Plasmon enhanced nonlinear absorption and refraction

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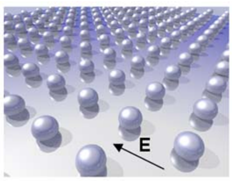
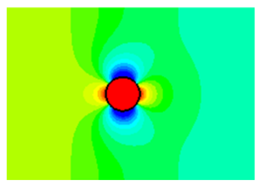
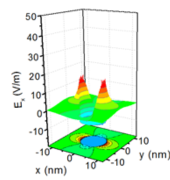
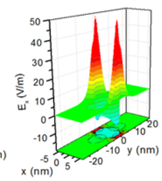
Calculations and simulations Dana Kohlgraf-Owens

Key idea: Use local fields to generate enhanced nonlinear optical response









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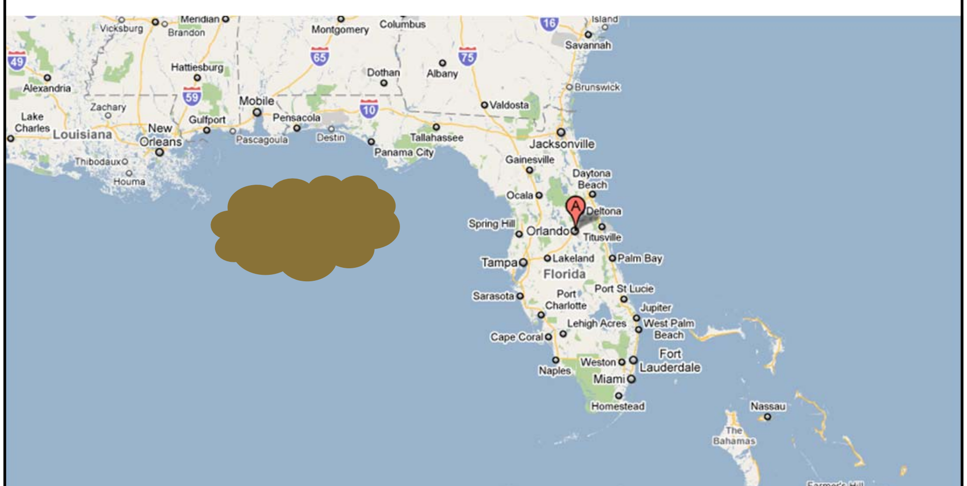
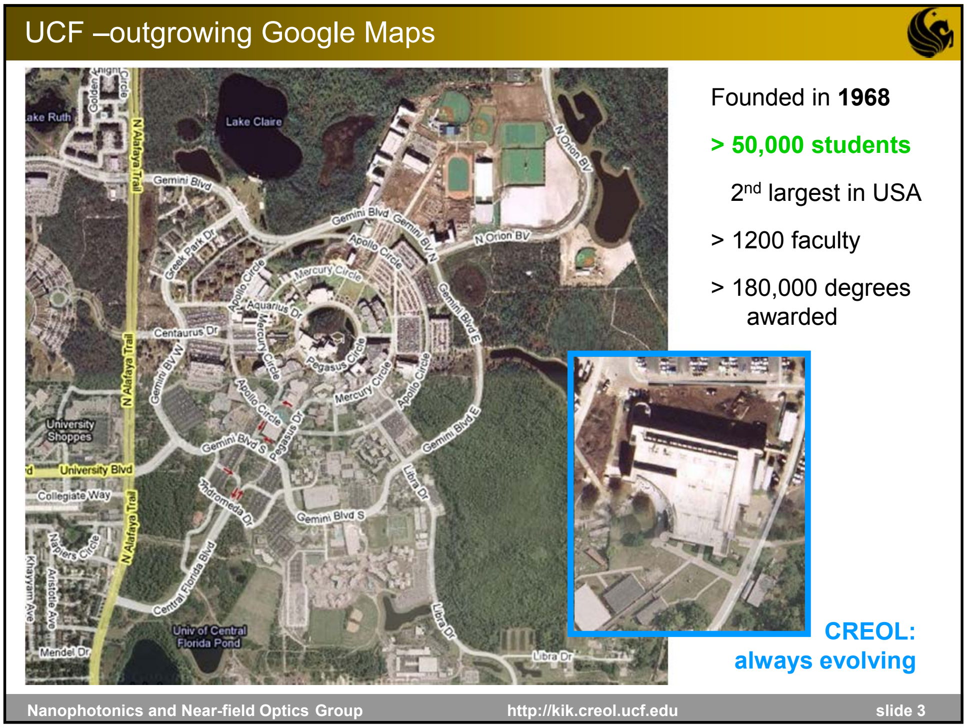
Orlando, FL

