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LIGHT-MATTER INTERACTIONS OF PLASMONIC NANOSTRUCTURES

by

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B.S. University of Central Florida, 2009

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the College of Science at the University of Central Florida Orlando, Florida

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Major Professor: Shengli Zou
ABSTRACT

Light interaction with matter has long been an area of interest throughout history, spanning many fields of study. In recent decades, the investigation of light-matter interactions with nanostructures has become an intense area of research in the field of photonics. Metallic nanostructures, in particular, are of interest due to the interesting properties that arise when interacting with light. The properties are a result of the excitation of surface plasmons which are the collective oscillation of the conduction electrons in the metal. Since the conduction electrons can be thought of as harmonic oscillators, they are quantized in a similar fashion. Just as a photon is a quantum of oscillations of an electromagnetic field, the plasmon is a quantum of electron oscillations of a metal. There are three types of plasmons:

1. Bulk plasmons, also called volume plasmons, are longitudinal density fluctuations which propagate through a bulk metal with an eigenfrequency of $\omega_p$ called the plasma frequency.
2. Localized surface plasmons are non-propagating excitations of the conduction electrons of a metallic nanoparticle coupled to an electromagnetic field.
3. Surface plasmon polaritons are evanescent, dispersive propagating electromagnetic waves formed by a coupled state between a photon and the excitation of the surface plasmons. They propagate along the surface of a metal-dielectric interface with a broad spectrum of eigenfrequencies from $\omega = 0$ to $\omega = \omega_p / \sqrt{2}$. 
Plasmonics is a subfield of photonics which focuses on the study of surface plasmons and the optical properties that result from light interacting with metal films and nanostructures on the deep subwavelength scale. In this thesis, plasmonic nanostructures are investigated for optical waveguides and other nanophotonic applications through computational simulations primarily base on electrodynamic theory. The theory was formulated by several key figures and established by James Clerk Maxwell after he published a set of relations which describe all classical electromagnetic phenomena, known as Maxwell’s equations. Using methods based on Maxwell’s equations, the optical properties of metallic nanostructures utilizing surface plasmons is explored.

In Chapter 3, light propagation of bright and dark modes of a partially and fully illuminated silver nanorod is investigated for waveguide applications. Then, the origin of the Fano resonance line shape in the scattering spectra of a silver nanorod is investigated. Next, in Chapter 4, the reflection and transmission of a multilayer silver film is simulated to observe the effects of varying the dielectric media between the layers on light propagation. Building on the multilayer film work, metal-insulator-metal waveguides are explored by perforating holes in the bottom layer of a two layer a silver film to investigate the limits of subwavelength light trapping, confinement, and propagation.

Lastly, in Chapter 5, the effect of surface plasmons on the propagation direction of electromagnetic wave around a spherical silver nanoparticle which shows an effective negative index of refraction is examined. In addition, light manipulation using a film of silver prisms with an effective negative index of refraction is also investigated. The silver prisms demonstrate
polarization selective propagation for waveguide and optical filter applications. These studies provide insight into plasmonic mechanisms utilized to overcome the diffraction limit of light. Through better understanding of how to manipulating light with plasmonic nanostructures, further advancements in nanophotonic technologies for applications such as extremely subwavelength waveguides, sensitive optical detection, optical filters, polarizers, beam splitters, optical data storage devices, high speed data transmission, and integrated subwavelength photonic circuits can be achieved.
"When we consider the magnitude and extent of his discoveries and their influence on the progress of science and of industry, there is no honour too great to pay to the memory of Faraday, one of the greatest scientific discoverers of all time" – Ernest Rutherford on Michael Faraday
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TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. xii

LIST OF TABLES ................................................................................................................... xix

CHAPTER 1 : INTRODUCTION .............................................................................................. 1

1.1 Light-Matter Interaction ................................................................................................. 1

1.1.1 Maxwell’s Wave Equations ..................................................................................... 1

1.1.2 Propagation of Electromagnetic Waves ................................................................. 5

1.1.3 Electromagnetic Waves at an Interface ................................................................. 11

1.1.4 Polarization of Electromagnetic Waves ............................................................ 23

1.2 Electromagnetic Wave Interactions with Metals ...................................................... 41

1.2.1 Lorentz Model ...................................................................................................... 41

1.2.2 Drude Model ........................................................................................................ 46

1.2.3 Surface Plasmons ............................................................................................... 48

1.2.4 Wavevectors at a Surface ................................................................................... 56

1.2.5 Conclusion ........................................................................................................... 71

CHAPTER 2 : METHODS ..................................................................................................... 72

2.1 Introduction ................................................................................................................ 72

2.2 Mie Theory ................................................................................................................. 73

2.3 Kramers-Kronig Relations ....................................................................................... 78
2.4 T-Matrix Method..................................................................................................85

2.5 Discrete Dipole Approximation Method..............................................................88

2.6 Coupled Dipole Approximation Method............................................................91

CHAPTER 3 : FANO RESONANCE AND DARK MODES IN NANORODS ..........93

3.1 General Introduction ...........................................................................................93

3.2 Dark Modes in Nanorods...................................................................................94

3.2.1 Introduction....................................................................................................94

3.2.2 Results and Discussion..................................................................................95

3.2.3 Summary.......................................................................................................105

3.3 Fano Resonance in Nanorods .........................................................................105

3.3.1 Introduction.................................................................................................105

3.3.2 Results and Discussion................................................................................106

3.3.3 Summary.......................................................................................................114

3.4 Conclusion.........................................................................................................114

CHAPTER 4 : PLASMONIC MIM STRUCTURES FOR WAVEGUIDING ..........116

4.1 General Introduction ..........................................................................................116

4.2 Multilayer Film ..................................................................................................117

4.2.1 Introduction...................................................................................................117

4.2.2 Results and Discussion................................................................................118
LIST OF FIGURES

Figure 1.1 Propagation vector, $\mathbf{k}'$, and two orthogonal polarization vectors, $\mathbf{e}_1$ and $\mathbf{e}_2$...........6

Figure 1.2 Reflection and transmission of a slab.................................................................17

Figure 1.3 Absorption and scattering processes of a spherical particle.............................18

Figure 1.4 Induced time-varying dipole moment in a dielectric sphere as a result of an incident electric field....................................................................................................................................19

Figure 1.5 Coordinate system for scattering of light in Rayleigh and Mie theory..............21

Figure 1.6 (a) Horizontal linear polarization where $E_x = 1$, $E_y = 0$, and $\Delta \phi = 0^\circ$, (b) right hand circular polarization where $E_x = 1$, $E_y = 1$, and $\Delta \phi = 90^\circ$, and (c) right hand elliptical polarization $E_x = 1$, $E_y = 1$, and $\Delta \phi = 45^\circ$..................................................25

Figure 1.7 Schematic for irradiance flux measurements........................................................29

Figure 1.8 Basis vectors for $+45^\circ$ and $-45^\circ$..............................................................30

Figure 1.9 Measurement of the polarization intensity of scattered light transmitted by a polarizer for different incident polarizations..............................................................................38

Figure 1.10 Lorentz harmonic oscillator.............................................................................43

Figure 1.11 Hypothetical oscillator response to a driving force at (a) low frequencies, (b) resonance frequency, $\omega_0$, and (c) high frequencies..............................................................................44

Figure 1.12 Frequency dependence of the real and imaginary parts of the dielectric constant of silver.........................................................................................................................46

Figure 1.13 (a) Bulk volume plasmons, (b) surface plasmon polaritons, (c) localized surface plasmons.........................................................................................................................50
Figure 1.14 Energy flux around a particle for a wavelength (a) much higher or lower than the resonance frequency and (b) at the resonance frequency ........................................................... 54

Figure 1.15 (a) Parallel (longitudinal mode) and (b) perpendicular (transverse mode) polarization of linear arrays of spheres when $k = 0$ ........................................................................... 55

Figure 1.16 Illumination of a metal-dielectric interface at an angle, $\theta$, produces polarization along the boundary with $k_x < k_0$ ........................................................................................................... 58

Figure 1.17 Surface plasmon dispersion relation ........................................................................ 66

Figure 1.18 Schematic of the Krestschmann configuration for the excitation of SPPs on a metal film. ............................................................................................................................. 68

Figure 1.19 Excitation of SPs on a nanoparticle placed on the surface of a metallic film which locally induces charge separation in the film and excites SPP modes travelling along the metal-dielectric boundary .................................................................................................................. 70

Figure 1.20 Excitation of SPP modes using a grating structure ................................................. 71

Figure 2.1 Cauchy’s contour of integration ............................................................................... 83

Figure 3.1 Schematic of a 250 nm long rod with (a) a fully illuminated region and (b) a partially illuminated region of 50 nm. ........................................................................................................... 96

Figure 3.2 Scattering spectra of a 50+200 nm partially illuminated silver rod (red) and scattering spectra of a 250 nm fully illuminated rod (black) .............................................................................. 97

Figure 3.3 The electric field distribution in the $YZ$ plane is shown for a partially illuminated 50+200 nm rod at wavelengths of (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis .............................................................................................................. 98
Figure 3.4 The electric field distribution in the $XZ$ plane for the rod at (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis.

