# Local Electromagnetic Fields Surrounding Gold Nano-Cap Particles

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***Abstract*— Using the discrete dipole approximation (DDA) the local electromagnetic fields surrounding gold nano-cap particles are investigated. Suitable k-vectors and polarization vectors of the incident light are used to determine the largest local electric field enhancement. The largest enhancement can be found for the 864 nm dipole resonance; where the field enhancement is approximately 30 000 times the applied field. The electric field contours surrounding the particle are used to assign the order of the surface plasmon resonances.**

***Keywords; Surface plasmon resonance; Plasmonics; Discrete Dipole Approximation; Gold nanoparticles; discrete nano-cap***

## I. INTRODUCTION

The strong interaction between the visible and infra-red regions of the electromagnetic spectrum and noble metal nanoparticles has led to the development of a new research field called plasmonics. The primary phenomenon, the surface plasmon resonance, is the fundamental premise underlying the plasmonics field. The plasmon resonance is the collective oscillation of conduction electrons in resonance with the frequency of the incident light, coupled with a local evanescent field. The plasmon resonance is the direct consequence of strong absorption [1, 2] of the incident light at the resonance frequency. The frequency of the resonance is determined by the physical attributes and surrounding medium of the nanoparticle. An informed description of the plasmon resonance can be found in for example ref. [2].

Typically, nanoparticles such as nanospheres, nanorods, nanoshells and nano-caps, have a plasmon resonance at a wavelength of the incident light ranging from 530 nm to 1um. It is important to be able predict and characterize the properties of the plasmon resonance. To do this the solutions to Maxwell's equations in metallic nanoparticles must be found. There exists only a handful of solutions to Maxwell's equations, such as for metallic spheres, ellipsoids, concentric shells and infinite cylinders. These solutions all fall under the banner of Mie theory. Numerical methods must be employed to calculate the optical response of arbitrarily shaped nanoparticles. One such numerical method is the DDA [3, 4]. The DDA method is suitable for isolated nanoparticles that are placed (in this case) in a non-absorbing medium. The nanoparticle is represented by a cubic array of point dipoles. Applying an electromagnetic field to the point dipoles, the optical response is determined by self-consistently finding the induced dipole moments of the point dipoles.

The current work concentrates on examining the electric field enhancements surrounding gold nano-cap particles using the DDA method implemented in the DDSCAT [3] program. The nano-caps can be created experimentally by thermally evaporating gold onto a template of polystyrene nanoparticle spheres (PSNS) [5, 6]. The nano-caps used in this investigation are created with a template of 200 nm PSNS and a deposition angle of 10°. The scattering and absorption cross-sections were calculated in a previous work [6]. The orders of the resonances, also discovered in the previous work, were found by analyzing the dipole moments induced within the nano-cap. By examining the electric field contours surrounding the nano-cap particle we will confirm the assigning of the order for each primary resonance.

## II. COMPUTATIONAL MODEL

### A. DDA Method

Although originally used exclusively with dielectrics, the DDA method has been used to computationally model the optical response of metallic nanoparticles.

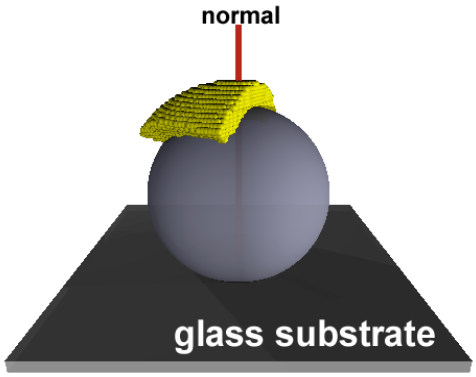


Figure 1. Schematic of the dipole representation used within the DDA calculations.

The applicability of the DDA method to metallic nanoparticles is best summarized in Kelly's paper [2]. The DDA method has been described in detail from other author's work [3, 4, 7]. The following is a brief qualitative description on the physics behind the method.

