Strong Interaction between Plasmonic Spheres

Sanghyeon Yu

ETH Zurich, Dept. of Math.

Workshop on Qualitative and Quantitative Approaches to Inverse Scattering Problems 2018. 9. 26. National University of Singapore

A classical problem in electromagnetism :

electromagnetic interaction between metallic (nano)particles



Modern applications :

Controlling light at the nanoscale (challenging due to Abbe's diffraction limit)

- ultra sensitive spectroscopy
- single molecule sensing
- optical integrated circuit or optical computer
- nonlinear optics

wavelength of visible light :





Sanghyeon Yu (ETH Zurich)

Strong Interaction between Plasmonic Spheres

What is so special about metallic particles?

- Surface Plasmon Resonances (SPRs) : oscillations of electron densities on the surfaces of the particles
- At certain frequencies, SPRs are excited -> confine light into their nanoscale volumes
- Origin: metal permittivity becomes negative at optical frequencies



What happens if they are close to touching?

When the metallic (or plasmonic) particles get closer.

- \rightarrow 1. extremely large EM field at the gap
- \rightarrow 2. light absorption for a broad range of frequency



*

So, the close-to-touching spheres are useful for controlling light on the nanoscale

* R.C. McPhedran and D.R. McKenzie, Applied Physics 23 (1980) 223–235
 R.C. McPhedran and W.T. Perrins, Applied Physics A 24 (1981) 311–318
 R.C. McPhedran and G.W. Milton, PRSA 411 (1987) 313–326
 A. Aubry, et al. Nano Lett. 10 (2010) 2574–2579
 J. B. Pendry, A.Aubry, D.R.Smith, S.A.Maier, Science 337 (2012) 549–552

Non-local effect

• When extreme small gap, the non-local effect becomes significant (below 0.25 nm). Even in touching case, the gap distance is effectively non-zero.



- Our focus is not on modelling the non-local effect but on the strong interaction between the particles.
 So we shall assume the gap distance is very small but not so much that the non-local effect is not significant.
- Non-local effect can be incorparated using the approach in Luo et al. PRL 111 (2013), 093901.

C. Ciracì. et al., Science 337 (2012), 1072–1074.
Y. Luo, R. Zhao, and J. B. Pendry, PNAS 111 (2014), 18422–18427.
O. Schnitzer, V. Giannini, R. V. Craster, and S. A. Maier, Phys. Rev. B, 93 (2016), p. 041409.

But, understanding their strong interaction is quite challenging. Why?



Difficulty 1: Analytical solution for two 3D spheres is not available (2D solution is known*).

* Ross.C. McPhedran and Graeme.W. Milton, PRSA 411 (1987) 313-326

Difficulty 2: (i) Numerical computation of EM field requires very fine mesh or a large number of spherical harmonics
(ii) The resulting linear system is ill-conditioned. Strong interaction between plasmonic spheres (S.Y. and H. Ammari, SIAM Review 2018)

- 1. Derive a fully analytic solution for two 'plasmonic' spheres (convergent quickly even in the nearly touching case)
- 2. Develop an efficient and accurate hybrid numerical scheme valid for arbitrary number of plasmonic spheres which can be nearly touching



Key idea : Clarify the connection between Transformation Optics and Image Charge Method

- Limitation: quasi-static approximation is assumed.
 - The retardation effect should be considered for large systems.
- But, even for large particles, the quasi-static term is dominant in the gaps.

Problem formulation: two plasmonic spheres

- Smallness of nanoparticles compared to wavelength → Quasi-static approximation
- Near field is described by electric potential:

$$\begin{cases} \nabla \cdot (\epsilon_B \nabla V) = 0 & \text{in } \mathbb{R}^3, \\ V(\mathbf{r}) = -E_0 z + O(|\mathbf{r}|^{-2}) & \text{as } |\mathbf{r}| \to \infty. \end{cases}$$

Here, the permittivity distribution is

$$\epsilon_B = \begin{cases} \epsilon & \text{in } B_+ \cup B_-, \\ 1 & \text{in } \mathbb{R}^3 \setminus (B_+ \cup B_-). \end{cases}$$

• Drude's model for metal permittivity

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$



• The metal permittivity is negative \rightarrow The problem is not uniformly elliptic.