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2nd largest in USA
> 1200 faculty
> 180,000 degrees awarded
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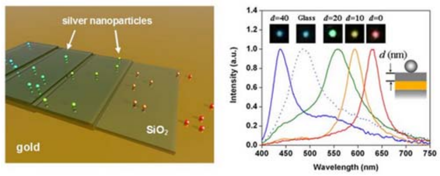
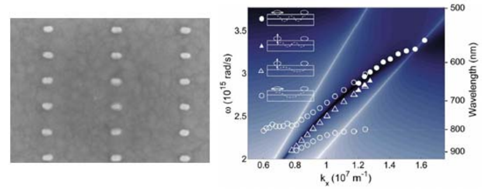
NPNO group – plasmon related work

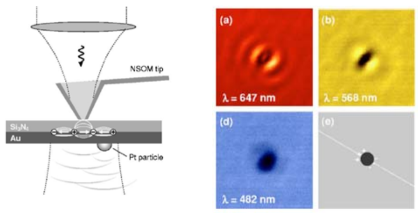
Dielectric control of SP resonances



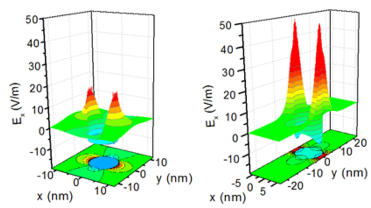
Strong coupling in surface coupled nanoparticle arrays (poster: Tuesday)



Near-field focusing using metal lenses



LSP enhanced nonlinear absorption



Outline

1. Introduction: nonlinear absorption
2. Intermezzo (recovery from equations)
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   ⇒ surprise: complex enhancement
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Nonlinear refraction

Nonlinear refractive and absorptive materials are of interest for

- Nonlinear transmission (power management)
- Self-focusing
- All-optical switching
- Sensor protection

Holy grail: achieve low threshold for NL absorption in thin-film coating

Challenge: **nonlinear optical response generally weak**

$\Rightarrow$ Extremely large irradiance needed to achieve any significant effects

Question: can plasmon resonance on spherical particles be used to increase the nonlinear absorption performance in a thin sample

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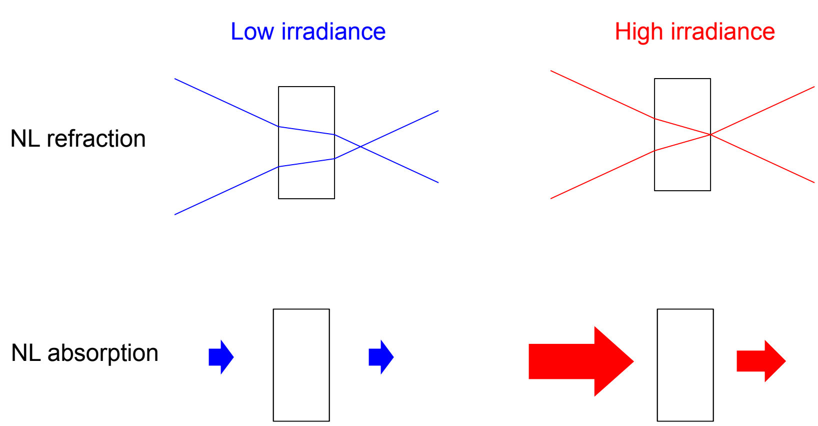
Complex nonlinear refractive index