An arbitrary continuum target geometry is represented by a set of finite polarizable dipole points (Fig. 1 shows a dipole representation of the nano-cap). The polarizable points acquire a dipole moment in response to the local electric field [4]. The interaction of the electric field from acquired dipole moments also contributes to the total resultant field. Hence, the local electric field consists of the incident field and the induced electric field caused by the other dipoles. The dipoles are positioned on a cubic lattice. There are two reasons for this. First, each dipole must have a polarizability to determine the dipole's resultant dipole moment. The polarizabilities for each point dipole must be somehow assigned. In 1909, Lorentz showed that the polarizabilities of each atom within a medium were related to the dielectric constant of the medium [8]. This relationship between the polarizabilities of each individual atom and the dielectric constant is called the Clausius-Mossotti relation [8]. The relationship, however, is only valid when the atoms are positioned on a cubic lattice. This relationship is the physical inspiration for the DDA method, forcing the dipoles to be positioned on a cubic lattice. The second reason involves efficiency; Fast Fourier Transform (FFT) methods can greatly reduce the calculation time for the scattering problem, only if the dipole lattice is periodic. The use of the FFT method is only for efficiency purposes and not required for the DDA method to function correctly. Hence, the first reason is the only reason the dipoles must be positioned on a cubic lattice.

A finite array of dipoles can only represent a continuum target if each dipole represents an individual atom. Because the particles in which we are interested contain numbers of atoms on the order $10^{10}$, it is computationally unfeasible to represent each atom with a single dipole. Hence, we let each dipole represent large numbers of atoms. This is essentially the only reason the DDA method is an approximation. The approximation works well when the inter-dipole distance (the distance between adjacent dipoles) is small compared to the length scales of the target. The accuracy of the method is only inhibited by the computational power of the hardware used to carry out the calculations.

The DDA method has been used to investigate particles such as nanodisks [9], nanorods [10] , dimer nanoparticles [11], nano-cups [12] and nano-caps [5, 6, 13]. Hao [11] has used this code to calculate the local near-fields of silver dimer nanoparticles. He showed that the DDA provides a good estimate of the local fields. The electric field intensity values will give quantitative evidence for the possible application of the discrete nano-caps for use in applications that take advantage of strong local fields. Others have used the DDA method to calculate the electric field intensity contours around

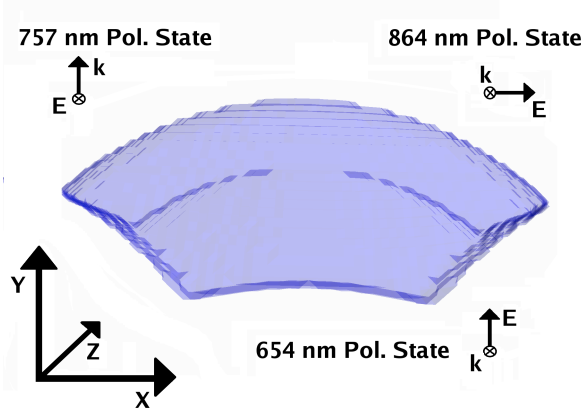


Figure 2. Polarization and k-vectors used to analyze the electric field enhancement. The k-vectors do not have a major influence on the enhancement. The polarization vectors are chosen to align with the major axes of symmetry.

particles [2, 11] and have found that the convergence of the electric field intensity magnitude is proportional to the number of dipoles used in the representation of the target. Hao and Schatz [11] found that the convergence of the calculated near field for triangle and ellipsoid monomer and dimer particles was dependant on the inter-dipole distance. That is the smaller the distance the more accurate the electric field.

### *B. Target Geometry*

The nano-caps studied in this work are created from a template of 200 nm PSNS, and are 94.6 nm x 46.2 nm x 143.0 nm in size. An inter-dipole distance of 2.2 nm was used for the electric field enhancement calculations, as to achieve a more accurate result in the near field [11]. The computational intensive nature of the DDA method prohibited using smaller inter-dipole distances with the relatively large discrete nano-caps.

## III. RESULTS AND DISCUSSION

The wavelengths, k-vectors and polarization vectors of the incident light used for this analysis, shown in Fig. 2, correspond to the plasmon resonance frequencies [6] and the maximum attainable electric field enhancements. There are three primary dipole resonances corresponding to the three axes of symmetry. The strongest resonance (i.e. strongest absorption) occurs at a wavelength of 865 nm with the polarization of the incident light in the x-direction. There is a corresponding quadrupole resonance, for this specific polarization, at 670 nm. The 755 nm dipole resonance occurs when the polarization of the incident light is in the z-direction. The quadrupole resonance occurs at 650 nm. The resonance at 654 nm occurs when the polarization of the incident light is in the y-direction. This resonance does not have a strong amplitude and will not be investigated any further.

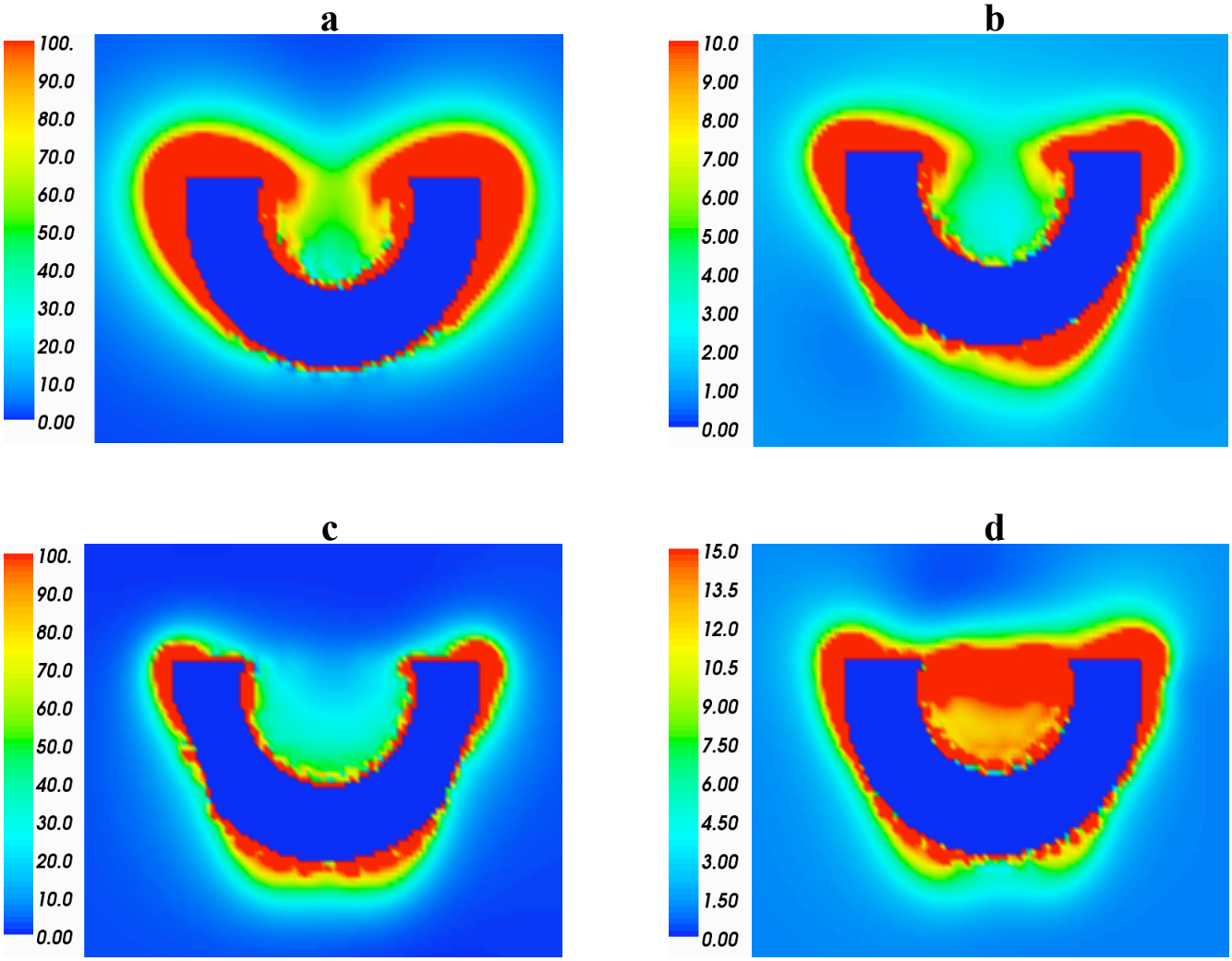


Figure 3. Electric field enhancement contours of a discrete gold nano-cap particle. The plots show a slice taken through target geometry. a) 865 nm dipole resonance. Polarization along x-direction. b) 670 nm quadrupole resonance. Polarization along x-direction. c) 755 nm dipole resonance. Polarization along z-direction. d) 650 nm quadrupole resonance. Polarization along z-direction.

The choice of k-vector has been found not to have a major impact [6] on the resonance amplitude. The electric field enhancement contours, $|\mathbf{E}|^2$, of the discrete nano-cap are displayed in Fig. 3. These plots confirm the assigning of the resonances, from [6], and show the magnitude of the electric fields at resonance conditions. They are well converged and display the exponential decay expected from near-fields (evanescent fields). The order of the resonances can be seen from these images.

For the polarization state in the x-direction, the 865 nm resonance has two field nodes, Fig. 3a, and is characteristic of a dipole resonance. The resonance at 670 nm has four field nodes, Fig. 3b, with slightly lobed shapes that are characteristic of a quadrupole resonance. For the 865 nm dipole resonance, the magnitudes of the fields are up to approximately 30 000 times stronger than the applied field. Where the strongest enhancement can be found surrounding the tips of the particle. The 670 nm quadrupole resonance has electric field enhancements of up to 4360 times the applied field. Once again the strongest enhancement can be found surrounding the tips of the particle.