→ singular behavior of the solution (plasmon resonances)

Mathematics of Surface Plasmons

• The PDE is equivalent to the following boundary integral equation:

$$(\lambda I - \mathcal{K}^*_{\partial B})[\varphi] = -E_0 \nu_z|_{\partial B} \qquad \lambda = \frac{\epsilon + 1}{2(\epsilon - 1)}$$

where \mathcal{K}_B^* is the Neumann-Poincaré (NP) operator given by

$$\mathcal{K}_B^*[\varphi](\mathbf{r}) = \frac{1}{2\pi} \int_{\partial B} \frac{(\mathbf{r} - \mathbf{r}') \cdot \mathbf{n}_{\mathbf{r}}}{|\mathbf{r} - \mathbf{r}'|^2} \varphi(\mathbf{r}') dS(\mathbf{r}'), \quad \mathbf{r} \in \partial B.$$

- The spectrum depends sensitively on the geometry.
- Geometrical singularity on the surfaces (corner, two touching surfaces..)
 - \rightarrow The NP-operator becomes **non-compact**
 - → continuous spectrum & singular behavior of (generalized) eigenfunctions



Mathematics of Surface Plasmons: Corner singularity

• An example of Lipschitz domains whose spectrum is continuous: 'the intersecting disks'



Spectral resolution of NP operator on intersecting disks (joint with Hyeonbae Kang & Mikyoung Lim, ARMA 2017)

$$\sigma_{ess}(\mathcal{K}^*_{\partial\Omega}) = [-b, b]$$
$$b = \frac{1}{2} - \frac{\theta_0}{\pi}$$

Remark A similar result was derived by T. Carleman in 1906 thesis. Not rigorous but idea was already there (Mihai Putinar at UCSB informed us its existence)

- Essential spectrum on general Lipschitz domains: Mihai Putinar and Karl-Mikael Perfekt, ARMA 2017
- Characterization of essential spectrum using Weyl sequence: Eric Bonnetier and Hai Zhang, RMI 2017
- 3D Rotationally symmetric domains : Johan Helsing and Karl-Mikael Perfekt, JMPA 2017
- Bowtie structures : Eric Bonnetier, Charles Dapogny, Faouzi Triki and Hai Zhang, arXiv 2018
- Embedded eigenvalues : Wei Li and Stephen Shipman, arXiv 2018

Mathematics of Surface Plasmons: Nearly Touching Surfaces

- Let us turn to the two spheres problem.
- The nearly touching spheres is also a geometrical singularity (a narrow gap region between the spheres).
- Two singular phenomena:
 (i) singular shift of resonance frequencies (or eigenvalues)
 (ii) high field concentration in the narrow gap
- Q: How can we capture the singular behaviours analytically?

Key : Clarify the connection between Transformation Optics and Image Charge Method



Brief Review: Transformation Optics and Image Charges Method

Approach 1 : Transformation Optics



- Inversion mapping => "two 3D spheres" become "concentric shell"
- TO solution uses spherical harmonics in the transformed frame

$$V(\mathbf{r}) = -E_0 z + \sum_{n=0}^{\infty} A_n \left(\mathcal{M}_{n,+}^0(\mathbf{r}) - \mathcal{M}_{n,-}^0(\mathbf{r}) \right)$$
$$\mathcal{M}_{n,\pm}^m(\mathbf{r}) = |\mathbf{r}' - \mathbf{R}_0'| (r')^{\pm (n+\frac{1}{2}) - \frac{1}{2}} Y_n^m(\theta', \phi')$$

• But the solution is not fully analytic.

