Lecture 12: Plasmonic nanoparticle imaging

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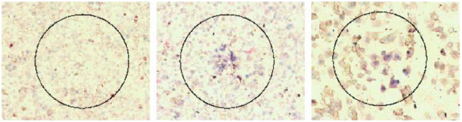
Plasmonic resonances for nanoparticles

- Gold nano-particles: accumulate selectively in tumor cells; bio-compatible; reduced toxicity.
- Detection: localized enhancement in radiation dose (strong scattering).
- Ablation: localized damage (strong absorption).
- Functionalization: targeted drugs.



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Plasmonic resonances for nanoparticles

- D: nanoparticle in $\mathbb{R}^d, d = 2, 3$; $\mathcal{C}^{1,\alpha}$ boundary ∂D, $\alpha > 0$.
- $\varepsilon_c(\omega)$: complex permittivity of D; $\varepsilon_m > 0$: permittivity of the background medium;
- Permittivity contrast: $\lambda(\omega) = (\varepsilon_c(\omega) + \varepsilon_m)/(2(\varepsilon_c(\omega) - \varepsilon_m))$.
- Causality $\Rightarrow$ Kramer-Krönig relations (Hilbert transform); Drude model for the dielectric permittivity $\varepsilon_c(\omega)$.
- G: Fundamental solution to the Laplacian; $\mathcal{S}_D$: Single-layer potential.
- Neumann-Poincaré operator $\mathcal{K}_D^*$:

$$\mathcal{K}_D^*[\varphi](x) := \int_{\partial D} \frac{\partial G}{\partial \nu(x)}(x-y)\varphi(y)\, ds(y) \ , \quad x \in \partial D.$$

  ν: normal to ∂D.
- $\mathcal{K}_D^*$: compact operator on $L^2(\partial D)$; Spectrum of $\mathcal{K}_D^*$ lies in $]-\frac{1}{2}, \frac{1}{2}]$ (Kellog).

Plasmonic resonances for nanoparticles

- $\mathcal{K}_D^*$ self-adjoint on $L^2(\partial D)$ iff D is a disk or a ball.
- Symmetrization technique for Neumann-Poincaré operator $\mathcal{K}_D^*$:
  - Calderón's identity: $\mathcal{K}_D \mathcal{S}_D = \mathcal{S}_D \mathcal{K}_D^*$;
  - In three dimensions, $\mathcal{K}_D^*$: self-adjoint in the Hilbert space $\mathcal{H}^*(\partial D) = H^{-\frac{1}{2}}(\partial D)$ equipped with

$$(u, v)_{\mathcal{H}^*} = -(u, \mathcal{S}_D[v])_{-\frac{1}{2},\frac{1}{2}}$$

    $(\cdot,\cdot)_{-\frac{1}{2},\frac{1}{2}}$: duality pairing between $H^{-\frac{1}{2}}(\partial D)$ and $H^{\frac{1}{2}}(\partial D)$.
  - In two dimensions: $\exists ! \widetilde{\varphi}_0$ s.t. $\mathcal{S}_D[\widetilde{\varphi}_0] =$ constant on ∂D and $(\widetilde{\varphi_0}, 1)_{-\frac{1}{2},\frac{1}{2}} = 1$. $\mathcal{S}_D \rightarrow \widetilde{\mathcal{S}}_D$:

$$\widetilde{\mathcal{S}}_D[\varphi] = \begin{cases} \mathcal{S}_D[\varphi] & \text{if } (\varphi, 1)_{-\frac{1}{2},\frac{1}{2}} = 0, \\ -1 & \text{if } \varphi = \widetilde{\varphi}_0. \end{cases}$$

