, PRB 56, 15873 (1997)  García de Abajo and Howie, PRB 65, 115418 (2002)

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Optical properties of metallic nanorings

\[ \frac{d}{a} \text{ smaller } \rightarrow \text{ red shift} \]


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Optical properties of metallic nanoshells

Mode tuning thanks to the aspect ratio

(a)

(b)

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Modes in a nanoring. The twisted slab

\[ \omega_\pm = \omega_s (1 \pm e^{-kd})^{1/2} \]

\[ kd = n \frac{2\pi}{L} \quad d = n \frac{d}{a} \]
Field-enhancement in a nanoring

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Different types of radio antennas

- **λ/4 antenna**
  - Horizontal radiation pattern
- **λ/2 Dipole**
  - Vertical radiation pattern
- **Yagi**
  - Horizontal radiation pattern
- **Parabolic**
  - Vertical radiation pattern

**Omnidirectional antenna**
- Commonly used at master station sites

**Directional Yagi antenna**
- Commonly used at remote field sites

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$\lambda/2$ nanoantenna

$\lambda/4$ optical antenna


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Different types of radio antennas

- **Vertical**
- **Dipole**
- **Yagi**
- **Parabolic**

**Omen-directional antenna**
Often used at master station sites

**Directional Yagi antenna**
Commonly used at remote field sites

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Yagi-Uda antenna

Taminiau et al.,
Optics Express 14, 10858 (2008)

J. Aizpurua, Lecture given at SSOP
Porquerolles, Sept. 2009
Different types of radio antennas

- **Horizontal radiation pattern**
- **Vertical radiation pattern**

**Omni-directional antenna**
- Often used at master station sites

**Dipole**
- Horizontal radiation pattern

**Yagi**
- Half-power beamwidth

**Parabolic**
- Half-power beamwidth

**Directional Yagi antenna**
- Commonly used at remote field sites

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Parabolic-like optical nanoantennas

N. Mirin and N. Halas, Nano Letters 9, 1255 (2009)

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Porquerolles, Sept. 2009
Resonant Optical Antennas

P. Mühlslagel,¹ H.-J. Eisler,¹ O. J. F. Martin,² B. Hecht,¹* D. W. Pohl¹

SCIENCE VOL 308 10 JUNE 2005

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\( \lambda/4 \) optical antenna


Bowtie antennas


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Outline

• Basics: Plasmonics

• Optical antennas for SERS
  (Surface-Enhanced Raman Scattering)

• $\frac{1}{2} \lambda$ dipole Infrared antennas for SEIRA

• Substrate-Enhanced Infrared Near-Field Microscopy

• THz Near-field Nanoscopy
Resonant antennas for enhanced signal of molecular vibrations

Concept

Surface-Enhanced Raman Scattering (SERS)

Identifying molecular vibrations for selective detection of species in small volumes

Molecular fingerprints

J. Aizpurua, Lecture given at SSOP Porquerolles, Sept. 2009
Surface Enhanced Raman Scattering, SERS

Electromagnetic effect

\[ M_i^{EM} = \left| \frac{E^L(\omega_i)}{E^I(\omega_i)} \right|^2 \left| \frac{E^L(\omega_i - \omega_v)}{E^I(\omega_i - \omega_v)} \right|^2 \]

If \( \omega_v << \omega_i \)

\[ M_i^{EM} = \left| \frac{E^L(\omega_i)}{E^I(\omega_i)} \right|^4 \]


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Near-field coupling – simple systems

Sphere - plane

Sphere - sphere

dipole – mirror dipole near-field interaction

dipole – dipole near-field interaction

→ High field enhancement in the gap due to resonant near-field coupling

→
  • local light sources
  • enhanced Raman signals (detection of single molecule Raman signals)
  • nonlinear effects

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Porquerolles, Sept. 2009
Dipolar sphere-sphere near-field interaction

Polarizability of spheres:  \[ \alpha_i = 4\pi \alpha_i^3 \frac{\varepsilon_i - 1}{\varepsilon_i + 2} \]

Scattered field:  \[ E_{sca} \propto \alpha_{eff} E_{in} \]

Effective polarizability of interacting dipoles (dipole approximation):

\[ \alpha_{eff} = \frac{\alpha_1 + \alpha_2 + \frac{\alpha_1 \alpha_2}{\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{4\pi^2 r^6}} \]

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**Resonance shift effects – two resonant spheres**

2 metal spheres: \( \varepsilon_1 = \varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \)

\( \gamma = 0.2 \)

\[
\alpha_{\text{eff}} = \frac{\alpha_1 + \alpha_2 + \frac{\alpha_1 \alpha_2}{\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{4 \pi^2 r^6}}
\]

dipolar approximation predicts

- resonance shifts
- field enhancement \( E_{\text{sca}} \propto \alpha_{\text{eff}} E_{\text{in}} \)

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Porquerolles, Sept. 2009
Dimers assisting in spectroscopy: SERS


Hot sites

Image obtained by R. Hillenbrand,
(Max Planck, Munich)

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Porquerolles, Sept. 2009
Two near-field interacting gold discs I

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Fig. 1. SEM images of particle pair samples with varying interparticle distance (center-to-center) of (a) 450 nm, (b) 300 nm and (c) 150 nm. The particle diameter is 150 nm, the particle height is 17 nm.