In the absence of 2nd order effects, polarization given by $P = \varepsilon_0 \chi^{(1)} E + \chi^{(3)} E^3 + \dots$

Finite $\chi^{(3)}$ leads to (complex) change in n: **n = n_0 + η_2 I = n_0 + (η_2'+i η_2'') I**



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Brief recap – propagation equations

In the absence of linear absorption, we have $\frac{dI}{dz} = -\beta I^2$

nonlinear absorption coefficient $\beta = 2 k_0 n_2''$

This leads to nonlinear signal propagation: $I(z) = \frac{I_0}{1+\beta I_0 z}$ (max $\frac{1}{\beta z}$)

Slab of NL absorptive medium ⇒ transmitted signal is limited

In the presence of linear absorption :

$$\frac{dI}{dz} = -(\alpha + \beta I)I \qquad I(z) = \frac{1}{e^{\alpha_c L} - \frac{\beta_c I_0}{\alpha_c}(1-e^{\alpha_c z})} I_0$$

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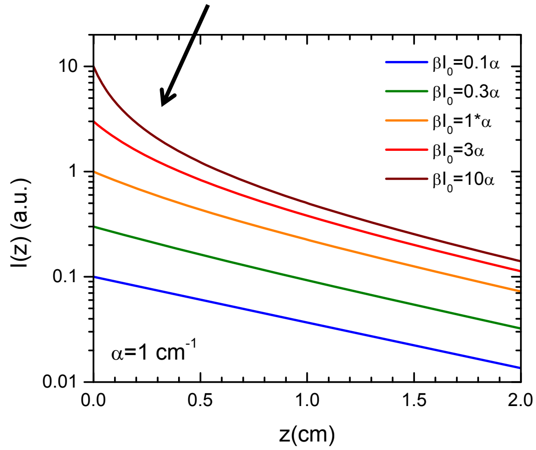
Example: nonlinear transmission

Initial absorption increases $\alpha_{tot} = \alpha + \beta I$

Incident irradiance up



Transmitted signal hits a limit

Challenge: irradiance required to achieve significant nonlinear absorption is high

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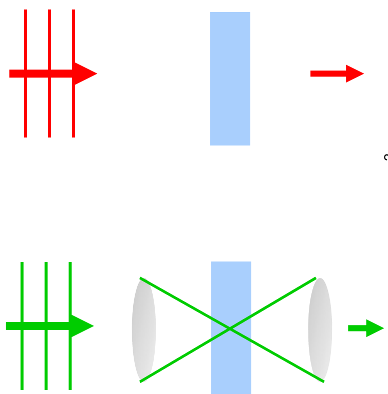
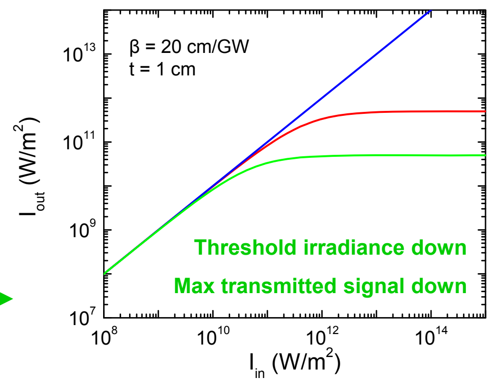
Effect of focusing on nonlinear absorption

Traditional solution: focusing incident radiation to increase irradiation





Practical issue: resulting system is large, relatively heavy

Enhancing local fields using surface plasmon resonance

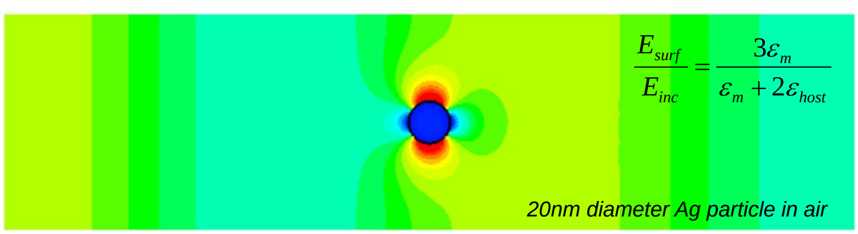
Known: large field strength ⇒ large nonlinear response

Clearly (..?) : plasmon resonance and field enhancement will improve performance

ARO MURI "*Engineered Multifunctional Nanophotonic Materials for Ultrafast Optical Switching*" (CREOL / GATech / UArizona / Purdue)

Abbreviated proposal text: "*Surround metal particle with nonlinear absorber ⇒ achieve enhanced NL absorption in small volume*?"

note!



First: evaluate using linear and 'nonlinear Maxwell Garnett theory'

Intermezzo – finding Maxwell Garnett

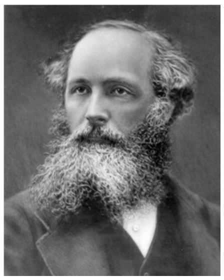
Who is J. C. Maxwell Garnett ?! Collaboration?

Google image search for a picture leads to many pictures of …

James Clerk Maxwell (1831 - 1879) Famous for .. Maxwell's equations

BUT.. Effective medium paper on colored glasses published in **1904**..

Apparently we have: James Clerk Maxwell ≠ James Clerk Maxwell Garnett



James Clerk Maxwell

Some internet searching reveals:

William Garnett, who was Maxwell's scientific demonstrator, was so impressed with Maxwell that he named his son James Clerk Maxwell Garnett

Mark I. Stockman Kik?

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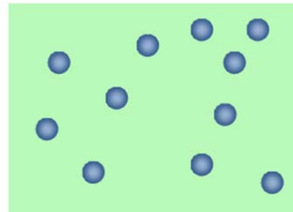
Analytical calculations – Maxwell Garnet theory

Consider dilute solution of silver nanoparticles in CS_2

CS_2 (fs) $n_2 = 6\times10^{-15}$ cm²/W and $\beta = 0.6$ cm/GW

Data for 440nm – assumed constant

Assume linear Ag particle in NL host
with fill fraction f = 0.1% and d=10 nm



Nonlinear susceptibility of the composite is enhanced relative to host:

$\chi_{eff}^{(3)} = g^{(3)} \chi_{host}^{(3)}$ and for NL index $n_{2,eff} = g_2\, n_{2,host}$

Analytic expression for the enhancement factor:

$$g^{(3)} \equiv 1 + \frac{f}{5}\left[8|\gamma|^2\gamma^2 + 6|\gamma|^2\gamma + 2\gamma^3 + 18\left(|\gamma|^2 + \gamma^2\right)\right]$$

M.I. Stockman et al., Phys. Rev. B 60, 17071 (1999)

Here γ is a complex field enhancement factor $\gamma = \dfrac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}$ ← plasmon resonance

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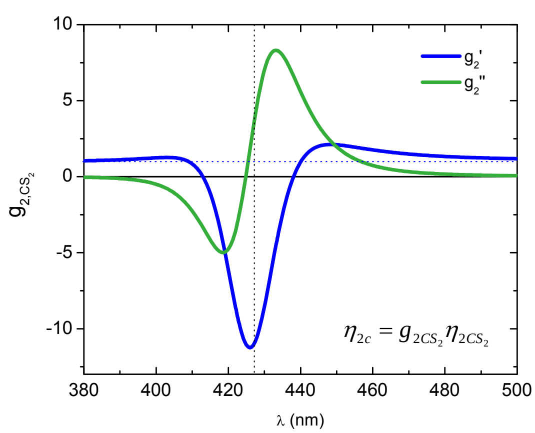
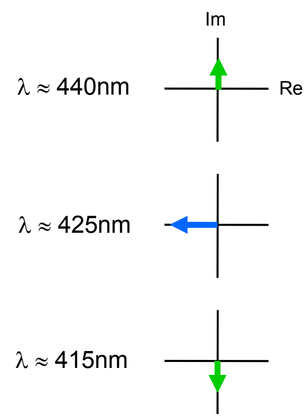
Nonlinear index enhancement: silver nanoparticles in CS_2





Good news: *small* amount of metal : f=0.001, but *large* enhancement factors

Surprise: at LSP resonance (~430nm) ⇒ CS_2 becomes saturable absorber !