The order of the resonances for the polarization state in the z-direction can also be allocated in the same way as stated above. Fig. 3c, shows the dipole resonance of the resonance found at 755 nm, and Fig. 3d shows the corresponding quadrupole resonance at the 650 nm resonance. The magnitude of the fields are up to approximately 8851 times the applied field for the 755 nm dipole resonance, and 3140 times for the 654 nm resonance.

The greatly enhanced electric fields can be suitable for applications involving bio-medical [14] (i.e. exciting attached fluorophores), wavelength selective window coatings [15, 16], plasmon polariton waveguiding [17, 18], and optical trapping experiments. Additionally, the polarization dependent resonances allow for polarization dependent applications, due to the strong electric field enhancements for each polarization of the incident light.

## IV. CONCLUSION

We have shown that the electric field enhancements can be found using the DDA method. The fields are well converged and display the characteristic exponentially decaying intensity that is expected from these fields. The electric field enhancement, with up to 30 000 times the applied field for the 865 nm dipole resonance, allow these particles to be applicable to many applications, that can take advantage of these strong fields. The other resonances, at 670 nm (quadrupole resonance), 755 nm (dipole resonance) and 650 nm (quadrupole resonance) provide strong enhancement with up to approximately 4360, 8851, and 3140 times the applied field respectively. These fields, although not as strong as the field produced by the 865 nm dipole resonance, can be still utilized within appropriate applications.

The polarization dependent resonances together with the fact that the nano-caps are created on an ordered array provide many opportunities to be incorporated within appropriate technologies. Especially with technologies involving plasmon waveguiding and optical trapping.

## V. ACKNOWLEDGEMENTS

This work was supported by the Australian Research Council, and the University of Technology, Sydney. Computing resources were provided by the Australian Centre for Advanced Computing and Communication (ac3) in New South Wales and the national facility at the Australian Partnership for Advanced Computing (APAC).

## REFERENCES

[1] B. C. F. and H. D. R., *Absorption and Scattering of Light By Small Particles*: Wiley-Interscience, 1998.