Fig. 2. Extinction (− log(1/Transmission)) spectra of a 2D array of the Au nanoparticle pairs with the interparticle center-to-center distances as the parameter. The orthogonal particle separation is kept constant, as can be seen in Fig. 1. The polarization direction of the exciting light is (a) parallel to the long particle pair axis and (b) orthogonal to it.
Field-enhancement: geometrical squeezing

\[ E_{loc} \approx E_0 (D + d) / d \]

\[ M = (\frac{D}{d} + 1)^4 \]
Dimers assisting in spectroscopy: SERS

\[ M_i^{EM} = \left| \frac{E^L(\omega_i)}{E^I(\omega_i)} \right|^4 \]

Plasmon hybridization

Sphere Coupled dimer Sphere

Sphere

\[ \omega = \frac{1}{\sqrt{2l+1}} \omega_p \]

\( l = 1 \)

\( l = 2 \)

Schmeits and Dambly,

Prodan et al,

Nordlander et al,
Nanoletters 4, 899 (2004)

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Porquerolles, Sept. 2009
Coupled modes in a metallic dimer

\[ \Psi^{(1)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l+1} \left( \frac{r_1}{a} \right)^l A_{lm} Y_{lm}(\theta_1, \varphi) e^{im\varphi} \quad \text{for } r_1 < a, \]

\[ \Psi^{(2)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l+1} \left( \frac{r_2}{b} \right)^l D_{lm} Y_{lm}(\theta_2, \varphi) e^{im\varphi} \quad \text{for } r_2 < b, \]

\[ \Psi^{(3)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l+1} \left[ \frac{\alpha^{l+1}}{r_1} B_{lm} Y_{lm}(\theta_1, \varphi) + \frac{b^{l+1}}{r_2} C_{lm} Y_{lm}(\theta_2, \varphi) \right] e^{im\varphi} \]

\[ \left( \frac{\omega_{m=0;l=1}}{\omega_p} \right)^2 = \frac{1 \pm 2 \left( \frac{D}{D+d} \right)^3}{3} \]

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Nanoparticles in the touching limit

Map of the resonances


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Charge density modes

Low frequency modes of non-touching and touching dimers are distinctly different

NOT TOUCHING

Neutral charge in each particle

TOUCHING

Net electrical charge in each half of the dimer

1st physical mode

1st physical mode

Unphysical mode

2nd physical mode

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Close Encounters between Two Nanoshells

J. Britt Lassiter, Javier Aizpurua, Luis I. Hernandez, Daniel W. Brandl, Isabel Romero, Surbhi Lai, Jason H. Hafner, Peter Nordlander, and Naomi J. Halas

J. Aizpurua, Lecture given at SSOP, Porquerolles, Sept. 2009
Outline

• Basics: Plasmonics

• Optical antennas for SERS

• Infrared antennas for SEIRA (Surface-Enhanced IR Absorption)

• Substrate-Enhanced Infrared Near-Field Microscopy

• THz Near-field Nanoscopy
Surface-enhanced IR absorption (SEIRA)

Resonant antennas for enhanced signal of molecular vibrations

Concept

IR radiation

$\mathbf{I}_0(\nu)$

Local Electric Field

Adsorbed Molecule

Substrate

Metal

$\mathbf{I}(\nu)$

SEIRA

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Metallic nanoparticle arrays for SERS and SEIRA

Halas group, Rice Univ.

Fei et al. ACS Nano. 2, 707 (2008)
In collaboration with P. Nordlander’s group

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Porquerolles, Sept. 2009
Metallic Nanoparticle Arrays: A Common Substrate for Both Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption

Fei Le,† Daniel W. Brandli,† Yaroslav A. Urzhumov,† Hui Wang,§ Janardan Kundu,§ Naomi J. Halas,§,∥ Javier Aizpurua,‡ and Peter Nordlander†,§,∥

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Porquerolles, Sept. 2009
Surface-enhanced IR absorption (SEIRA)

Resonant antennas for enhanced signal of molecular vibrations
Single antenna for infrared resonant spectroscopy

- Resonant structure
- Layer to be investigated
- Non-resonant structure

- Resonant triangles (coated)

- Nanoshell arrays
  - H. Wang et al., Angew. Chem. 46, 9040 (2007)

- Resonant particle (coated) (embedded)

- Resonant rod (coated)
Basics of nanorods


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Calculation of gold antenna modes

Antenna modes:
D=80nm, L=200nm; ratio=2.5

Dipole response:
\( L \alpha \lambda/2 \)

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\[
\begin{align*}
\text{Dipole response:} & \\
L & \propto \frac{\lambda}{2} \\
\end{align*}
\]
Metallic nanorod as a $\lambda/2$ optical antenna

