Design of Nanosurfaces With Optimized Optical Properties Using the DDA Algorithm

by
Myria Angelidou

Submitted to the University of Cyprus in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering
Department of Electrical and Computer Engineering
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Examination committee:

Dr. Constantinos Pitris
Assistant Professor, Department of ECE, Research Supervisor

Dr. Stavros Iezekiel
Associate Professor, Department of ECE, Committee Member

Dr. George E. Georghiou
Assistant Professor, Department of ECE, Committee Member
Abstract

According to recent statistics, 11% of all women will exhibit urine tract infections (UTI) each year and up to 50% of women will have at least one infection during their lifetime. A specific diagnosis of a UTI is obtained with a culture of a specimen of urine and identification of the involved bacteria. With the techniques used today, it takes 24-48 hours until the pathogenic organism is cultured and identified and its sensitivity to antibiotics determined. It would be of great benefit if there existed an easy and practical method which could identify UTIs immediately and reliably. Such a method could be Surface Enhanced Raman Scattering (SERS). The success of SERS depends on specially designed nanosurfaces which enhance the normally weak signal of the Raman effect.

This thesis investigates the design and development of nanosurfaces (or nanoparticles) with optical properties optimized to provide a high electromagnetic field enhancement factor for the SERS effect. These optical properties depend on the size, shape, material and external dielectric environment of the nanosurface. The designs are developed using suitable theoretical estimations, so that the appropriate sizes and shapes can be chosen, based on the materials and optical devices that are available. There are many available methods for calculating the optical properties of nanoparticles. Mie theory provides accurate solutions of Maxwell’s equations, but it can be applied only to spheres and spheroids with arbitrary radius and dielectric constants. For nanosurfaces with rough or asymmetrical characteristics, such as cubes and tetrahedrons, various approximation methods exist. This project uses the Discrete Dipole Approximation (DDA), which is a method that provides accurate results of the optical properties such as the extinction efficiency factor of the nanoparticles if some limitations of the algorithm are taken into account.

Before designing any of the nanosurfaces some test simulations were performed to validate the results of the algorithm. The results produced agreed with key reference articles. Subsequently, considering that the nanosurfaces will most likely be fabricated with commonly used techniques, such as Electron Beam Lithography and Nanosphere Lithography, the design of appropriate nanoparticles, such as cubes and tetrahedra, was investigated. The properties of such particles made from silver, gold, aluminum and nickel were determined. With the above mentioned
techniques, it is important to characterize not only the effects of shape, size, and material of the surface, but also the effect of the substrate onto which the nanoparticles are fabricated. The simulations determined how the material of the substrate and its dimensions affect the optical properties of the nanostructures. To conclude, a comparison was made between the different nanostructure particles to determine which nanostructure results in optimized optical properties appropriate for use in SERS experiments.

Περίληψη

Σύμφωνα με πρόσφατες έρευνες, κάθε χρόνο ένα 11% όλων των γυναικών θα παρουσιάσουν λοιμώξεις του ουροποιητικού συστήματος και περισσότερες από 50% γυναίκες θα έχουν τουλάχιστον μία λοιμώξη κατά την διάρκεια της ζωής τους. Μία συγκεκριμένη διάγνωση για τις ουρολοιμώξεις λαμβάνεται με καλλιέργεια ενός δείγματος ούρων και αναγνώρισή του βακτηρίου που προκάλεσε αυτή την λοιμώξη. Με τις τεχνικές που χρησιμοποιούνται σήμερα, χρειάζεται 24-48 ώρες μέχρι ο παθογόνος οργανισμός να καλλιεργηθεί, αναγνωριστεί και καθοριστεί η ευαισθησία του στα αντιβιοτικά. Το όφελος θα ήταν σημαντικό αν υπήρχε μία εύκολη και πρακτική μέθοδος, με την οποία θα γινόταν η διάγνωση ουρολοιμώξεων άμεσα και αξιόπιστα. Μια τέτοια μέθοδος μπορεί να είναι η φασματοσκοπία από σκέδαση Raman με ενίσχυση επιφάνειας (Surface Enhanced Raman Spectroscopy ή SERS). Η επιτυχία της SERS βασίζεται πάνω σε συγκεκριμένα σχεδιασμένες νανοεπιφάνειες οι οποίες βελτιώνουν το συνήθως ασθενές σήμα Raman.

Αυτό το ερευνητικό έργο διερευνά την ανάπτυξη τέτοιων βελτιστοποιημένων νανοεπιφανειών (ή νανοσωματιδίων) με οπτικές ιδιότητες οι οποίες παρέχουν ένα υψηλό παράγοντα ενίσχυσης του ηλεκτρομαγνητικού πεδίου που συνεισφέρει στο μηχανισμό της SERS. Οι οπτικές ιδιότητες εξαρτώνται από το μέγεθος, το σχήμα και το υλικό του νανοσωματιδίου καθώς επίσης και από το εξωτερικό διηλεκτρικό περιβάλλον που βρίσκεται το νανοσωματίδιο. Πρέπει αυτές οι νανοεπιφάνειες να σχεδιαστούν χρησιμοποιώντας θεωρητική αποτίμηση, ούτως ώστε τα κατάλληλα μεγέθη και σχήματα να επιλεγούν, βάση των υλικών και οπτικού εξοπλισμού που είναι διαθέσιμα. Υπάρχουν διάφοροι μέθοδοι για τον υπολογισμό των οπτικών ιδιοτήτων των νανοσωματιδίων. Η θεωρεία του Mie παρέχει τις ακριβείς λύσεις των
εξισώσεων του Maxwell, αλλά μπορεί να εφαρμοστεί μόνο σε σφαιρικά και σφαιροειδή νανοσωματίδια με τυχαία ακτίνα και διηλεκτρική σταθερά (δηλαδή υλικό). Για νανοσωματίδια με τραχιά ή ασύμμετρα χαρακτηριστικά, όπως ο κύβος και το τετράεδρο, διάφορες προσεγγιστικές μέθοδοι υπάρχουν. Σε αυτό το ερευνητικό έργο χρησιμοποιείται η Προσέγγιση Διακριτών Διπόλων (Discrete Dipole Approximation), η οποία παρέχει ακριβή αποτελέσματα των οπτικών ιδιοτήτων και ιδιαίτερα του παράγοντα ικανότητας της εξάλειψης (extinction efficiency factor) όταν φυσικά λαμβάνονται υπ’ ώρα κάποιοι περιορισμοί της προσέγγισης.

Πριν αρχίσει ο σχεδιασμός των νανοεπιφανειών, έγιναν κάποιες δοκιμές οι οποίες επιβεβαίωσαν ότι ο αλγόριθμος δίνει τα επιθυμητά αποτελέσματα τα οποία και συμφωνούν με τις βιβλιογραφικές αναφορές. Κατόπιν, θεωρώντας ότι για την κατασκευή των νανοεπιφανειών θα χρησιμοποιηθούν γνωστές μεθόδους, όπως η Λιθογραφία Ηλεκτρονικής Δέσμης (Electron Beam Lithography) και η Νανοσφαιρική Λιθογραφία (Nanosphere Lithography), εξερευνήθηκε ο σχεδιασμός ανάλογων νανοσωματιδίων όπως παραλληλεπίπεδα και τετράεδρα. Εξερευνήθηκαν, με προσομοιώσεις, οι ιδιότητες τέτοιων σωματιδίων από άργυρο, χρυσό, αλουμίνιο και νικέλιο. Με τις προαναφερθείσες τεχνολογίες, δεν αρκεί μόνο να υπολογιστεί η επιρροή του μεγέθους, σχήματος και υλικού του νανοσωματιδίου αλλά και η επιρροή του υποστρώματος πάνω στο οποίο κατασκευάζονται τα νανοσωματίδια. Υπολογισμοί που έγιναν καθορίζουν πώς το υλικό του υποστρώματος και οι διαστάσεις του επηρεάζουν τις οπτικές ιδιότητες των νανοσωματιδίων. Καταλήγοντας, έγινε μία σύγκριση μεταξύ των διαφόρων νανοσωματιδίων, έτσι ώστε να διασαφηνιστεί ποια αποδίδουν τις βέλτιστες οπτικές ιδιότητες κατάλληλες για χρήση σε πειράματα SERS.
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Chapter 1: Introduction

Spectroscopic techniques have long been a very useful tool for the early diagnosis of disease and monitoring of treatment. One of the most useful techniques is Raman spectroscopy which can provide information regarding the biochemical constituents of tissue. However, for most molecules, the intensities of Raman signals are very low compared to Rayleigh scattering (where the scattered photon has the same energy as the incident photon). One way to amplify the normally weak Raman signal, by as much as $10^6$, is using Surface Enhanced Raman Scattering (SERS). [1] As it will be discussed later, SERS amplification depends upon various features of a metal nanosurface, such as size, shape, arrangement and surrounding environment. This thesis examines these aspects and simulates possible geometries which can be used to enhance the Raman signals.

In this chapter, the basic theory of the Raman effect is introduced. Then, plasmons, the effect of plasmon resonance and their relation to SERS is discussed. Afterwards a brief description of the mechanism of SERS is included.

1. Introduction to the Raman Effect

The Raman effect was discovered by Chandrasekhara Venkata Raman in 1928. He was the first Indian who received a Nobel prize for his discovery two years later. [2] The Raman effect deals with the interaction of light with the vibrational levels of biomolecules in tissue. It is an inelastic, non-irradiative process where light incident on to matter is scattered with a shift in its frequency.

1.1 Raman scattering

In Raman scattering the incident photon is scattered by biomolecules in tissue, into another photon with less or more energy as compared to the incident one. The energy difference is due to the interaction of the photon with the vibrational levels of the molecule and is proportional to the vibrational energy gained or lost. If the scattered photon has lower energy than the incident photon then a vibrational transition is induced from a lower level to a higher level. This process is called \textit{Stokes}}
Raman Scattering. If the scattered photon has higher energy than the incident photon then a transition is induced from a higher thermally populated vibrational level to a lower level. This process is called anti-Stokes Raman Scattering. [3] These transitions are shown in figure 1.1.

\[\hbar \omega_L \quad \hbar \omega_S \quad \hbar \omega_{as}\]

Figure 1.1: Model for the illustration of Stokes-Raman and anti-Stokes-Raman scattering [4] \(\omega_L\) is the frequency of the incident, \(\omega_S\) of a Stokes-scattered and \(\omega_{as}\) of an anti-Stokes scattered photon.

1.2 Fluorescence

Transition may also occur between electronic states of the molecule or tissue in a radiative manner. [3] This radiational process is called fluorescence and, for most biomolecules, is many orders of magnitude more intense than the vibrational excitation of the Raman effect. This causes significant problems when measuring the Raman signal of a biomolecule since fluorescence overlaps with Raman emissions. As shown in the middle panel of figure 1.2, if the excited light is in the visible region, the fluorescence wavelength and the Raman scattered wavelength, are similar. Therefore, in a measured spectrum the Raman bands can not be distinguished from the fluorescence background. One way of avoiding the problem is by using a near-IR excitation source which does not excite any fluorescence. Alternatively the problem of fluorescence can be eliminated by using UV light at wavelengths below 270nm. [2] In this case the fluorescence is in the visible region and does not overlap with the UV Raman bands.

1.3 UV resonance Raman scattering

The wavelength of the excitation source used to perform Raman Spectroscopy is usually below the first energy state of most molecules. [4] When the excitation
wavelength is close to or concurs with an energy transition of the scattering biomolecule, usually for UV wavelengths, we the process is called UV resonance Raman scattering. [5]

In biological materials, when the upper energy states are excited by UV light often relax to lower energy levels with non-radiative process, thereby radiating fluorescence at a sufficiently different wavelength compared to the excitation light. In contrast, Raman scattered light is emitted in the UV because it occurs before relaxation sets in. The result is that fluorescence occurs in wavelengths which are outside the spectral region of the Raman bands, and Raman spectra can be obtained without a fluorescence background. Another advantage of UV excitation is that many biomolecules absorb very highly in the UV region and Raman intensity is significantly increased. [2]

![Figure 1.2: Raman effect: UV, visible and near-IR excitation processes. S₀ is the ground energy state; S₁ and S₂ are the excited energy states. The horizontal lines indicate vibrational energy levels. νₑ: excitation frequency, νₐ: Raman frequency, νᵢ: fluorescence frequency. Curved lines indicate non irradiative processes. [2]](image)

1.4. Applications of Raman spectroscopy

The major advantage of Raman spectroscopy is that it provides detailed information regarding the chemical structure and composition of the molecules. It also provides information on intermolecular interactions. [3] Biological applications of
Raman include structural investigation of hormone receptors, structural studies on soil components, localization and identification of single bacteria, etc. [4] Some of the clinical applications of Raman spectroscopy include the diagnosis of atherosclerosis, breast cancer, Alzheimer’s disease, and analysis of blood analytes. The potential of using Raman spectroscopy to get accurate diagnosis of human disease is very significant. [2]

2. Introduction to Plasmonics

Plasmonics is an area, which deals with the interaction of waves with metallic surfaces and nanostructures, such as metallic nanoparticles, nanorods and nanoshells, and their applications. A metal-dielectric boundary on the scale of nanometers produces observable changes in the optical properties, making them size and shape dependent. Plasmon resonance, at the boundary between the metal nanostructures and the surrounding dielectric, also produces an enhanced electromagnetic field at the interface. The optical properties of metallic nanostructures are not derived from quantum confinement of electrons and holes as in the bulk form of the material but from electrodynamic effects and from modification of the dielectric environment. [6]

2.1 Plasmon resonance

Interactions of metallic nanoparticles with light can produce a resonance, which gives rise to a plasmon absorption band at a specific wavelength range. There are specific wavelengths of light absorption that produce plasmon oscillations and are called surface plasmon bands. The effect is due to the coherent, collective oscillation of electrons at the surface, which is induced by interaction with the electromagnetic field of the incident light. These oscillations produce surface plasmon waves. In the case of metal particles, as opposed to metal surfaces, these excitations at the metal-dielectric interface form localized surface plasmons and a local field enhancement is observed. When the wavelength of the incident light is close to the wavelength of the plasmons of the metal, electrons from the surface are excited to an upper energy level (plasmon resonance). [6]
2.2. Dipoles and higher-order poles

An electric dipole is a separation of positive and negative charge. Its field at large distances, large compared to the separation of the poles, depends almost entirely on the dipole moment. This electric dipole moment would point from the negative charge towards the positive charge, and have a magnitude equal to the strength of each charge times the separation between the charges. A higher-order pole is the quadrupole which is a combination of two opposite dipole sources. The quadrupole, as well as the dipole, are two of a sequence of configurations of electric charge, usually part of a multipole expansion of a more complex structure reflecting various orders of complexity. This means that there are charges of positive and negative signs that are separated in a more complicated way than the dipole. Configurations of electric charges of dipole and higher multipolar nature that change in time radiate electromagnetic waves, according to a specific pattern generated by such sources.

2.3. Metallic nanostructures

Metallic nanoparticles exhibit major changes in their optical spectra derived from effects that can be explained using a classical dielectric picture. Their surface plasmon band depends on their size, shape and the surrounding dielectric medium. For nanorods, the surface plasmon band splits into two bands. More details regarding these nanostructures will be discussed later.
2.4. Metallic nanoshells

Metallic nanoshells consist of two different materials, a dielectric core and a shell. When the shell is metallic, dramatic changes are observed in the surface plasmon resonance. The optical resonance shifts to a longer wavelength than those in the corresponding solid metal nanoparticles. Nanoshells have found applications in whole-blood immunoassays and prevention of photo-oxidation of semiconducting polymers based devices. [6]

2.5. Applications of metallic nanostructures

A well-established application of use of metallic nanostructures is Surface-Enhanced Raman Spectroscopy (SERS). More recently metallic nanostructures have found new applications. The effect of plasmon resonance is utilized, primarily, in three ways:

- Local field enhancement near the surface of a metallic nanostructure
- Evanescent wave derived from the surface, when exciting a surface plasmon resonance
- The sensitivity of the surface plasmon resonance to the dielectric medium surrounds the metallic nanostructure.