RemarkThe same solution was derived 42 years ago. \rightarrow A. Goyette and A. Navon, PRB 13 (1976), 4320A more extensive study in the plasmonics context \rightarrow R. Ruppin, PRB 26 (1982), 3440

Sanghyeon Yu (ETH Zurich)

Strong Interaction between Plasmonic Spheres

Approach 2 : Image charges method

- Image charge method is to find fictitious sources which generate the desired field.
- Two 2D cylinders (R.C.McPhedran, L.Poladian and G.W.Milton, PRSA 415 (1988) 185-196)
- Two 3D spheres (L. Poladian, PRSA 426(1989) 343-359, Poladian's PhD thesis)
- Asymptotic solution by continuous density approximation of discrete image sources



- Potential generated by image charges

$$U(\mathbf{r}) = \sum_{k=0}^{\infty} u_k (G(\mathbf{r} - \mathbf{z}_k) - G(\mathbf{r} + \mathbf{z}_k))$$

- Image charges strength

$$u_k = \tau^k \frac{\sinh(s+t_0)}{\sinh(ks+s+t_0)} \qquad \tau = \frac{\epsilon-1}{\epsilon+1}$$

G: potential by a point charge

• However, the image series solution is not valid for "plasmonic" spheres due to non-convergence.

<u>Remark</u> The asymptotics of the multipole coefficients are valid for the plasmonic case. But computing the field enhancement is still challenging.

Sanghyeon Yu (ETH Zurich)

Strong Interaction between Plasmonic Spheres

Leon Poladian & his thesis (1/2)

- A former student of Ross C. McPhedran (Univ. of Sydney)
- His thesis: a complete image charges method for two 3D spheres and its applications to composite materials

L. Poladian, Effective Transport and Optical Properties of Composite Materials. Ph.D. thesis, University of Sydney, 1990

- Every textbook on classical electromagnetism discusses the image charge method but not for 3D dielectric spheres (3D case is extremely difficult..).
- Image charge method for a 'single' 3D dielectric sphere was discovered by several people independently.

(Neumann 1883, Iossel 1971, Poladian 1989, Lindell 1992, Norris 1995)

• But, **Poladian** is the first to solve two 3D dielectric spheres problem.



Leon Poladian

Leon Poladian & his thesis (2/2)

- In 2014 Summer, Mikyoung Lim (KAIST) and I were visiting Univ. of Utah.
- Mikyoung Lim and I got an asymptotic result for two 2D circlular cylinders (M. Lim and S.Y. 2015).
- Our proof shows the connection between the image charges and TO for 2D case. So the next step was to extend it to 3D.
- Graeme Milton and Ross McPhedran informed us the Poladian's thesis.
- Poladian's 3D solution became the key to solving the plasmonic spheres problem.



Moab

Poladian's thesis is a long and rich work.. It deserves a more attention.

Result 1 Analytic solution for two plasmonic spheres (connection between image charges method and TO) Main obstacle - Non-convergence of the image series Our idea - Converting image series into TO-type solution

B+

Image Charges Method $-u_0 - u_1 - u_2 ...$ R (0,0,-z_k)



Transformation Optics (TO)



$$U(\mathbf{r}) = \sum_{k=0}^{\infty} u_k (G(\mathbf{r} - \mathbf{z}_k) - G(\mathbf{r} + \mathbf{z}_k))$$

$$\mathcal{M}_{n,\pm}^{m}(\mathbf{r}) = |\mathbf{r}' - \mathbf{R}_{0}'|(r')^{\pm(n+\frac{1}{2})-\frac{1}{2}}Y_{n}^{m}(\theta',\phi')$$
$$V(\mathbf{r}) = -E_{0}z + \sum_{n=0}^{\infty}A_{n}\left(\mathcal{M}_{n,+}^{0}(\mathbf{r}) - \mathcal{M}_{n,-}^{0}(\mathbf{r})\right)$$

Β.