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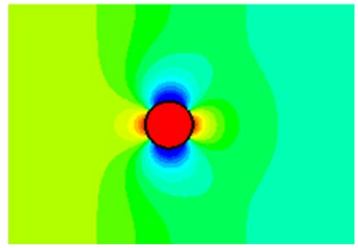
Nonlinear index enhancement: silver nanoparticles in CS_2

Origin of change in response:

$$P^{(3)} = \varepsilon_0 \chi^{(3)} E^3$$



Locally enhanced fields in host:

90° phase delayed relative to incident light

$$P_{loc}^{(3)} = \varepsilon_0 \chi^{(3)} E_{loc}^3$$

$$E_{loc} \propto iE_{in} \quad \Rightarrow \quad P_{loc}^{(3)} \propto -i\chi^{(3)} E_{in}^3$$

"Clearly plasmon resonance and field enhancement will improve performance .." - P.G. Kik, GRC 2010

Field enhancement does NOT simply enhance nonlinear absorption

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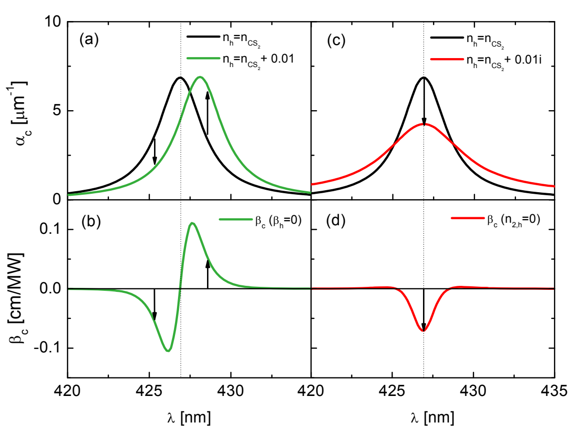
Interpretation: light-induced resonance changes

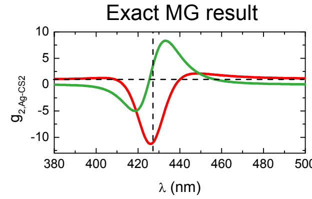


$$\sigma_{ext} = 9\frac{\omega}{c}\epsilon_h'^{3/2} V \frac{\epsilon_m''}{(\epsilon_m' + 2\epsilon_H')^2 + \epsilon_m''^2}$$

ε_H' up ⇒ resonance redshifts

ε_H'' up ⇒ resonance broadens

Exact MG result



Damping reduced 10x
large Δn_H and $\Delta\kappa_H$ assumed

Wrong viewpoint: 'the enhanced local fields enhance the response of the host'

Correct: the nonlinear host polarizability affects the composite polarizability

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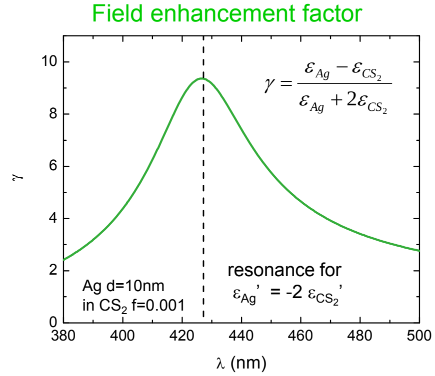
Trade-off: field enhancement vs. linear absorption

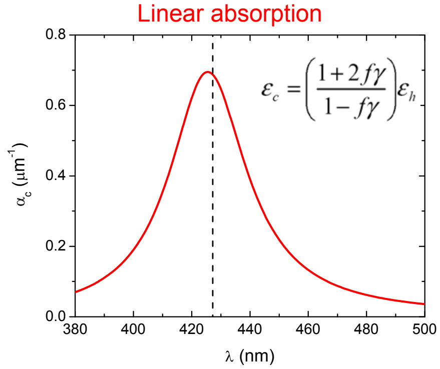
Second challenge: metal nanoparticles introduce linear absorption

