High-order nonlinearities in disordered media

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Second lecture
Transverse high-order nonlinear phenomena in composites
Metal-dielectric nanocomposites

- Glasses (bulk and thin films) with metallic NPs
- Polymers with metallic nanostructures
- Liquid colloids with metallic NPs

Optical response is controlled through the volume fraction of the NPs
Metallic NPs as optical nanoantennas

Optical response may be enhanced due to the NPs

\[ E_{\text{local}} = \eta E_{\text{light}} \]

\[ \eta = \frac{3 \varepsilon_{NP}(\omega)}{\varepsilon_{NP}(\omega) + 2 \varepsilon_h(\omega)} \]

\[ \text{Re} \left[ \varepsilon(\omega_{sp}) + 2 \varepsilon_m(\omega_{sp}) \right] = 0 \]
Colloids with Ag spherical NPs

Stabilizing agents to prevent aggregation

Diameter: 4 nm ≈ 1500 atoms ≈ 30% in the surface

Spheres and several shapes and sizes

Sodium citrate, PVP, PVA
**Metallic nanoshells**

Plasmon frequency depends on the ratio between the shell thickness and the core radius

Hallas et al.  
*Langmuir* 2013  
29, 4366-4372

**Silver Nanoprisms**

Synthesis of silver nanoprisms: A photochemical approach using light emission diodes

Saade, de Araújo  

**High-order nonlinearity of silica-gold nanoshells in chloroform at 1560 nm**

Falcão-Filho et al.  
*Opt. Express* 18 (2010) 21616

**Improved synthesis of gold and silver nanoshells**

Brito-Silva et al.  
*Langmuir* 29 (2013) 4366
Large optical nonlinearity and fast response

Fast response is due to the
induced dipole relaxation

Surface plasmon optical dephasing, $T_2$

Measured using the “Persistent Hole-Burning Technique”

$T_2 < 3fs$

$T_2$ is influenced by the environment

Nonlinear optics of a nanocomposite

\[ P_L + P_{NL} = \epsilon_0 \sum_{N=0}^{\infty} \chi_{eff}^{(2N+1)} E^{(2N+1)} \]

**Effective 3rd. order susceptibility**

\[ \chi_{eff}^{(3)} = f L^2 \left| L \right|^2 \chi_{np}^{(3)} + \chi_h^{(3)} , \]

Centro-symmetric media

\[ \chi_{eff}^{(even)} = 0 \]

**Local field factor**

\[ L = 3\epsilon_h^{(L)}/(\epsilon_{np}^{(L)} + 2\epsilon_h^{(L)}) \]

Nonlinear response depends strongly on the laser frequency

\[ n_2 \propto \text{Re} \chi_{eff}^{(3)} \]

Nonlinear refraction

\[ \alpha_2 \propto \text{Im} \chi_{eff}^{(3)} \]

Nonlinear absorption
When high-order nonlinearities are present:

**Self-focusing medium**

**NL refraction**

"Closed-aperture" Z scan

\[ \Delta T \propto n_2 I + n_4 I^2 + n_6 I^3 + \ldots \]

**NL absorption**

"Open-aperture" Z scan

\[ \Delta T \propto \alpha_2 I + \alpha_4 I^2 + \alpha_6 I^3 + \ldots \]
\[ \chi^{(3)}_{\text{eff}} \approx f (2.3 + i1.0) \chi^{(3)}_{NP} + \chi^{(3)}_{\text{host}} \]

\[ n_2 \propto \left\{ f \left( 2.3 \Re \chi^{(3)}_{NP} - 1.0 \Im \chi^{(3)}_{NP} \right) + \Re \chi^{(3)}_{\text{host}} \right\} \]

\[ \alpha_2 \propto \left\{ f \left( 2.3 \Im \chi^{(3)}_{NP} + 1.0 \Re \chi^{(3)}_{NP} \right) + \Im \chi^{(3)}_{\text{host}} \right\} \]

\[ \chi^{(3)}_{\text{host}} = 2.9 \times 10^{-20} + i3.5 \times 10^{-22} (m/V)^2 \]

\[ \chi^{(3)}_{NP} = -(6.3 - i1.9) \times 10^{-16} (m/V)^2 \]
Observation of fifth-order refraction in a metal-colloid

Silver NPs in acetone

Z-scan
532 nm
Single pulses
5 GW/cm²

\( f = 5.0 \times 10^{-5} \)

\( n_2 \)

\( n_4 \times I \)

\( f (10^{-4}) \)