Mapping the plasmon resonances of metallic nanoantennas

\[
(q^2 - \varepsilon k^2)^{1/2} I_0((q^2 - \varepsilon k^2)^{1/2} R)K_1((q^2 - k^2)^{1/2} R) + \varepsilon (q^2 - k^2)^{1/2} I_1((q^2 - \varepsilon k^2)^{1/2} R)K_0((q^2 - k^2)^{1/2} R) = 0
\]

\[q = \pi/L_{\text{tot}}\]
Optical nanoantenna resonant at $\lambda=3.41\mu m$
with $L=1.31\mu m$ and $D=100nm$
Finding the right nanowire resonance for IR spectroscopy

Experiments by Prof. A. Pucci’s group (Heidelberg, Germany)

Gold nanowire (L=1.5μm and D=100nm, on a silicon wafer)

SEM image: perfect cylindrical shape

Relative IR transmittance spectra
Electric field along the long wire axis

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Near-field mapping of IR nanoantennas

Experiment by Martin Schnell, R. Hillenbrand’s group

Calculation by A. Garcia-Etxarri, San Sebastian

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(M. Schnell, Nat. Phot. 3, 287 (2009))
λ/2 antenna enhanced IR spectroscopy
Relative IR transmittance of ODT molecules on a gold nanowire

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Outline

• Basics: Plasmonics

• Optical antennas for SERS

• $\frac{1}{2}\lambda$ dipole Infrared antennas for SEIRA

• Substrate-Enhanced Infrared Near-Field Microscopy

• THz Near-field Nanoscopy
Resonant structure
Layer to be investigated
Non-resonant structure

Resonant triangles (coated)


Resonant particle
(coated)
(embedded)


Resonant rod (coated)

F. Neubrech et al., APL 89, 253104 (2006)

Near-field IR spectroscopy

Nanoshell arrays

H. Wang et al., Angew. Chem. 46, 9040 (2007)

Resonant substrate

J. Aizpurua et al., Optics Exp 16, 1529 (2008)
Scattering–type Near Field Optical Microscopy
Rainer Hillenbrand

[Image of a tip-like structure emitting light towards a surface with a fractal-like pattern]
Localization of plasmons by a probe

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Porquerolles, Sept. 2009
Dipolar sphere-plane near-field interaction

Polarizability of the tip

\[ \alpha = 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2} \]

Effective polarizability of interacting dipoles

\[ \alpha_{\text{eff}} = \frac{\alpha (1 + \beta)}{1 - \frac{\alpha \beta}{16\pi (z + a)^3}} \quad \text{with} \quad \beta = \frac{\epsilon - 1}{\epsilon + 1} \]

- Near-field interaction modifies amplitude and phase of \( E_{\text{sca}} \)
- Resonance through a) sphere \( \epsilon_p = -2 \)
  b) plane \( \epsilon = -1 \)

No multipoles included in this description

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s-SNOM contrast of SiC/Au

phonon-enhanced near-field interaction
- strong signals
- high spectral sharpness
- optical fingerprint

identification of materials at nanoscopic spatial resolution
< $\lambda / 100$ !
Can we do the same in a simple optical antenna?

Mapping the fields of a metal-nanoparticle

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Label-free high-resolution optical imaging of nanoparticles

Probing - tip based chemicaly specific methods

- IR
  \[ C_{\text{sca}} \sim d^6/\lambda^4 \]
  \[ 10^{-28} \text{ cm}^2 \]
  (1 nm particle @ mid-IR)

- Raman
  \[ C_{\text{sca}} \sim 10^{-30} \text{ cm}^2 \]
  (typical molecule)

extremely small scattering cross-sections!

Solution → field enhancement in an antenna cavity!

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Substrate-enhanced IR microscopy

Dielectric
\( \varepsilon = 3 \)

Metal mirror
\( \varepsilon = -5000 \)

Phonon polariton resonant
\( \varepsilon = -2 \)

Field amplitude

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Outline

• Basics: Plasmonics

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Terahertz radiation (THz, T-RAYS)

Frequencies between IR and THz (far-IR) are highly sensitive to
- molecular vibrations → chemical composition
- crystal lattice vibrations → structural properties
- plasmons in doped semiconductors → electron properties
- ....

BUT: spatial resolution > \( \lambda/2 \approx 10-100 \, \mu m \)

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Theory predicts nanoscale confined THz fields

- Full electrodynamic calculation
- For 2.54 THz ($\lambda \approx 118 \mu m$) predicts field enhancement at tip apex
- Tip length: 1 µm ($\approx \lambda / 118$)
- 30 nm field confinement at tip apex, like for VIS or IR frequencies
- Mechanism: lightning-rod effect

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Lightning rod effect

- Lightning rod effect
  Needs:
  - Geometric singularity
  - Proper polarization
  - Good conductor
THz s-SNOM can map free carriers in semiconductor devices

Test structure containing transistors of 65 nm - technology

THz image exhibits material and free-carrier contrast

THz s-SNOM can map free carriers in semiconductor devices

For doped semiconductors $\varepsilon(\omega)$ depends on concentration of free carriers:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right) \text{ with } \omega_p^2 = \frac{n e^2}{\varepsilon_0\varepsilon_\infty m^* m_0}$$

Dipole model explains free-carrier contrast

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