Plasmonic resonances for nanoparticles

- Symmetrization technique for Neumann-Poincaré operator $\mathcal{K}_D^*$:
  - Spectrum $\sigma(\mathcal{K}_D^*)$ discrete in $]-1/2, 1/2[$;
  - Ellipse: $\pm\frac{1}{2}(\frac{a-b}{a+b})^j$, elliptic harmonics ($a, b$: long and short axis).
  - Ball: $\frac{1}{2(2j+1)}$, spherical harmonics.
  - Twin property in two dimensions;
  - (λ_j, φ_j), $j = 0, 1, 2, \ldots$: eigenvalue and normalized eigenfunction pair of $\mathcal{K}_D^*$ in $\mathcal{H}^*(\partial D)$; $\lambda_j \in]-\frac{1}{2}, \frac{1}{2}]$ and $\lambda_j \to 0$ as $j \to \infty$;
  - φ_0: eigenfunction associated to $1/2$ ($\widetilde{\varphi}_0$ multiple of φ_0);
  - Spectral decomposition formula in $H^{-1/2}(\partial D)$,

$$\mathcal{K}_D^*[\psi] = \sum_{j=0}^{\infty} \lambda_j (\psi, \varphi_j)_{\mathcal{H}^*} \varphi_j.$$

Plasmonic resonances for nanoparticles

- u^i: incident plane wave; Helmholtz equation:

$$\begin{cases} \nabla \cdot \Big(\varepsilon_m \chi(\mathbb{R}^d \setminus \bar{D}) + \varepsilon_c(\omega)\chi(\overline{D}) \Big) \nabla u + \omega^2 u = 0, \\ u^s := u - u^i \text{ satisfies the outgoing radiation condition.} \end{cases}$$

- Uniform small volume expansion with respect to the contrast: $D = z + \delta B$, $\delta \to 0$, $|x - z| \gg 2\pi / k_m$,

$$u^s = -M(\lambda(\omega), D) \nabla_z G_{k_m}(x - z) \cdot \nabla u^i(z) + O\left(\frac{\delta^{d+1}}{\mathrm{dist}(\lambda(\omega), \sigma(\mathcal{K}_D^*))}\right).$$

- G_{k_m}: outgoing fundamental solution to $\Delta + k_m^2$; $k_m := \omega / \sqrt{\varepsilon_m}$;
- Polarization tensor:

$$M(\lambda(\omega), D) := \int_{\partial D} x (\lambda(\omega) I - \mathcal{K}_D^*)^{-1}[\nu](x) \, ds(x).$$

Plasmonic resonances for nanoparticles

- Spectral decomposition: (l, m)-entry

$$M_{l,m}(\lambda(\omega), D) = \sum_{j=1}^{\infty} \frac{(\nu_m, \varphi_j)_{\mathcal{H}^*} (\nu_l, \varphi_j)_{\mathcal{H}^*}}{(1/2 - \lambda_j)(\lambda(\omega) - \lambda_j)}.$$

- $(\nu_m, \varphi_0)_{\mathcal{H}^*} = 0$; φ_0: eigenfunction of $\mathcal{K}_D^*$ associated to $1/2$.
- Quasi-static plasmonic resonance: $\mathrm{dist}(\lambda(\omega), \sigma(\mathcal{K}_D^*))$ minimal ($\Re e\, \varepsilon_c(\omega) < 0$).

Plasmonic resonances for nanoparticles

- $M(\lambda(\omega), B) = (\frac{\varepsilon_c(\omega)}{\varepsilon_m} - 1) \int_B \nabla v(y) dy$:

$$\begin{cases} \nabla \cdot \Big(\varepsilon_m \chi(\mathbb{R}^d \setminus \bar{B}) + \varepsilon_c(\omega)\chi(\overline{B})\Big) \nabla v = 0, \\ v(y) - y \to 0, \qquad |y| \to +\infty. \end{cases}$$

- Corrector v:

$$v(y) = y + \mathcal{S}_B(\lambda(\omega) I - \mathcal{K}_B^*)^{-1}[\nu](y), \quad y \in \mathbb{R}^d.$$