Figure 3.5 The electric field vector plot inside the rod in the $XZ$ plane for wavelengths at (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis.

Figure 3.6 (a) A schematic of the partially illuminated 1050 nm rod. (b) The total scattering spectrum and the scattering spectrum along the $Z$ axis, perpendicular to the incident wave and polarization directions, of a 50+1000 nm long rod when the polarization is parallel to the rod axis. (b) The extinction, scattering, and absorption spectra of the rod when the incident polarization is perpendicular to the rod axis.

Figure 3.7 (a) The electric field distribution at a wavelength of 2800 nm when the incident polarization is perpendicular to the rod axis, (b) the electric field distribution at a wavelength of 1060 nm when the incident polarization is parallel to the rod axis, and (c) the electric field distribution for a 50+5000 nm rod at a wavelength of 1230 nm.

Figure 3.8 Surface plasmon dispersion relation curves for a single Ag-air interface (green) and nanorods with varied length. Wavevector (square) for 250 nm rods, (diamond) for long nanorods (red, orange = 1000 nm; blue = 5050 nm) calculated using the DDA method are plotted. The free space wavevector, $k_0$ (navy), and the plasma frequency of bulk Ag (dark grey) is also plotted for comparison.

Figure 3.9 (a) Scattering and (b) absorption spectra of silver rods with different lengths.

Figure 3.10 Electric field vector plot inside a rod with a length of 300 nm at a resonance wavelength of 480 nm, where the plane is in the $XY$ plane and through the rod center.
Figure 3.11 Scattering spectra of a rod with a 20 nm cut at different distances ($l_c$) from one end.

Figure 3.12 Electric field contour plots at (a) 450, (b) 480 and (c) 570 nm wavelength for rods of a cut at $l_c = 100$ nm and (d) for $l_c = 150$ nm rods at 620 nm wavelength.

Figure 3.13 (a) Schematic of cutting positions on the nanorod. (b) Scattering spectra of a single rod, a rod with one or two cuts at nodal positions and the rod center.

Figure 3.14 Scattering spectra of the left and right circularly polarized light along the direction perpendicular to the incident wave and polarization directions for (a) a 300 nm long rod and (b) a 100 nm radius spherical particle when the incident light is left circularly polarized. Equal magnitude indicates a linearly polarized light.

Figure 4.1 Schematic of a two layer film made up of two parallel infinite silver layers. $L$ refers to the distance between the two layers; $d_1$ and $d_2$ are the thicknesses of the first and the second layer, respectively; $N_1$, $N_2$, $N_3$, $N_4$, and $N_5$ represent the index of refraction of each layer and surrounding medium. $N_2$ equals $N_4$ in the current studies.

Figure 4.2 (a) Absorption, (b) scattering, and (c) extinction spectra of a two-layer silver film with $40(d_1)$ and $60(d_2)$ nm thickness and $L = 150$ nm separation. (d) Enhanced electric field, $|E|^2$, along the $X$ axis at corresponding resonance wavelength.

Figure 4.3 (a) Absorption spectra of the two layer film when the media, $N_3$ and $N_5$, are fixed as water and the medium $N_1$ is changed from vacuum (solid line), water (dotted line), to glass (dashed line); (b) absorption spectra of the two layer film when the media, $N_1$ and $N_3$, are fixed as water and the medium, $N_5$, is changed from vacuum, water, to glass.
Figure 4.4 Absorption spectra of the film when the second layer is 60 nm, as $N_5$ is water and varying $N_1$ from vacuum (solid line) to water (dotted line) and finally, to glass (dashed line). (a) The first layer is 10 nm, (b) the first layer is 20 nm, and (c) the first layer is 30 nm. (d) Schematic of the film structure with the varied parameters highlighted in red........................................124

Figure 4.5 Absorption spectra when the first layer is 40 nm, $N_1$ is water and varying $N_5$ from vacuum (solid line) to water (dotted line) then glass (dashed line). (a) The second layer is 30 nm; (b) the second layer is 40 nm, (c) the second the layer is 50 nm. (d) Schematic of the film structure with the varied parameters highlighted in red...........................................................126

Figure 4.6 Absorption (blue), scattering (green), and transmission (red) for a periodically perforated film with a distance between layers of 10 nm..........................................................130

Figure 4.7 (a) Schematic of an open array of holes periodic at 10 microns along the Z axis and 400 nm along the Y axis. Electric field contour plots between the two layers in the YZ plane with a distance between films of (b) 40 nm and (c) 30 nm at a wavelength of 800 nm and (d) 10 nm at a wavelength of 1300 nm. .......................................................................................................131

Figure 4.8 Surface plasmon dispersion relation curves for a single Ag-air interface (green) calculated from equation (4.7) and MIM structures with varied $L$ (teal, maroon, indigo) calculated from equations (4.8)-(4.10). Wavevector (diamond) for each of the periodic hole array structures from Figure 4.7 (b)-(d) calculated using the DDA method are plotted with corresponding colors to the MIM counterparts. The free space wavevector, $k_0$ (navy), and the plasma frequency of bulk Ag (dark grey) is also plotted for comparison........................................135
Figure 4.9 (a) Schematic of an isolated hole array separated by 100 nm walls to form isolated channels along the Z axis. The electric field contour plots between the two layers in the YZ plane at a wavelength of 1020 nm are plotted for channel widths of (b) 400 nm and (c) 300 nm. ...... 137

Figure 4.10 (a) Schematic of an open hole array with ridges along the Z axis with 10 micron periodic holes. Electric field contour plots between the two layers in the YZ plane of the ridge structures with a spacing between the coaxial and top film of 10 nm and \( L = (b) \) 30 nm and (c) 40 nm at an incident wavelength of 1300 nm................................................................................ 139

Figure 5.1 (a) Absorption spectrum of a 10 nm silver particle in a vacuum. (b) Effective indices of refraction of the particle obtained from the Kramers-Kronig transformation method. .......... 147

Figure 5.2 Real and imaginary polarizabilities of a silver particle with a 10 nm radius......... 148

Figure 5.3 Electric field vector plots for a 10 nm radius silver particle at (a) 345 and (b) 371 nm wavelengths and Poynting vector plot for the silver particle at wavelengths of (c) 345 nm and (d) 371 nm. All the plots are in the XZ plane and through the particle center.............................. 149

Figure 5.4 Sketches of light rays through (a) a right handed and (b) a left handed film comprised of periodic triangular prisms............................................................... 152

Figure 5.5 Spectra of silver films comprised of periodic triangular prisms for (a) Z polarized incident light and (b) Y polarized incident light. ................................................................. 153

Figure 5.6 Electric field \( |E_r|^2 \) contour plots of silver prism films in the XZ plane (a) at 600 nm and (b) 700 nm wavelength for the Z polarized incident light; (c) at 600 nm and (d) 700 nm wavelength for the Y polarized incident light. The incident wave vector is parallel to the \( X \) axis. .................................................................................................................. 154
Figure 5.7 Poynting vector plots of a single silver prism in the $XZ$ plane (a) at 600 nm and (b) 700 nm wavelength for the $Z$ polarized incident light. ............................................................. 156

Figure 5.8 The angle of incidence versus the angle of refraction, which are the angles between the incident and refracted light rays and the upper surface normal, at different wavelengths for silver prism films of different heights and periodic distances when the polarization direction is in the plane of incidence.................................................................157

Figure A.1 Electric and magnetic field vectors at an interface between two media..................166

Figure A.2 Gaussian pillbox showing the flux of the electric field out of a surface at the interface between two media.................................................................167

Figure A.3 Application of Faraday’s Law of Induction to a rectangular loop across an interface between two media showing electric field flux across the boundary. ........................................169