Transmittance

GW/cm²

9 GW/cm²
Generalized Maxwell-Garnet model

\[ \chi_{\text{eff}}^{(3)} = f \ L^2 \ |L|^2 \ \chi_{\text{np}}^{(3)} + \chi_{h}^{(3)}, \]

\[ L = 3\varepsilon_{h}^{(L)}/(\varepsilon_{\text{np}}^{(L)} + 2\varepsilon_{h}^{(L)}) \]

\[ \chi_{\text{eff}}^{(5)} = f \ L^2 \ |L|^4 \ \chi_{\text{np}}^{(5)} - \frac{6}{10} f \ L^3 \ |L|^4 \ (\chi_{\text{np}}^{(3)})^2 - \frac{3}{10} f \ L |L|^6 |\chi_{\text{np}}^{(3)}|^2, \]

\[ \chi_{\text{eff}}^{(7)} = f \ L^2 \ |L|^6 \ \chi_{\text{np}}^{(7)} + \frac{12}{35} f \ L^4 \ |L|^6 \ (\chi_{\text{np}}^{(3)})^3 + \frac{3}{35} f |L|^8 \left[ 4L^2 \chi_{\text{np}}^{(3)} + |L|^2 (\chi_{\text{np}}^{(3)})^* \right] |\chi_{\text{np}}^{(3)}|^2 \]

\[ -\frac{4}{7} f \ L |L|^6 \left[ 2L^2 \chi_{\text{np}}^{(3)} + |L|^2 (\chi_{\text{np}}^{(3)})^* \right] \chi_{\text{np}}^{(5)}, \]

Reyna, de Araújo, Optics Express 22 (2014) 22456

Ag NPs in acetone

\[ \chi_{\text{host}}^{(5)} - \text{negligible} \]
Nonlinearity Management

A procedure to obtain exotic metal-dielectric composites

It is possible to suppress one specific order of nonlinearity and enhance another one

Example: \( n_2 = 0 \) and \( n_4 \neq 0 \)

\[ n_2 \propto \text{Re} \chi_{\text{eff}}^{(3)} \quad \text{and} \quad n_4 \propto \text{Re} \chi_{\text{eff}}^{(5)} \]
Nonlinearity management: Silver NPs + CS$_2$

\[ I = 4 \times 10^{12} \text{ W/m}^2 \]

\[ n_4 I \]

\[ n_6 I^2 \]

\[ 4 \times 10^8 \text{ W/cm}^2 \]

\[ 1 \times 10^8 \text{ W/cm}^2 \]

Effective $\chi^{(7)}$
Self-defocusing due to $\chi^{(7)}$ \( f = 3.3 \times 10^{-5} \)

\begin{align*}
\text{Input plane out of the lens focus} \\
I &= 70 \text{ GW/cm}^2
\end{align*}

Cross-phase modulation with two counter–propagating beams

\[-\frac{\partial A_1}{\partial z} - \frac{i}{2k} \left( \frac{\partial^2 A_1}{\partial x^2} + \frac{\partial^2 A_1}{\partial y^2} \right) = \frac{ikn_2}{n_0} \left( |A_1|^2 + 2|A_2|^2 \right) A_1 + \frac{ikn_4}{n_0} \left( |A_1|^4 + 6|A_1|^2 |A_2|^2 + 3|A_2|^4 \right) A_1,\]

\[\frac{\partial A_2}{\partial z} - \frac{i}{2k} \left( \frac{\partial^2 A_2}{\partial x^2} + \frac{\partial^2 A_2}{\partial y^2} \right) = \frac{ikn_2}{n_0} \left( |A_2|^2 + 2|A_1|^2 \right) A_2 + \frac{ikn_4}{n_0} \left( |A_2|^4 + 6|A_1|^2 |A_2|^2 + 3|A_1|^4 \right) A_2,\]

Third-order

Fifth-order
Spatial Cross-Phase Modulation

NPs: 9 nm, L=5 cm, $I_{\text{pump}}=2 \text{ GW/cm}^2$, $I_{\text{probe}} = 0.1 I_{\text{pump}}$
Counter-propagating beams
First observation of Spatial Modulational Instability due to $\chi_{\text{eff}}^{(5)}$

Profiles from the images

Theory

Ag NPs + acetone

$Re \chi^{(3)} = 0$

$Re \chi^{(5)} > 0$

$n_2 = 0$

$n_4 = +3.2 \times 10^{-25} \text{ cm}^4 / \text{W}^2$

Reyna, de Araújo, Phys. Rev. A 89 (2014) 063803
Cross-phase modulation
Co-propagating beams

\[ -2ik \frac{\partial E_1}{\partial z} + \Delta E_1 = -\frac{\omega^2}{c^2} \left[ \frac{3}{2} \chi^{(3)}_{\text{eff}} \left( |E_1|^2 + 2 |E_2|^2 \right) E_1 
+ 10 \chi^{(5)}_{\text{eff}} \left( |E_1|^4 + 6 |E_1|^2 |E_2|^2 + 3 |E_2|^4 \right) E_1 
+ 35 \chi^{(7)}_{\text{eff}} \left( |E_1|^6 + 18 |E_1|^2 |E_2|^4 + 12 |E_1|^4 |E_2|^2 + 4 |E_2|^6 \right) E_1 \right] \]