- Inner expansion: $\delta \to 0$, $|x - z| = O(\delta)$,

$$u(x) = u^i(z) + \delta v(\frac{x - z}{\delta}) \cdot \nabla u^i(z) + O(\frac{\delta^2}{\mathrm{dist}(\lambda(\omega), \sigma(\mathcal{K}_D^*))}).$$

- Monitoring of temperature elevation due to nanoparticle heating:

$$\begin{cases} \rho C \frac{\partial T}{\partial t} - \nabla \cdot \tau \nabla T = \frac{\omega}{2\pi} (\Im(\varepsilon_c(\omega)) \, |u|^2 \chi(D), \\ T\big|_{t=0} = 0. \end{cases}$$

ρ: mass density; C: thermal capacity; τ: thermal conductivity.

Plasmonic resonances for nanoparticles

- Scattering amplitude:

$$u^s(x) = -ie^{-\frac{\pi i}{4}} \frac{e^{ik_m|x|}}{\sqrt{8\pi k_m |x|}} A_\infty[D, \varepsilon_c, \varepsilon_m, \omega](\theta, \theta') + o(|x|^{-\frac{1}{2}}),$$

  $|x| \to \infty$; θ, θ': incident and scattered directions.

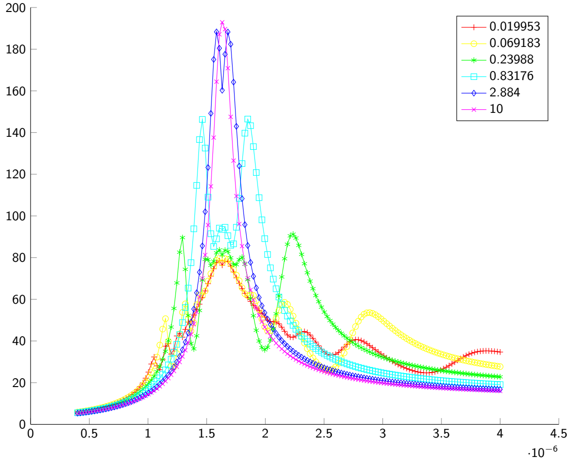
- Scattering cross-section:

$$Q^s[D, \varepsilon_c, \varepsilon_m, \omega](\theta') := \int_0^{2\pi} \left| A_\infty[D, \varepsilon_c, \varepsilon_m, \omega](\theta, \theta') \right|^2 d\theta.$$

- Enhancement of Q^s at plasmonic resonances:

$$Q^s \propto \left| \mathrm{tr}(M(\lambda(\omega), D)) \right|^2.$$

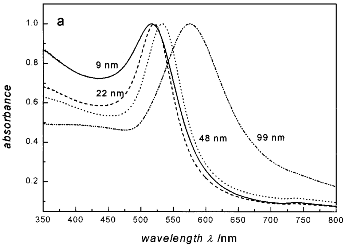
Plasmonic resonances for nanoparticles



Norm of the polarization tensor for two disks for various separating distances.

Plasmonic resonances for nanoparticles

- $\mathcal{K}_D^*$: scale invariant $\Rightarrow$ Quasi-static plasmonic resonances: size independent.
- Analytic formula for the first-order correction to quasi-static plasmonic resonances in terms of the particle's characteristic size δ:



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Plasmonic resonances for nanoparticles

- Helmholtz equation:

$$\begin{cases} \nabla \cdot \Big(\varepsilon_m \chi(\mathbb{R}^d \setminus \bar{D}) + \varepsilon_c(\omega)\chi(\overline{D}) \Big) \nabla u + \omega^2 u = 0, \\ u^s := u - u^i \text{ satisfies the outgoing radiation condition.} \end{cases}$$

u^i: incident plane wave; $k_m := \omega\sqrt{\varepsilon_m}$, $k_c := \omega\sqrt{\varepsilon_c(\omega)}$.