Figure A.4 Gaussian pillbox showing the flux of the magnetic field out of a surface at the interface between two media. .................................................................172

Figure A.5 Ampère’s Law applied to a rectangular loop across an interface between two media showing magnetic flux across the boundary....................................................173

Figure B.1 Schematic of an experimental setup to measure the intensity of a specific polarization of light scattered by a particle and further transmitted by a polarizer for incident light at various polarizations.................................................................177
LIST OF TABLES

Table 1.1 Signs of Stokes parameters. .................................................................26
Table 1.2 Stokes parameters for polarized light ...................................................33
Table 1.3 Scattering matrix elements obtained from scattering amplitude matrix elements. 35
Table 1.4 Mueller matrices for optical elements with the resulting Stokes vectors of the transmitted, polarized light .................................................................37
Table 1.5 Combination of scattering matrix elements to give the intensity of different measured transmitted polarizations for parallel and perpendicular incident polarizations ........40
Table 2.1 Parametric representations of the four curves in Cauchy’s contour of integration. 83
CHAPTER 1: INTRODUCTION

1.1 Light-Matter Interaction

Nanostructured optical materials with dimensions in the subwavelength regime exhibit unusual behavior when interacting with electromagnetic (EM) waves and can be utilized for a variety of novel applications. Such behavior can be seen in conductive nanoparticles that display collective resonances called localized surface plasmons (LSPs) which have resonantly enhanced absorption and scattering. Spectral control of the plasmon resonance of the particles can be done by tuning the shape, size, material composition, and local environment, for applications such as surface enhanced Raman spectroscopy (SERS), subwavelength waveguiding, biological imaging, and labeling. In addition to metal nanoparticles, metallic films also support surface plasmons (SPs) in the form of evanescent surface waves called surface plasmon polaritons (SPPs) for use in applications such as optical circuitry and waveguiding. Understanding the plasmonic properties of metallic nanostructures allows for the manipulation of light on the subwavelength scale, giving rise to novel technologies and opening the doors to new avenues of scientific advancement.

1.1.1 Maxwell’s Wave Equations

The interaction of light and matter, even on the subwavelength scale, can be described classically by a set of macroscopic equations, called Maxwell’s equations. Specifically, Maxwell’s equations are a set of differential equations which describe the relationship between the macroscopic electric and magnetic fields of an electromagnetic wave at any point in space-time, \((x, y, z, t)\). The propagation of the wave through a medium is determined by several
parameters of the medium: the electric permittivity, \( \varepsilon(x, y, z, t) \); magnetic permeability, \( \mu(x, y, z, t) \); and the electric conductivity, \( \sigma(x, y, z, t) \). At an interface, or boundary, the microscopic properties gradually change on the atomic scale which, macroscopically, is seen as a drastic change in the media properties. The equations are valid when the parameters of the medium do not change drastically. For the purpose of treating wave propagation classically, the macroscopically averaged parameters of the medium are sufficient.

Electromagnetic fields are comprised of two constant vectors, \( E \) and \( H \), for the electric and magnetic components, respectively. The existence of propagating electromagnetic fields in an infinite, non-conducting medium with constant permittivity, \( \varepsilon = \varepsilon' + i\varepsilon'' \), and permeability, \( \mu = \mu' + i\mu'' \), in the direction of the complex wave vector, \( k = k' + ik'' \), is given by Maxwell’s plane wave equations

\[
\begin{align*}
k \cdot D &= 0, \\
k \cdot B &= 0, \\
k \times E + \frac{\partial B}{\partial t} &= 0, \\
k \times H - \frac{\partial D}{\partial t} &= 0.
\end{align*}
\]

(1.1) \hspace{2cm} (1.2) \hspace{2cm} (1.3) \hspace{2cm} (1.4)

The above equations are for a plane wave in source-free regions of space. Charge density, \( \rho \), and external current density, \( J_{\text{ext}} \), are sources for electromagnetic wave and with their addition, Maxwell’s equations (1.1) and (1.4) take on a new form,
\[ \mathbf{k} \cdot \mathbf{D} = \rho, \tag{1.5} \]

\[ \mathbf{k} \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{j}_{\text{ext}}, \tag{1.6} \]

where equations (1.2) and (1.5) are known as Gauss’ laws for electric and magnetic fields. The first two constitutive relations relate the electric and magnetic field intensities, \( \mathbf{E} \) and \( \mathbf{H} \), to the electric and magnetic flux densities, \( \mathbf{B} \) and \( \mathbf{D} \), respectively, which are in the form of \( \mathbf{D} = \varepsilon \mathbf{E} \) and \( \mathbf{B} = \mu \mathbf{H} \). In a vacuum, \( \varepsilon \) is designated as \( \varepsilon_0 \) and is equal to \( 8.854 \times 10^{-12} \) farad/m and \( \mu \) becomes \( \mu_0 \) and is equal to \( 4\pi \times 10^{-7} \) henry/m. The speed of light in a vacuum is defined as

\[ c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} = 2.998 \times 10^{-8} \frac{m}{\text{sec}}. \tag{1.7} \]

The relations demonstrate that the field intensity and flux density are dependent on the medium in which the wave exists. Assuming that the medium is uniform, isotropic, and linear, where both \( \varepsilon(\omega) \) and \( \mu(\omega) \) are positive and real, equations (1.3) and (1.4) become

\[ \mathbf{k} \times \mathbf{E} + \mu_0 \frac{\partial \mathbf{H}}{\partial t} = 0, \tag{1.8} \]

\[ \mathbf{k} \times \mathbf{H} - \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} = 0. \tag{1.9} \]

Equation (1.8) is known as Faraday’s Law. By taking the third constitutive relation, \( \mathbf{j}_{\text{ext}} = \sigma \mathbf{E} \), and substituting it into a modified equation (1.9), Ampere’s Law is derived as
\[ k \times H - \varepsilon \frac{\partial E}{\partial t} - \sigma E = 0. \quad (1.10) \]

A combined wave equation can be obtained by assuming a harmonic time dependence, \( e^{-i\omega t} \), and with writing equations (1.8) and (1.9) in terms of \( E \) and \( B \) as

\[ k \times E - i\omega B = 0, \quad (1.11) \]
\[ k \times B - i\omega\mu\varepsilon E = 0, \quad (1.12) \]

to yield the combined Helmholtz wave equation,

\[ (k^2 + \omega^2\mu\varepsilon) \frac{[E]}{[B]} = 0. \quad (1.13) \]

The combined Helmholtz wave equation can be written terms of for \( E \) and \( H \) by taking the curl of equation (1.8) and substituting in equation (1.10) to give the wave equation for the electric field intensity,

\[ k^2 E - \mu\sigma \frac{\partial E}{\partial t} - \mu\varepsilon \frac{\partial^2 E}{\partial t^2} = 0, \quad (1.14) \]

and following similar steps, the wave equation for the magnetic field intensity,

\[ k^2 H - \mu\sigma \frac{\partial H}{\partial t} - \mu\varepsilon \frac{\partial^2 H}{\partial t^2} = 0. \quad (1.15) \]
1.1.2 Propagation of Electromagnetic Waves

Now that the electric and magnetic fields of a wave have been described, it is pertinent to discuss the propagation of the wave through space. The simplest case is the propagation of a wave in a vacuum, which will be discussed first, leading up to the propagation of a wave in a medium. In doing so, the optical constants of the medium will be related to the propagation of the wave itself.

1.1.2.1 Propagation in vacuo

A wave propagating in a vacuum in the positive $x$ direction with a complex wavevector, $\mathbf{k} = k' + ik''$, is homogenous, meaning that $k'$ and $k''$ are parallel vectors. A solution to the second order differentials given in equations (1.14) and (1.15) for the wave takes on the familiar form for the wave equations:

$$E = E_0 e^{(-k''x)} e^{(ik' \cdot x - i\omega t)},$$  \hspace{1cm} (1.16)

$$H = H_0 e^{(-k''x)} e^{(ik' \cdot x - i\omega t)},$$  \hspace{1cm} (1.17)

where $k'$ and $k''$ are real vectors. The first part of the wave equation gives the amplitude of each of the wave component, $E_0 e^{(-k''x)}$ and $H_0 e^{(-k''x)}$, and the second part of the equation gives the phase, $\phi = (k' \cdot x - \omega t)$, where $k'$ is perpendicular to surfaces of constant phase and $k''$ is perpendicular to surfaces of constant amplitude. A change in a distance, $\Delta z$, over a change in time, $\Delta t$, for the propagation of surfaces of constant phase, where $k' \cdot x = kz$ and $kz - \omega t = \phi$ gives the phase, $\phi$,
\[ k z - \omega t = k - \omega (t + \Delta t) = \phi, \]  

(1.18)

and phase velocity, \( v \),

\[ v = \frac{\omega}{k}. \]  

(1.19)

For homogeneous waves in a vacuum, the real components of \( E_0 \) and \( H_0 \) are perpendicular to the direction of propagation, \( k' \), and therefore reside in the same plane as shown in Figure 1.1.