The local field enhancement has been proposed for a new method called plasmonic printing for photofabrication of nanostructures. [6] This local field enhancement also contributes to the enhancement of the linear and nonlinear optical transitions in molecules that are in a nanoscopic distance from a metallic nanostructure. [6]

Evanescent electromagnetic waves produced when light is coupled as a surface plasmon excitation in a metallic nanostructure, emanate from the surface and are exponentially decaying into the surrounding dielectric field. This wave can be utilized to preferentially excite an optical transition in fluorescent molecules or nanospheres near the surface of a metallic nanostructure. It has also been utilized to convert a propagating plasmon wave in a plasmon waveguide to a fluorescent optical signal.

The surface plasmon resonance frequency and its width are both sensitive to the surrounding dielectric. This sensitivity forms a basis for detection of biological
analytes, which can bind to the surface of the metallic nanostructures through a typical antigen-antibody type coupling chemistry. [6]

3. Surface Enhanced Raman Scattering (SERS)

When molecules are absorbed onto certain metals (such as silver, gold and copper), an enhanced Raman effect is observed when the incident light excites the free electrons in the metal’s conduction band and induces plasmon resonance. This phenomenon is called Surface Enhanced Raman Scattering (SERS) [5] and is observed in a variety of morphologies of metals and physical environments. [9] The major contribution to SERS enhancement, for a system of a nanosurface with a molecule on, comes from the scattering by the metal particle rather than by the molecule. However, the Raman spectrum of the molecule is reflected in the SERS spectrum of the light scattered by the metal. [10] SERS results in an enhancement factor of up to about $10^6$ in scattering efficiency over normal Raman scattering. [11] The largest enhancement occurs for surfaces which are rough on the nanoscale (10-100 nm) and when there is a direct contact between the molecules under investigation and these surfaces. [6] SERS excitation is a near field phenomenon [10] meaning that SERS enhancement drops off rapidly with distance from the surface. [11]

3.1. Mechanisms of SERS:

The total enhancement of the SERS effect is explained by two processes: 1) an electromagnetic enhancement effect and 2) a charge-transfer mechanism also referred to as chemical enhancement. [12] SERS enhancement comes mostly from the first mechanism. [13] This mechanism can be attributed to surface plasmon oscillations (plasmon excitations in the metallic nanostructure create an enhanced electromagnetic field near the metal). [12,13] Chemical enhancement also contributes to SERS [9], which is in broad terms a charge transfer interaction between the metal and adsorbed molecules [4], and acts independently from the electromagnetic mechanism. It has been very difficult to separate these effects in relatively complicated systems. [9]. In most cases, these two very different mechanisms act together in varying proportions, which are extremely difficult to verify and distinguish. [1]
Electromagnetic enhancement:

The electromagnetic field of the light at the surface can be greatly enhanced under conditions of surface plasmon excitation. The reinforcement (amplification) of both the incident wave field and the scattered Raman field through their interaction with the surface constitutes the electromagnetic SERS enhancement [9].

For a spherical metallic nanostructure in an external electric field, whose radius is much smaller than the wavelength of the incident light, the electromagnetic field is uniform across the metal and can be approximated by electrostatics. The field induced at the surface of the sphere is related to the applied external field as shown in the equation:

\[ E_{\text{induced}} = \left[ \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2} \right] E_{\text{laser}} \]

where \( \varepsilon_1(\omega) \) is the complex, frequency-dependent dielectric function of the metal and \( \varepsilon_2 \) is the relative permittivity of the surrounding environment. A resonant is observed at the frequency for which \( \text{Re} (\varepsilon_1) = -2\varepsilon_2 \) while \( \text{Im} (\varepsilon_1) \) is as close to zero. [9] (The numerical factor of 2 in the resonance equation will simply be different for different structures.)

Chemical enhancement:

Chemical enhancement or charge transfer can be explained by two observations. [9] First, charge transfer involves the formation of a bond between the molecule and the surface. This bond is believed to produce a surface form which includes the molecule and some surface atoms. This makes it possible for electrons or holes to transfer from the metal to the molecule and new electronic states arise from the formation of the bond between the metal and molecule. Chemical enhancement occurs only when the molecules are directly attached to the surface. [11] Another observation that explains chemical enhancement is that when the molecule is absorbed on the metal’s surface, its electronic state is broadened and shifted. [9]
3.2. Applications of SERS:

SERS is a well-known method for improving the signal level in Raman scattering. [14] Because SERS provides both rich spectroscopic information and high sensitivity, as a result of the large enhancement effect, it is ideally suited for trace analysis. [4] Also SERS has a fluorescence-quenching effect [15] and is extremely useful when examining microorganisms, which often exhibit a high fluorescence background under excitation in the near-infrared to visible regions of the electromagnetic spectrum. [12]

References:

Chapter 2: Theory

1. Introduction

In this chapter, a more detailed view of the electromagnetic theory of SERS will be introduced. Also a discussion of the spectral properties of surface plasmons of the metal nanostructures is included. As will be described in this chapter, a sphere (or a particle with arbitrary shape), with dimensions smaller than the wavelength of the excitation light, will maintain oscillating surface plasmon multipoles of various orders induced by the time-varying field vector of the light. When the sphere is small enough all but the dipolar plasmon can be ignored. [1] In the last few years, several studies have aimed at using computational electrodynamics to provide a realistic and quantitative description of SERS. [2] Based on these studies, some electrodynamic methods will be introduced in this chapter. These methods can be used to estimate the SERS effect for particles with various shapes, sizes and materials.

2. Electromagnetic Mechanism of SERS

Systems with free or almost free electrons can maintain oscillating fields, under excitation, and the freer the electrons, the sharper and more intense the dipolar plasmon resonance will be. [1] The Electromagnetic (EM) enhancement is based on the significantly amplified electromagnetic fields (E) generated by the localized surface plasmon resonance (LSPR) of nanoscale surface roughness features. [3] SERS-active metals such as Ag, Au and Cu exhibit free electron-like behaviour at long wavelengths thus are the most usable metals in SERS experiments. The enhancement may be estimated using only the size, shape and the dielectric constant of the metal particle or surface involved. [4]

First, it must be noted that the major contribution to SERS, for a system of a nanosurface with a molecule on, comes from the scattering by the metal particle rather than by the molecule. However the Raman spectrum of the molecule is reflected in the SERS spectrum of the light scattered by the metal. Also, SERS excitation is a near field phenomenon meaning that the molecule must be as close as possible to the surface. [1]
The particle size plays a major role in the SERS mechanism. As noted above, the particle that interacts with light must be small compared to the incident wavelength. If the features of the particle are of the order of the wavelength or larger, the optical field no longer excites dipolar plasmons exclusively but also high order multipoles which must be considered in the estimations. Unlike the dipoles, higher order multipoles are non-radiative and hence not efficient in exciting Raman. Therefore, the SERS efficiency drops until, for large enough particles, the exciting radiation is locked up in higher order plasmon multipoles and SERS is all but eliminated. As the nanostructures responsible for SERS become too small the effective conductivity of the metal nanoparticle diminishes as a result of electronic scattering processes at the particle’s surface. As a result, the quality factor of the dipolar plasmon resonance is annulled and the re-radiated field strength is reduced. When the particle becomes too small, the pseudo-bulk description eventually no longer holds in the definition of the surface plasmon. Instead, one needs to treat the metal particle as a fully quantum object whose electronic properties show quantum size effects. [1]

Electromagnetic theory can be used to calculate the extinction and scattering cross-sections for the nanoparticles and determine how these are related to the SERS electromagnetic field enhancement. These cross-sections may be obtained from the solution of Maxwell’s equation. They depend on the asymptotic properties of the solutions rather than the surface fields as the SERS model. For very small particles, there is a close relationship between the extinction and scattering cross-sections and the SERS excitation profiles, since both have plasmon peaks at the same wavelength. However, for large spherical and nonspherical particles there are significant differences in wavelength dependence. These differences can provide information about the factors affecting the electromagnetic mechanism. [4] Much of the work presented in the next chapters, comes from studies of extinction spectra, which can lead to a better understanding of the dependence of the optical properties of metal nanoparticles on size, shape, arrangement and dielectric environment.
2.1 Dipole plasmon resonances for small spherical particles

The theory focuses on isolated small, spherical particles, as this provides the simplest problem that still exhibits all the features of SERS which are also found in more complex systems. The molecule is ignored in determining the optical properties and electric field near the surface. [4] As noted above, the spherical particle is much smaller than the wavelength of light so the incident electric field can be considered to be constant (independent of coordinates for distances at least as large as the sphere [4]), and the interaction is governed by electrostatics rather than electrodynamics. This is often called the \textit{quasistatic approximation}. [5]

The nanoparticle is typically large enough that classical electromagnetic theory can accurately describe the interaction with light but small enough so that there are strong variations in optical properties with particle size, shape and local environment. [6] The spherical particle has a dielectric constant $\varepsilon_i$ and is assumed that it is embedded in a medium of dielectric constant $\varepsilon_0$. The dielectric constant of the metal sphere is taken to be independent of the size. [4] Let’s denote the electric field of the incident electromagnetic wave by the constant vector $\mathbf{E}_0$ along the direction z. To determine the electromagnetic field surrounding the particle, the Laplace’s equation must be solved. The resulting field outside the sphere, $\mathbf{E}_{\text{out}}$, can then be written as:

\begin{equation}
\mathbf{E}_{\text{out}} = \mathbf{E}_0 \mathbf{z} - \alpha \mathbf{E}_0 \left[ \frac{z}{r^3} - \frac{3z}{r^5} (z \mathbf{x} + x \mathbf{z} + y \mathbf{y}) \right]
\end{equation}

where the first term is the applied field, and the second is the induced dipole that results from polarization of the sphere conduction electron density, $\alpha$ is the metal polarizability, $x$, $y$, $z$, $r$, $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ are the Cartesian coordinates, radial distance and Cartesian unit vectors, respectively and $\mathbf{E}_0$ is the magnitude of $\mathbf{E}_0$. For a metal sphere with the dielectric constant indicated above, the polarizability is [4,5]

\begin{equation}
\alpha = ga^3
\end{equation}

where $a$ is the sphere radius and
\[ g = \frac{\varepsilon_i - \varepsilon_0}{\varepsilon_i + 2\varepsilon_0} \]  

(3)

Clearly, \( g \) depends on the dielectric constants of the metal and the surrounding medium. Since the dielectric constants vary for different wavelengths, \( g \) also depends on laser frequency. [7]

Also, note that \( \alpha \) is a number that is on the order of the sphere volume in the limit \( k \to 0 \), as in that case \( \varepsilon_i \) is \(-\infty\). However, when the real part of \( \varepsilon_i \) equals \(-2\varepsilon_0\) and the imaginary part is small, the polarizability becomes very large, and as a result the induced field becomes large. This plasmon resonance condition requires the real part of \( \varepsilon_i \) to be large in magnitude and negative, and this is always the case for free electron metals at long enough wavelengths. In addition, the formula states that the plasmon resonance wavelength will change if the \( \varepsilon_0 \) changes.

The Raman intensity depends on the magnitude square of \( E_{\text{out}} \) which is denoted as \( E_{\text{out}}^2 \), evaluated at the surface of the sphere \((r=\alpha)\). From eq. 1 this is given by

\[ E_{\text{out}}^2 = E_0^2 \left[ |1 - g|^2 + 3 \cos^2 \theta \left( 2 \Re(g) + |g|^2 \right) \right] \]  

(4)

where \( \theta \) is the angle between the applied field direction and the vector \( r \) that defines positions on the sphere surface. Note that if \(|g|\) is large, eq. 4 reduces to

\[ E_{\text{out}}^2 = E_0^2 |g|^2 \left( 1 + 3 \cos^2 \theta \right) \]  

(5)

This indicates that the larger field intensities occur for angles \( \theta \) equal to zero or 180°. Now consider a molecule that is located at the position of maximum enhancement and take the limit \(|g|\gg1\), then the overall enhancement arising from the incident and scattered fields is approximately

\[ E_R = \frac{E_{\text{out}}^2}{E_0^4} = 16 |g|^2 |g|^2 \]  

(6)
where the primed symbols refer to fields evaluated at the scattered frequency. For small Stokes shifts, \(|g|\) and \(|g'|\) are maximum at approximately the same wavelength. [4]

Bohren and Hoffman demonstrate the absorption and scattering efficiencies of a small sphere where small can be defined as

\[
x \ll 1 \quad \text{and} \quad |m| x \ll 1
\]

These equations can be obtained by treating the sphere as an ideal dipole with moment given by electrostatics theory such as above. [8] There is one exception, eq. 8 is accurate only if scattering is small compared with absorption). Thus, although the dipole field in eq. 1, is that of a static dipole, it is actually a radiating dipole and contributes to extinction and Rayleigh scattering by the sphere. The extinction and scattering efficiency factors for a radiating dipole, therefore, are:

\[
Q_{ext} = 4x \text{Im}(g)
\]

\[
Q_{sca} = \frac{8}{3} x^4 |g|^2
\]

where \(x = \frac{2\pi \alpha (\epsilon_0)^{1/2}}{\lambda}\). The efficiency is the ratio of the cross-section to the geometrical cross-section \(\pi \alpha^2\). Note that the factor \(g\) from eq. 3 plays the key role in determining the wavelength dependence of these cross-sections, as the metal dielectric constant depends strongly on the wavelength. [4,5]

As long as the plasmon width is much smaller than the plasmon energy, the extinction cross-section has the same wavelength dependence (after leaving out the \(x\) factor) as the large \(|g|\) limit of eq. 4. Therefore, in the small particle limit, SERS excitation and extinction plasmon peaks and widths should be the same. [4]
2.2 Electromagnetic fields for spherical particles

For SERS, the electromagnetic field at or near the particle surfaces determines the measured intensities. Thus, the SERS intensity is determined by:

\[
E = \left\langle |E(\omega)|^2 |E(\omega')|^2 \right\rangle
\]

(10)

where \(E(\omega)\) is the local electric-field at the incident frequency \(\omega\), \(E(\omega')\) is the corresponding factor at the Stokes-shifted frequency \(\omega'\) and the brackets are used to denote an average over the particle surface. [2, 7]

At the dipole level, the field outside a particle is given by eq. 1. This expression determines the near-fields at the particle surfaces quite accurately for small enough particles; however, the field beyond 100nm from the center of the particle exhibits radiative contributions that are not contained in the equation. To describe this, the dipole field must be replaced by its radiative counterpart, thus is given by:

\[
E_{\text{dipole}} = k^2 e^{ikr} \frac{r \times (r \times P)}{r^3} + e^{ikr} \left(1 - ikr\right) \frac{\left[r^2P - 3r(r \cdot P)\right]}{r^3}
\]

(11)

where \(P\) is the dipole moment. Note that this reduces to the static field since, in the limit \(k \to 0\), only the term in square brackets remains. However, at long ranges, the first term becomes dominant as it falls off more slowly with \(r\) than the second. [5]

Further, since the field is inversely proportional to \(r^3\), the magnitude of the SERS enhancement drops off rapidly with distance from the surface. [7]

3. Spectral Properties of Surface Plasmon Resonance in Metallic Nanostructures

It is important to investigate how the localized surface plasmon resonance in metallic nanostructures depends on size, shape and arrangement, and which conditions induce a larger local electromagnetic field enhancement near the structure surface. When metallic nanoparticles take the form of nanorods or triangular prisms the surface plasmon resonances are strongly affected. [9]
3.1. Spectral features of monomers:

Nanospheres, nanorods and triangular prisms:

The wavelength of the maximum absorption peak of the surface plasmon band depends on the size of the nanospheres. It is also dependent on the surrounding dielectric environment of the particles. Increasing, for example, the dielectric function of the surrounding medium leads to an increase in the plasmon band intensity and bandwidth and as well as a red shift of the plasmon band maximum.