Connection between Transformation Optics and Image charges method

Theorem 1 (S.Y. and H. Ammari, SIAM Rev. 2018)

We have the following connection formula:

$$u_k G(\mathbf{r} \mp \mathbf{z}_k) = \frac{\sinh(s+t_0)}{4\pi\alpha} \sum_{n=0}^{\infty} \left[\tau e^{-(2n+1)s}\right]^k$$

$$\underset{\text{Image charge}}{\overset{\text{for}}{\overset{for}{\overset{fo}}{\overset{f$$

LHS : The potential generated by k-th image charge

RHS : The potential which is represented in terms of TO basis functions

f

Theorem 2 (S.Y. and H. Ammari, SIAM Rev. 2018)

The following approximation for the electric potential V holds:

$$V(\mathbf{r}) \approx -E_0 z + \sum_{n=0}^{\infty} \widetilde{A}_n \left(\mathcal{M}_{n,+}^0(\mathbf{r}) - \mathcal{M}_{n,-}^0(\mathbf{r}) \right)$$

where

$$\widetilde{A}_{n} = E_{0} \frac{2\tau\alpha}{3-\tau} \cdot \frac{2n+1-\gamma_{0}}{e^{(2n+1)s}-\tau}$$
fully analytic!
$$\gamma_{0} = \sum_{n=0}^{\infty} \frac{2n+1}{e^{(2n+1)s}-\tau} \Big/ \sum_{n=0}^{\infty} \frac{1}{e^{(2n+1)s}-\tau}$$

convergent for the plasmonic case

Comparison between our analytical approx. and exact sol.



Result 2 : Hybrid numerical scheme for an arbitrary number of nearly touching spheres.



Review: Cheng and Greengard's hybrid numerical scheme for "dielectric" spheres

- hybrid method combining the image charge method and the multipole expansion method
- extremely efficient and accurate even when nearly touching
- But it cannot be applied to plasmonic spheres (due to the divergence of the image series).



Hongwei Cheng and Leslie Greengard, SIAM Appl. Math. 1998

Our method: Hybrid numerical scheme for plasmonic spheres (S.Y. and H. Ammari, SIAM Review 2018)

• We modify Cheng & Greengard's hybrid scheme

by replacing image source series with their TO versions



Sanghyeon Yu (ETH Zurich)



• Field enhancement at the gap center

(Radius: 30nm Gap distance: 0.3nm)

~2,000 times more efficient

Numerical result: Potential distribution



(Radius: 30nm Gap distance: 0.3nm)

The field concentration is clearly shown.

Sanghyeon Yu (ETH Zurich)

Strong Interaction between Plasmonic Spheres

Part II

A similar problem in linear elasticity : Stress concentration



Linear elasticity for two rigid inclusions (general shapes)

- Lamé system with <u>high-contrast</u> coefficients

$$\begin{cases} \mathcal{L}_{\lambda,\mu} \mathbf{u} = 0 & \text{in } \widetilde{\Omega}, \\ \mathbf{u} = \sum_{j=1}^{3} c_{ij} \Psi_j(\mathbf{x}) & \text{on } \partial D_i, \quad i = 1, 2 \\ \mathbf{u} = \mathbf{g} & \text{on } \partial \Omega, \end{cases}$$

- Lame operator $\mathcal{L}_{\lambda,\mu}\mathbf{u} := \mu\Delta\mathbf{u} + (\lambda + \mu)\nabla\nabla\cdot\mathbf{u}$

- Bdry conditions on the inclusions

$$\int_{\partial D_i} \partial_{\nu} \mathbf{u}|_+ \cdot \Psi_j \, d\sigma = 0, \quad i = 1, 2, \ j = 1, 2, 3.$$





stress tensor

- Rigid motions: $\Psi_1(\mathbf{x}) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \Psi_2(\mathbf{x}) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad \Psi_3(\mathbf{x}) = \begin{bmatrix} -y \\ x \end{bmatrix}$

Stress Concentration

- When ϵ goes to zero, the stress may blow up in the narrow gap region.
- asymptotic behavior of the gradient $\, \nabla {f u}$?

Strong Interaction between Plasmonic Spheres

Elasticity case is difficult to solve..