![Propagation vector, \( k' \), and two orthogonal polarization vectors, \( e_1 \) and \( e_2 \).](image)

Figure 1.1 Propagation vector, \( k' \), and two orthogonal polarization vectors, \( e_1 \) and \( e_2 \).

The conditions for a transverse plane wave are given by Maxwell’s equations,

\[ k \cdot E_0 = k \cdot H_0 = H_0 \cdot E_0 = 0, \]  

(1.20)

which state that the electric field component and the magnetic field component must be perpendicular to each other.
When \( k' \) and \( k'' \) are not parallel and the surfaces do not coincide, the wave is said to be inhomogeneous.

The complex wavevector, \( k \), is strictly a property of the wave and it can be rewritten from the relationship between \( E \) and \( H \) in Maxwell’s equations to elucidate a relationship between the wave and the medium it travels through as

\[
k \cdot k = \varepsilon \mu \omega^2. \tag{1.21}
\]

The wave vector \( k = (k' + ik'')\hat{e} \), with \( \hat{e} \) as a real unit vector and positive values of \( k' \) and \( k'' \), is related to the wavenumber, \( k = k' + ik'' \). When \( k \) is combined with equation (1.22), it is revealed that in a vacuum with permittivity, \( \varepsilon_0 \), and permeability, \( \mu_0 \),

\[
k = \frac{\omega}{c} = \omega \sqrt{\varepsilon_0 \mu_0} = \frac{1}{v}, \tag{1.22}
\]

where \( v \) is the phase velocity and the speed of light, \( c \), is

\[
c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}, \tag{1.23}
\]

leading to a new optical property of the medium, the refractive index, \( n \), where

\[
n = \frac{c}{v}, \tag{1.24}
\]

which shows that the propagation velocity of a wave through a material is decreased with increased refractive index. From equations (1.167) and (1.169), it can be seen that the phase
velocity is dependent on the wavevector and refractive index of the medium, giving rise to the
dispersion of light.

1.1.2.2 Propagation of electromagnetic waves in a medium

In a medium other than a vacuum, the permittivity and permeability are affected by the
polarization properties of the material called the electric and magnetic susceptibilities, $\chi$ and $\chi_m$, respectively, which relates $\varepsilon_0$ and $\mu_0$ to that of $\varepsilon$ and $\mu$ in the medium as

$$\varepsilon = \varepsilon_0(1 + \chi), \quad (1.25)$$
$$\mu = \mu_0(1 + \chi_m). \quad (1.26)$$

The relative permittivity, $\varepsilon_{relative} = (\varepsilon/\varepsilon_0)$, and permeability, $\mu_{relative} = (\mu/\mu_0)$, then define a material’s response to an electromagnetic wave as the refractive index, $n$, by

$$n = \sqrt{\varepsilon_{relative} \mu_{relative}}. \quad (1.27)$$

It can be seen from equation (1.27) that $n$ is a complex vector where

$$n = n + i\kappa. \quad (1.28)$$

From the susceptibilities, the polarization, $P$, and magnetization, $M$, of the material can be derived using the first two constitutive relations where the polarization is defined as the average electric dipole moment per unit volume of the medium,

$$E = \varepsilon D = \varepsilon_0(1 + \chi)E = \varepsilon_0 E + \varepsilon_0 \chi \varepsilon E = \varepsilon_0 E + P, \quad (1.29)$$
to give \( P = \varepsilon_0 \chi E \). The magnetization is defined as the average magnetic dipole moment per unit volume of the medium,

\[
B = \mu H = \mu_0 (1 + \chi_m) H = \mu_0 (H + \chi_m H) = \mu_0 (H + M),
\]

(1.30)
to give \( M = \chi_m H \).

The energy flux of a plane wave is given by the Poynting vector,

\[
S = \frac{1}{2} Re \{ E \times H^* \} = Re \left\{ \frac{E \times (k^* \times E^*)}{2 \omega \mu^*} \right\},
\]

(1.31)

where

\[
E \times (k^* \times E^*) = k^* (E \cdot E^*) - E^* (k^* \cdot E).
\]

(1.32)

For a homogenous wave,

\[
k \cdot E = 0,
\]

(1.33)

\[
k^* \cdot E = 0,
\]

(1.34)

propagating in the direction \( \hat{e} \), gives

\[
S = \frac{1}{2} Re \left\{ \frac{\varepsilon}{\mu} |E_0|^2 \exp \left( -\frac{4\pi k z}{\lambda} \right) \hat{e} \right\},
\]

(1.35)
where the magnitude of $S$ is called the irradiance, $I$, is attenuated exponentially as it propagates through a medium as

$$ I = I_0 e^{-\alpha z}, $$

(1.36)

yielding the absorption coefficient as

$$ \alpha = \frac{4\pi\kappa}{\lambda}, $$

(1.37)

which shows that the imaginary part of the refractive index determines the rate at which electromagnetic energy is removed from the wave as it propagates through any medium.

**1.1.2.3 Right hand rule**

An incident electric field residing the $XY$ plane, $E_i$, can be resolved into two components, the parallel, $E_{i\parallel}$, and perpendicular, $E_{i\perp}$,

$$ E_i = (E_{0\parallel}\hat{e}_{i\parallel} + E_{0\perp}\hat{e}_{i\perp}) e^{(ikz-iot)} = E_{i\parallel}\hat{e}_{i\parallel} + E_{i\perp}\hat{e}_{i\perp}, $$

(1.38)

with the wavenumber in the surrounding medium, $k$, given by

$$ k = \frac{2\pi n}{\lambda}, $$

(1.39)

the refractive index of the medium, $n$, the wavelength in vacuo, $\lambda$, and orthogonal basis vectors,

$$ \hat{e}_{i\parallel} = \cos \phi \hat{e}_x + \sin \phi \hat{e}_y, $$

(1.40)
\[
\mathbf{e}_{\perp} = \sin \phi \mathbf{e}_x - \cos \phi \mathbf{e}_y,
\]

which form a right hand triad, termed the right hand rule, with the basis vector for the direction of propagation, \(\mathbf{e}_z\),

\[
\mathbf{e}_z = \mathbf{e}_{\perp} \times \mathbf{e}_{\parallel} \quad (1.42)
\]

where \(\mathbf{e}_z\) and \(\mathbf{e}_\parallel\), which is the scattering direction, form the scattering plane upon interaction with a scattering particle. The incident, \(\mathbf{E}_i\), and scattering, \(\mathbf{E}_s\), fields are written in matrix forms as follows,

\[
\mathbf{E}_i = \begin{pmatrix} E_{i\parallel} \\ E_{i\perp} \end{pmatrix},
\]

\[
(1.43)
\]

\[
\mathbf{E}_s = \begin{pmatrix} E_{s\parallel} \\ E_{s\perp} \end{pmatrix},
\]

\[
(1.44)
\]

### 1.1.3 Electromagnetic Waves at an Interface

After describing the propagating properties of a wave in different media, the interaction of an EM wave at the boundary between two media can now be discussed. An electromagnetic wave propagating through different media is affected by interactions with each medium as it traverses across the boundary between one medium and another. Two general cases will be discussed in this section to illustrate the interactions. The first case is the reflection and transmission of a wave with a planar film and the second case is the absorption and scattering of a wave by a particle. Due to the nature of the interactions, the polarization of the wave is
inconsequential at this point in the discussion. However, it is to be noted that regardless of the polarization of the incident wave, the scattered light becomes polarized to some degree where the polarization of the scattered wave is determined by the properties of the scattering species. Since it is not pertinent in determining the reflection or transmission of a film or the scattering of a particle, the polarization properties of a wave will be discussed in section 1.1.4.

