Linear and nonlinear optical properties of metal nanoparticles

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Nanomaterials

Semiconductor or metal nanoparticles in a transparent matrix or deposited

- Quantum confinement:
  - modification of the electronic wave functions
  - quantized vibration modes

- Dielectric confinement:
  - Sizes \(<\) optical wavelength
  → Modification of the optical properties

Semiconductor nanoparticles → quantum confinement
Metal nanoparticles → dielectric confinement

→ "small solids" + modifications due to confinement
(N > 300 atoms / particle ⇔ nanosphere with diameter D > 2nm)

⇒ Noble Metals (Ag, Au): synthesis - model
Metal nanoparticles: optical properties at equilibrium

Silver nanoparticles in glass matrix

Interfaces:
Visible absorption enhancement ⇒ Surface Plasmon Resonance
Optical Properties of Metal Clusters (I)

Metal Nanospheres ($\varepsilon = \varepsilon_1 + i\varepsilon_2$)  
($R << \lambda$) in a matrix ($\varepsilon_m$):

→ effective dielectric constant:

$$\tilde{\varepsilon} = \varepsilon_m + p \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} (\varepsilon - \varepsilon_m)$$

($p << 1$ : volume fraction)

Medium absorption (spheres):  
$\alpha(\omega) \propto \frac{\varepsilon_2(\omega)}{(\varepsilon_1(\omega) + 2\varepsilon_m)^2 + \varepsilon_2^2(\omega)}$

→ Resonance for $\varepsilon_1 + 2\varepsilon_m = 0$: surface plasmon resonance  
→ Resonance frequency depends on: - shape  
- structure  
- environment
Optical Properties of Metal Clusters (II)

Metal dielectric function:

\[ \varepsilon(\omega) = \varepsilon^b(\omega) - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \]

- bound electrons (interband)
- free electrons (intraband)

Ag - D = 13 nm - p = 2 \times 10^{-4}

Surface Plasmon Resonance

- frequency: \( \Omega_R = \omega_p / \sqrt{\varepsilon_1^b(\Omega_R) + 2 \varepsilon_m} \)
- width: \( \Gamma = 1/\tau = 1/\tau_o + g v_F/R \)
Non-equilibrium Femtosecond studies

**Fundamental properties of metal nanoparticles**
(Silver or Gold in a matrix, solution or deposited)
→ out-of-equilibrium electronic properties

Optical excitation → Ultrafast response
of an ensemble of nanoparticles or a single unit

- Size evolution of the properties
- Mechanisms of energy and charge transfer at interfaces

Experiments: **femtosecond pump-probe setup**

Optical « pump » pulse:
⇒ modification of the **electronic and optical properties** of the system

Optical « probe » pulse:
⇒ optical transmission changes $\Delta T/T$
**Experimental setup : femtosecond pump - probe**

**Pump:** infrared pulses (25 fs)

**Probe:** infrared pulses (25 fs)
  - blue (30 fs)
  - or UV (55 fs)

**Weak perturbation :** $\Delta T_e \sim 100K$

**Sensitivity:** $\Delta T/T \sim 10^{-7}$
Nanomaterials: Ag, Au nanoparticles in a matrix

<table>
<thead>
<tr>
<th>Hoya - Japan</th>
<th>LASIM - Lyon</th>
<th>LM2N - Paris / ICMCB - Bdx</th>
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<tbody>
<tr>
<td>Synthesis:</td>
<td>fusion + trait. th.</td>
<td>deposition (LECBD)</td>
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<td>Diameter D:</td>
<td>4 &lt; D &lt; 30 nm</td>
<td>2 &lt; D &lt; 4 nm</td>
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<tr>
<td>Dispersion:</td>
<td>&lt; 10 %</td>
<td>~ 10 %</td>
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<tr>
<td>Vol. Fraction:</td>
<td>~ 2.10^{-4}</td>
<td>~ 2 %</td>
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<td>Matrix:</td>
<td>50 BaO - 50P_{2}O_{5}</td>
<td>Al_{2}O_{3} ou MgF_{2}</td>
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TEM

![TEM image](image)

![Histogram](image)
Selective electron excitation ($h\nu$) \rightarrow response of nonequilibrium electrons

$\rightarrow$ **Intrinsic electron scattering processes**
  - Internal thermalization ($\rightarrow T_e$) \rightarrow electron-electron : $\tau_{\text{th}} \sim 300 \text{ fs}$
  - External thermalization ($T_e \rightarrow T_L$) \rightarrow electron-lattice : $\tau_{\text{e-ph}} \sim 1 \text{ ps}$

$\rightarrow$ **Confined vibrational modes**
Femtosecond excitation and probing

**Femtosecond excitation:** intraband absorption

- Intraband absorption
- Athermal electron distribution
- Thermalization + Cooling

**Femtosecond probing:**
- Transmission change $\Delta T/T \iff$ dielectric function change $\Delta \varepsilon(t_D)$
- Probe wavelength $\rightarrow$ different electron interactions

Diagram:
- Pump $\rightarrow$ Sample $\rightarrow$ Probe
- $I_s$ $\rightarrow$ $T \times I_s$
- $\Delta T/T$

Graphs:
1. $f_0$ $\rightarrow$ $T_c = T_0$
2. $t < 0$ $\rightarrow$ $E_F$
3. $t = 0$ $\rightarrow$ $\hbar \omega_p$
4. $t > 0$ $\rightarrow$ $T_c > T_0$
Ultrafast dynamics

*First hundreds fs:
→ Internal thermalisation of the electron gaz at $T_e > T_0$

$\tau_{th} (Ag) = 350\text{ fs dans le massif}$

* First ps:
→ Energy transfer from the electrons to the lattice

$\tau_{e-ph} (Ag) = 850\text{ fs dans le massif}$

* Longer time scale:
→ Energy transfer to the matrix
→ Acoustic vibrations

![Graph showing Ultrafast dynamics](image)
Metal Nanoparticles (I)

Internal electron thermalization
Internal electron thermalization: Ag - Au

- Probing energies close to the Fermi level from \textit{d-bands}
  \rightarrow \text{electronic distribution close to } E_F \rightarrow \text{Internal electron thermalization}

- Probe pulse:  
  - Ag: \( \hbar \Omega_{ib} \sim 4\,\text{eV} \ (310\,\text{nm}) \) \rightarrow \text{Titane - Saphir x 3}
  - Au: \( \hbar \Omega_{ib} \sim 2.5\,\text{eV} \ (500\,\text{nm}) \) \rightarrow \text{Titane - Saphir x 2}

- Low perturbation regime: dynamics independent from \( I_{pompe} \)
**Electron thermalization kinetics (Ag nanoparticles)**

**Rise time : thermalization time**

**response:**

Faster thermalization for the smaller sizes

**Phenomenological**

\[ h(t) = A \{1 - \exp(-t/\tau_{th})\} \exp(-t/\tau_{rel}) + B \]

⇒ caracteristic time \( \tau_{th} \)
Electron internal thermalization: size dependence

(C. Voisin et al., PRL 85, 2200 (2000))

- Increase of electron – electron scattering: intrinsic effect
- Modification of the electronic environment at surfaces:
  - spill-out → reduction of the electron density $n_e \rightarrow R + b$
  - reduced polarisability of $d$-electrons → $R - a$

Fermi liquid Theory (bulk): \[ \tau_{e-e} \propto (n_e)^{5/6} (\varepsilon_d)^{1/2} \]

⇒ increase of e-e scattering close to the surfaces (screening reduction)
Metal Nanoparticles (II)

Electrons - lattice energy transfer
Electron energy losses: electron-phonon coupling

Ag - D = 3 nm in Al₂O₃

UV probe: Risetime: electron thermalization $\rightarrow$ electron-electron interactions
Decay: energy transfer to the lattice $\rightarrow$ electron-lattice coupling

Blue probe: $\Delta T/T \propto$ excess energy in the electron gas $\rightarrow$ electron-lattice coupling

 Probe Delay (ps)

UV probe: IR (930nm)
probe: Blue (465nm) or UV (310 nm)

Size effect?
Electron - Phonon Coupling in Ag Clusters: Size effect

Exponential decay: electrons - lattice energy transfer time,
\[ \tau_{e-ph} \]

- Large nanoparticles: same as bulk
- Small nanoparticles: increased electron-lattice energy exchanges
Electron-phonon scattering: size effects

(A. Arbouet et al., PRL 90, 177401 (2003))

- Similar to electron-electron scattering modifications
- Tin and Gallium: $\tau_{e-ph} \propto D$ (M. Nisoli et al., PRL 78, 3575 (1997))
- Theory: coupling modification (electron-ion screening $\rightarrow$ full line)?
  - Quantized vibrations?

No matrix or growing method dependence $\Rightarrow$ Intrinsic effect

![Graph showing electron-phonon scattering for Ag and Au nanoparticles]

- Nanoparticle Diameter (nm) vs. $\tau_{e-ph}$ (ps)
- Ag and Au nanoparticles with different matrices and growing methods.

- No matrix or growing method dependence $\Rightarrow$ Intrinsic effect
- Similar to electron-electron scattering modifications
- Tin and Gallium: $\tau_{e-ph} \propto D$ (M. Nisoli et al., PRL 78, 3575 (1997))
- Theory: coupling modification (electron-ion screening $\rightarrow$ full line)?
  - Quantized vibrations?
Metal Nanoparticles (III)

Acoustic Vibrations of nanospheres
Electron-lattice quasi-equilibrium: acoustic mode
Ag spherical nanoparticles in glass

Transmission change probed at the surface plasmon resonance:

⇒ Oscillating signal \[ \Delta T/T \propto A \exp(-\gamma t) \cos (\omega t + \phi) \]
⇒ Coherent (in phase) motion of the spherical nanoparticles

⇒ Fundamental radial mode (n = 0): "breathing" of an elastic sphere
**Excitation mechanism**

Fast lattice heating by the electrons: $\tau_{e-ph} < T_{osc}$

$\Rightarrow$ fast increase of the equilibrium size $R_{eq}(T_L)$ (dilation)

Probe mechanism

Modulation of the position of the surface plasmon resonance:

\[
\Omega_R = \frac{\omega_p}{\sqrt{\varepsilon_1(\Omega_R) + 2\varepsilon_m}}
\]

Ensemble of nanoparticles:

⇒ Coherent (in-phase) oscillations
Vibration modes of a sphere

- Silver nanoparticles in glass matrix: elastic homogeneous media
- Vibration modes of a free sphere: Lamb (1882)
- Embedded sphere:
  - Excitation mechanism: isotrope (via the electrons)
    → radial vibration modes (dilation and contraction)
Size effects

Dependence of period and damping with nanoparticle size

Size reduction:

\[ R = 13 \text{ nm} \]
\[ R = 3 \text{ nm} \]

\[ T_{osc} = \frac{2\pi}{\omega} \propto R \]
\[ \tau = \frac{1}{\gamma} \propto R \]
Origin of damping: *homogeneous* and *inhomogeneous*

**Inhomogeneous**: nanoparticle *size distribution*

**Homogeneous**: energy transfer to the matrix → nanoparticle - matrix acoustic coupling

- Ag - R = 3nm in glass
- Ag - R = 2.5nm in water
Acoustic vibrations: fundamental radial mode

Fundamental radial mode \((n = 0)\):

- Period \(T_{n=0} \rightarrow \) average diameter

Homogeneous damping:
- \(\tau_h \propto E_{\text{volume}} \left/ \left( \frac{dE}{dt} \right)_{\text{surface}} \right. \propto R \)
- \(\rightarrow \) contact / interface quality
Higher order radial modes

with: \( T_{n=1} = T_{n=0} / 2.1 \) (period)

\( \tau_{n=1} \approx \tau_{n=0} \) (damping)

lower excitation (1:6)
(dilation model)
Conclusion

• Femtosecond perturbation of the electron gas
  → Electron interaction processes in a nanoparticle

• Nonequilibrium electrons: establishment of a collective response

• Electron dynamics:    ⇒  e - e and e - phonon interactions increase for D ≤ 10nm
  ⇒  Confinement effects

• Nanoparticle lattice dynamics
  ⇒  Real time detection of nanoparticle coherent oscillations
  ⇒  Radial mode frequency and damping    -   Optical control

• Charge transfer
• Single nanoparticle
# Acknowledgements

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