As shown in figure 2.1, for small particles (<15nm for gold) the plasmon band peak does not shift significantly when the size changes. In addition, the bandwidth of the peak is broadening. These spectra features for small nanoparticles are referred to as intrinsic size effects. For larger particles (>25nm for gold particles) the peak is red shifted and the bandwidth increases because of extrinsic size effects.

For nanoparticles smaller than about 20nm, only the dipole term is assumed to contribute to the absorption. It is well established that the bandwidth of the plasmon absorption is inversely proportional to the radius $r$ of the particle. Consider eq.7 describing the absorption efficiency. If $g$ is a weak function of wavelength over some interval, then for sufficiently small particles $Q_{abs} \sim 1/\lambda$. The size dependence of
the plasmon absorption in the quasi-static regime is introduced by assuming a size-dependent material dielectric function, \( \varepsilon(\omega, R) \), due to interband transitions, from inner d orbitals to the conduction band. This is the reason why the related changes in the optical absorption spectra are referred to as the **intrinsic size effects**.

For larger particles, higher order multipole terms (which are functions of \( r \)) contribute to the absorption and an inhomogeneous polarization of the particle is observed by the electric field. For these particles the plasmon bandwidth increases and the efficiency drops with increasing size as the wavelength \( \lambda \) of the incident light becomes comparable to the dimension of the nanoparticle. The increased line width is caused by the excitation of different multipole modes, which peak at different energies. This behavior is referred to as an **extrinsic size effect** and the size dependence comes from the full expression of Mie’s theory. [10]

![Figure 2.2: Absorbance of gold nanorods.](image)

For a **nanorod**, the surface plasmon band splits into two. One peak corresponds to the oscillation of free electrons in the longitudinal direction and the other peak to the transverse compared to the long axis of the rod. [11] The transverse mode resembles the observed mode for spherical particles while the longitudinal mode is red-shifted and depends strongly on the aspect ratio, i.e. the length of the rod.
divided by its width. Also for a fixed aspect ratio, the maximum peak red shifts with increasing the dielectric function of the surrounding medium. [10]

For a **triangular prism**, the extinction spectrum is sensitive to its edge length, thickness and snipping. The long wavelength dipole resonance red shifts when the edge length is increased or the thickness decreased, while snipping blue shifts the plasmon resonance. [9] Figure 2.3 illustrates the effect of snipping on the efficiency factor of a triangular prism.

![Figure 2.3: Effect of snipping to the extinction efficiency of triangular prisms.](image)

The efficiency factor variance with the particle’s shape is presented in figure 2.4. Consider the shapes of a sphere, a cylinder, a cube, a prism, and a pyramid, all with the same volume as the sphere. The maximum plasmon resonance is strongly shaped dependent. A sphere gives the shortest peak wavelength of all the particles. Particles such as truncated tetrahedrons, with sharp points, give the more red shifted spectrum. [13]
It has been noted from Hao, and C. Schatz, [9] that isolated nonspherical particles show typically larger local electromagnetic field enhancement than isolated spheres because of their ability to support plasmon resonance at long wavelengths while the effective radius is kept small.

3.2. Spectral properties of dimers:

Dimers of spheres:

A dimer is a structure that consists of two particles that nearly touching. From experimental data, it was observed that the extinction spectra of dimers are very sensitive to separation distance. The dipole resonance red shifts and the quadrupole resonance becomes more intense as the particles approach. The separation between the spheres has to be in the order of a few nanometers. Larger particles give the same enhancements for larger distances. [9]

Dimers of triangular prisms:

A pair of triangular prisms can be positioned with a common perpendicular bisector and with corresponding tips directed toward each other and separated by a distance in the order of a few nanometers. The extinction spectra obtained for polarization along the perpendicular to the plane of the triangles, and perpendicular to the inter particle axis, are very similar with those found for uncoupled triangles.
However, when the polarization is along the inter-particle axis a significant red shift of the dipole plasmon resonance is observed and an additional weak peak appears. The maximum enhancement occurs at the interface between the two prisms. [9]

![Figure 2.5: Electromagnetic field contours for a monomer and dimers of triangular prisms. [9]](image)

As demonstrated in figure 2.5, for the case of a monomer prism, the maximum enhancement for the dipole resonances occurs at the particle tips. The largest fields ($|E|^2$) for dipole resonance are 3500x the applied field at the peak resonance wavelength near 700nm. The second contour shows the E-field for the head to head configuration of a dimmer of prisms separated by 2nm, at the wavelength of 932nm that corresponds to dipole resonance. The largest fields ($|E|^2$) are 53000x the applied field. The right contour shows the E-field enhancement for a head to tail configuration of a dimmer of prisms separated by 2nm, at 852nm with the induced polarization along the interparticle axis. The largest fields ($|E|^2$) are 57000x the applied field. Indeed the E-field enhancement produced between two prisms is larger than the E-field enhancement produced at the tips of a monomer. [9]

4. Electrodynamic Methods for Nonspherical Particles

The classical electromagnetic theory of metal nanoparticles has a long history. Maxwell’s equations describe the field in the presence of matter. A century ago, Mie introduced exact solutions of Maxwell’s equations for the scattering of light of a spherical particle. Unfortunately, Mie’s theory is limited to spheres. [6] For particles
that do not allow analytical solutions of Maxwell’s equations (or Laplace’s equation), it is necessary to introduce numerical methods. [7]

In the last few years, estimates of SERS enhancement factors have been achieved, for nonspherical nanoparticle surfaces, using computational electrodynamic methods such as the discrete dipole approximation (DDA), the modified long wavelength approximation (MLWA) which uses the quasistatic approximation corrected for finite wavelength effects, and the finite difference time-domain (FDTD) method to solve Maxwell’s equations to determine the local fields $E(\omega)$. These methods can be used to describe any kind of particle, but they are ultimately limited by the total number of elements and computations needed for the calculations to converge. [2, 5]

For isolated nanoparticles of arbitrary shape and a complex surrounding environment, a particularly powerful method is the DDA. It can treat complex particles in heterogeneous environments and determine far-field properties such as extinction and scattering spectra [5], even though it has limitations in determining the electromagnetic field around the particles. [6] In addition to the fact that the estimate of the electric field close to the particle surfaces is inaccurate, there is another important weakness. The total volume of material that can be described is limited by available computer resources to dimensions of a few hundred nanometers. [5] However, the strength of this method depends on its ability to directly calculate the optical response of a nanoparticle without any fitting parameters given that the following aspects are known:

1) Nanoparticle size and shape
2) Bulk dielectric constants of each material (the dielectric depends only on the incident wavelength, not on the size of the particle)
3) Incident wavelengths. [14]

Another advantage of DDA is computational speed. Consider $N$ to be the number of dipoles. Due to the fact that DDA uses the FFT algorithm, it converges in $N\ln(N)$ steps compared to other methods that converge in $N^2$.
References:


Chapter 3: DDA Theory and Algorithm

1. Discrete Dipole Approximation

The discrete dipole approximation (DDA) was originally proposed by Purcell and Pennypacker [1] in 1973 and has undergone a number of theoretical developments since then, including the introduction of radiative reaction corrections by Draine [2] in 1988. Since then, it has become an important computational tool.

1.1 DDA theory

The DDA is an approximation of the continuum target by a finite array of polarizable points. Each of these points is small enough that interacts only through dipole-dipole interactions with an external electromagnetic field and with induced fields from other dipolar points that need to be considered. [2-5] The optical response of the collection of dipoles to the applied field can then be described by self-consistently determining the induced dipole in each element. [6,7] In the limit of an infinite number of dipole elements, the DDA provides a nearly exact solution to Maxwell’s equations. [7]

Figure 3.1: Representation of a sphere by a number $N=17904$ dipoles [8]
In the DDA, the particle is divided into a cubic array of N-point dipoles. The N-point dipoles have positions \( r_i \) and polarizabilities \( \alpha_i \). The polarization induced in each dipole, as a result of interaction with the local electric field \( E_{\text{loc}} \), will be:

\[
P_i = \alpha_i E_{\text{loc}}(r_i) \tag{1}
\]

\( E_{\text{loc}} \), for isolated particles, is the sum of the incident field and a contribution from all other dipoles in the same particle:

\[
E_{\text{loc}}(r_i) = E_{\text{inc},i} + E_{\text{self},i} = E_0 \exp(ik_r r_i) - \sum_{j \neq i} A_{ij} P_j \tag{2}
\]

\( E_0 \) and \( k \) are the amplitude and wave vector of the incident wave, respectively, and the interaction matrix \( A \) has the following form:

\[
A_{ij} P_j = \frac{\exp(ik_r r_i)}{r_i^3} \left\{ k^2 r_j \times (r_j \times P_j) + \frac{(1-ik_r r_j)}{r_j^2} \times \left[ r_i \times P_j - 3r_j (r_j \cdot P_j) \right] \right\} \quad (j \neq i) \tag{3}
\]

where \( k = \omega/c \) and \( r_{ij} = r_i - r_j \). [2-5] The diagonal elements \( (i=j) \) of the matrix \( A \) are equal to the inverse polarizability of the \( j \)th dipole. [2,5]

If the system of interest consists of many metal particles on top of a flat substrate, \( E_{\text{loc},i} \) will have additional contributions, including a field \( E_{\text{ref},i} \) arising from reflection of the incident field from the substrate, a field \( E_{\text{others},i} \) due to fields from dipoles on other particles (the interparticle interaction) and a field \( E_{\text{sub},i} \) from the reflection of dipole radiation due to all the particles from the substrate (the substrate effect). So in more general case the local field is

\[
E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{ref},i} + E_{\text{self},i} + E_{\text{others},i} + E_{\text{sub},i} \tag{4}
\]

where

\[
E_{\text{ref},i} = F_{\|,i} E_0 \exp(k_r r_i), \tag{5}
\]
\[
E_{\text{others},i} = - \sum_j A_{ij} \cdot P_j
\]
\[
E_{\text{sub},i} = - \sum_j A_{ij} \cdot P_j
\]

In eq. 5, the field \(E_{\text{ref},i}\) includes the Fresnel coefficient \(F\) for either parallel or perpendicular polarization and the wave vector of the reflected field is denoted \(k'\).

Also note that the fourth term in eq. 4 includes the contribution of other particles, i.e. sums over all dipoles except those on the same particle as \(i\), while the last term, the substrate effect, includes contribution from all dipoles including \(i\). For both these terms, the interaction matrix is given by eq. 3. The polarization \(P_j\) appearing in the substrate term is obtained from \(P_j\) using the image model formulas:

\[
P_{||,j} = \frac{\varepsilon_{\text{subs}} - 1}{\varepsilon_{\text{subs}} + 1} P_{||,j}
\]
\[
P_{\perp,j} = \frac{\varepsilon_{\text{subs}} - 1}{\varepsilon_{\text{subs}} + 1} P_{\perp,j}
\]

where \(\parallel\) and \(\perp\) refer to the parallel and perpendicular components relative to the surface of the substrate and \(\varepsilon_{\text{subs}}\) is the substrate dielectric constant. [4,7]

Substituting eqs. (4) or (5) into eq. (1) and rearranging terms in the equation, we generate an equation of the form

\[
A' \cdot P = E
\]

where \(A'\) is a matrix which is built out of the matrix \(A\) from eq. (3). For a system with a total of \(N\) dipoles, \(E\) and \(P\) in eq. (8) are \(3N\)-dimensional vectors, and \(A'\) is a \(3Nx3N\) matrix. By solving these \(3N\) complex linear equations, polarizations, local fields and Raman enhancements can be calculated. [2-5]

DDA can also describe clusters and periodic arrays of identical particles, either by locating dipoles on all the particles and letting them interact or by having
dipoles on only one particle, and using the approximation for the induced polarization of dipoles in the other particles:

$$P(r_\alpha) = P_0 \exp(i k r_\alpha)$$  \hspace{1cm} (9)

where $P_0$ is the polarization of each dipole in the particle at the origin, and $r_\alpha$ an integer multiple of the lattice vector that locates the $\alpha^{th}$ particle. This approximation requires that interactions between dipoles on the same particles be larger than between dipoles of different particles. [4]

### 1.2 Properties of DDA

As discussed above using DDA the polarization $P$, the extinction and absorption cross sections and the electromagnetic field enhancement factor can be calculated.

Extinction and absorption cross-sections:

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{inc,j}^* P_j)$$  \hspace{1cm} (10)

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \left\{ \text{Im}(P_j (\alpha_j^{-1})^* P_j^*) - \frac{2}{3} k^3 |P_j|^2 \right\}$$  \hspace{1cm} (11)

The scattering cross section is equal to $C_{ext} - C_{abs}$. [2,4-5] The absorption cross section in obtained by summing over the rate of energy dissipation by each of the dipoles. [2]

Also the extinction efficiency can be obtained as it is the ratio of the extinction cross section to effective particle area where the effective area is defined as the area of a sphere with the same volume as the particle. [3,4]

The electromagnetic field enhancement factor $F(\omega)$ is determined by averaging the square of $E_{loc,i}(\omega)$ over the exposed surfaces, and normalizing by the incident field,
\[ F(\omega) = \frac{\langle |E_{loc}(\omega)|^2 \rangle}{E_0^2} \]  

An expression for the SERS enhancement factor involves multiplying field enhancement factors for the incident and Stokes shifted frequencies, \( \omega \) and \( \omega' \)

\[ R(\omega, \omega') = F(\omega)F(\omega') \]  

It is only an approximation to the true Raman enhancement factor (valid in the limit that particle size is small compared to the wavelength \( \lambda \)), but it is adequate for these problems. [4]

2. DDA Algorithm

In the previous section, the theory of the discrete dipole approximation was explained. To solve the system of 3N complex linear equations (eq. (8)) for the induced polarizations, Draine and Flatau [9] developed an algorithm that performs the sum over dipole fields in eq. (2) using fast Fourier transform methods and solves eq. (8) by complex conjugate gradient methods. This facilitates the treatment of targets of a very large number of dipoles (>10⁴). The polarizability of each dipole is assumed to follow the lattice dispersion relation (LDR) proposed by Draine and Goodman [8]. They derive the dispersion relation for electromagnetic waves propagating on a lattice of polarizable points. Then, from this dispersion relation, they obtain a prescription for choosing dipole polarizabilities so that an infinite lattice with finite lattice spacing will mimic a continuum with dielectric constant \( \varepsilon(\omega) \). These polarizabilities are related to the dielectric constant \( \varepsilon \) of the particle by eq. 26. [8]

This expression forces the optical response of a dipole lattice for an infinite solid to match that of bulk material once the calculation has converged with respect to the dipole density. [3,4,10]

3. The DDSCAT Scattering Algorithm

The DDSCAT algorithm was developed by B. T. Draine and P. J. Flatau to carry out calculations of scattering and absorption of electromagnetic waves by
targets with arbitrary geometries using the discrete dipole approximation (DDA). The DDSCAT code is publicly available [11,12]. The code allows accurate calculations of electromagnetic scattering from targets with "size parameters" $2\pi\alpha_{\text{eff}} / \lambda < 15$ provided the refractive index $m$ is not large compared to unity ($|m-1| < 2$). (The size parameter is explained in paragraph 3.3) Target materials may be both inhomogeneous and anisotropic. [12]

3.1 What does it calculate?

DDSCAT solves the problem of scattering and absorption by an array of polarizable point dipoles interacting with a monochromatic plane wave incident from infinity. The code has the capability of automatically generating dipole array representations for various target geometries and can also accept dipole array representations of targets supplied by the user. The incident plane wave can have arbitrary elliptical polarization and the target can be arbitrarily oriented to the incident radiation.