To evaluate quality of NL absorber, consider Figure of Merit **FOM = β / α**

Field enhancement factor



Linear absorption



Max $|g^{(3)}|$ occurs at frequency for max linear absorption

Next: calculate figure of merit vs. fill fraction

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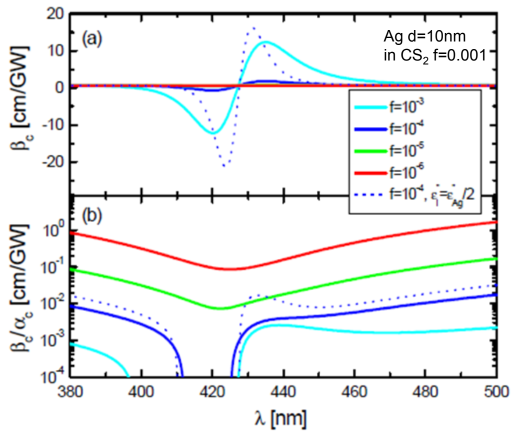
Composite β and Figure Of Merit



For large (10^{-3}) fill fraction, NL absorption coefficient significantly enhanced

However: linear absorption increases, leading to an overall reduced figure of merit

Next: try top-down nanostructuring to improve figure of merit

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Structural engineering for optimum NLO absorption

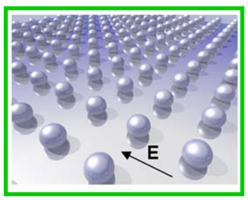
Numerical simulations based on frequency domain simulations in CST Studio

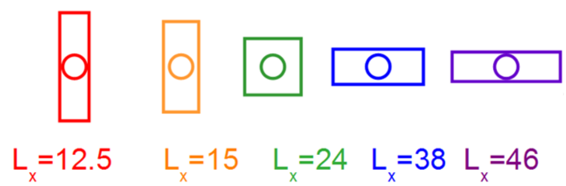
Rectangular arrays of silver np (10nm diam, f=3%) single layer (xy plane), n_{host}=1.5

Change inter-particle interaction by varying unit cell aspect ratio

Monitor geometry dependence of field enhancement and NLO response

Top view of geometries, incident E-field along x (horizontal), layer thickness 30nm





Effective medium response through numerical intregration

Dense arrays: no analytical formulas available

Based on numerically computed field distributions in different unit cells we calculate linear dielectric properties using

$$\varepsilon_c(\omega) = \frac{\left\langle \varepsilon(\omega,\vec{r})\vec{E}(\omega,\vec{r})^2 \right\rangle_V}{\left\langle \vec{E}(\omega,\vec{r}) \right\rangle_V^2}$$

And nonlinear optical properties using

$$\chi_c^{(3)}(\omega) = \frac{\left\langle \chi^{(3)}(\omega,\vec{r})\left|\vec{E}\right|^2 \vec{E}^2 \right\rangle_V}{\left|\left\langle \vec{E}\right\rangle_V\right|^2 \left\langle \vec{E}\right\rangle_V^2}$$

Note: χ values represents χ_{xxxx}, only valid along certain structural symmetry axes

Definition of enhancement factor

Composite NL susceptibility can be written in terms of enhancement factors g:

$$\chi_c^{(3)} = f_{in} g_{in}^{(3)} \chi_{in}^{(3)} + f_h g_h^{(3)} \chi_h^{(3)}$$

Note: fill fraction no longer part of the enhancement factor. New factors given by :

$$g_j^{(3)} = \frac{\left\langle \vec{E}^2 |\vec{E}|^2 \right\rangle_{V_j}}{\left\langle \vec{E} \right\rangle_V^2 \left| \left\langle \vec{E} \right\rangle_V \right|^2}$$

V_j = volume of inclusion or of host (j=in or h)