\[ 2ik \frac{\partial E_2}{\partial z} + \Delta E_2 = -\frac{\omega^2}{c^2} \left[ \frac{3}{2} \chi^{(3)}_{\text{eff}} \left( 2 |E_1|^2 + |E_2|^2 \right) E_2 
+ 10 \chi^{(5)}_{\text{eff}} \left( 3 |E_1|^4 + 6 |E_1|^2 |E_2|^2 + |E_2|^4 \right) E_2 
+ 35 \chi^{(7)}_{\text{eff}} \left( 4 |E_1|^6 + 12 |E_1|^2 |E_2|^4 + 18 |E_1|^4 |E_2|^2 + |E_2|^6 \right) E_2 \right] \]
Induced focusing due to the seventh-order susceptibility

\[ n_2 = 0; \quad n_4 = 0; \quad n_6 < 0 \]
Bright Spatial Soliton

Diffraction

Self-focusing

Nonlinear medium
First demonstration of (2+1)D soliton propagating in a homogeneous medium with local nonlinearity

Falcão-Filho, de Araújo, Boudebs, Leblond, Skarka
Robust two-dimensional spatial solitons in liquid carbon disulfide

Very important: contributions of third and fifth order of opposite signs
CS$_2$: stable (2+1)D soliton

\[ Re \chi^{(3)} > 0 \quad Re \chi^{(5)} < 0 \]

Is it possible to observe a stable (2+1)D soliton in a system with:

\[ Re \chi^{(3)} = 0 \quad Re \chi^{(5)} > 0 \quad Re \chi^{(7)} < 0 \]

\[
2ik \frac{\partial E}{\partial z} + \Delta E = -\frac{\omega^2}{c^2} \left[ 3\chi^{(3)} |E|^2 E + 10\chi^{(5)} |E|^4 E + 35\chi^{(7)} |E|^6 E \right]
\]
First observation of 2D Spatial-Solitons in a quintic-septimal medium

\[ n_2 = 0; \quad n_4 > 0; \quad n_6 < 0 \]

Silver NPs in acetone

J. Lumin. 169 (2016) 492-496
$2ik \frac{\partial E}{\partial z} + \Delta E = -\frac{\omega^2}{c^2} \left[ 3 \chi^{(3)}_{\text{eff}} |E|^2 E + 10 \chi^{(5)}_{\text{eff}} |E|^4 E + 35 \chi^{(7)}_{\text{eff}} |E|^6 E \right]$
Guiding and confinement of light induced by optical vortex solitons in a cubic–quintic medium

Albert S. Reyna* and Cid B. de Araújo

Optics Letters 41 (2016) 191

Z= 0          3              5           10 mm

0.1

3.0

GW/cm²

10 mm - 25 Zₘ
$I_{OVS} = 3.0 \text{ GW/cm}^2$

$I_{HeNe} = 0.1 \text{ GW/cm}^2$
How to address the long standing problem of discovering a very good material for all-optical switching?

We need a material with large NL refraction and low NL absorption.

In general large NL refraction presents large NL absorption.
**PbO-GeO$_2$ films with gold NPs for all-optical switching**

**RF sputtering**

800 nm \[ \text{150 fs} \]

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**Germanate film**

<table>
<thead>
<tr>
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<th>( n_2 / \lambda \alpha_2 )</th>
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<tbody>
<tr>
<td>As grown</td>
<td>( 8.3 \times 10^{-4} )</td>
</tr>
<tr>
<td>With Au NPs</td>
<td>( &gt;2.1 \times 10^{-1} )</td>
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*Figure-of-merit enhanced by two orders of magnitude*

*de Araújo et al. J. Luminescence 133 (2013) 180*
Optimization procedure for the design of all-optical switches based on metal-dielectric nanocomposites

\[ \Delta n = n_2 I + n_4 I^2 + n_6 I^3 + \cdots = n_{NL} I \]

\[ \chi^{(2N+1)} \]

\[ W = \frac{\Delta n}{\lambda \alpha_0} > 1 \]

\[ \alpha_{NL} = \alpha_2 + \alpha_4 I + \alpha_6 I^2 + \cdots \]

\[ T = \frac{\lambda \alpha_{NL}}{n_{NL}} < 1 \]

Reyna, de Araújo, Opt. Express 23 (2015) 7659
These results show that it is possible to have an efficient all-optical switch if a nanocomposite is made according to the nonlinearity management procedure presented.

Challenge for materials scientists.
Summary

Metal composites present large NL susceptibility which depends on the shape and volume fraction of NPs.

Metallic NPs can be nucleated inside different media allowing enhancement of:
- luminescence properties (Stokes and anti-Stokes)
- optical gain/amplification in waveguides
- random lasers, DFB lasers
- all-optical switching, etc.

Nonlinearity Management

The control of NPs volume fraction allows suppression and/or enhancement of nonlinear optical contributions.


Thank you for your attention

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