The following quantities are calculated:

- Absorption efficiency factor $Q_{\text{abs}} \equiv C_{\text{abs}} / \pi\alpha_{\text{eff}}^2$, where $C_{\text{abs}}$ is the absorption cross section;
- Scattering efficiency factor $Q_{\text{sca}} \equiv C_{\text{sca}} / \pi\alpha_{\text{eff}}^2$, where $C_{\text{sca}}$ is the scattering cross section;
- Extinction efficiency factor $Q_{\text{ext}} \equiv Q_{\text{sca}} + Q_{\text{abs}}$;
- Phase lag efficiency factor $Q_{\text{pha}}$, defined so that the phase-lag (in radians) of a plane wave after propagating a distance $L$ is just $nLQ_{\text{pha}}/2\alpha_{\text{eff}}^2$, where
- The 4x4 Mueller scattering intensity matrix $S_{ij}$ describing the complete scattering properties of the target for scattering directions specified by the user.

DDSCAT also calculates the radiation force efficiency factor $Q_{\text{rad}}$, and the radiation torque efficiency factor $Q_{\Gamma}$ but these are irrelevant to the current project. [12]

Definitions of absorption, scattering, extinction and phase-lag cross sections are given by Draine [2] and C F Bohren, D R Huffman [13]. Consider $W_s$ to be the rate at which energy is scattered across the surface $A$, $W_a$ to be the rate at which energy is absorbed by the particle and $W_{\text{ext}}$ to be the sum of the energy absorption rate
and the energy scattering rate \( W_{\text{ext}} = W_a + W_s \). The ratio of \( W_{\text{ext}} \) to \( I_i \), the incident irradiance, is a quantity with dimensions of area and is called extinction cross section \( C_{\text{ext}} = W_{\text{ext}} / I_i \). The same stands for absorption and scattering. The efficiencies (or efficiency factors) are the dimensionless cross sections. The extinction efficiency is \( Q_{\text{ext}} = C_{\text{ext}} / G \) where \( G \) is the particle cross-sectional area projected onto a plane perpendicular to the incident beam. \( G = \pi a_{\text{eff}}^2 \) [13] The efficiencies computed by the algorithm are actually the ratios of the cross-sections for the target geometry to the geometrical cross-sections of the equal-volume spheres, \( \pi a_{\text{eff}}^2 \), and when requested averaged over two polarizations, which is convenient for comparing the optical properties of particles of different shapes. [14]

### 3.2 Application to targets in dielectric media

The materials of the targets used for the calculations are characterized by a complex refractive index (\( n \)) or a complex dielectric functions (\( \varepsilon \)). The refractive index depends on the material and the wavelength of the incident radiation. The complex index of refraction (\( m = n - i k \)), is the material property of a dielectric that determines its radiative properties. [15] The complex dielectric constant \( \varepsilon \) for such a material is \( \varepsilon = \varepsilon_1 + i \varepsilon_2 \) where the dielectric constants are related to the optical constants by:

\[
\varepsilon_1 = n^2 - k^2 \quad \quad \quad \quad \varepsilon_2 = 2nk
\]

The optical constants can be obtained from the dielectric constants using the following equations: [16]

\[
n = \sqrt{\frac{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} + \varepsilon_1}{2}} \quad \quad \quad k = \sqrt{\frac{\left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2} - \varepsilon_1}{2}}
\]

In many applications, the target is essentially in vacuum. However, sometimes the "target" body is embedded in a nonabsorbing dielectric medium (a purely real dielectric constant) \( \varepsilon_{\text{med}}(\omega) \) or a real refractive index \( m_{\text{med}}(\omega) = \sqrt{\varepsilon_{\text{med}}(\omega)} \). The DDSCAT algorithm is fully applicable to these scattering problems, as long as: [10,12]
- The "dielectric function" or "refractive index" supplied to DDSCAT should be the *relative* dielectric function

\[ \varepsilon(\omega) = \frac{\varepsilon_{\text{target}}(\omega)}{\varepsilon_{\text{medium}}(\omega)} \]  

(14)

Or relative refractive index:

\[ m(\omega) = \frac{m_{\text{target}}(\omega)}{m_{\text{medium}}(\omega)} \]  

(15)

- The wavelength \( \lambda \) specified should be the wavelength *in the medium*:

\[ \hat{\lambda} = \frac{\lambda_{\text{vac}}}{m_{\text{medium}}} \]  

(16)

### 3.3 Applicability and validity criteria of DDA

The principal advantage of the DDA approach is that it is completely flexible regarding the geometry of the target, being limited only by the need to use an interdipole separation \( d \) small compared to (i) any structural lengths in the target and (ii) the wavelength \( \lambda \). As noted from the authors, \( d \) should follow the criterion \( d \leq 8 \) nanometers [17]. Numerical studies [1,8,18] indicate that the second criterion(ii) is adequately satisfied if

\[ |m|kd < 1 \]  

(17)

where \( m \) is the complex refractive index of the target material, and \( k \equiv 2\pi / \lambda \), where \( \lambda \) is the wavelength in vacuum.

Let \( V \) be the target volume. If the target is represented by an array of \( N \) dipoles, located on a cubic lattice with lattice spacing \( d \), then

\[ V = Nd^3 \]  

(18)
N must be as large as feasible, in order that the dipole array accurately mimics the target geometry [18] and thus diminish the inaccuracy originating from the surface granularity resulting from approximating arbitrary surfaces with discrete dipoles. [2,14] It is common to specify the size of particles of an arbitrary shape and volume V by an "effective radius", which is the radius of a sphere having an equal volume to that of the particle: [14]

\[
\alpha_{\text{eff}} \equiv \left( \frac{3V}{4\pi} \right)^{1/3} = \left( \frac{3N}{4\pi} \right)^{1/3} \quad d
\]

A given scattering problem is characterized by the dimensionless "size parameter":

\[
x \equiv k\alpha_{\text{eff}} = \frac{2\pi\alpha_{\text{eff}}}{\lambda}
\]

The size parameter can be related to N and |m|kd:

\[
x = \frac{2\pi\alpha_{\text{eff}}}{\lambda} = \frac{62.04 \left( \frac{N}{10^6} \right)^{1/3}}{|m|kd}
\]

Equivalently, the target size can be written as:

\[
a_{\text{eff}} = 9.873 \frac{\lambda}{|m|} \left( \frac{N}{10^6} \right)^{1/3} |m|kd
\]

For calculations of the total cross sections $C_{\text{abs}}$ and $C_{\text{sca}}$, is required $|m|kd < 1$ or:

\[
a_{\text{eff}} < 9.88 \frac{\lambda}{|m|} \left( \frac{N}{10^6} \right)^{1/3} \quad \text{or} \quad x < \frac{62.04 \left( \frac{N}{10^6} \right)^{1/3}}{|m|kd}
\]

From eq. 23 it is clear that the DDA is not suitable for very large values of the size parameter x, or very large values of the refractive index m. [12] For smaller values of |m-1| the accuracy for a given N and |m|kd is generally better. [18] With the present code, good accuracy can be achieved for |m-1|<2. [12]
3.4 Dipole polarizabilities

Since the intention of the algorithm is for the dipole array to mimic a continuum material of dielectric constant $\varepsilon$, a natural way to specify the polarizabilities $\alpha$ is to require that an infinite number of lattice points have the same dispersion relation, $k(\omega)$, as the continuum material they are intended to mimic. Using the "lattice dispersion relation" (LDR) approach, Draine and Goodman [8] obtained a prescription for assigning dipole polarizabilities. [18] Recently, Gutkowicz-Krusin & Draine [20] corrected an error in the analysis of Draine & Goodman. [8] The polarizability in ref. 20 differs somewhat from that of ref. 8 but the differences in calculated scattering cross sections are relatively small. [12]

3.4.1 Lattice dispersion relation (LDR)

The continuum medium is characterized by its complex dielectric function $\varepsilon$, or its refractive index $m = \varepsilon^{1/2}$. In the limit $k_0d \to 0$, the dipole polarizabilities $\alpha_i$ must be given by the "Clausius-Mossotti" polarizability function

\[
a_i^{(0)} = \frac{3d^3}{4\pi} \left( \frac{m_i - 1}{m_i + 2} \right)
\]

where $m_i$ is the refractive index at lattice side $i$. Draine [2] showed that when $k_0d$ was finite the polarizabilities $\alpha_i$ should include a radiative-reaction correction:

\[
a_i = \frac{a_i^{(nr)}}{1 - (2/3)i \left( a_i^{(nr)} / d^3 \right) (k_0d)^3}
\]

where the "nonradiative" polarizability $a_i^{(nr)}$ is the polarizability in the absence of the radiative reaction correction. Draine and Goodman [8] studied electromagnetic wave propagation on an infinite lattice. They required that the lattice reproduce the dispersion relation of a continuum medium. The lattice dispersion relation may be found analytically; in the long-wavelength limit $kd << 1$, the polarization is given as a series expansion in powers of $kd$ and $m^2 = \varepsilon$: 

35
\[ a^{LDR} \approx \frac{a^{(0)}}{1 + \left( \frac{a^{(0)}}{d^3} \right) \left[ \left( b_1 + m^2 b_2 + m^2 b_3 S \right) (kd)^2 - \left( \frac{2}{3} i (kd)^3 \right) \right]} \]  

(26)

\[ b_1 = -1.891531 \quad b_2 = 0.1648469 \]

\[ b_3 = -1.7700004 \quad S = \sum_{j=1}^{3} \left( \hat{a}_j \hat{e}_j \right)^2 \]

where \( \hat{a} \) and \( \hat{e} \) are unit vectors defining the incident direction and the polarization state. The LDR prescription appears to be best for \( |m| kd < 1 \). [8,9,19] Also, the LDR ensures that in the limit of an infinite number of dipoles the correct Maxwell solution will be obtained. [7]

3.5 Solution method

3.5.1 Complex-conjugate gradient method

Rather than direct methods for solving eq. 8, CCG methods proved to be more effective and efficient for finding \( \mathbf{P} \) iteratively. As \( \mathbf{P} \) has 3N unknown elements, CCG methods in general converge in 3N iterations. When N is large, these methods are much faster than are direct methods for finding \( \mathbf{P} \). The fact that CCG methods in practice converge relatively rapidly is presumably a consequence of the basic symmetries of \( \mathbf{A} \). [9]

Beginning from an initial guess \( \mathbf{p}_0 \), the CCG method generates a sequence \( \mathbf{p}_n \) (n=1,2,...) that converges monotonically to the exact solution for n→3N and may yield an excellent approximation in far fewer than 3N iterations. The CCG method does not require the actual components of \( \mathbf{A} \) but only matrix-vectors of the form \( \mathbf{A} \mathbf{X} \) and \( \mathbf{A}^\dagger \mathbf{X} \), where \( ^\dagger \) signifies the Hermitian conjugate. The matrix \( \mathbf{A}^\dagger \) is independent of the direction of \( \mathbf{k} \) and of polarization of \( \mathbf{E}_{\text{inc}} \) and does not change between CCG iterations but is computed only once for each \( \mathbf{k} \). The iteration number \( n \) is an increasing function of both \( |\varepsilon-1| \) and \( x \). However, it does not appear to depend significantly on \( N \) as noted by Goodman, Draine and Flatau. [21]
The accuracy to which an estimate $p^{(n)}_j$ is a solution to equation 27 (obtained from eq. 1 and 2) may be measured by the tolerance error $h$, the rms residual in eq. 27 per occupied site divided by $|E_0|$. 

\[
(a_n)^{-1} p_j + \sum_{j \neq i} A_{ji} P_j = E_{inc,i}
\]  

(27)

\[
\left| A^+ A P - A^+ E \right| < h
\]

(28)

where $A^+$ is the Hermitian conjugate of $A$, and $h$ is the error tolerance. Typically $h$ is taken to be equal to $10^{-5}$ in order to satisfy eq. 8. [12, 18, 21]

### 3.5.2 Fast Fourier Transforms

The fast Fourier transform can be used to evaluate the matrix-vectors multiplications of the form $A.X$ if the dipoles are located on a cubic lattice:

\[ i = (i_x, i_y, i_z), r_i = (i_x d, i_y d, i_z d) + r_0 \]

where $i_x \in \{1, 2, \ldots, N_x\}, i_y \in \{1, 2, \ldots, N_y\}$ e.t.c.; $N_x$, $N_y$, $N_z$ is the number of lattice sites in a rectangular volume containing the $N$ occupied sites. If $N_x$, $N_y$ and $N_z$ are highly factorizable, the Fourier transforms require $O(N L \ln NL)$ operations; thus $A.X$ can be evaluated in $O(N L \ln NL)$ rather than $O(N^2)$ operations that are required for general matrix-vector multiplication. [9, 21]

Goodman, Draine and Flatau [21] note the following points:

- The use of FFT is not limited to homogeneous solids, since the $A_{ij}$ do not depend on the potentially position-dependent polarizabilities $\alpha_i$.
- The method is not limited to brick-shaped solids: an arbitrarily shape can be represented by zeroing the polarizations at lattice sites that lie outside its boundary before evaluating $P$.
- Evaluation of $A.X$ by FFT's is formally exact and is probably less sensitive to round-off errors than direct evaluation because it requires fewer operations per lattice site.
- Since $A$ is symmetric, the product $A^+.X = (A.X^*)^*$.
Most of the computational time is spent until the solution vector $\mathbf{P}$ satisfies eq. 8 to the required accuracy. The time spent per iteration scales approximately as $N_L$. For a given scattering problem, the number of iterations required is essentially independent of $N_L$, so the overall CPU time per scattering problem scales approximately linearly with $N_L$.[18]

3.6 Target orientation

Consider a "Lab Frame" where the incident radiation is always assumed to propagate in the $+x$ direction. The incident polarization state $\hat{e}_{0i}$ is specified to be along the $y$ axis. DDSCAT automatically constructs a second polarization state $\hat{e}_{02} = \hat{x} \times \hat{e}_{0i}$ orthogonal to $\hat{e}_{0i}$ (meaning it would be along the $z$ axis). The target is assumed to have two vectors $\hat{a}_1$ and $\hat{a}_2$ embedded in it (where $\hat{a}_2$ is orthogonal to $\hat{a}_1$). The target orientation in the Lab Frame is set by three angles: $\beta$, $\Theta$, and $\Phi$.

![Figure 3.2: Target orientation in the Lab Frame][12]
Θ and Φ specify the direction of \( \hat{a}_i \) in the Lab Frame. Θ is the angle between \( \hat{a}_i \) and \( \hat{x} \). When Φ=0, \( \hat{a}_i \) will lie in the \( \hat{x}, \hat{y} \) plane. When Φ is nonzero, it will refer to the rotation of \( \hat{a}_i \) around \( \hat{x} \). The target is assumed to be rotated around \( \hat{a}_i \) by an angle β.

Figure 3.3: Array of N=61432 dipoles representing a regular tetrahedron. It is oriented at an angle Θ=30° relative to the x axis. [18]

In the input file only the length/d (d=interdipole spacing) of one edge is defined meaning the z-direction of the tetrahedron. For most of the examples in this thesis, one face of the tetrahedron is parallel to y,z plane, the opposite "vertex" is in +x direction, and one edge is parallel to z axis. Target axes \( \hat{a}_1 = (1,0,0) \) [emerging from one vertex] is in the x-y plane (Φ=0°) at an angle Θ=0° from the x axis (i.e. along the x axis), while \( \hat{a}_2 = (0,1,0) \) [emerging from an edge] is also in the x-y plane at β=0° (i.e. along the y axis). The incident radiation is propagating in the x direction. [12,18]
3.7 Scattering directions

DDSCAT calculates scattering in selected directions. These directions are specified through angles $\theta_s$ and $\phi_s$. The scattering angle $\theta_s$ is simply the angle between the incident beam (along the $\hat{x}$ direction) and the scattered beam ($\theta_s = 0$ for forward scattering, $\theta_s = 180^\circ$ for backscattering). The scattering angle $\phi_s$ specifies the orientation of the "scattering plane" relative to the $\hat{x}, \hat{y}$ plane in the Lab Frame. When $\phi_s = 0$ the scattering plane is assumed to coincide with the $\hat{x}, \hat{y}$ plane. When $\phi_s = 90^\circ$ the scattering plane is assumed to coincide with the $\hat{x}, \hat{z}$ plane. Within the scattering plane the scattering directions are specified by $0 \leq \theta_s \leq 180^\circ$. The only limitation (due to computational limits) is that the number of scattering directions not exceeds the number 1000. [12]

References:


Chapter 4: Validation and Effects of Nanoparticle Characteristics

1. Introduction

The DDSCAT algorithm provides a convenient tool for calculating the SERS properties of nanoparticles. Before embarking in the investigation of novel particles, the algorithm was tested against known nanosurfaces. There are several articles in the literature [1-3] that provide theoretical and experimental results which can be used as standards to validate this technique. Most refer to silver particles of various shapes. In this chapter, the general properties and results of the surface plasmon resonance regime, as calculated by the DDSCAT algorithm, are presented and compared to similar findings from various references. Further, tests of how a substrate (with varied dimension of thickness) of a certain material can affect the surface plasmon resonance peak value are implemented and demonstrated.

2. Electrodynamics of Metal Nanoparticles

The wavelength corresponding to the extinction maximum, $\lambda_{\text{max}}$, of the localized surface plasmon resonance (LSPR) is highly dependent on the size, shape, interparticle spacing, and wavelength-dependent dielectric constants of the material from which the nanoparticles are composed. In addition the $\lambda_{\text{max}}$ of the LSPR is dependent on the dielectric properties of the local environment that surrounds the particles and the substrate on which the particles are supported. [3]

2.1 Effect of particle size

The first test was to calculate the extinction spectra of silver spheres with varying radii (40-100nm) and compare with bibliographic data [1], which presents Mie theory results and DDA calculations. The dielectric constants used for the calculations were obtained from Palik [4], and the particles are assumed to be in vacuum. The number of dipoles used was $N_x=32768$ (ellipse with $x/d=y/d=z/d=32$ dipoles where $d$ is the interdipole spacing) and the effective radius, $a_{\text{eff}}$ is equivalent with the particle radius.
The results obtained agree with the references, which examine the dipole plasmon resonance for silver particles. As the particle radius increases the plasmon resonance is red-shifted and broadened. Moreover, a quadrupole resonance starts to appear at the particle radius of 80nm. However, its contribution is overwhelmed by the dipole resonance until the latter is shifted significantly to the red. The quadrupole resonance also red-shifts as the particle radius increase, but the effect is much smaller than for the dipole resonance. Note that for particles with radius 80nm and higher, the quadrupole resonance is more intense than the dipole resonance. [1]

2.2 Effect of particle shape

Particle shape plays an important role in determining the plasmon resonance spectrum of a silver particle. The extinction efficiency was examined for silver nanoparticles with shapes of sphere, cube and tetrahedron all with the same effective radius equal to \( a_{\text{eff}} = 50 \text{nm} \). This corresponds to a sphere with radius 50nm, a cube with side length \( \sim 80 \text{nm} \), and a tetrahedron with side length \( \sim 164 \text{nm} \). The number of dipoles used were \( N_s = 17256 \) (ellipse with \( x/d = y/d = z/d = 32 \)) dipoles for the sphere,
Ns=32768 (rectgl with x/d=y/d=z/d=32) dipoles for the cube and Ns=3850 (tetrah with x/d=25, y/d=27, z/d=32) dipoles for the tetrahedron. The dielectric constants used for the calculations were obtained from Palik [4], and the particles were assumed to be in vacuum.

![Graph showing extinction efficiency for different shapes](image)

Figure 4.2: Shape dependence of extinction efficiency for silver nanoparticles. The shapes considered are sphere, cube and tetrahedron with all the same effective radius.

As illustrated in figure 4.2, the extinction efficiency is shape-dependent as also mentioned in chapter 2. The spectrum of the tetrahedron has the longest plasmon resonance maximum wavelength at 583nm, while the spectrum of the sphere gives the shortest at $\lambda_{\text{max}}=405$nm. The efficiency factor of the cube is the largest, approximately 9.4, followed by the tetrahedron with $\sim 8.2$ and, last, the sphere with $\sim 6.85$. It is also observed that the spectrum of the tetrahedron appears and a quadrupole peak at 408nm. These results agree with the bibliography. [6]

2.2.1 Truncated tetrahedrons

A particle of particular interest is the truncated tetrahedron. This shape is defined by slicing off one tip from a regular tetrahedron in such a way that the plane of the slice is parallel to the plane associated with the opposite face of the tetrahedron.
This shape approximately describes particles which have been made in recent nanosphere lithography experiments. The dimensions of the truncated tetrahedron are described using the length $\alpha$ of the perpendicular bisector of the opposite face and the distance $b$ between the two parallel planes. \[1-2\]

![Figure 4.3: A schematic representation of truncated tetrahedron [2]](image)

DDA calculations for a sphere with a 30nm radius and for a truncated tetrahedron with a height $b$ of 45nm and a perpendicular bisector $a$ of 85nm were executed (same as the particle in ref. 1). This gives a particle volume that is the same as that for the sphere of 30nm radius and, therefore, the effective radius of the two is the same. The field polarization was taken to be along the y-axis (perpendicular bisector). The number of dipoles used $N_{t}=11402$ (tetrah with $x/d=21$, $y/d=40$ and $z/d=46$ dipoles) for the tetrahedron and $N_{s}=32768$ ($x/d=y/d=z/d=32$ dipoles) for the sphere. The shape of a truncated tetrahedron is structured with a data file of a tetrahedron and removing a number of dipoles in $x/d$ location to obtain a comparable height as that of the real particle (see also the example in appendix). The results obtained using dielectric constants from Palik [4], and assuming that the truncated tetrahedron is in vacuum.
In ref. 1 the authors observed that the plasmon resonance of the truncated tetrahedron is significantly more red-shifted than a corresponding 2:1 oblate spheroid. They also note that the plasmon resonance profile is somewhat more complicated than for the oblate spheroid with a slightly broader width, and a more noticeable quadrupole resonance peak. The same effects are observed in figure 4.4. Other effects noted include that decreasing the particle height causes a red-shift to the plasmon resonance wavelength. Also, if the in-plane shape changes from triangular to circular the SPR maximum wavelength shifts to the blue. [5]

2.2.1.1 Polarization dependence

Figure 4.5 shows the electric field polarization dependence of the calculated extinction spectrum of a single isolated truncated tetrahedron. The nanoparticle has dimensions of \( \alpha = 120\text{nm} \) (perpendicular bisector) and \( b = 46\text{nm} \) (height). The results obtained using dielectric constants from Palik [4], and assuming that the truncated tetrahedron is in vacuum. Note that there is a small difference in the extinction spectra corresponding to y- and z-polarized light. That is because the size and shape of the particle along its y- and z- axes are very similar. A blue-shift is
observed for x-polarization compared to y- and z-polarizations. Since the incident beam propagates along the x-axis, the major components of the polarization vectors will lie in the y-z plane. The x-polarization can be omitted and an average of y- and z-polarizations be used.

Figure 4.5: Polarization dependence of the extinction efficiency for the same particle calculated using 10234 dipoles. $\lambda_{\text{max(yz-pol)}}=577\text{nm}$ [2]

DDA calculation were obtained for a similar truncated tetrahedron having a width $a=120\text{nm}$, and a height $b=46\text{nm}$, with averaged y-z polarization. The number of dipoles used $N_{tt}=10330$ (tetrah with x/d=16, y/d=40, and z/d=47 dipoles) and the dielectric constant of silver is taken from ref. 4. The particle is assumed to be in vacuum. The effective radius, $a_{\text{eff}}$, is calculated to be equal to 38nm. An example of the calculations of the effective radius, $a_{\text{eff}}$ of the truncated tetrahedron is given in appendix.
Figure 4.6: Extinction efficiency versus wavelength for a truncated tetrahedron with a width equals to 120nm and a height= 46nm.

The result is equivalent to that from the ref. 2 with a slide difference in the maximum SPR peak value. Here, \( \lambda_{\text{max}}(yz\text{-pol})=565\text{nm} \) as opposed to 577nm but the efficiency factor is the same. This slide variation in the maximum SPR wavelength is due slightly different shapes used.

2.2.1.2 Dielectric constant dependence

One limitation of the computational electrodynamics methods is that the results are only as good as the dielectric constants (for the particle) used. Ideally one would be able to calculate such information directly from electronic structure calculations, but in reality this is not practical for metals like silver and gold so the information is derived from experimental data that is obtained for bulk metal. The use of bulk dielectric constants for nanoparticle calculations is appropriate for particles that are large enough (larger than the conduction electron mean free path), such as particles having radii greater than \( \geq 20\text{nm} \) [6]
The authors in ref. 2 examine the effect of dielectric constant on the calculated extinction spectrum for three different sets of values from the literature: those of (1) Palik, (2) Hagemann, Gudat, and Kunz, and (3) Johnson and Christy.

Figure 4.7 shows the calculated extinction spectrum of a single truncated tetrahedron for the three different sets of values of the dielectric constant for bulk silver. The differences in the extinction spectra based on the choice of $\varepsilon_{Ag}$ are very significant. The maximum calculated SPR wavelength for the data from Johnson and Christy is $\lambda_{\text{max}} = 550$nm, for the data from Hagemann, Gudat and Kunz is $\lambda_{\text{max}} = 548$nm, while the value from Palik is $\lambda_{\text{max}} = 574$nm. The most commonly used dielectric constants are from Palik because the values in the wavelength region of interest represent measurements obtained in an ultrahigh vacuum environment, and are considered to be more reliable. [2]

2.2.1.3 Interparticle distance $d_{\text{tt}}$ dependence

Until now, only dipole interactions for a particle are considered. For an array of particles the particle-particle interaction between two truncated tetrahedrons should be examined. Ref. 2 shows that the maximum wavelength of the SPR shifts to the red
as the particles are brought closer together. When the particles are separated by \( d_{it} = 100 \text{nm} \) and larger the interaction between two particles causes only a very small red-shifting in the peak of the extinction spectrum. Thus, particles in an array that have interparticle separation larger than 100nm are influenced only to a small degree by their neighbors and for simplicity can be treated as though they were an array of individual, isolated particles. [2] This is the case of the structures of interest in this thesis.

### 2.2.2 Non-truncated tetrahedrons

#### 2.2.2.1 Polarization and rotation dependence

Additional simulations were performed for a silver, non-truncated, tetrahedrons with \( a=150 \text{nm} \) side length, with different polarizations and different orientations relative to the incident beam. The incident electromagnetic wave was propagating along the +x-axis and the particle was assumed to be in vacuum. The dielectric constant used for the calculation was obtained from ref. 4. The number of dipoles used were \( N_i=3850 \), \( x/d=25 \), \( y/d=26 \) and \( z/d=32 \) dipoles). The effect of rotation of the particle (angle theta) with respect to polarization, was also examined. The particle is as shown in figure 4.8.

![Figure 4.8 The tetrahedron with (A) theta=0 and (B) theta=90 relative to the incident beam (k)](image)
Figure 4.9: Extinction efficiency versus wavelength for a silver tetrahedron with $a=150\,\text{nm}$ for polarization $y,z$ and two different orientations of the target. Theta is the angle between $\hat{a}_i$ and $\hat{x}$ (direction of the incident radiation).

It is observed that for $z$-polarization the orientation $\theta=0$ and $\theta=90^\circ$ give exactly the same result, (same maximum wavelength and same bandwidth) while for $y$-polarization the two orientations have the same maximum wavelength but a slightly different maximum value. Also the bandwidth for $\theta=90^\circ$ is smaller compared to that of $\theta=0$. Note that all four situations give the same plasmon resonance wavelength. This can be explained by the fact that the projected area that a plane, perpendicular to the incident wave, sees is almost the same for the cases of $\theta=0$, or $\theta=90^\circ$. Consider the spectra of $\theta=0$ and $\theta=90^\circ$ for polarization along the $y$-axis. In the first case the polarization lies along the perpendicular bisector of the base of the tetrahedron. For the second situation the polarization lies along the height of the tetrahedron, which is larger compared to the width. So, the projected areas onto the plane are different, with the second be larger from the first one, giving a smaller efficiency factor. In the case of the $z$-polarization, both for $\theta=0$ and $\theta=90^\circ$ the area projected onto the plane is the same, so the same extinction efficiency factor is obtained.
Now consider the situation of y-polarization and 3 different theta angles for the same particle as above.

Here, the orientations of theta=0 and theta=180° give exactly the same results. For theta=90° there is a small variation as before. The polarization y lies along the perpendicular bisector of the particle, so the particle cross-sectional area projected onto a plane perpendicular to the incident beam is the same for the case of θ=0 and θ=180° while differs slightly for the case of θ=90° due to the fact that the polarization y lies along the height of the tetrahedron. It must be noted that all spectra have the same dipole resonance maximum wavelength.

### 2.2.2.2 DDA convergence

The DDA calculations can generally be made to converge with respect to the bulk properties as the number of point elements used to represent the particle in the electrodynamics calculations increases. Typically this convergence is demonstrated...
by increasing the number of dipoles used to represent the particles until the results are stationary. [1] The following figure shows the calculated extinction spectrum using 682 (z/d=18), 936 (z/d=20), 2578 (z/d=28), 3850 (z/d=32), 7530 (z/d=40), 13024 (z/d=48) and 22986 (z/d=58) dipoles. The particle was assumed to be in vacuum. The dielectric constant used for the calculation was obtained from ref. 4. The polarization is taken to be along the y-axis. Figure 4.11 illustrates the convergence properties of the DDA calculations for a single isolated tetrahedron. The result using about 7530 dipoles represents a satisfactory balance between sufficient convergence of the calculation and practical time constraints involved in the calculation.

Simulations were also performed for the same nanoparticle as above (a silver tetrahedrons with a=150nm side length), for different tolerance error h. (see chapter 3). The particle was assumed to be in vacuum. The dielectric constant used for the calculation was obtained from ref. 4. The polarization is taken to be along the y-axis. The number of dipoles used was Nt=3850. (x/d=25, y/d=26 and z/d=32 dipoles) for all the cases of tolerance.
Figure 4.12: Extinction spectra for a silver tetrahedron with a tolerance error varying.