V = volume of unit cell

These represent *enhancement of $\chi^{(3)}$ contribution from host or inclusion, relative to the expected value based on a homogeneous E distribution*

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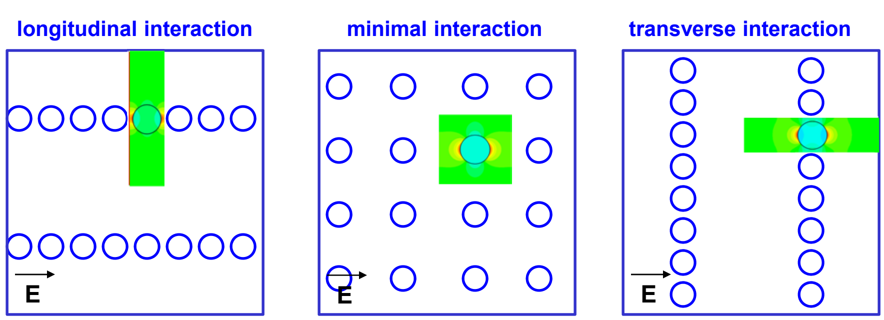
Simulation structure

- Simulate 5 geometries ; maintain fixed fill fraction **f=0.03**
- 10 nm diameter Ag spheres in host index **n=1.5**
- Incident E field polarized along x direction



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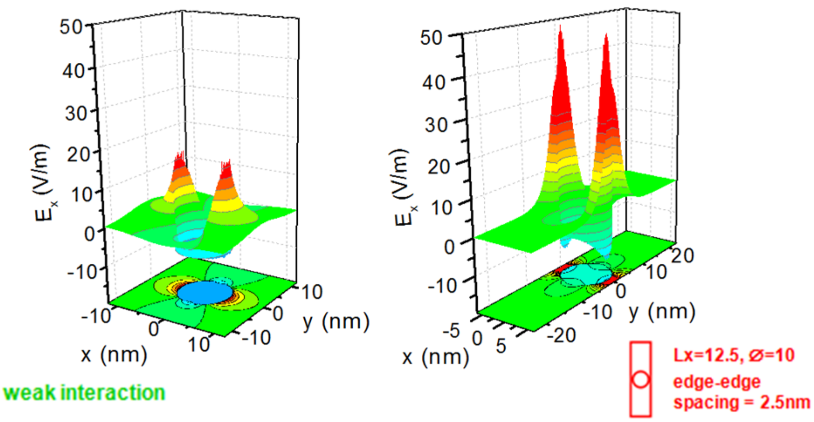
Calculated field distributions



Calculated E_x fields in xy plane for two geometries: square array (left) for weak interaction and small inter-particle spacing. E-field is aligned along x-axis

Note: higher enhancement for small spacing, but in small volume

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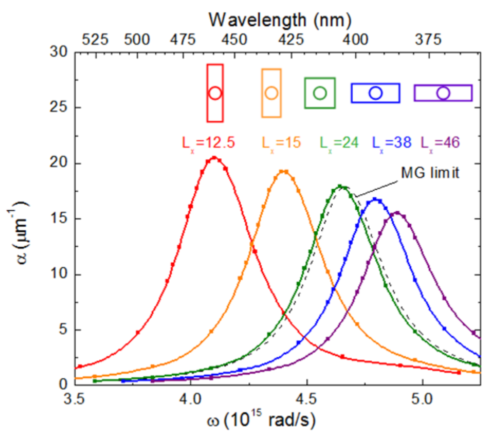
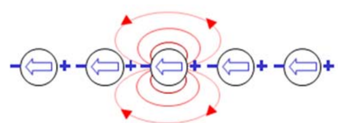
Linear absorption vs. geometry



Small longitudinal spacing



⇒ Near-field interaction reduce Internal fields : redshift

Square unit cell result close to known analytical MG result (dashed line)

Significant absorption in less than a micron: final structure thin by necessity

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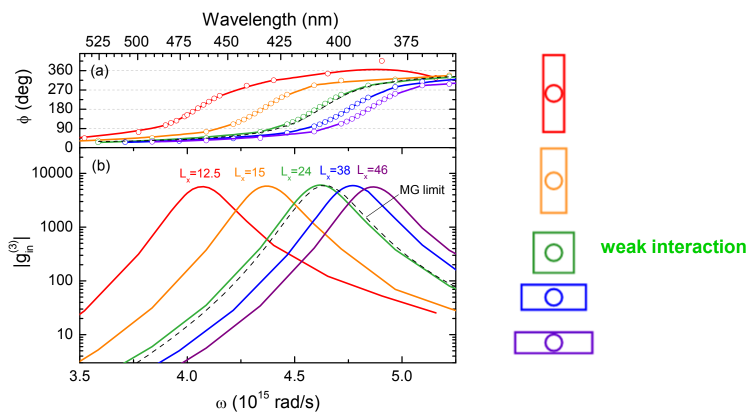
Inclusion enhancement factors vs. geometry

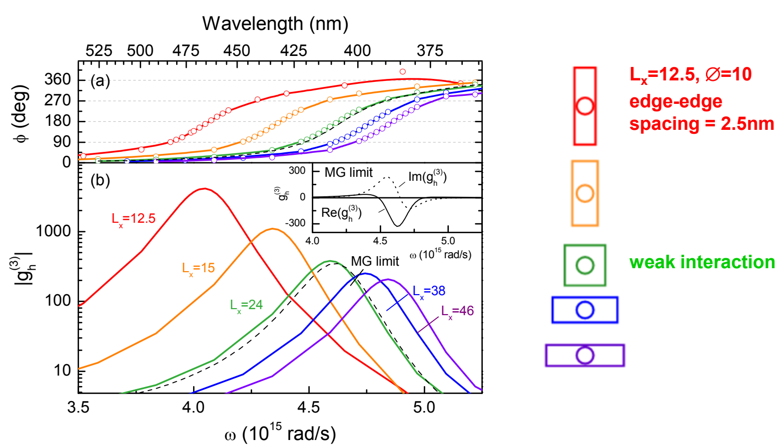


Maximum enhancement occurs near array plasmon resonance

Metal NLO response only weakly affected by geometry

Reason: *internal* field distribution not strongly affected by neighbor particles

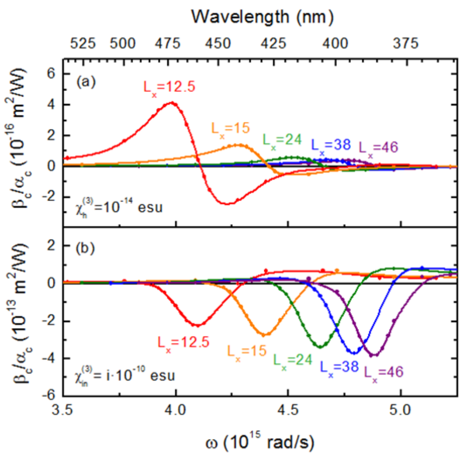
Host enhancement factors vs. geometry



Field concentration is beneficial:

At 2.5nm edge-edge spacing, enhancement up ~10x compared to weak interaction

Figures of Merit for Nonlinear Absorption



Top panel: assumes only host nonlinear, assume realistic but large nonlinear refraction

Lower panel: assume only metal nonlinear, assume imaginary freq. independent $\chi^{(3)}$

⇒ Host figure of merit can be significantly improved using geometry by optimizing local field enhancement while maintaining similar absorption

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Summary

Holy grail: achieve low threshold for NL absorption in thin-film coating

Dilute metal nanoparticle solutions:

- Small metal fill fractions generate large changes (>10x) in $\chi^{(3)}$ and n_2
- Enhancement is complex: NL absorptive host not best choice?
- Understand in terms of linear absorption spectra
- Figure of merit is reduced in presence of metal due to linear absorption, BUT thin film response is improved

Metal nanoparticle arrays

- Additional field enhancement at small spacing improves FOM

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Questions?
CREOL professor
CREOL student