- Integral formulation on ∂D:

$$\begin{cases} \mathcal{S}_D^{k_c}[\phi] - \mathcal{S}_D^{k_m}[\psi] = u^i, \\ \varepsilon_c\big(\frac{I}{2} - (\mathcal{K}_D^{k_c})^*\big)[\phi] - \varepsilon_m\big(\frac{I}{2} + (\mathcal{K}_D^{k_m})^*\big)[\psi] = \varepsilon_m \partial u^i/\partial \nu. \end{cases}$$

- Operator-valued function $\delta \mapsto \mathcal{A}_\delta(\omega) \in \mathcal{L}(\mathcal{H}^*(\partial B), \mathcal{H}^*(\partial B))$:

$$\mathcal{A}_\delta(\omega) = \overbrace{(\lambda(\omega)I - \mathcal{K}_B^*)}^{\mathcal{A}_0(\omega)} + (\omega\delta)^2 \mathcal{A}_1(\omega) + O((\omega\delta)^3).$$

- Quasi-static limit:

$$\mathcal{A}_0(\omega)[\psi] = \sum_{j=0}^{\infty} \tau_j(\omega)(\psi, \varphi_j)_{\mathcal{H}^*} \varphi_j, \quad \tau_j(\omega) := \frac{1}{2}(\varepsilon_m + \varepsilon_c(\omega)) - (\varepsilon_c(\omega) - \varepsilon_m)\lambda_j.$$

Plasmonic resonances for nanoparticles

- Shift in the plasmonic resonances:

$$\arg\min_{\omega} \left| \frac{1}{2}\left(\varepsilon_m + \varepsilon_c(\omega)\right) - \left(\varepsilon_c(\omega) - \varepsilon_m\right)\lambda_j + (\omega\delta)^2 \tau_{j,1} \right|$$

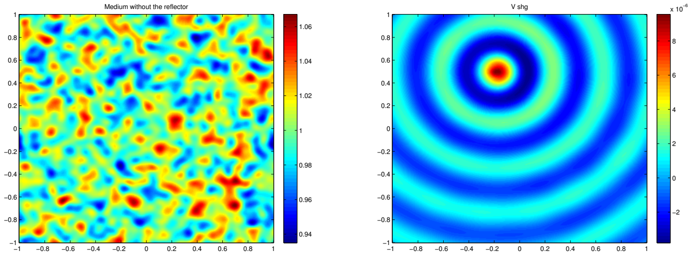
- $\tau_{j,1} := (\mathcal{A}_1(\omega)[\varphi_j], \varphi_j)_{\mathcal{H}^*}$.

Nanoparticle imaging

- Single nanoparticle imaging:

$$\max_{z^S} I(z^S, \omega)$$

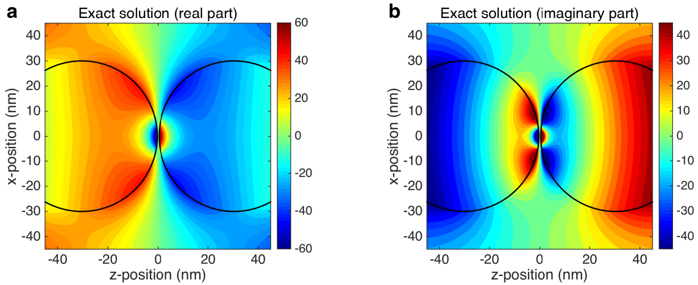
- $I(z^S, \omega)$: imaging functional; z^S: search point.
- Resolution: limited only by the signal-to-noise-ratio.
- Cross-correlation techniques: robustness with respect to medium noise.



Nanoparticle imaging

- Blow-up of the electric field in the gap at the plasmonic resonances:

$$\nabla u = O\left(\frac{1}{(\delta/R)^{3/2}\ln(R/\delta)}\right).$$



Nanoparticle imaging

- Reconstruction from plasmonic spectroscopic data: