Analysis of biological liquids by metal enhanced fluorescence from gold nanoparticles

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with great appreciation
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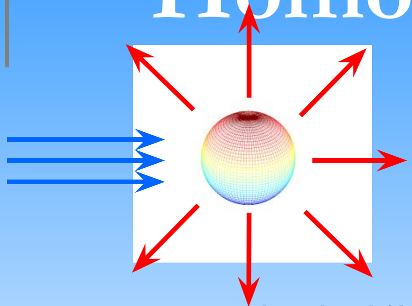
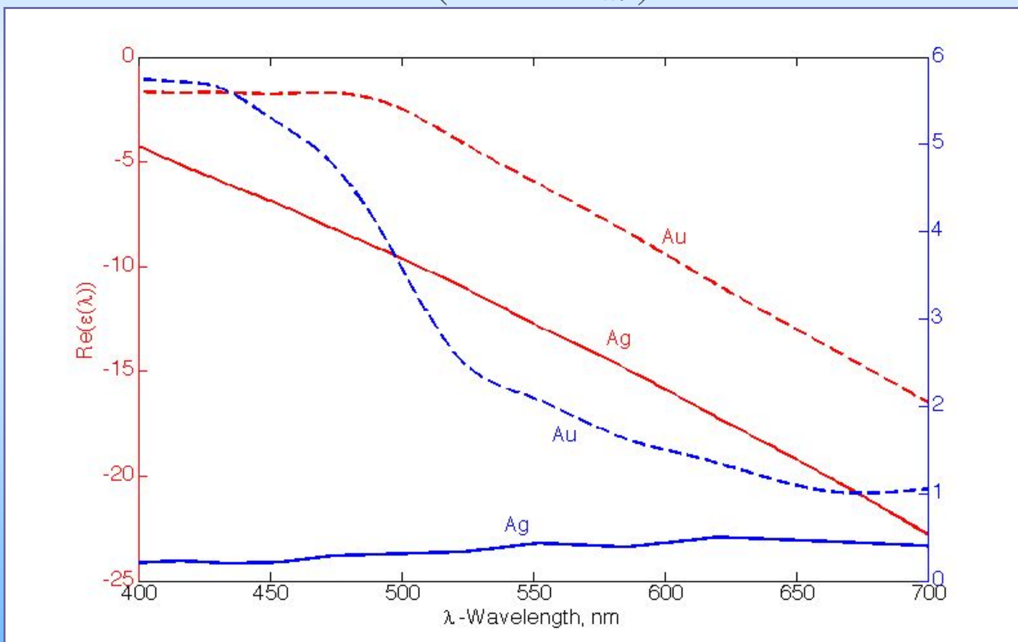
Homogeneous Spheres: Mie Theory



$$\varepsilon(\lambda) = \varepsilon'(\lambda) + i\varepsilon''(\lambda)$$

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2}, \quad 2R << \lambda$$



Spectrum of the dielectric functions for gold and silver

Applications in nanobiotechnology and biomedicine:

- Biosensorics
- Optical imaging of biological cells
- Detection and control of microorganisms
- Optical coherence tomography
- Cancer cell photothermolysis
- Therapy of bacterial infection
- Targeted delivery of drags directly to tumor cells
- Drag development
  - decrease of toxicity,
  - increase of antibacterial activity

References:

- C.F. Boren and D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983)
- P.B. Johnson and R.W. Christy, Phys. Rev. B 6, 4370 (1972)

Nanodevices

Materials:
(Au, Ag, Cu)

→ **Length scales:**
particles are smaller than the excitation wavelength.

→ **Excitation:**
Time-harmonic:
Electromagnetic Plane Wave
Optical Dipole Source

→ **Shapes:**
very primitive, mostly smooth.

↓ **Geometrical settings:**
Strongly coupled nanodetails

← **Mathematical model:**
transmission problem for Maxwell's equations on the entire space

Strong dispersion

$$\varepsilon(\vec{r},\omega)=\varepsilon_1(\vec{r},\omega)+i\varepsilon_2(\vec{r},\omega)$$

Negative refraction

$$\varepsilon_1(\omega) << 0$$

Nonnegligible losses

$$\varepsilon_2(\omega) >> 0$$

Chalenges:

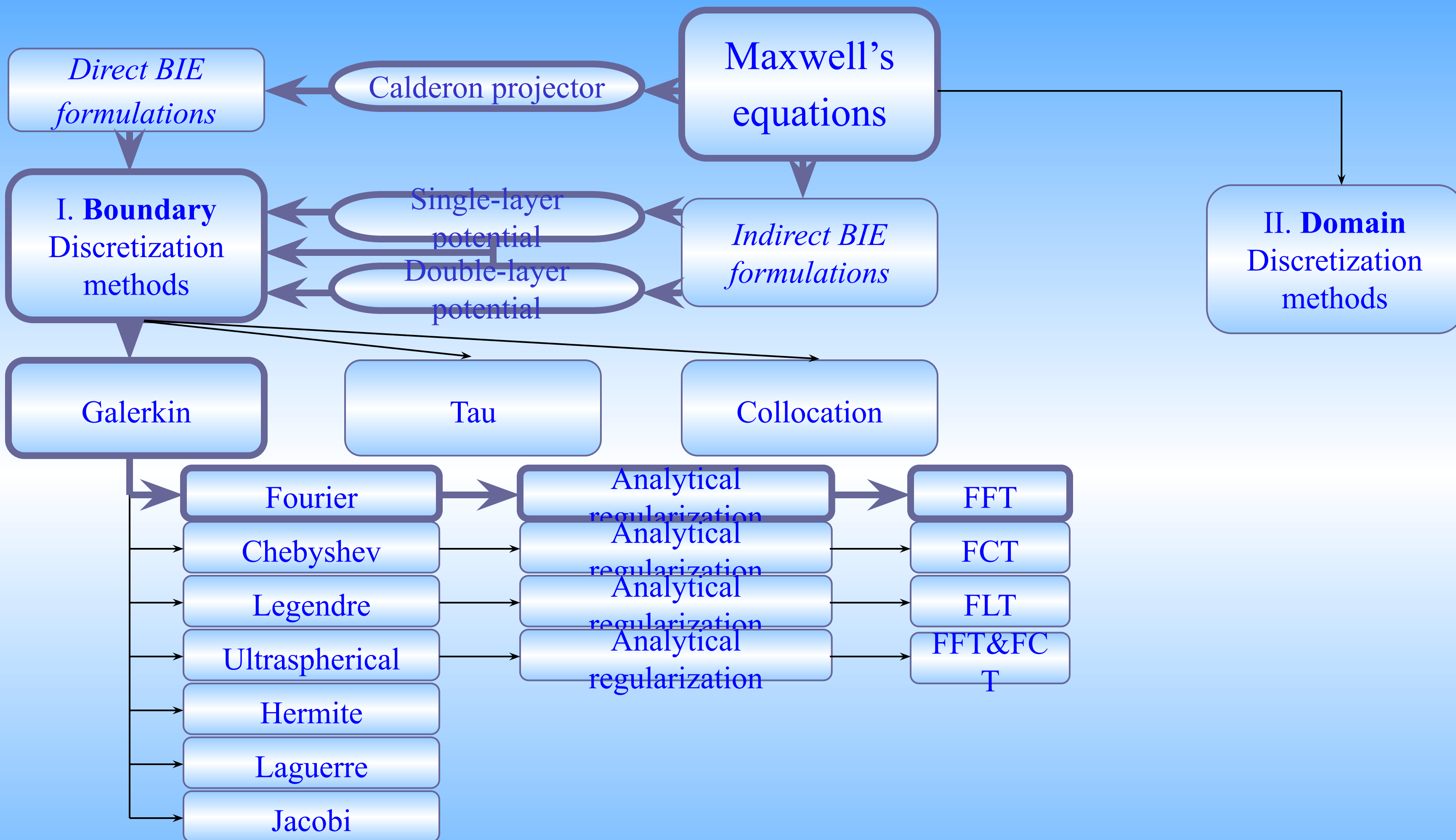
❶ Transmission problem must be solved over whole range of possible excitation wavelength
❷ Local near-field enhancements, amplitudes might reach hundreds of those of illumination
❸ Details smaller than a wavelength may make strong impact on the near-field behavier.

Needed:

- Fast numerical algorithm with
- High accuracy
- Accurate description of the shapes

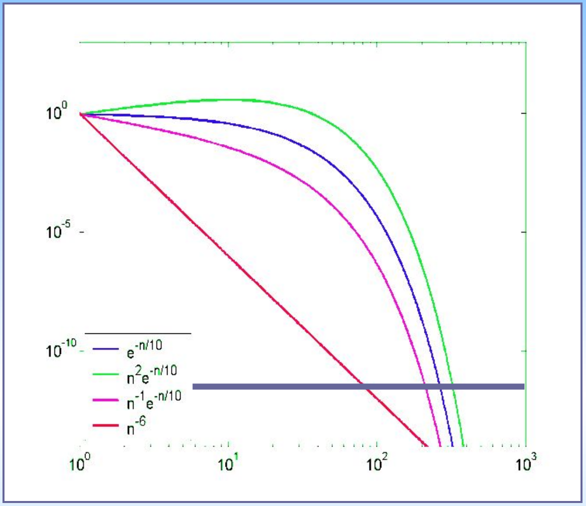
Advanced numerical simulation algorithms are tailored to application !
[Prof. C. Fumeaux, Mr. G. Almpanic, private communication]

Spectral methods



For smooth boundaries the solution provided by spectral BIE method converges much faster than those of BEM! [K.E. Atkinson].

Choice of basis functions and the convergence rate



- Definition of the convergence rate based on asymptotic behavior of the series expansions for large number N of unknowns may be highly misleading if applied for small or moderate N.

  [J. P. Boyd, 2001].

- The choice of basis functions is responsible for the superior approximation of spectral methods when compared with FD, FEM and BEM.

  [E.H. Doha & A.H. Bhrawy, Appl. Num. Math. 58, 2008].

  Fourier polynomials – for periodic problems;

  Legendre polynomials and Chebyshev polynomials – for non-periodic problems on finite intervals;

  Laguerre polynomials – for problems on the half line;

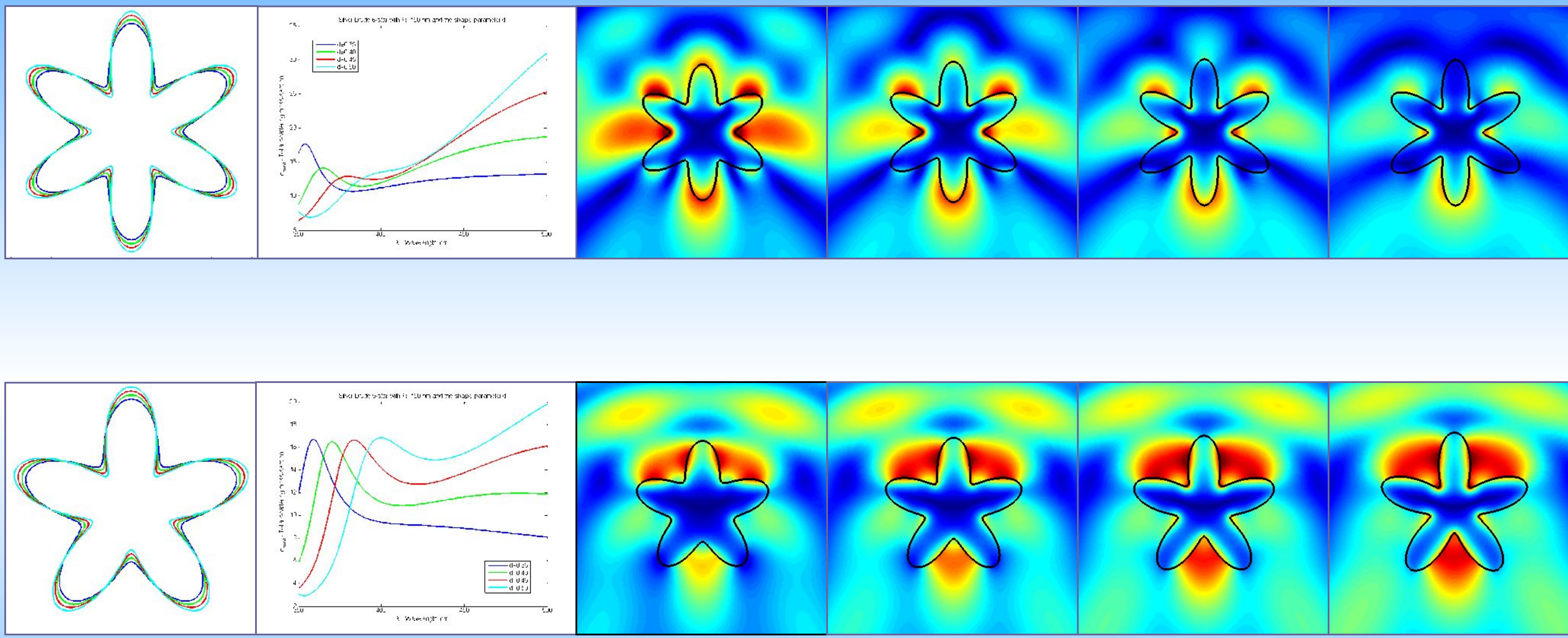
  Hermite polynomials – for problems on whole line

  [G. Ben-Yu, 1998].

- Nanoparticles have smooth regular shape, approximation of their boundaries by non-smooth curves leads to dramatic error in numerical solution because the energy of plasmon modes is concentrated in thing region surrounding the realistic boundary of smooth nanoparticle.

I have no satisfaktion in formulas unless I feel their numerical magnitude !
[Sir William Thomson, 1st Lord Kelvin (1824-1907)]

Nanostars



Geometry, total scattering cross-section as a function on excitation wavelength for Drude silver 6- and 5-pointed stars and normilized near-field distributions corresponding to several wavelength (λ=354, 365, 380, 395 nm and λ=359, 370, 380, 395 nm).

Electromagnetic Transmission Problem

- The problem is formulated in the two-dimensional space assuming invariance along the z-direction. Harmonic time dependence is assumed.

- The total field in presence of plasmonic nanoparticle is presented as follows:

$$H^{tot}(\vec{r}) = \begin{cases} H_e(\vec{r}) = H_e^{sc}(\vec{r}) + H_e^{inc}(\vec{r}), & \vec{r} \in \Omega^+ = \mathbf{R}^2 \backslash \Omega^- \\ H_i(\vec{r}) = H_i^{sc}(\vec{r}) + H_i^{inc}(\vec{r}), & \vec{r} \in \Omega^- \end{cases}$$

- The function H represents the z-component of magnetic field

$$\vec{H}(\vec{r}) = (0, \quad 0, \quad H_z(\vec{r})) \qquad \vec{E}(\vec{r}) = (E_x(\vec{r}), E_y(\vec{r}), 0)$$

- The components of electric field may be found by using

$$E_x(\vec{r}) = \frac{i}{\omega\varepsilon(\vec{r},\omega)} \frac{\partial H_z(\vec{r})}{\partial y} \qquad E_y(\vec{r}) = -\frac{i}{\omega\varepsilon(\vec{r},\omega)} \frac{\partial H_z(\vec{r})}{\partial x}$$

- ***TE*** and ***TM*** modes may be considered independently in the similar manner
- Surface Plasmon Polariton Resonances appear only in ***TE*** polarization case [S. Maier, 2007]

Electromagnetic Transmission Problem

- Helmholtz (wave) equations

$$\Delta U^-(\vec{r}) + (k^-)^2 U^-(\vec{r}) = 0, \quad \vec{r} \in \Omega^-,$$
$$\Delta U^+(\vec{r}) + (k^+)^2 U^+(\vec{r}) = 0, \quad \vec{r} \in \Omega^+.$$

- The boundary conditions on the contour of plasmonic particle are:

$$\left(U^{inc} + U^+\right)\Big|_\Gamma = U^-\Big|_\Gamma, \quad \frac{1}{p^+}\frac{\partial\left(U^{inc} + U^+\right)}{\partial \vec{n}}\Bigg|_\Gamma = \frac{1}{p^-}\frac{\partial U^-}{\partial \vec{n}}\Bigg|_\Gamma,$$

where for TM-polarization

$$p^- = \mu^- \qquad p^+ = \mu^+$$

for TE-polarization

$$p^- = \varepsilon^- \qquad p^+ = \varepsilon^+$$

- Outgoing wave condition:

$$\left|\frac{\partial H_j^{sc}}{\partial r} - ikH_j^{sc}\right| \le \frac{c_3}{r^2}, \quad r = |\vec{r}| \to \infty, \quad j = 1, \dots, N$$

Layer-Potential Technique

Green function of infinite dielectric medium:

$$G^{\pm}(\vec r,\vec r\,')=\frac{i}{4}H_0^{(1)}\left(k\sqrt{\varepsilon^{\pm}(\omega)}\left|\vec r-\vec r\,'\right|\right),\quad \vec r,\vec r\,'\in R^2$$

Let S and D be single- and double-layer potentials associated with Green function:

$$S^{\pm}\varphi(\vec r)=\int_L G^{\pm}(\vec r,\vec r\,')\varphi(\vec r\,')dl',\qquad \vec r\in R^2$$

$$D^{\pm}\varphi(\vec r)=\int_L \frac{\partial G^{\pm}(\vec r,\vec r\,')}{\partial n}\varphi(\vec r\,')dl',\quad \vec r\in R^2\setminus L$$

which satisfy

$$\left(\Delta+k^2\varepsilon^{\pm}(\omega)\right)S^{\pm}\varphi(\vec r)=\left(\Delta+k^2\varepsilon^{\pm}(\omega)\right)D^{\pm}\varphi(\vec r)=0,\ \vec r\in\Omega^{\pm}$$

- One can seek the solution of the boundary value problem as a set of single- or double-layer potentials (or their combination) [Colton & Kress, 1983] satisfying the Helmholtz equation and radiation condition.

Analytical Regularization for Spectral Fourier BIE method (Singularity Subtraction)

$$S\varphi = S_0\varphi + (S - S_0)\varphi = S_0\varphi + \hat{S}\varphi$$

- Fourier harmonics to span the space of trial and test functions $\quad t \to e^{int}, \quad -N \le n \le N$
- Parameterization of boundary in terms of mapping on a circle $\quad \gamma(t) : [0, 2\pi] \to L$

$$(S\varphi)(t) = \frac{i}{4}\int_0^{2\pi} \psi(s) H_0^{(1)}\left(a\left|\gamma(s) - \gamma(t)\right|\right) ds \qquad \psi(s) = \varphi(\gamma(s))\left|\gamma'(s)\right|$$

$$(S_0\psi)(t) = \frac{i}{4}\int_0^{2\pi} \psi(s) H_0^{(1)}\left(2a\sin\frac{|s-t|}{2}\right) ds \qquad (\hat{S}\psi)(t) = \frac{i}{4}\int_0^{2\pi} \hat{S}(t,s)\psi(s)\, ds$$

- Spectral properties of the single-layer potential operator on a circle with wavenumber *a*

$$\frac{1}{2\pi}\int_0^{2\pi} e^{ins} H_0^{(1)}\left(2a\sin|s-t|/2\right) ds = e^{int} J_n(a) H_n^{(1)}(a)$$

$$\hat{S}(t,s) = \begin{cases} H_0^{(1)}(a|\gamma(s)-\gamma(t)|) - H_0^{(1)}(2a\sin|s-t|/2), & s-t \ne 2m\pi \\ -\dfrac{2i}{\pi}\log|\gamma'(s)|, & s-t = 2m\pi \end{cases}$$

1) Fast Fourier Transform
2) Multiple Multipole Method

- Spectral Fourier-Galerkin BIE methods with singularity subtraction lead to a system of Fredholm equations of the second kind for both direct and indirect formulations.

Conclusions

- New fast and efficient numerical simulation algorithms at nanoscale are required to capture essential physics of new EM effects at nanoscale!
- Advanced numerical simulation algorithms are tailored to application !
- The energy of plasmon modes is strongly localized having extremely high near-field amplitude enhancements and fast decay inside and outside of nanoparticle.
- Due to nature of plasmonic effects BIE based numerical algorithms appear more promising than those on Finite Difference (FD) and Finite Element Methods (FEM).
- For smooth boundaries the solution provided by spectral BIE method converges much faster than those of Boundary Element Method (BEM)! [K.E. Atkinson].
- The choice of basis functions is responsible for the superior approximation of spectral methods when compared with classical FD, FEM and BEM schemes.
- The selection of the basis functions must be guided by geometry of the problem.
- Spectral Fourier discretization merged with Singularity Subtraction lead to system of Fredholm equations of the second kind.

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