Figure 4.12 demonstrates the calculated extinction spectra for the silver tetrahedron with side length $a=150\text{nm}$. It is observed that even using an error tolerance of $x10^{-3}$ the DDA algorithm gives accurate results. All estimations in this thesis were calculated using a tolerance error $x10^{-5}$.

2.3 Effect of the substrate

Because nanoparticles are often produced on substructures, it is important to understand how their interaction with the substrate influences their plasmon resonance properties. This adds a new level of complexity to the electromagnetic modeling due to the asymmetric environment. However the DDA method can handle these situations.

2.3.1 Truncated tetrahedron on a substrate

For estimations of the effect of substrate, consider silver truncated tetrahedrons with perpendicular bisector (100nm) and height (25nm). The substrate is approximated to be finite, flat, cylindrical slab. The size of the slab is restricted by the computational resources, but results converge when (1) the slab thickness is larger
than the particle height and (2) the slab width extends past each edge of the silver nanoparticle by approximately the length equivalent to the particle radius. [3, 7] The dipole grid spacing is constant and the same in both the particle and the associated substrate. [5] The effective radius of the truncated tetrahedron is 29.67nm and that of the total system, nanoparticle and substrate, is 60.24nm. The substrate slab is considered to be a part of the target in the DDA calculations. Propagation is along the x-axis and the polarization state is y-z averaged.

Figure 4.13: Schematic diagram of the DDA target. (A) Perspective view. (B) Cross-sectional view. The silver truncated tetrahedron with base perpendicular bisector=100nm and height=25nm, sits on top of a cylindrical slab of substrate, diameter=200nm and height=27nm. The total number of dipoles used to represent the silver nanoparticle is 11218 and the total for the nanoparticle and substrate is 93911. (Particle and slab have the same grid spacing) [3]

Figure 4.14: DDA calculations for the particle with cylindrical slabs of substrate with various dielectric constants. The dielectric constant of the external environment is $n_{ext}=1.0$ (A) No substrate, (B) Fused Silica $n_{sub}=1.46$, (C) Borosilicate glass $n_{sub}=1.52$, (D) Mica $n_{sub}=1.6$, (E) SF-10 $n_{sub}=1.73$, (F) $n_{sub}=1.77$ [3]
Figure 4.14 shows the calculated extinction spectra for single nanoparticles on cylindrical slabs of substrate with substrate refractive indices varying from 1.46 to 1.77. The maximum wavelength shifts to the red from 652nm for $n_{\text{sub}}=1.46$ to 696nm for $n_{\text{sub}}=1.73$. Thus, DDA predicts, for truncated tetrahedrons with aspect ratio of 4:1 in a controlled N$_2$ environment, that the maximum wavelength of the SPR will shift to the red as the refractive index of the substrate is increased. In addition, ref. 6 compares the extinction spectrum of a truncated tetrahedron with an oblate ellipsoid-shaped particle, both on a substrate. The spectrum of the short truncated tetrahedral particle was further red-shifted by the inclusion of substrate interactions than the oblate ellipsoid-shaped particle as it had more direct contact with the substrate.

A simulation was performed to obtain the extinction spectra of the truncated tetrahedron of ref. 3 with mica substrate and without a substrate. The target was the same as that of figure 4.13. The number of dipoles used for the tetrahedron $N_{\text{trun tet}}=10023$ (tetrahedron with $x/d=11$, $y/d=45$ and $z/d=51$) and for the total (particle+substrate) $N_{\text{tot}}=92911$ (cylinder with $x/d=13$, $y/d=90$ and $z/d=90$). Note that the same $d$ (interdipole spacing) was used for both the particle and the substrate. The target was assumed to be in vacuum. The dielectric constant for silver was taken from ref. 4, and for mica from ref. 9. The polarization state was assumed to be the average over the y-z polarization states. The effective radius of the particle was $a_{\text{eff}}=29.67$nm and the total was $a_{\text{eff}}=62.54$nm. More details are given in appendix.
Figure 4.15: Extinction efficiency versus wavelength for a truncated tetrahedron with $\alpha=100\text{nm}$ and $b=25\text{nm}$. The particle is assumed to be on a mica substrate with diameter=200nm and height=27nm.

Although the maximum SPR wavelength occurs at $\lambda_{\text{max}}=685\text{nm}$ which is correct, the extinction efficiency of the target with particle and substrate is significant smaller than that expected. A correction is needed to correct for the fact that the algorithm calculates the extinction coefficient considering a Rayleigh scattering cross-section associated with the slab+particle instead of the cross-section of the particle alone. [8] To rescale the extinction efficiency based on the effective radius of particle and particle+slab targets one can use:

$$Q'_{\text{ext}} = Q_{\text{ext}} \frac{a^2_{\text{eff,slab+particle}}}{a^2_{\text{eff,particle}}}$$

This corrects for the $\lambda^{-4}$ scattering off the slab that can dominate the slab+particle system if the slab is large. Notice that the results obtained after the correction are identical to that for the ref. 3. (Cases A&D of figure 4.14)
Some extra simulations, which illustrate the effects of different shapes and sizes of the substrate, where performed. The material of the substrate remained mica. First, consider the truncated tetrahedron with $a=100\,\text{nm}$, $b=25\,\text{nm}$ dimensions as above but on a rectangular substrate (rcntgl with $x/d=13$, $y/d=80$, and $z/d=78$ dipoles, $N_s=81120$) with the same volume as the cylindrical slab used above, thus the total effective radius of the system is the same as before. Second, consider the same truncated tetrahedron with a rectangular substrate (rcntgl with $x/d=13$, $y/d=58$, and $z/d=57$ dipoles $N_s=42978$) with the same height as the cylindrical but with different $y=z$ dimensions. The total effective radius is equal to $52.172\,\text{nm}$. Third, consider a tetrahedron with $a=175\,\text{nm}$ (side length) (tetrah with $x/d=38$, $y/d=40$, $z/d=48$ dipoles, $N_t=13024$) with a rectangular substrate but with varied height ($z/d=48$, $y/d=40$ and $x/d=1,5,10$, and 15 dipoles, $N_s=1920, 9600, 19200$, and $28800$ respectively). The effective radius of the target was $53.2\,\text{nm}$ while the total $\alpha_{\text{eff}}$ were $55.9\,\text{nm}$, $64.63\,\text{nm}$, $73\,\text{nm}$ and $79.8\,\text{nm}$, respectively. All extinction efficiencies shown below were corrected. The polarization state was taken to be the average over the y-z polarization states for the two first cases, while for the third was taken to be along the y-axis.

![Figure 4.16: Corrected extinction efficiency versus wavelength for a truncated tetrahedron with a mica cylindrical slab.](image-url)
The slab shape and dimension can affect the extinction spectrum. Substrates with the same volume but different shapes give approximately the same maximum SPR wavelength and almost the same spectrum. For a much smaller slab in the $y,z$ dimensions a blue shift occurs as well as a smaller extinction efficiency. Therefore if the substrate is not large enough in the $x,y$ dimensions, errors will occur in $\lambda_{\text{max}}$ and the bandwidth.
Figure 4.18: Extinction efficiency versus wavelength for a tetrahedron with $w=175\text{nm}$ and a mica substrate with $z/d=48$, $y/d=40$ and a varying $x/d=1, 5, 10$ and $15$ dipoles.

Figure 4.18 shows the extinction efficiency versus wavelength for various substrate heights it illustrates that varying the height of the substrate in the simulations results in a different extinction spectrum. The higher the substrate the more red-shift to the $\lambda_{\text{max}}$ occurs and larger maximum extinction efficiency. However, the continuous increase in the slab’s thickness results in a convergence of the extinction spectrum. For $x/d=5$, $10$ and $15$ dipoles the spectra obtained are approximately the same, with only a very small shift of the wavelength that can be consider negligible. The shape of the substrate in the simulations plays an important role in the calculation of the SPR $\lambda_{\text{max}}$, as seen in the examples and simulations. To approximate the effect of real substrates, which can be orders of magnitude thicker than the particles, one must use a sufficient number of dipoles.

2.4 Effect of the surrounding medium

Another important factor in the calculation of the SERS properties of a nanostructured surface is the medium that surrounds the particle. The effect can be easily understood using the plasmon resonance condition for spherical
nanoparticles: Re(ε) + 2ε₀ = 0. The maximum plasmon wavelength depends linearly with the index of refraction of the surrounding solvent. [7]

![Figure 4.19: Effect of the surrounding medium (n is the index of refraction of the medium) on the extinction spectrum of a 50nm silver nanoparticle [5]](image)

The effect of a solvent on the plasmon lineshape is as shown in figure 4.19. [6] It demonstrates an expected red shifting and broadening of the dipole resonance as the refractive index is increased from 1.0 to 2.0. [5] In addition, a quadropole peak appears and becomes more noticeable as the index is increased. [6]

It is interesting to note that nanoparticles have higher sensitivities to the bulk solvent environment (external dielectric medium) than to the substrate because a larger fraction of the surface area is exposed to solvent than to the substrate. [3] As an example, for a truncated tetrahedron with a perpendicular bisector of 100nm and height of 25nm, the surface area exposed to solvent (the three truncated sides plus the top face) is approximated to be 11063nm², while the surface exposed to the substrate is 5774nm². Therefore, the solvent per substrate exposed surface area ratio is nearly 2:1.
3. Efficiency Factors

The extinction efficiency factor depends on the effects of both absorption and scattering. It may be of interest to examine the contribution of each. Consider, as an example, a silver sphere with radius 50nm and compare the calculated absorption, scattering and extinction efficiencies. The nanoparticle is assumed to be in vacuum. The dielectric constant used for the calculations was taken from Johnson and Christy [10] as used by the authors in ref. 11. The number of dipoles taken to be $N_e=64000$ (ellips with $x/d=y/d=z/d=40$) in order to have a good convergence.

![Figure 4.19: Efficiencies versus wavelength for a sphere with r=50nm and dielectric constant taken from ref. 11](image)

The results are in good agreement with the literature. [11] In the spectra, at about 320nm all the efficiencies have a local minimum that corresponds to the wavelength at which the dielectric function of silver, both real and imaginary parts, almost vanishes. Therefore, this feature of the spectra is inherent to the material properties and is independent of the particle geometry. Below 320nm, the absorption of light is mainly due to the intra-band electronic transitions of silver. Also this feature of the spectra is independent of the shape and size of the particles. A peak appears in the spectrum of $Q_{abs}$, at about 350nm that is related to the excitation of the surface plasmon of the sphere, therefore this feature is inherent to the geometry of the
particle, although the position depends on the material properties. At larger wavelengths the spectrum $Q_{\text{abs}}$ has smaller peaks that correspond to plasmon excitations due to higher multipolar charge distributions.

The $Q_{\text{sca}}$ spectrum shows a broad peak with a maximum at about 400nm, which is three times more intense than the maximum of $Q_{\text{abs}}$. The characteristics of the $Q_{\text{sca}}$ spectrum are mainly due to the size of the particle. As the radius of the sphere increases the maximum is less pronounced and decays slowly for $Q_{\text{sca}}$. This means that as the sphere becomes larger it scatters light at longer wavelengths. The extinction efficiency is the sum of absorption and scattering and, for large particles, the scattering overlaps with the higher multipolar characteristics of the absorption. [11]

References:

Appendix

As an example for the calculation of the effective radius, $a_{\text{eff}}$, is given for the particle in ref. 2. Consider a truncated tetrahedron with perpendicular bisector $a=100\text{nm}$ and height $b=25\text{nm}$. The effective radius is calculated with a cylindrical slab, a rectangular slab of substrate and without a substrate.

Useful formulas:

Volume of a rectangular: $V = xyz$

Volume of a cylindrical slab: $V = \pi R^2 h$

Volume of the tetrahedron: $V = \frac{1}{12}\sqrt{2}w^3$ where $w$ is the side length

Volume of a truncated tetrahedron: $V = \frac{1}{12}\sqrt{2}\left(w^3 - w_1^3\right)$

Here the volume of the truncated tetrahedron is the difference between the total volume minus the tetrahedron that is been removed (with side length $w_1$)

Perpendicular bisector-side length relation: $w = \frac{2a}{\sqrt{3}}$ (Pythagorean Theorem)

Height of the tetrahedron: $h = \frac{1}{3}\sqrt{6}a$

Effective radius: $a_{\text{eff}} = \left(\frac{3V_{\text{tot}}}{4\pi}\right)^{1/3} = \left(\frac{3N_{\text{tot}}}{4\pi}\right)^{1/3}d$

Consider a tetrahedron with $x/d=42$, $y/d=45$ and $z/d=51$ dipoles.
The perpendicular bisector is \( \alpha = 100\text{nm} \) so the side length \( w \) is equal to \( w = 115.47\text{nm} \).

Then, the height equals to \( h = 94.28\text{nm} \).

Now to create a truncated tip with a certain height must slice-off. The remained truncated have \( b = 25\text{nm} \). So from the total height abstract the truncated height and the remained is a tetrahedron smaller from the first one with height \( h - b \) and side length \( w_i = \frac{3(h - b)}{\sqrt{6}} \). For this case, \( w_i = 84.85\text{nm} \).

Now, the volume of the truncated can be calculated. Setting the values in the equation, the result is \( V_{\text{trunc,tet}} = 1.0945\times10^{-22}\text{ m}^3 \).

The effective radius for an isolated truncated tetrahedron without a substrate is \( \alpha_{\text{eff}} = 29.67\text{nm} \)

Before continuing with the calculation of the effective radius of a particle with a substrate, the number of dipoles in the \( x, y \) and \( z \) direction must be denoted. Also they have to be in such a way so to represent a truncated tetrahedron.

There is a subroutine, calltarget, in DDSCAT, which generates data files containing dipole representation of various targets. A tetrahedron data file can be generated and then a number of dipoles in the \( x/d \) direction (height of the particle) must cut-off to obtain a truncated-shaped. (\( d \) is the interdipole spacing)

The dimensions of the tetrahedron are \( x = 94.28\text{nm} \) (height), \( y = 100\text{nm} \) (perpendicular bisector) and \( z = 115.47\text{nm} \) (side length). The number of dipoles set to the \( z/d \) equals to 51. The program generates automatically the \( x/d \) and \( y/d \).

So \( z/d = 51 \), \( y/d = 45 \) and \( x/d = 42 \).

Now, the number of dipoles in \( y \) and \( z \) stays the same.

The truncated tetrahedron has a height of 25nm, \( h - b = 69.28\text{nm} \) the height that was removed. What number of dipoles this height corresponds?
\( \frac{x}{d} = 42 \Rightarrow d = 2,245nm \)

\[ \frac{h-b}{d} = \frac{69,28nm}{2,245nm} = 30,8597 \approx 31 \] is the number of dipole that must be removed in the x direction.

So, the truncated tetrahedron has z/d=51, y/d=45 and x/d=11 dipoles \( \Rightarrow N_{tet}=25245 \)

Now, the case of a particle with a substrate is considered.

Let the substrate be a cylindrical slab with diameter=200nm and height of 27nm.

The dipoles used in y/d=z/d=90 and x/d=13 (given by reference 2) \( \Rightarrow N_{sub}=105300 \).

The total number of particle+substrate of dipoles is \( N_{tot}=130545 \).

The volume of the substrate is calculated to be \( V_{cylind.sub}=9.1504E-22 \text{ m}^3 \), thus the total volume is \( V_{tot}=1.0245E-21 \text{ m}^3 \). The effective radius is calculated to be \( \alpha_{eff}=62.54nm \).

References:
Chapter 5: Design of Cubical and Tetrahedral Nanoparticles

1. Introduction

There are several methods for constructing nanosurfaces. The most utilized are (1) Thermal Evaporation Deposition, (2) Electron-Beam Lithography and (3) Nanosphere Lithography. This chapter provides a brief overview of these methods. Using these techniques various shapes of nanoparticles can be fabricated on substrates of different materials. An examination of the extinction efficiency for such nanoparticles is demonstrated and analyzed so as to compare each. Such results can help determine the method of fabrication which could provide the optimal surfaces for SERS. In this chapter, a number of simulations will be presented for nanoparticles from a variety of materials such as gold, nickel and aluminium.

2. Thermal Evaporation Deposition

Of the wide array of techniques available for the production of nanostructures, thermal evaporation is one of the oldest and most inexpensive methods known. [1] Evaporation is a common method for thin film deposition [2]

The thermal evaporation deposition technique consists of two basic processes: a hot source material evaporates and condenses in the form of a thin film on the cold substrate surface and on the vacuum chamber walls. [2,3]. An evaporation system operates in a vacuum. It also includes an energy source that evaporates the material to be deposited. The source material is placed in a crucible, which is radiatively heated by an electric filament and is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the substrate, without colliding with the background gas, where the particles condense back to a solid state. [2]

Surfaces, produced using this method, are characterized as island films consisting of small metal particles. Thermal evaporation is well suited for producing metal films with controlled surface plasmon resonance wavelength characteristics, when the thermal evaporator operates entirely under manual control. [1] The key deposition parameters which must be evaluated are substrate temperature, deposition rate and film thickness. Ranges for these parameters can be chosen to produce surface plasmon resonance wavelength (SPRW) values throughout the visible region of the
electromagnetic spectrum. The spectra obtained and the SPRW are not simple functions of any one of the deposition parameters since a direct correlation between extinction and SPRW is not observed. The SPRW was found to decrease (shift to shorter wavelengths) with increasing substrate temperature and increase (shifts to longer wavelengths) with increasing deposition rate and film thickness.

With this kind of fabrication there is a great disparity in shape and distribution of metallic nanoparticles. [4] Because of the broad distribution in particle size and shape as well as a random arrangement of the particles on the substrate surface, nanostructured surfaces, produced with this technique, exhibit a broad inhomogeneous absorption band. [5] Changing the evaporation metal mass thickness and post annealing can change the overall characteristics of the surface and consequently the position and the full width at half maximum of the plasmon resonance but the process is not very accurate. [4] Therefore, only poor control of surface optical properties is possible. [5] Although metal island films provide good enhancement, their applicability is hindered by the lack of control of the fabrication, inadequate reproducibility of the preparation process, lack of homogeneity and limited durability of the structures. [4-6] Moreover, due to difficulty obtaining the distribution parameters of the nanoparticles, a check of theoretical models is very problematic. [5] For these reasons, the design of such nanostructured surfaces was not further explored in this thesis.

3. Electron-Beam Lithography (EBL)

Arrays of nanoparticles can be fabricated by EBL, using a scanning electron microscope equipped with a lithographic system, which enables the fabrication of highly reproducible patterns with a great variety of geometries and uniformly sized and shaped particles. [7] First, the electron beam is used to etch a nanostructure pattern onto a resist layer, followed by formation the surface and substrate. Two different methods of surface-substrates fabrication exist. [6] Regular fields of nanoparticles can be produced by a lift-off technique. A silver layer is evaporated on the structured resist and the resist is removed afterwards. With this method, the metal between the nanoparticles is completely removed by lift-off and the particles are more similar to silver island films of periodic structures. With the second method, gratings
or crossed gratings are transferred into a silicon wafer with a thermal oxide surface layer by reactive ion etching (RIE). Then, the e-beam resist is removed and finally a silver layer is evaporated. In order to avoid charging up of the sample during the electron beam exposure, electrically conducting substrates must be used which must, also, be optically highly transparent. [5] These methods are demonstrated in figure 5.1

Figure 5.1: Schemes of etching and lift-off methods of substrate fabrication by e-beam lithography on oxidized silicon substrates. [6]

The EBL method offers a great variability in the structural properties by precise control and independent variation of numerous parameters. [6] The two most important parameters, namely particle shape and interparticle distance can be tuned independently, thus the spectral position and width of the extinction band can be tailored. [5] This technique allows good control of the surface plasmon resonance thus providing tuning to almost any desirable wavelength by varying the particle shape, size, and spacing. [4, 7] However, a disadvantage of the method is the high cost and inability of mass production due to inherent low throughput in a serial processing tool. [6]
4. Properties of Cubical Structures

Surfaces, produced by the EBL technique, are usually cubical in shape. So a number of DDA simulations were performed to estimate the extinction efficiency of cubes with different parameters such as the height of the particle, the z, y dimensions or dielectric substrates. The particles were assumed to be either gold, aluminum or nickel.

4.1 Optical properties of silver and gold cubic nanoparticles

First, consider the silver and gold cubic nanoparticles with sides of 83nm. [8] The nanoparticles are assumed to be in vacuum. The dielectric constants are taken from Johnson and Christy [9] as used by the authors in ref. 8. The effective radius is equal to 51.5nm. The number of dipoles is N_c=64000 (x/d=y/d=z/d=40 dipoles). The direction of propagation of the electromagnetic wave is in +x and the polarization is in the y direction.

The results obtained are in good agreement with those in the bibliography. [8] The maximum at 410nm, of the silver spectrum, is due to absorption and corresponds
to dipolar resonance, while at 450nm is due to scattering. Contrary to the rich structure in the spectrum of the silver cube, the spectrum of gold has a very smooth curve of lower extinction efficiency. [8]

It is interesting to also explore the effect of variations in the dielectric constants used. Take the cubic nanoparticle as before, with the same parameters (effective radius, number of dipoles and same polarization) but slightly different dielectric constants. As noted in chapter 4, the results of the algorithm are as good as the dielectric constants used. Variations in the spectra are observed. Using the dielectric constants from Palik [10] the width of the spectrum is different from that of the spectrum of Johnson and Christy [9]. The peak at 550nm is the dipolar plasmon and the peak at 580nm is due to scattering. In the spectrum of Johnson and Christy the two peaks can not be discriminated. So the dielectric constant obtained from Palik is believed to give accurate results.

Figure 5.3: Extinction efficiency versus wavelength for a cubic nanoparticle with sides 83nm and polarization along the y-axis.
4.2 Optical properties of cubical nanoparticles from other materials

The extinction efficiency factor is estimated for cubic-shaped nanoparticles made from materials with different dielectric properties, such as gold, aluminum and nickel. Consider a cube with side lengths x=y=z=100nm and is assumed to be in vacuum. The number of dipoles used N_ε=6859 (x/d=y/d=z/d=19 dipoles). The effective radius is 62.035nm. The dielectric constants for nickel and aluminum are taken from ref. 11, while for gold from ref. 10. The polarization of the incident electromagnetic wave is taken to be an average of the y- and z- polarizations.

![Figure 5.4: Extinction efficiency versus wavelength for rectangle nanoparticles, with side length 100nm, for various materials](image)

It is observed, from the spectra of figure 5.4, that an intense peak exists for the gold nanoparticle at λ=600nm, while the peaks for nickel and aluminum are blue-shifted. Another important observation is that the spectrum of gold gives the highest extinction efficiency factor at the maximum wavelength. Also, the bandwidth of gold is more narrow than for nickel and aluminum.

It is also interesting to illustrate how the extinction efficiency of the same particle as before is affected by a substrate with various materials. The particle is
assumed to be on a substrate of Pyrex glass or silicon. The substrate has dimensions of $x/d=5$, $y/d=29$, $z/d=29$ dipoles. The same $d$ (interdipole spacing) is used both for the particle and the substrate. The total number of dipoles for the target (particle plus substrate) is $N_t=11064$. The effective radius is 72.74nm. The polarization of the incident electromagnetic wave is taken to be an average of the y- and z- polarizations. It must be mentioned that the efficiency factors given for the nanoparticle plus substrate were corrected using the equation provided in chapter 4.

![Ni rectangle with $x=y=z=100$nm](image)

**Figure 5.5: Extinction efficiency versus wavelength for nickel rectangle with side length 100nm on a substrate of (a) glass Pyrex [12] and (b) silicon [13]**

Comparing the spectra for the nickel nanoparticle on a Pyrex glass substrate, and without a substrate, only small variations are observed. A slide shift to the red of the maximum wavelength and a small increase of the extinction efficiency are noticed compared to the spectrum without a substrate. For a silicon substrate, things are different because the dielectric constant is highly wavelength depended and has a real and imaginary part. Thus, it changes the overall optical properties of the target. It appears to have a plasmon resonance at $\lambda=450$nm with an extinction efficiency factor at 6.5, which is much higher than that with a Pyrex glass substrate.
Nanosurfaces fabricated by EBL can take cubical structures of certain dimension (determined by the apparatus used) and can be made using a variety of metals. Here the nanoparticles are assumed to have dimensions of \( y=z=200 \text{nm} \) so the extinction spectrum in the range of 400-900nm has a maximum. We examine such particles made from a variety of materials. First, the particles are considered to be in vacuum. The dielectric constants for nickel and aluminum are taken from ref. 11 and for gold from ref. 10. The number of dipoles used for the dimensions of \( x=100 \text{nm} \) and \( z=y=200 \text{nm} \) is \( N_c=62500 \) (\( x/d=25 \), \( y/d=z/d=50 \) dipoles). The effective radius, for all particles, is equivalent to 98.5nm. The polarization of the incident electromagnetic wave is taken to be an average of the \( y- \) and \( z- \) polarizations for all the simulations.

![Figure 5.6: Extinction efficiency versus wavelength for cubic nanoparticles with dimensions \( y=z=200 \text{nm} \) and \( x=100 \text{nm} \) for differently materials. The nanoparticles assumed to be in vacuum.](image)

The results obtained from the simulations are demonstrated in figure 5.6. The spectrum from gold nanoparticles, as expected, has the most intense extinction efficiency factor (~ 9) at \( \lambda=705 \text{nm} \). Aluminum and nickel result in less efficiency (~ 7 and 6, respectively). The \( \lambda_{\text{max}} \) occurs at 685nm for an aluminum and 785nm for a nickel nanoparticle. The bandwidth of the gold spectrum is the most narrow of the three.
Usually the cubic nanoparticles constructed by the EBL method, are fabricated on a substrate. Suppose the substrate is made of Pyrex glass. The cubic nanoparticle has the same dimensions as before but with a different number of dipoles, \( N_c = 55296 \) \((x/d=24, \ y/d=z/d=48 \) dipoles). The number of dipoles used for the substrate are \( N_s = 16820 \) \((x/d=5, \ y/d=z/d=58 \) dipoles). So, this makes the total number \( N_t = 72116 \) dipoles. The effective radius for the particle is 98.5nm while the total is equivalent to 107.6nm. The polarization of the incident light is taken to be an average of y- and z-polarizations for all the simulations. Also, the extinction efficiencies were corrected.

![Figure 5.7: Extinction efficiency versus wavelength of cubic nanoparticles with dimensions \( y=z=200nm \) and \( x=100nm \) for differently materials. The nanoparticles are on a substrate of Pyrex glass](image)

As illustrated in figure 5.7, the spectrum of gold nanoparticles, as expected, has the most intense extinction efficiency factor (~9.7). Aluminum and nickel result in less efficiency (7.6 and 6.7 respectively). The \( \lambda_{\text{max}} \) of the gold spectrum lies between the \( \lambda_{\text{max}} \) of aluminum and nickel. The bandwidth of gold is the narrowest. A shift is observed in the peak which is most significant for gold, from \( \lambda = 705nm \) to \( \lambda = 787nm \), while the aluminum peak shifts about 30nm and nickel shifts only 15nm. In general, when a substrate contributes to the optical properties of a nanoparticle, a shift of the
plasmon resonance occurs, a broadening of the bandwidth of the spectrum is observed and the extinction efficiency factor is enhanced.

Another question is how the spectrum of extinction efficiency varies when the dimensions of $x, y$ and $z$ are varied independently. Consider a cubical nickel nanoparticle with a constant $x=100\text{nm}$ and varied $y=z$ dimensions. The particle is assumed to be in vacuum. The dielectric constant is taken from ref. 11. The number of dipoles used and the effective radii are

I. $z=y=150\text{nm}$, $N_r=82500$ ($x/d=33$, $y/d=z/d=50$ dipoles) and $\alpha_{\text{eff}}=81\text{nm}$.
II. $z=y=200\text{nm}$, $N_r=62500$ ($x/d=25$, $y/d=z/d=50$ dipoles) and $\alpha_{\text{eff}}=98.5\text{nm}$.
III. $z=y=250\text{nm}$, $N_r=43776$ ($x/d=19$, $y/d=z/d=48$ dipoles) and $\alpha_{\text{eff}}=114\text{nm}$.
IV. And $z=y=300\text{nm}$, $N_r=63916$ ($x/d=19$, $y/d=z/d=58$ dipoles) and $\alpha_{\text{eff}}=128.3\text{nm}$.

The polarization of the incident electromagnetic wave is taken to be an average of the $y$- and $z$- polarizations for all the simulations.

![Figure 5.8: Extinction efficiency versus wavelength for a nickel rectangular-shaped nanoparticle with $x=100\text{nm}$ and variable $y, z$ dimensions](image)

The polarization of the incident electromagnetic wave is taken to be an average of the $y$- and $z$- polarizations for all the simulations.
From the spectra obtained, it appears that, when the height (x dimension) stays constant, as the width of the particle (y and z dimensions) increases, the $\lambda_{\text{max}}$ shifts noticeably to the red with a gain in the extinction efficiency factor. At the same time, the bandwidth of the spectrum gets broader.

Alternatively, if the width of the cubical nanoparticle stays constant, at $y=z=200\,\text{nm}$ and the height is changing, the extinction efficiency spectrum is also affected. The particle is assumed to be in vacuum. The dielectric constant is taken from ref. 11. The number of dipoles used for the dimensions of $y=z=200\,\text{nm}$ and the effective radii are

I. $x=100\,\text{nm}$, $N_r=62500$ ($x/d=25$, $y/d=z/d=50$ dipoles) and $\alpha_{\text{eff}}=98.5\,\text{nm}$.
II. $x=50\,\text{nm}$, $N_r=27648$ ($x/d=12$, $y/d=z/d=48$ dipoles) and $\alpha_{\text{eff}}=78.16\,\text{nm}$.
III. $x=25\,\text{nm}$, $N_r=13824$ ($x/d=6$, $y/d=z/d=48$ dipoles) and $\alpha_{\text{eff}}=62.035\,\text{nm}$.

The polarization of the incident electromagnetic wave is taken to be an average of the y- and z- polarizations for all the simulations.

![Figure 5.9: Extinction efficiency versus wavelength for a nickel cubical-shaped nanoparticle with the same $y=z=200\,\text{nm}$ and an alterable x dimension](image)

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Simulations presented in figure 5.9, indicate that reducing the particle height the extinction efficiency increases but the $\lambda_{\text{max}}$ remains about the same. The small shifts in $\lambda_{\text{mac}}$ are negligible since the bandwidth of the spectra is broad (covers a large region in the visible-NIR.)

5. Nanosphere Lithography (NSL)

The most common method which is used to fabricate truncated tetrahedrons, is Nanosphere Lithography (NSL). [14] NSL is a powerful fabrication technique for producing regular, nearly homogeneous arrays of nanoparticles with tunable shapes, sizes and spacing. The method involves drop-coating a suspension of size-mono-disperse polystyrene nanospheres of a uniform diameter D onto a substrate and allowing them to self-assemble into a hexagonal close-packed monolayer. (Fig. 5.10) The monolayer of nanospheres acts as a deposition mask through which a metal is deposited either by thermal evaporation, electron beam deposition or pulsed laser deposition to a target metal thickness, $d_m$. The nanosphere mask is then removed, leaving behind surface-confined nanoparticles with triangular footprints. Independent tuning of the width and height of the nanoparticles is allowed by controlling the size of the polystyrene nanospheres and the amount of material deposited. [15-17]

![Figure 5.10: Nanosphere lithography fabrication of triangular particle array. Polystyrene microspheres of uniform diameter are self-assembled into hexagonally close-packed array on supporting substrate. Metal (typically Ag or Au) is deposited through sphere array, which serves as deposition shadow mask. [9]](image-url)
6. Properties of Tetrahedral Structures

Nanoparticles constructed using nanosphere lithography have the shape of a tetrahedron or truncated tetrahedron, if proportion of the material is missing from the top part. An example of a material leading to truncated tetrahedrals is silver which is a soft metal. Here, all the particles are assumed to have tetrahedral shape regardless of the material.

6.1 Tetrahedrons of various materials

To estimate the extinction efficiency of tetrahedrons with side length $a=250\text{nm}$, assumed to be in vacuum, the number of dipoles used is $N_t=13024$ ($x/d=38$, $y/d=40$, $z/d=48$ dipoles) and the effective radius is equal to $76.04\text{nm}$. The dielectric constants used for Ni and Al taken from ref. 11 and for Au from ref. 10. The incident electromagnetic wave propagates in $+x$ axis while the polarization is taken to be an average of $y$- and $z$- polarizations.

![Figure 5.11: Extinction efficiency versus wavelength for a tetrahedron with $a=250\text{nm}$ without any substrate for the materials (a) Ni, (b) Au, and (c) Al.](image-url)
Figure 5.11 demonstrates the extinction efficiency of Au, Al and Ni tetrahedrons with the same volume, without substrate. The gold spectrum has a narrow peak at $\lambda=735\text{nm}$ with an efficiency factor maximum at almost 9. Gold provides the best efficiency factor at plasmon resonance. The spectrum of aluminum presents a wide bandwidth at $\lambda=610\text{nm}$, it is blue-shifted compared to gold, and the efficiency factor maximum is approximately 7. Nickel nanoparticles exhibit the widest plasmon resonance bandwidth, the smallest value of the efficiency factor (approximately 5) and a maximum wavelength between the maxima of Al and Au.

6.2 Effect of substrate

The effect of the substrate on the extinction efficiency factor is investigated assuming a nickel tetrahedron with sides $a=250\text{nm}$. The particle dipoles are as noted above. The same $d$ (interdipole spacing) is used for both the particle and the substrate. The number of dipoles used for the substrate is $N_s=9600$ ($x/d=5$, $y/d=40$, $z/d=48$ dipoles). Note that the $z$ and $y$ dimensions of the substrate are the same as the $z$ and $y$ dimension of the nanoparticle. The total number of dipoles is $N_{tot}=22624$. The effective radius is equal to 92.313nm. The dielectric constant of nickel is taken from ref. 11, for mica ($n=1.58$) from ref. 18 and from Pyrex glass from ref. 12. The polarization of the incident electromagnetic wave is taken to be an average of the $y$- and $z$- polarizations. All extinction efficiencies were corrected.
Figure 5.12: Extinction efficiency versus wavelength for a nickel tetrahedron with $\alpha=250\text{nm}$ (a) with substrate mica ($n=1.58$) (b) with substrate glass Pyrex ($n=1.474$) and (c) without any substrate.

Figure 5.12 illustrates that the spectrum of a Ni tetrahedron without a substrate has a maximum wavelength $\lambda_{\text{max}}=675\text{nm}$ and an extinction efficiency maximum at 5.25. The spectra with substrates have a red-shifted peak and an increased extinction efficiency. The Pyrex glass substrate gives a peak maximum at $\lambda=725\text{nm}$ with the efficiency factor approximately 6, while with the mica substrate the plasmon resonance peaks at $\lambda_{\text{max}}=740\text{nm}$ with an extinction efficiency equal to 5.5. So for different substrate materials both the maximum wavelength and the spectrum of the efficiency factor vary.

Now, consider a tetrahedron with side length $a=250\text{nm}$ ($x/d=38$, $y/d=40$, $z/d=48$ dipoles, $N_t=13024$) with a cubic mica substrate of varied height ($z/d=48$, $y/d=40$ and $x/d=1,5,10$ dipoles, that correspond to $N_s=1920, 9600, 19200$, number of dipoles) The interdipole separation, d is the same for the particle and the substrate. The $z$ and $y$ dimensions of the substrate are the same with the $z$ and $y$ dimension of the nanoparticle. The effective radius of the tetrahedron is equal to 76.04nm, while the total effective medium is equal to 79.844nm, 92.313nm and 104.27nm, respectively.
The dielectric constant of nickel is taken from ref. 11 and for mica (n=1.58) from ref. 18. The polarization is along the y axis. All extinction efficiencies were corrected.

![Graph](image)

**Figure 5.13**: Extinction efficiency versus wavelength for nickel tetrahedron with side length \(a=250\text{nm}\), and a mica substrate with \(z/d=y/d=48\) dipoles and \(x/d=1,5,10\) dipoles.

When modifying the thickness of the substrate a red-shift of the maximum wavelength is observed as well a small increase in the extinction efficiency factor. Figure 5.13 shows that when the substrate thickness is increased a gain in the extinction efficiency is attained which reaches a maximum value after a thickness of 10 dipoles.

Now consider a tetrahedron as before, lying on a rectangular substrate of mica, with a height \((x/d)\) of 5 dipoles but varied side lengths \(y\) and \(z\). The first substrate has \(y/d=z/d=58\) dipoles, corresponding to \(N_s=16820\) dipoles. The second, has \(y/d=48, z/d=58\) dipoles (\(N_s=13920\) dipoles) and the third has \(y/d=58, z/d=48\) dipoles (\(N_s=13920\) dipoles). The interdipole separation, \(d\) is the same for the particle and the substrate. The total effective medium for each substrate is equal to 101.56nm, 98.056nm and 98.056nm, respectively. The polarization is along the y axis. All extinction efficiencies were corrected.
Figure 5.14: Extinction efficiency versus wavelength for nickel tetrahedron with side length a=250nm, and a mica substrate with the same number of dipoles in x/d but different number in the z/d and y/d direction.

In figure 5.14, the spectra of the extinction efficiency for substrates with a variety y,z dimensions are plotted. For comparison the spectrum of the tetrahedron without substrate is plotted. It is observed that although the size of the substrate does not significantly affect the wavelength of the maximum of the extinction efficiency, it may lead to wrong estimates in the value of the peak efficiency. This appears to be particularly so in the direction of the polarization (in this example y) where 48 dipoles did not appear to be an adequate approximation of a large enough substrate.

6.3 Tetrahedrons of different materials on a Pyrex glass substrate

After the short investigation about the effects of the substrate the extinction efficiency of tetrahedrons of a variety of materials with side length a=250nm on a Pyrex glass substrate is estimated. The characteristics of the particle are the same as the previous examples. The number of dipoles used for the substrate $N_s=16820$ (x/d=5, y/d=58, z/d=58 dipoles). The total number of dipoles is $N_{tot}=29844$. The effective radius is equal to 101.56nm. The dielectric constants used for Ni and Al taken from
ref. 11 and for Au from ref. 10. The incident electromagnetic wave propagates in +x axis while the polarization is taken to be an average of the y- and z- polarizations.

Figure 5.15: Extinction efficiency versus wavelength for a tetrahedron with $\alpha=250\text{nm}$ and a Pyrex glass substrate.

Figure 5.15 illustrates the extinction spectra of gold, aluminum and nickel tetrahedrons on Pyrex glass substrate. As expected from previous simulations, the $\lambda_{\text{max}}$ is shifted to the red, the bandwidth of the spectra is broader, and an increase in the efficiency factor is observed. Again the spectrum from gold nanoparticles has the most intense extinction efficiency factor (~10.2) while aluminum and nickel result in less efficiency (8.2 and ~6 respectively). For aluminum, the wavelength shifts by 88nm, for nickel by 80nm and for gold by 80nm. The $\lambda_{\text{max}}$ of the nickel spectrum lies between the $\lambda_{\text{max}}$ of aluminum and gold. The bandwidth of gold is the narrowest. Therefore, for several particle materials with a tetrahedron shape and the same substrate, the shift of the maximum wavelength is almost the same but it depends on the dielectric properties of the particle and the y, z dimensions (base) of the substrate.

7. Discussion

As demonstrated in this chapter, particles with different shapes and materials results in different characteristics in their extinction spectra. Mainly, the maximum
wavelength, extinction efficiency peak at the $\lambda_{\text{max}}$ and bandwidth of their spectrum varie significantly.

The optical properties of cubical nanoparticles depend on the size of their x,y and z dimensions. If the y,z dimensions are constant and the x (height) decreases then the extinction efficiency increases but the maximum wavelength remains almost constant. Increasing the y,z dimensions and keeping the height constant, the maximum wavelength red-shifts and the extinction efficiency rises significantly.

Particles that are fabricated using the EBL technique are, on a Pyrex glass substrate, give very broad spectra, with gold demonstrating a quadrupole peak as well. The extinction efficiency of gold nanoparticles is larger compared to other materials such as aluminum and nickel. The nickel cubes produce the longest while aluminum cubes produce the shortest maximum wavelength. Nickel nanoparticle also result in the broadest bandwidth.

Tetrahedral nanoparticles, fabricated using the NSL method, on a Pyrex glass substrate exhibit narrower spectra compared to the cubical particles. Also, the extinction efficiency appears to be smaller for nickel tetrahedrons compared to aluminum and gold tetrahedrons as in the case of cube nanoparticles. The spectrum of nickel results in the broadest bandwidth. Another important observation is that now the gold tetrahedron exhibits the longest $\lambda_{\text{max}}$ while aluminum still gives the shortest.

An important consideration when examining the optical properties of such nanoparticles is the substrate effect. Changing the material of the substrate can affect the extinction spectrum of the nanoparticles. For example, changing the material of the substrate can cause a small red shift in the $\lambda_{\text{max}}$ and an increase in the extinction maximum. If the height of the substrate is considered constant and the dimensions of y and z are increased, (dimensions of the base) the same thing is observed, meaning an increment in the extinction efficiency and a red shifting in the maximum wavelength are observed.

Now, considering the y and z dimensions constant, and changing the substrate’s height, it is observed that the extinction spectrum differs. While increasing the substrate height, the plasmon resonance maximum wavelength shifts to the near-infrared region, and also the efficiency factor increases. For nanoparticles with different materials, but the same shape of the particle and substrate, different shifts of the $\lambda_{\text{max}}$ occurs. Also the increase of the efficiency factor differs. What it is observed for a nanoparticle of a certain material, is that the continuous increase of the
substrate’s height results in a convergence of the extinction spectrum. The height of the substrate is not a parameter for we will be varying, so it is important to be thick enough, in the simulations, so that the solution converges and the optical properties of nanoparticles do not change significantly.

References:


Conclusions

With the techniques used today, it takes 24-48 hours until the pathogenic organism is cultured and identified and its sensitivity to antibiotics determined. It would be of great benefit if the method called Surface Enhanced Raman Scattering (SERS) could identify UTIs immediately and reliably in an easy and practical way. The success of SERS depends on specially designed nanosurfaces which enhance the normally weak signal of the Raman effect. It is investigated the design and development of nanosurfaces (or nanoparticles) with optical properties optimized to provide good extinction efficiency factors. The extinctions are related to SERS electromagnetic field enhancement effects. These optical properties depend on the size, shape, material and external dielectric environment of the nanosurface.

In this thesis, the extinction efficiency factor for various nanosurfaces with different sizes, shapes, materials and external dielectric environments is estimated with a method called Discrete Dipole Approximation. Of the many available methods for calculating the optical properties of nanoparticles, the DDA approximation was chosen because it is most appropriate for surfaces with rough characteristics, such as cubes and tetrahedrons. The DDA approximation gives very accurate results if a large number of dipoles used and the limitation of $|m|kd < 1$ are obeyed.

At the University of Cyprus, two methods are available for the fabrication of nanostructures. These methods are the Electron-Beam Lithography (EBL) and Nanosphere Lithography (NSL). Nanosurfaces fabricated by EBL can take cubical structures of certain dimension (determined by the apparatus used) and can be made using a variety of metals. In the case of the UCY EBL system the minimum dimensions of the nanoparticles can be $z=y=250\text{nm}$. Nanoparticles, constructed using nanosphere lithography, have the shape of a tetrahedron or truncated tetrahedron, if proportion of the material is missing from the top part. Here, all the particles were assumed to have tetrahedral shape. In the case of UCY there are no limitations of fabrication in the method of NSL.

We have examined such particles, which were fabricated from these methods, made from a variety of materials on a Pyrex glass substrate. Since our Raman system operates at 785nm, the nanoparticles were designed with their extinction spectrum maximum wavelength $\lambda_{\text{max}}$, including the effect of the substrate, approaching 785nm.
Using the EBL method, the extinction spectra of nanoparticles with dimensions $z=y=250\text{nm}$, the $\lambda_{\text{max}}$ is shifted to the red and is not in the range of 750-800nm which is of interest. Since the limitations of the EBL system are unavoidable, the closest particles were designed and the extinction efficiency at 785nm was calculated for comparison.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Shape</th>
<th>Substrate</th>
<th>Material</th>
<th>Dimensions (nm)</th>
<th>Extinction Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$x$  $y$  $z$</td>
<td>$\lambda_{\text{max}}$ at 785nm</td>
</tr>
<tr>
<td>EBL</td>
<td>Cubical</td>
<td>Pyrex glass</td>
<td>Gold</td>
<td>25  250  250</td>
<td>9,6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nickel</td>
<td></td>
<td>9,9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aluminum</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gold</td>
<td>100  250  250</td>
<td>8,2</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Nickel</td>
<td></td>
<td>6,7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aluminum</td>
<td></td>
<td>8,5</td>
</tr>
<tr>
<td>NSL</td>
<td>Tetrahedral</td>
<td>Pyrex glass</td>
<td>Gold</td>
<td>204  216  250</td>
<td>9,7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nickel</td>
<td></td>
<td>5,9</td>
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<tr>
<td></td>
<td></td>
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<td>Aluminum</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>245  260  300</td>
<td>6,2</td>
</tr>
</tbody>
</table>

There is still a lot to be done for this research to be considered complete. In the future the electromagnetic field enhancements produced at the surface of the nanoparticles will be estimated using the electrodynamic method of DDA. Another important factor which must be calculated is the SERS enhancement factor from the e-field enhancement. It is important to estimate these e-fields enhancements before constructing the nanosurfaces since it is possible for slightly different dimensions and/or shapes to produce different SERS enhancement. After the confirmation that the nanoparticles produce good SERS enhancement factors, the surfaces will be constructed using the methods indicated above. The e-fields produced will be
measured experimentaly at the surface of the nanoparticles and compared with the theoretical estimations to confirm the results. Finally, the surfaces will be used for SERS experiments with bacteria to obtain spectra for different pathogens and proceed with the identification and characterization of the various species and antibiotic susceptibilities.