- difficulty 1 : elliptic system -> no maximum principle
- difficulty 2 : Keller's function doesn't work

Previous works

- upper estimate of the gradient by H. Li, Y.Y. Li, and J. Bao (ARMA 2015)

$$\|\nabla \mathbf{u}\|_{L^{\infty}(\Omega)} \leq \frac{C}{\sqrt{\epsilon}}$$

- lower estimate of the gradient (H. Li et al. 2017)

$$\frac{|Q(g)|}{\sqrt{\epsilon}} \le \|\nabla \mathbf{u}\|_{L^{\infty}(\Omega)}$$

- Single inclusion close to the boundary (J. Bao, H. Ju, H. Li 2017, H. Li, L.Xu 2017)
- Continuous density approximation approach (R.C.McPhedran and A.B.Movchan, 1994)

Conductivity case (scalar PDE) : well understood..

occurrence of the gradient blow-up blow-up rate of gradient etc..



Ammari-Kang-Lim(05), Ammari-Kang-Lee-Lee-Lim(07), Yun(07), Ammari-Kang-Lee-Lim-Zribi(09), Yun(09), Bonnetier-Vogelius (00), Ammari-Ciraolo-Kang-Lee-Yun (ARMA '13), Bowtie case: Kang-Yun (17) Bao-Li-Yin(ARMA 09,10), Lim-Yun(09), Bonnetier-Triki, ARMA (13)

• Elasticity case (system of PDEs) : much less is known..

optimal blow-up rate was not proved.

- upper estimate of the gradient by Haigang Li, YanYan Li, and Jiguang Bao (ARMA 2015, Adv. Math. 2017)
- lower estimate of the gradient by Yuanyuan Hou, Hongjie Ju, and Haigang Li (2017)

Our recent work

Quantitative characterization of stress concentration (joint work with Hyeonbae Kang, ARMA 2018)

1. We **completely characterize** the gradient blow-up (stress concentration) by explicit singular functions.

2. The optimality of the blow-up rate is proved.

3. New method based on variational principles



Problem formulation

Characterization of the stress concentration by singular functions

Decompose the solution as

$$\mathbf{u} = \mathbf{s} + \mathbf{b}$$

where **s** is an explicit function and **b** satisfies $\|\nabla \mathbf{b}\|_{L^{\infty}} \leq C$.

 \rightarrow Then the function s completely characterize the gradient blow-up of the solution.

How can we find singular functions for **linear elasticity**?

point sources in elasticity - nuclei of strains

$$egin{array}{ccc} \Gamma(\mathbf{x}) \mathbf{e}_1 & \Gamma(\mathbf{x}) \mathbf{e}_2 & rac{\mathbf{x}}{|\mathbf{x}|^2} & rac{\mathbf{x}^{\perp}}{|\mathbf{x}|^2} \end{array}$$
 point forces point pressure point moment

Singular functions (H. Kang and S.Y. ARMA 2018)

They are defined as follows:

$$\begin{aligned} \mathbf{q}_{1}(\mathbf{x}) &:= \mathbf{\Gamma}(\mathbf{x} - \mathbf{p}_{1})\mathbf{e}_{1} - \mathbf{\Gamma}(\mathbf{x} - \mathbf{p}_{2})\mathbf{e}_{1} + \alpha_{2}a\left(\frac{\mathbf{x} - \mathbf{p}_{1}}{|\mathbf{x} - \mathbf{p}_{1}|^{2}} + \frac{\mathbf{x} - \mathbf{p}_{2}}{|\mathbf{x} - \mathbf{p}_{2}|^{2}}\right) \\ \mathbf{q}_{2}(\mathbf{x}) &:= \mathbf{\Gamma}(\mathbf{x} - \mathbf{p}_{1})\mathbf{e}_{2} - \mathbf{\Gamma}(\mathbf{x} - \mathbf{p}_{2})\mathbf{e}_{2} - \alpha_{2}a\left(\frac{(\mathbf{x} - \mathbf{p}_{1})^{\perp}}{|\mathbf{x} - \mathbf{p}_{1}|^{2}} + \frac{(\mathbf{x} - \mathbf{p}_{2})^{\perp}}{|\mathbf{x} - \mathbf{p}_{2}|^{2}}\right) \\ \mathbf{q}_{3}(\mathbf{x}) &:= \mathbf{\Gamma}^{\perp}(\mathbf{x} - \mathbf{p}_{1})\mathbf{e}_{1} + \mathbf{\Gamma}^{\perp}(\mathbf{x} - \mathbf{p}_{2})\mathbf{e}_{1} + \alpha_{2}a\left(\frac{(\mathbf{x} - \mathbf{p}_{1})^{\perp}}{|\mathbf{x} - \mathbf{p}_{1}|^{2}} - \frac{(\mathbf{x} - \mathbf{p}_{2})^{\perp}}{|\mathbf{x} - \mathbf{p}_{2}|^{2}}\right) \end{aligned}$$