[2] K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, "Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, The," *J. Phys. Chem. B*, vol. 107, pp. 668 - 677, 2003.

[3] B. T. Draine, "Discrete-Dipole Approximation and Its Application to Interstellar Graphite Grains, The," *Astrophys. J.*, vol. 333, pp. 848-872, 1988.

[4] B. T. Draine and P. J. Flatau, "Discrete-Dipole Approximation for Scattering Calculations," *J. Opt. Soc. Am. A*, vol. 11, pp. 1491 - 1499, 1994.

[5] J. Liu, B. Cankurtaran, G. McCredie, M. J. Ford, L. Wieczorek, and M. B. Cortie, "Investigation of the optical properties of hollow aluminium 'nano-caps'," *Nanotechnology*, vol. 16, pp. 3023-3028, 2005.

[6] J. Liu, B. Cankurtaran, L. Wieczorek, M. J. Ford, and M. B. Cortie, "Anisotropic Optical Properties of Semitransparent Coatings of Gold Nanocaps," *Adv. Funct. Mater.*, 2006.

[7] B. T. Draine and J. Goodman, "Beyond Clausius-Mossotti: Wave Propagation On a Polarizable Point Lattice and the Discrete Dipole Approximation.," *Astrophys. J.*, vol. 405, pp. 685-697, 1993.

[8] D. J. Griffiths, *Introduction to Electrodynamics*: Prentice-Hall Inc., 1981.

[9] E. Hao, G. C. Schatz, and J. T. Hupp, "Synthesis and Optical Properties of Anisotropic Metal Nanoparticles," *J. Fluoresc.*, vol. 14, pp. 331 - 341, 2004.

[10] A. Brioude, X. C. Jiang, and M. P. Pileni, "Optical Properties of Gold Nanorods: DDA Simulations Supported By Experiments," *J. Phys. Chem. B*, vol. 109, pp. 13138 - 13142, 2005.

[11] E. Hao and G. C. Schatz, "Electromagnetic Fields Around Silver Nanoparticles and Dimers," *J. Chem. Phys.*, vol. 120, pp. 357 - 366, 2004.

[12] C. Charnay, A. Lee, S. Q. Man, C. E. Moran, C. Radloff, R. K. Bradley, and N. J. Halas, "Reduced Symmetry Metallodielectric Nanoparticles: Chemical Synthesis and Plasmonic Properties," *J. Phys. Chem. B*, vol. 107, pp. 7327 - 7333, 2003.

[13] J. Liu, A. I. Maaroof, L. Wieczorek, and M. Cortie, "Fabrication of Hollow Metal 'Nano-Caps' and Their Red-Shifted Optical Absorption Spectra," *Adv. Mater.*, vol. 17, pp. 1276-1281, 2005.

[14] C. Loo, A. Lin, L. Hirsch, M. H. Lee, J. Barton, N. Halas, J. West, and R. Drezek, "Nanoshell-Enabled Photonics-Based Imaging and Therapy of Cancer," *Technol. Cancer Res. Treat.*, vol. 3, pp. 33-40, 2004.

[15] S. Schelm and G. B. Smith, "Dilute LaB6 Nanoparticles in Polymer As Optimized Clear Solar Control Glazing," *Appl. Phys. Lett.*, vol. 82, pp. 4346-4348, 2003.

[16] X. D. Xu, M. Stevens, and M. B. Cortie, "In Situ Precipitation of Gold Nanoparticles Onto Glass For Potential Architectural Applications," *Chem. Mater.*, vol. 16, pp. 2259-2266, 2004.

[17] S. A. Maier, M. L. Brongersma, P. G. Kik, and H. A. Atwater, "Observation of Near-Field Coupling in Metal Nanoparticle Chains Using Far-Field Polarization Spectroscopy," *Phys. Rev. B*, vol. 65, 2002.

[18] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. Requicha, and H. A. Atwater, "Plasmonics - A Route to Nanoscale Optical Devices," *Adv. Mater.*, vol. 13, pp. 1501-1505, 2001.