Collective Optical Excitations in Nanoparticle Chains for Potential Applications in Optical Sensing and Imaging

Vadim Markel
University of Pennsylvania
Departments of Radiology and Bioengineering
Philadelphia

vmarkel@mail.med.upenn.edu
http://whale.seas.upenn.edu/vmarkel/
Potential Uses of Metal Nanoparticles

- SERS
- Biosensors
- Imaging beyond diffraction limit
- Therapy
Figure 5: FE-SEM images (1.2μm × 1.2μm) of AMF of 11-nm mass thickness before (top) and after protein deposition and washing inside spot (bottom).

Figure 6: SERS spectra at 568nm incident laser wavelength for human insulin (blue) and insulin lispro (red) on AMF substrates. The SERS difference spectrum (insulin lispro) in the lower panel clearly shows the observed spectral differences between the two isomers.

THE ABOVE IMAGES IMAGES HAVE BEEN PUBLISHED IN:


(Experiments were performed in Shalaev’s group, ECE, Purdue)
Why Metal Nanoparticles are Useful?

- Field Enhancement
- Field Localization

\[ \alpha = \frac{V}{4\pi} \left( \frac{1}{\varepsilon - 1} + \nu \right) ; \quad 0 < \nu < 1 \quad [\nu = \frac{1}{3} \text{ for a sphere}] \]

\[ \varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad \Rightarrow \quad \alpha = -\frac{V}{4\pi} \frac{\omega_p^2}{\omega^2 - \omega_F^2 + i\gamma \omega} \]

\[ \omega_F = \sqrt{\nu \omega_p} \]
Resonance polarizability

\[ \alpha_{\text{res}} = \alpha(\omega = \omega_F) = i \frac{V}{4\pi} \frac{\omega_p}{\gamma \sqrt{\nu}} \]
\[ \omega_p / \gamma \approx 500 \text{ (silver)} \]

First radiative correction to the polarizability:
\[ \frac{1}{\alpha} = \frac{1}{\alpha_{\text{quasistatic}}} - i \frac{2k^3}{3} ; \quad [k = \frac{\omega}{c}] \]
\[ \alpha = \frac{\alpha_{\text{quasistatic}}}{1 - i2k^3\alpha_{\text{quasistatic}} / 3} \]

Resonance Field Enhancement Near a Sphere Surface

\[ |E_{\text{surface}}| = \frac{|\alpha|}{a^3} E_0 \sqrt{1 + 3\cos^2 \theta} \]
\[ \frac{|\alpha_{\text{res}}|}{a^3} = \frac{\omega_p}{\gamma \sqrt{3}} \sim 300 ; \quad G_{\text{SERS}} \sim \left| \frac{E_{\text{surface}}}{E_0} \right|^4 \]
From Single to Aggregated Nanoparticles

Even stronger local field enhancements

-- Single molecule SERS in a nanojunction

-- Nanoscale focusing in a “nanolens”

[K. Li, M.I. Stockman, D.J. Bergman, PRL 91, 227402-1-4 (2003)]
Collective optical excitations allow even more controllability

From surface plasmons to surface polaritons
Linear chains have been lately of particular interest...
Physical Model

\[ n = 1 \quad d_{n-1} \quad d_n \quad d_{n+1} \]

NF tip operating in the illumination mode

NF tip operating in the collection mode
The Dipole Approximation

\[ d_n = \alpha_n \left[ E_n + \sum_{m \neq n} \hat{G}_k(x_n, x_m) d_m \right] \]

- \( \alpha_n \) - Polarizability of the \( n \)-th particle
- \( \hat{G}_k(x_n, x_m) \) - Green's function for the electric field in vacuum
- \( E_n \propto \delta_{n1} \) - Electric field produced by the first tip
- (the incident field)

The coupled-dipole equation in the frequency domain

\[ k = \frac{\omega}{c} = \text{const} \]
Model for the Polarizability, $\alpha$

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$  
[Drude model for the dielectric function]

$$\text{Re}\left(\frac{1}{\alpha}\right) = \frac{1}{a^3}\left[1 - \left(\frac{\omega}{\omega_F}\right)^2\right]$$

$$\text{Im}\left(\frac{1}{\alpha}\right) = -i\left(\frac{2k^3}{3} + \frac{1}{a^3} \frac{\omega \gamma}{\omega_F^2}\right)$$  
[Quasistatic approximation + first radiative correction]

$a$ - Nanosphere radius

$\omega_F = \omega_p / \sqrt{3}$ - Frohlich frequency

$k = \omega / c$
Simulation in a Finite Chain of $N=1000$ Identical Nanospheres

Parameters:
- $\omega = \omega_F$
- $\frac{\gamma}{\omega_F} = 0.002$
- $\lambda = \frac{2\pi c}{\omega} = 10h$
- $h = 4a$
Analytical Solution in an Infinite Periodic Chain

\[
d_{n}^{(\parallel, \perp)} = \int_{-\pi/h}^{\pi/h} \frac{E_{n}^{(\parallel, \perp)} e^{i q x_{n}}}{1/\alpha - S^{(\parallel, \perp)}(k, q) \ 2\pi} \ dq
\]

\[
S^{(\parallel, \perp)}(k, q) = 2 \sum_{n>0} G_{k}^{(\parallel, \perp)}(0, x_{n}) \cos(q x_{n}) \quad \text{[The dipole sum]}
\]

If \( q > k \), \( \text{Im}[S^{(\parallel, \perp)}(k, q)] = -\frac{2k^{3}}{3} \)

The dispersion equation:

\[
Z(k, q) = 1/\alpha - S^{(\parallel, \perp)}(k, q) = 0 \quad \Rightarrow \quad \omega = f(q)
\]
Let, for a given value of $k$, $Z(k, q_0) \approx 0$ and $q_0 > k$

$$Z(k, q_0) = 1/\alpha - S(k, q_0) \approx 0$$

Then we write approximately:

$$S(k, q) \approx \text{Re} S(k, q_0) + (q - q_0) \frac{\partial \text{Re} S(k, q)}{\partial q} \bigg|_{q=q_0} - i \frac{2k^3}{3}$$

$$\ell = \frac{1}{\delta} \left| \frac{\partial \text{Re} S(k, q)}{\partial q} \right|_{q=q_0}$$  [Decay length]

$$\delta = -\text{Im}(1/\alpha) - 2k^3/3$$  [Absorption strength]
The Dipole Sum (Transverse Oscillations in an Infinite Periodic Chain)

\[ l^3 \text{Re}[S(k,q)] \]

- \( k h = 0.4 \pi \) (purple)
- \( k h = 0.2 \pi \) (blue)
- \( k h = 0.1 \pi \) (green)
- Quasi-Static Limit (red)

(Transverse Oscillations)

\[ q h / \pi \]
The Dispersion Curve (Transverse Oscillations in an Infinite Ordered Chain)
Dispersion Curves (continued)
Simulation in a Finite Chain of $N=1000$ Identical Nanospheres

Parameters:

\[ \omega = \omega_F \]
\[ \frac{\gamma}{\omega_F} = 0.002 \]
\[ \lambda = \frac{2\pi c}{\omega} = 10h \]
\[ h = 4a \]
Effect of Ohmic Losses

Parameters:
- $\omega = \omega_F$
- $\gamma = \frac{\gamma}{\omega_F}$ varies
- $\lambda = \frac{2\pi c}{\omega} = 10h$
- $h = 4a$
Effects of Disorder

• Off-diagonal disorder (disorder in the nanoparticle positions)

We assume here that the position of the $n$-th particle is evenly distributed in the interval $[h(n-A), h(n+A)]$, $A<<1$

• Diagonal disorder

[A more subtle effect, not considered in this talk; see Phys.Rev.B 75, 085426 (2007)]
Off-Diagonal Disorder in the Absence of Ohmic Losses

Parameters:

\[ \omega = \omega_F \]
\[ \gamma = 0 \]
\[ \frac{\lambda}{\omega_F} = 10h \]
\[ h = 4a \]
Different Realization of Disorder at the Level $A=0.01$
Different Realization of Disorder at the Level $A=0.02$
Non-Quasistatic SP at Different Levels of Disorder

Let the frequency be small enough so that the ordinary SP is not excited.

Quasistatic (ordinary) SP

Non-Quasistatic (extraordinary) SP
Non-Quasistatic SP at Different Levels of Disorder (continued)

\[ \frac{\omega}{\omega_F} = 0.984 \]

(small enough so that the ordinary SP is not excited)
Specific Extinction for Excitation by a Plane Wave $\exp(iq\mathbf{x})$
(e.g., created by the TIR, $q$ can be larger than $k$)
II. SURFACE PLASMON POLARITONS IN CHAINS OF NANOPARICLES

\[ n = 1 \]

\[ d_{n-1} \]

\[ d_n \]

\[ d_{n+1} \]

\[ \theta \]

\[ 2a \]

\[ h \]

NF tip operating in the illumination mode

NF tip operating in the collection mode
Dispersion Relations and Group Velocity for Different Aspect Ratios of Nanoparticles
Propagation of SPP Wave Packets in Chains

\[ E_n(t) = \delta_{n1} A \exp[-i\omega_0 t] \exp \left[ -\left( \frac{t - t_0}{\Delta t} \right)^2 \right] \]

\[ \tilde{E}_n(\omega) = \delta_{n1} A \sqrt{\pi \Delta t} \exp \left[ -\left( \frac{\omega - \omega_0}{\Delta \omega} \right)^2 \right] \]

\[ \Delta \omega = \frac{2}{\Delta t} \]
Chain Parameters:
- \( h = 40 \text{ nm} \)
- \( b = 10 \text{ nm} \)
- \( \xi = \frac{b}{a} = 0.15 \)
- \( N = 5000 \)
- \( \tau = \frac{h}{c} = 0.133 \text{ fsec} \)

Metal Parameters (Ag):
- \( \varepsilon = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \)
- \( \lambda_p = \frac{2\pi c}{\omega_p} = 136 \text{ nm} \)
- \( \gamma/\omega_p = 0.002 \)
- \( \varepsilon_0 = 5 \)

Host Medium:
- \( \varepsilon_h = 2.5 \)

Pulse Parameters:
- \( \omega_0 = 0.1\omega_p \) \( [\lambda_0 = 1.36 \mu \text{m}] \)
- \( \Delta t = 7.2 \text{ fsec} \)
- \( \Delta \omega/\omega_0 = 0.2 \)

\( \nu_g \approx 0.58c \)

\( x = 200 \mu \text{m} \)
Pulse Parameters Different from the Previous Graph:

- $\omega_0 = 0.05 \omega_p \ [\lambda_0 = 2.72 \mu m]$ 
- $\Delta t = 14.2 \ fsec$ 
- $\Delta \omega / \omega_0 = 0.2 \ [\text{same as before}]$ 

$v_g \approx 1.17c$
THE END
Depolarization factors

Prolate:

\[ v = \frac{1 - \zeta^2}{\zeta^2} \left[ -1 + \frac{1}{2\zeta} \ln \left( \frac{1 + \zeta}{1 - \zeta} \right) \right] \]

Oblate:

\[ v = \frac{g(\zeta)}{2\zeta^2} \left[ \frac{\pi}{2} - \arctg(g(\zeta)) \right] ; \quad g(\zeta) = \sqrt{\frac{1 - \zeta^2}{\zeta^2}} \]

\[ \zeta = 1 - \xi^2 ; \quad \xi = \frac{a_\leq}{a_>} < 1 \]
I. COHERENTLY TUNABLE THIRD-ORDER NONLINEARITY IN THE NANOJUNCTION OF TWO METAL SPHERES
\[ d_{z}^{(NL)}(t) = \alpha^{(3)} E_{z} |E_{z}|^{2} = \alpha_{\text{eff}}^{(3)} E_{0} |E_{0}|^{2} \exp(-i\omega t). \]

\[ \alpha_{\text{eff}}^{(3)} = G \alpha^{(3)} \]

\[ G = \frac{E_{z} |E_{z}|^{2}}{E_{0} |E_{0}|^{2}} \]