where

$$\boldsymbol{\Gamma}(\mathbf{x}) = \alpha_1 \log |\mathbf{x}| \mathbf{I} - \alpha_2 \mathbf{x} \otimes \nabla(\ln |\mathbf{x}|),$$
$$\boldsymbol{\Gamma}^{\perp}(\mathbf{x}) = \alpha_1 \arg(\mathbf{x}) \mathbf{I} - \alpha_2 \mathbf{x} \otimes \nabla(\arg(\mathbf{x})).$$

Theorem 1 (H. Kang and S.Y. ARMA 2018)

The solution can be decomposed as

$$\begin{split} \mathbf{u}(\mathbf{x}) &= \mathbf{b}_{\Omega}(\mathbf{x}) - \sum_{j=1}^{3} \mathcal{K}_{\Omega,j} \mathbf{q}_{j}(\mathbf{x}), \quad \mathbf{x} \in \widetilde{\Omega}, \\ \end{split}$$
where the regular part \mathbf{b}_{Ω} satisfies
$$\| \nabla \mathbf{b}_{\Omega} \|_{L^{\infty}(\widetilde{\Omega})} \lesssim \| \mathbf{g} \|_{C^{1,\gamma}(\partial \Omega)}$$

Corollary (optimality of the blow-up rate)

The blow-up estimate of the gradient

$$\frac{\sum_{j=1}^2 |\mathcal{K}_{\Omega,j}|}{\sqrt{\epsilon}} \lesssim \|\nabla \mathbf{u}\|_{L^{\infty}(\widetilde{\Omega})} \lesssim \frac{\|\mathbf{g}\|_{C^{1,\gamma}(\partial\Omega)}}{\sqrt{\epsilon}}$$

Question : Can we achieve the condition $1 \leq |\mathcal{K}_{\Omega,j}|$? Yes.

Theorem 2 (joint with Hyeonbae Kang, ARMA 2018)

Assume the inclusions are circular disks. Then, under **some condition on Lame parameters**, the followings hold:

(i) If $g(\mathbf{x}) = (Ax, By)$ with $A \neq 0$, then

 $|\partial_1 u_1(0,0)| \approx \epsilon^{-1/2}$ and $|\partial_2 u_1(0,0)| + |\partial_1 u_2(0,0)| + |\partial_2 u_2(0,0)| \lesssim 1.$

(ii) If
$$g(\mathbf{x}) = C(y, x)$$
 with $C \neq 0$, then

 $|\partial_1 u_2(0,0)| \approx \epsilon^{-1/2}$ and $|\partial_1 u_1(0,0)| + |\partial_2 u_1(0,0)| + |\partial_2 u_2(0,0)| \lesssim 1.$

Effective Properties of Elastic Composites

Effective bulk and shear modulus Flaherty and Keller derived the following asymptotic formulas (CPAM 1974)

$$E_* = E \frac{L_1}{L_2} \frac{\pi}{\sqrt{\kappa_0}} \frac{1}{\sqrt{\epsilon}} + O(1)$$
$$\mu_* = \mu \frac{L_1}{L_2} \frac{\pi}{\sqrt{\kappa_0}} \frac{1}{\sqrt{\epsilon}} + O(1)$$



Rigourous Justificatoin (joint work with H. Kang, 2018)

 Based on Primal-dual variational principles with our new singular functions (Keller's function doesn't work as test function)

Thank you.