1.1.3.1 Planar film

Upon interaction with an interface of a medium with a refractive index of \( N_1 = n_1 + i\kappa_1 \), a propagating plane wave with an electric field amplitude, \( E_i \), in a nonabsorbing medium with a refractive index of \( N_2 = n_2 \) can either be reflected, \( E_r \), transmitted, \( E_t \), or both. Maxwell’s equations yield plane wave solutions in the interior of both media. When the distance, \( z \), from the interface, where \( z = 0 \), is \( z > 0 \), the solution is

\[
E_t \exp \left[ i\omega \left( \frac{N_1 z}{c} - 1 \right) \right],
\]

and when \( z < 0 \), it becomes

\[
E_i \exp \left[ i\omega \left( \frac{N_2 z}{c} - 1 \right) \right] + E_r \exp \left[ -i\omega \left( \frac{N_2 z}{c} + 1 \right) \right].
\]

Boundary conditions require the tangential components of the electric field to be continuous across the boundary, when \( z = 0 \), to give

\[
E_i + E_r = E_t.
\]
Taking into account the continuity of the tangential magnetic field gives

\[ E_i - E_r = \frac{N_1}{N_2} E_t \]  \hspace{1cm} (1.48)

Assuming the permeabilities of the two media are equivalent and solving equations (1.47) and (1.48) for the electric field amplitudes relates the incident and reflected terms by the reflection coefficient, \( \tilde{r} \),

\[ E_r = \tilde{r} E_i, \] \hspace{1cm} (1.49)

and the incident and transmitted terms by the transmitted coefficient, \( \tilde{t} \),

\[ E_t = \tilde{t} E_i, \] \hspace{1cm} (1.50)

where

\[ \frac{1 - m}{1 + m} = \tilde{r}, \] \hspace{1cm} (1.51)

\[ \frac{2}{1 + m} = \tilde{t}, \] \hspace{1cm} (1.52)

with \( m \) representing the refractive index of medium 1 relative to medium 2,

\[ m = \frac{N_1}{N_2} = n + ik. \] \hspace{1cm} (1.53)
The ratio of reflected to incident radiation is the reflectance, \( R \), which is the square of the modulus of the reflection coefficient,

\[
R = |\hat{r}|^2 = \left|\frac{1 - m}{1 + m}\right|^2 = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2}.
\] (1.54)

It is more useful to look at the reflection and transmission by a plane-parallel slab, giving two boundaries for a plane wave of the form,

\[
E_i \exp\left[i\omega\left(\frac{N_2 z}{c} - t\right)\right],
\] (1.55)

to traverse. In this case, the reflected wave is given as

\[
E_r \exp\left[-i\omega\left(\frac{N_2 z}{c} + t\right)\right],
\] (1.56)

and the transmitted wave as,

\[
E_t \exp\left[i\omega\left(\frac{N_2 z}{c} - t\right)\right].
\] (1.57)

Following the reflected and transmitted waves comes the equation for a wave inside the slab propagating in the +z direction,
\[ E_1^+ \exp \left[ i\omega \left( \frac{N_1 z}{c} - t \right) \right], \]  
\( (1.58) \)

and in the \(-z\) direction,

\[ E_1^- \exp \left[ -i\omega \left( \frac{N_1 z}{c} + t \right) \right]. \]  
\( (1.59) \)

Satisfying the boundary conditions from equations (1.47) and (1.48) at the first interface where \( z = 0 \), gives

\[ E_1 + E_r = E_1^+ + E_1^-, \]  
\( (1.60) \)

\[ E_1 - E_r = \frac{N_1}{N_2} (E_1^+ - E_1^-), \]  
\( (1.61) \)

and at the second boundary where \( z = h \), gives

\[ E_1^+ (i k N_1 h) + E_1^- (-i k N_1 h) = E_t \exp (i k N_2 h), \]  
\( (1.62) \)

\[ E_1^+ (i k N_1 h) - E_1^- (-i k N_1 h) = \frac{N_1}{N_2} [E_t \exp (i k N_2 h)]. \]  
\( (1.63) \)

Following equations (1.51) and (1.52), the reflection and transmission coefficients now become

\[ \hat{r}_{\text{slab}} = \frac{E_r}{E_i} = \frac{\hat{r} [1 - \exp (i 2 k N_1 h)]}{1 - \hat{r}^2 \exp (i 2 k N_1 h)}, \]  
\( (1.64) \)
\[ \tilde{t}_{\text{slab}} = \frac{E_t}{E_i} = \frac{4m}{(m+1)^2} \frac{\exp(-ikN_2h)}{\exp(-ikN_1h) - \tilde{r}^2 \exp(i2kN_1h)} \] (1.65)

The transmittance of a slab with a complex refractive index of \( N_1 = n_1 + i\kappa_1 \) in a nonabsorbing medium with a refractive index of \( N_2 = n_2 \) is given by

\[ T_{\text{slab}} = |\tilde{t}_{\text{slab}}|^2 = \frac{(1 - R)^2 + 4R \sin^2 \psi}{R^2 e^{-ah} + e^{ah} - 2R \cos(\zeta + 2\psi)}. \] (1.66)

where the attenuation of the wave is a result of \( \kappa_1 \) of the slab which is found in the absorption coefficient given by

\[ \alpha = \frac{4\pi\kappa_1}{\lambda}, \] (1.67)

and the phase difference, \( \zeta \), or optical path, is affected by the real part of the refractive index, \( n_1 \), for a slab with a thickness \( h \), which is given by

\[ \zeta = \frac{4\pi n_1 h}{\lambda} \] (1.68)

with an additional phase term \( \psi \), taking into account the phase difference due to the refractive indices of both materials,

\[ \psi = \tan^{-1}\left( \frac{2n_2\kappa_1}{n_1^2 + \kappa_1^2 - n_2^2} \right). \] (1.69)
where $0 \leq \psi \leq \pi$. A schematic demonstrating the transmission by a slab is shown in Figure 1.2.

![Diagram of reflection and transmission of a slab]

Figure 1.2 Reflection and transmission of a slab.

1.1.3.2 Absorption and scattering by discrete particles

The two main interactions between incident light and a discrete particle are absorption and scattering. Scattering can be inelastic, where the wavelength of the scattered radiation is different from the incident wavelength, or elastic, where the scattered radiation has the same wavelength as the incident light. Examples of elastic scattering are Rayleigh scattering from small, dielectric (nonabsorbing) spherical particles and Mie scattering from spherical particles with no limitations on size or dielectric properties. Mie theory will be discussed in section 2.2 of the Methods chapter; therefore the discussion here will be limited to Rayleigh scattering. A
schematic of the different types of mechanisms which occur for the absorption and scattering of light by a particle is shown in Figure 1.3.

Figure 1.3 Absorption and scattering processes of a spherical particle.

Scattering is governed by the wavelength of incident light on the particle, the size of the particle, given by the size parameter, \( x \), where

\[
x = \frac{2\pi a}{\lambda},
\]

(1.70)

and the refractive index, \( n = n + i\kappa \). The refraction of light is handled by the real part of the refractive index, \( n \), and the absorption is handled by the imaginary part, \( \kappa \). In Rayleigh theory, spherical particles scatter light as a result of the dipole moment induced inside the particle. One important limitation of the theory is that it is only valid when the size of the particle is very small. In terms of what is considered small for the Rayleigh scattering process to occur, the size parameter must be much less than 1, \( x \ll 1 \), or the relative refractive index,
\[ m = \frac{(n + i\kappa)_\text{in}}{(n + i\kappa)_\text{out}}, \quad (1.71) \]

when multiplied by the size parameter, must be much less than one, \( |m|x \ll 1 \).

Figure 1.4 Induced time-varying dipole moment in a dielectric sphere as a result of an incident electric field.

For isotropic spherical particles with dimensions in the Rayleigh regime in an isotropic environment, the polarizability, \( \alpha \), is related to the dipole moment, \( p \), and electric field, \( E \), by

\[ p(\omega) = \alpha(\omega)E(\omega). \]

The induced dipole, \( p \), in a particle with a radius, \( a \), as shown in Figure 1.4, oscillates as a result of the oscillation of the incident electric field, \( E_\text{in} \), given by

\[ p = 4\varepsilon_\text{out}a^3 \left( \frac{\varepsilon_\text{in} - \varepsilon_\text{out}}{\varepsilon_\text{in} + 2\varepsilon_\text{out}} \right) E_0, \quad (1.72) \]
where the frequency of radiation from oscillating dipole is at the same frequency as the incident light. In the presence of an electric field, $E_0$, oriented along the $z$-axis, the total electric potential inside the sphere, $\phi_{in}$, is given by

$$\phi_{in} = -\left(\frac{3\varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}}\right)E_0 z,$$

and outside, $\phi_{out}$,

$$\phi_{out} = \left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}} \frac{a^3}{r^3} - 1\right)E_0 z,$$

where $z$ is the distance along the propagation axis. From the electric potentials in and out of the sphere, the internal electric field can be obtained as a function of the change in electric potential over a change in distance, $z$,

$$E_{in} = -\frac{d\phi_{in}}{dz} = \left(\frac{3\varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}}\right)E_0,$$

which leads to the field enhancement inside a particle,

$$\frac{E_{in}}{E_0} = \left(\frac{3\varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}}\right),$$

and outside the sphere,
\[ \frac{E_{\text{out}}}{E_0} = \left( \frac{3\varepsilon_{\text{in}}}{\varepsilon_{\text{in}} + 2\varepsilon_{\text{out}}} \right). \]  

(1.77)

Figure 1.5  Coordinate system for scattering of light in Rayleigh and Mie theory.

A schematic of the coordinate system and scattering angles for Rayleigh theory, which is also used in Mie Theory, is shown in Figure 1.5. The scattering intensity of light, \( I_s \), is given by

\[ I_s = \left( \frac{8^4 N a^6}{\lambda^4 r^2} \right) \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 (1 + \cos^2 \theta) I_l, \]  

(1.78)

where \( N \) is the number of scattering species, \( a \) is the radius of the particle, \( r \) is the distance from the particle origin, and \( \theta \) is the angle along the propagation axis, as shown in Figure 1.5. In Rayleigh theory, the term \( |(m^2 - 1)/(m^2 + 1)|^2 \) is weakly dependent on the wavelength and the scattered irradiance is proportional to the wavelength as
\[ I_s \propto \frac{1}{\lambda^4}, \quad (1.79) \]

which demonstrates that shorter wavelengths are scattered more efficiently than longer wavelengths, which explains why the sky appears blue. Scattered light during the day occurs along non-zero angles, \( \theta \), efficiently scattering blue radiation, while in the evening, the scattered angles are closer to zero and longer wavelengths are scattered resulting in the observed red sunsets.

The efficiency, \( Q \), is defined as the optical cross-section, \( \sigma \), divided by the physical cross-sectional area, \( \pi a^2 \),

\[ \sigma = Q \times \pi a^2. \quad (1.80) \]

The extinction efficiency is given by

\[ Q_{ext} = 4 \pi \text{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \left[ 1 + \frac{x^2}{15} \left( \frac{m^2 - 1}{m^2 + 2} \right) \frac{m^4 + 27m^2 + 38}{2m^2 + 3} \right] \right. \]

\[ + \left. \frac{8}{3} x^4 \text{Re} \left\{ \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 \right\} \right\}, \quad (1.81) \]

the scattering efficiency is given by the second term in equation (1.81)

\[ Q_{sca} = \frac{8}{3} x^4 \left\{ \frac{m^2 - 1}{m^2 + 2} \right\}^2, \quad (1.82) \]
and the absorption efficiency \( Q_{abs} = Q_{ext} - Q_{sca} \), where the absorption comes from the first term of equation (1.81). From the criteria for Rayleigh scattering, \(|m|x \ll 1\), \( Q_{abs} \) simplifies to

\[
Q_{abs} = 4x \Im \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \left[ 1 + \frac{4x^3}{3} \Im \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \right],
\]

(1.83)

where, for particles that are sufficiently small, the second term \( (4x^3/3) \Im \{(m^2 - 1)/(m^2 + 2)\} \) is \( \ll 1 \) and the absorption further simplifies to

\[
Q_{abs} = 4x \Im \left\{ \frac{m^2 - 1}{m^2 + 2} \right\}.
\]

(1.84)

The proportionality of the intensity of scattered light on the wavelength, as given in equation (1.79), can then be written in terms of the scattering efficiency,

\[
Q_{sca} \propto \frac{1}{\lambda^4},
\]

(1.85)

and absorption efficiency,

\[
Q_{abs} \propto \frac{1}{\lambda^4}.
\]

(1.86)

1.1.4 Polarization of Electromagnetic Waves

A propagating time harmonic, electromagnetic wave, \( E_0 \), in any medium, it will generate an electric and magnetic field, which are described by three properties: frequency, irradiance, and polarization state. Frequency and irradiance have been addressed in the previous sections,
which leaves the last property, the polarization of an EM wave, to be discussed. Polarization is conventionally defined by the electric field, therefore only the electric field component will be discussed. The three properties of an electric field, the irradiance, frequency, and the state of polarization, are a function of the amplitude and relative phase of the horizontal and vertical components.

1.1.4.1 Stokes vector

The parallel and perpendicular components can also be written as $E_x$ and $E_y$, respectively. Therefore, the polarization state of an EM wave is a function of the relative magnitude of the horizontal, $E_x$, and vertical, $E_y$, orthogonal components of the electric field vector and the correlation between them. The correlation is a function of the degree of polarization of the wave and the phase angle, $\phi$, between the horizontal and vertical components to give linear, circular, or elliptical polarizations. For linear polarization, the amplitudes $E_x$ and $E_y$ are in phase and the relative amplitude of each component ultimately determines the polarization direction. Figure 1.6 (a) shows an example of a horizontally polarized wave where the relative magnitude of the horizontal component is $E_x = 1$ and the vertical component is $E_y = 0$. The phase difference between the two components is $\Delta \phi = 0^\circ$.

For circular polarization, both $E_x$ and $E_y$ have a relative magnitude of 1, but their phases are offset by $\Delta \phi = 90^\circ$. Depending on which orthogonal component is phase lagged by $90^\circ$, the circular polarization can either be right-handed or left-handed. A schematic for a right handed polarized wave is shown in Figure 1.6 (b). If the relative phase difference and/or the relative amplitude are not equal, then elliptical polarization occurs. As in circular polarization, the
handedness can be either left or right. Right handed, elliptical polarization is shown in Figure 1.6 (c) where the relative amplitudes are the same, $E_x = 1$ and $E_y = 1$, and but the phase difference is $\Delta \phi = 45^\circ$.

![Diagram showing linear horizontal, right hand circular, and right hand elliptical polarization](image)

Figure 1.6 (a) Horizontal linear polarization where $E_x = 1$, $E_y = 0$, and $\Delta \phi = 0^\circ$, (b) right hand circular polarization where $E_x = 1$, $E_y = 1$, and $\Delta \phi = 90^\circ$, and (c) right hand elliptical polarization $E_x = 1$, $E_y = 1$, and $\Delta \phi = 45^\circ$.

To describe the polarization properties of a wave, a set of four values called the Stokes parameters are used. These parameters form the Stokes vector, written as a 4x1 matrix,
\[ \text{Stokes vector} = \begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix}, \]  \hspace{2cm} (1.87)

where \( I \) = total irradiance, \( Q \) = degree of linear polarization, \( U \) = extent of \(+45^\circ/-45^\circ\) linear polarization, and \( V \) = rotation handedness.

Table 1.1 Signs of Stokes parameters.

<table>
<thead>
<tr>
<th>100% Linear Polarization</th>
<th>100% ±45 Polarization</th>
<th>100% Circular Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>+Q ( y ) - ( x )</td>
<td>+U ( y ) (-45^\circ ) ( x )</td>
<td>+V ( y ) ( x ) right</td>
</tr>
<tr>
<td>-Q ( y ) ( x )</td>
<td>-U ( y ) ( 45^\circ ) ( x )</td>
<td>-V ( y ) ( x ) left</td>
</tr>
</tbody>
</table>

If the tip of the electric field vector is traced out in space in time, the Stokes parameters can be visualized as a horizontal line for horizontal polarization, a vertical line for vertical polarization, a positively sloped line at \( 45^\circ \) for \( 45^\circ \) linear polarization, a negatively sloped line at \(-45^\circ \) for \(-45^\circ \) linearly polarized light, a circle or ellipse being traced out clockwise for right
circular, or elliptical, polarization, and finally a circle or ellipse being traced out counter
clockwise for left circular, or elliptical, polarization. There is some ambiguity in defining what
constitutes clockwise or counter clockwise since the designation depends on whether the wave is
viewed along the direction of the $k$-vector propagating toward the viewer or away from the
viewer. For this work, a wave is designated right handed if the electric field vector traces out a
circle or ellipse clockwise as the viewer looks toward the light source. The shape and sign of Q,
U, and V are shown in Table 1.1.

The Stokes parameters can be written in terms of $E_x = E_x + iE_x^*$ and $E_y = E_y + iE_y^*$,
starting with a wave in the standard form,

$$E = E_0 e^{(ikx - i\omega t)},$$

where $E_0$ is given by the amplitudes $E_x$ and $E_y$ with orthogonal basis vectors, $\hat{e}_x$ and $\hat{e}_y$,

$$E_0 = E_x \hat{e}_x + E_y \hat{e}_y,$$

$$E_x = a_x e^{-i\delta_x},$$

$$E_y = a_y e^{-i\delta_y},$$

where the real amplitude is given by $a_x$ and $a_y$, and the phase is given by $\delta_x$ and $\delta_y$. The four
parameters, with the prefactor $\frac{k}{2\omega \mu_0}$ omitted for simplicity, are therefore

$$I = E_x E_x^* + E_y E_y^* = |E_x|^2 + |E_y|^2 = a_x^2 + a_y^2,$$

(1.92)
\[ Q = E_x E_x^* - E_y E_y^* = |E_x|^2 - |E_y|^2 = a_x^2 - a_y^2, \]  

(1.93)

\[ U = E_x E_y^* + E_y E_x^* = 2 \text{Re}(E_x E_y) = 2(a_x a_y) \cos \delta, \]  

(1.94)

\[ V = i(E_x E_y^* - E_y E_x^*) = 2 \text{iIm}(E_x E_y) = 2(a_x a_y) \sin \delta. \]  

(1.95)

Cumulatively, the parameters are related by

\[ I^2 = Q^2 + U^2 + V^2, \]  

(1.96)

where the degree of polarization can be determined by

\[ \text{Degree of polarization} = \frac{\sqrt{Q^2 + U^2 + V^2}}{I}. \]  

(1.97)

Understanding the interpretation of the Stokes vector can be done by generalizing how the terms are obtained experimentally through six polarization measurements each detecting the irradiance flux of one polarization component of a monochromatic incident beam transmitting through one of the following ideal polarizers: \( P_H \) = horizontal linear polarizer (0°), \( P_V \) = vertical linear polarizer (90°), \( P_{+45°} \) = 45° linear polarizer, \( P_{-45°} \) = -45° linear polarizer, \( P_R \) = right circular polarizer, and \( P_L \) = left circular polarizer. A schematic showing the basic experimental setup is shown in Figure 1.7.
Figure 1.7 Schematic for irradiance flux measurements.

An unpolarized beam of light with irradiance, $I$, is detected in the absence of any polarizing element and is given by

$$I_{\text{unpolarized}} = (E_x E_x^* + E_y E_y^*),$$  \hspace{1cm} (1.98)

which gives the total intensity of the beam, usually normalized to 1. The prefactor $\frac{k}{2\omega\mu_0}$ is still omitted. To obtain the irradiance of linear polarized light with parallel, $x$, and perpendicular, $y$, components, irradiance flux measurements using the horizontal polarizer, $P_H$, for the measurement of irradiance, $I_x$, and the vertical polarizer, $P_V$, for the measurement of irradiance, $I_y$, with corresponding transmitted amplitudes $E_x$ and $E_y$, respectively, gives

$$I_x = E_x E_x^*, \hspace{1cm} (1.99)$$

$$I_y = E_y E_y^*, \hspace{1cm} (1.100)$$

where

$$I_{\text{linear}} = I_x - I_y = (E_x E_x^* - E_y E_y^*).$$  \hspace{1cm} (1.101)
Therefore, the difference between the two transmittance measurements gives the amount of horizontal or vertical polarization of the beam. It can now be seen how the value of $U$ for a beam that is completely horizontally polarized has a value of 1 and a beam that is completely vertically polarized has a value of -1. The same can be done for $+45^\circ$ and $-45^\circ$ linear polarization, where $\hat{e}_x$ is rotated by $+45^\circ$ and $-45^\circ$ as shown in Figure 1.8.

![Figure 1.8 Basis vectors for $+45^\circ$ and $-45^\circ$](image)

The basis vectors now become $\hat{e}_{+45^\circ}$ for $+45^\circ$ and $\hat{e}_{-45^\circ}$ for $-45^\circ$, with the electric field, $E_0$ and amplitudes, $E_{+45^\circ}$ and $E_{-45^\circ}$, given by

$$E_0 = E_{+45^\circ}\hat{e}_{+45^\circ} + E_{-45^\circ}\hat{e}_{-45^\circ}, \quad (1.102)$$

which are related to the linear polarization orthogonal components in equations (1.89) - (1.91) by
\[ E_{+45^\circ} = \frac{1}{\sqrt{2}}(E_x + E_y), \quad (1.103) \]

\[ E_{-45^\circ} = \frac{1}{\sqrt{2}}(E_x - E_y), \quad (1.104) \]

\[ \hat{e}_{+45^\circ} = \frac{1}{\sqrt{2}}(\hat{e}_x + \hat{e}_y), \quad (1.105) \]

\[ \hat{e}_{-45^\circ} = \frac{1}{\sqrt{2}}(\hat{e}_x - \hat{e}_y), \quad (1.106) \]

For a wave with an amplitude of \( (E_x + E_y)/\sqrt{2} \), the measured irradiance of the transmitted beam passing through a 45° polarizer is

\[ I_{+45^\circ} = \frac{1}{2}(E_x E_x^* + E_y E_y^* + E_x E_y^* + E_y E_x^*), \quad (1.107) \]

and passing through a -45° polarizer is

\[ I_{-45^\circ} = \frac{1}{2}(E_x E_x^* - E_y E_y^* - E_x E_y^* + E_y E_x^*), \quad (1.108) \]

to give the overall difference between the irradiances as

\[ I_{+45^\circ} - I_{-45^\circ} = (E_x E_y^* + E_y E_x^*). \quad (1.109) \]

For the circular polarization measurements, the basis vectors become \( \hat{e}_R \) for right circular and \( \hat{e}_L \) for left circular polarizations, with the electric field, \( E_\theta \) and amplitudes, \( E_R \) and \( E_L \), now given by
\[ E_0 = E_R \hat{e}_R + E_L \hat{e}_L, \]  

which are related to the linear polarization orthogonal components in equations (1.89) - (1.91) by

\[ E_R = \frac{1}{\sqrt{2}} (E_x - iE_y), \]  

(1.111)

\[ E_L = \frac{1}{\sqrt{2}} (E_x + iE_y), \]  

(1.112)

\[ \hat{e}_R = \frac{1}{\sqrt{2}} (\hat{e}_x + i\hat{e}_y), \]  

(1.113)

\[ \hat{e}_L = \frac{1}{\sqrt{2}} (\hat{e}_x - i\hat{e}_y), \]  

(1.114)

where the conditions for \( \hat{e}_R \) and \( \hat{e}_L \) to be orthogonal are \( \hat{e}_R \cdot \hat{e}_R^* = 1, \hat{e}_L \cdot \hat{e}_L^* = 1 \), and \( \hat{e}_R \cdot \hat{e}_L^* = 0 \).

The measured irradiance of the transmitted beam passing through a right circular polarizer is

\[ I_R = \frac{1}{2} \left( E_x^* E_x - iE_x^* E_y + iE_y^* E_x + E_y E_y^* \right), \]  

(1.115)

and passing through a -45° polarizer is

\[ I_L = \frac{1}{2} \left( E_x^* E_x + iE_y E_x^* - iE_x^* E_y + E_y E_y^* \right), \]  

(1.116)

to give the overall difference between the irradiances as

\[ I_R - I_L = (E_y E_x - E_x^* E_y). \]  

(1.117)
Irradiance flux measurements are summarized in the matrix below, where the results of the measurements yield the four parameters that make up the complete Stokes vector:

\[
\mathbf{S}_{\text{Stokes vector}} = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix} = \begin{bmatrix} P_H + P_V \\ P_H - P_V \\ P_{45} - P_{135} \\ P_R - P_L \end{bmatrix}.
\] (1.118)

An important relationship emerges from the polarization measurements, where \( P_H + P_V = P_{+45°} + P_{-45°} = P_R + P_L \), which shows that any monochromatic beam of light, regardless of polarization, can be decomposed to two orthogonal components of another polarization set. The Stokes parameters for various polarization conditions for 100% polarized waves are summarized in Table 1.2.

Table 1.2 Stokes parameters for polarized light.

<table>
<thead>
<tr>
<th>Linear Polarization</th>
<th>Linear Polarization</th>
<th>Circular Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>90°</td>
<td>+45°</td>
</tr>
<tr>
<td>[1]</td>
<td>[1]</td>
<td>[1]</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1.1.4.2 Amplitude matrix and scattering matrix

The relation between incident and scattered electric fields is contained in a 2x2 amplitude scattering matrix which describes the transformation of \( \mathbf{E}_i \) to \( \mathbf{E}_s \). It contains 4 elements, each
containing a real and imaginary part as the amplitude and phase, respectively, which are dependent on the scattering angle, $\theta$, and azimuthal angle, $\phi$, given by

$$\left(\begin{array}{c}
E_s \parallel \\
E_s \perp
\end{array}\right) = \left(\begin{array}{c}
e^{i k r} \\
-i k r
\end{array}\right) \left[\begin{array}{cc}
S_2(\theta, \phi) & S_3(\theta, \phi) \\
S_4(\theta, \phi) & S_1(\theta, \phi)
\end{array}\right] \left(\begin{array}{c}
E_{i \parallel} \\
E_{i \perp}
\end{array}\right).$$

(1.119)

where at some distance, $r$, from the center of a scattering particle in the far field region where $k r \gg 1$, $E_s$, can be approximated as being transverse,

$$\hat{e}_r \cdot E_s \approx 0,$$

(1.120)

giving

$$\left(\begin{array}{c}
E_s \parallel \\
E_s \perp
\end{array}\right) = \left(\begin{array}{c}
e^{i k r} \\
-i k r
\end{array}\right) A,$$

(1.121)

where $A$ is the amplitude of the scattering electric field.

An example of the amplitude scattering matrix transformation from an incident electric field with orthogonal components decomposed into parallel and perpendicular to the scattered electric field decomposed into left and right handed orthogonal components is

$$\left[\begin{array}{c}
E_L \\
E_R
\end{array}\right] = \frac{1}{\sqrt{2}} \left[\begin{array}{cc}
1 & i \\
1 & -i
\end{array}\right] \left[\begin{array}{c}
E_{i \parallel} \\
E_{i \perp}
\end{array}\right].$$

(1.122)

where, if the transformation was reversed, the new amplitude scattering matrix becomes
\[
\begin{bmatrix}
\hat{E}_{\parallel} \\
\hat{E}_{\perp}
\end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix}
1 & 1 \\
-i & i
\end{bmatrix}
\begin{bmatrix}
\hat{E}_L \\
\hat{E}_R
\end{bmatrix},
\] (1.123)

From the amplitude scattering matrix, the polarization of the angular scattering of light by an optical element can be obtained. The state of polarization of an incident wave can be transformed by an optical element such as a polarizer, retarder, or reflector. The optical element can be described by the 16 elements contained in a 4x4 Mueller matrix, called the scattering matrix, where the 16 elements are obtained from the real and imaginary components of the amplitude scattering matrix shown in Table 1.3.

Table 1.3 Scattering matrix elements obtained from scattering amplitude matrix elements.

<table>
<thead>
<tr>
<th>Scattering Mueller Matrix Elements</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{11} = \frac{1}{2} \left(</td>
<td>S_1</td>
</tr>
<tr>
<td>( S_{12} = \frac{1}{2} \left(</td>
<td>S_2</td>
</tr>
<tr>
<td>( S_{13} = \text{Re} { S_2 S_3^* + S_4 S_4^* } )</td>
<td>( S_{33} = \text{Re} { S_1 S_2^* + S_3 S_4^* } )</td>
</tr>
<tr>
<td>( S_{14} = \text{Im} { S_2 S_3^* - S_4 S_4^* } )</td>
<td>( S_{34} = \text{Im} { S_2 S_3^* + S_4 S_4^* } )</td>
</tr>
<tr>
<td>( S_{21} = \frac{1}{2} \left(</td>
<td>S_2</td>
</tr>
<tr>
<td>( S_{22} = \frac{1}{2} \left(</td>
<td>S_2</td>
</tr>
<tr>
<td>( S_{23} = \text{Re} { S_2 S_3^* - S_4 S_4^* } )</td>
<td>( S_{43} = \text{Im} { S_2 S_2^* - S_3 S_4^* } )</td>
</tr>
<tr>
<td>( S_{24} = \text{Im} { S_2 S_3^* + S_4 S_4^* } )</td>
<td>( S_{44} = \text{Re} { S_2 S_2^* - S_3 S_4^* } )</td>
</tr>
</tbody>
</table>
The scattering matrix relates the incident, $i$, and scattered, $s$, EM waves described by the Stokes vectors through

$$\begin{bmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{bmatrix} = \frac{1}{k^2 r^2} \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix}. \quad (1.124)$$

For unpolarized incident light scattered by some optical element, the resulting Stokes vector for the scattered light is

$$\begin{bmatrix} S_{11} \\ S_{21} \\ S_{31} \\ S_{41} \end{bmatrix} = \frac{1}{k^2 r^2} \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (1.125)$$

where each of the Stokes parameters are normalized by $I_s/I_i = S_{11}$, $Q_s/I_i = S_{21}$, $U_s/I_i = S_{31}$, and $V_s/I_i = S_{41}$, thus demonstrating that scattering by an optically active particle is a mechanism for polarization. Optical elements described by Mueller matrices are shown in Table 1.4.
Table 1.4 Mueller matrices for optical elements with the resulting Stokes vectors of the transmitted, polarized light.

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>Scattering Mueller Matrix</th>
<th>Scattered Stokes Vector</th>
<th>Transmitted Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ 1 \ 0 \ 0 \end{bmatrix} ]</td>
<td>0° Linear</td>
</tr>
<tr>
<td>Linear Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 1 &amp; 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ -1 \ 0 \ 0 \end{bmatrix} ]</td>
<td>90° Linear</td>
</tr>
<tr>
<td>Linear Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 1 &amp; 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ 0 \ 0 \ 0 \end{bmatrix} ]</td>
<td>+45° Linear</td>
</tr>
<tr>
<td>Linear Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ -1 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ 0 \ -1 \ 0 \end{bmatrix} ]</td>
<td>-45° Linear</td>
</tr>
<tr>
<td>Circular Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 1 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ 0 \ 0 \ 0 \end{bmatrix} ]</td>
<td>Right Handed</td>
</tr>
<tr>
<td>Circular Polarizer</td>
<td>[ \frac{1}{2} \begin{bmatrix} 1 &amp; 0 &amp; 0 &amp; -1 \ 0 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 \ -1 &amp; 0 &amp; 0 &amp; 1 \end{bmatrix} ]</td>
<td>[ \begin{bmatrix} 1 \ 0 \ 0 \ -1 \end{bmatrix} ]</td>
<td>Left Handed</td>
</tr>
</tbody>
</table>
By combining optical elements, the change in polarization of a wave can be obtained by multiplying the associated Mueller matrices in the correct order for each element. An example of the creation of a right-handed circular polarizer from a linear polarizer and a retarder are shown in equation (1.126).

\[
\begin{align*}
1 \begin{bmatrix}
1 & 1 & 0 & 0 \\
1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}_{\text{linear}} & \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 \\
0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0
\end{bmatrix}_{\text{retarder}} = \frac{1}{2} \begin{bmatrix}
1 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
1 & 1 & 0 & 0
\end{bmatrix}_{\text{right}} \\
\end{align*}
\]

(1.126)

The polarization of the scattered wave is determined by the addition and subtraction of different scattering Mueller matrix elements to give the polarization intensity, $I_s$, for a scattered wave at a specific angle, $\theta$, for a given incident polarization, $I_i$. A schematic of the general experimental set up to determine the measurements is shown in Figure 1.9.

Figure 1.9 Measurement of the polarization intensity of scattered light transmitted by a polarizer for different incident polarizations.
Table 1.5 gives the combination of scattering matrix elements for incident light which is linearly polarized parallel, $I_{i,||}$, and perpendicular, $I_{i,\perp}$, and for the measured scattered light transmitted by the polarizer for polarizations of total, or unpolarized, $I_{s,u}$, linear parallel, $I_{s,||}$, linear perpendicular, $I_{s,\perp}$, right circular, $I_{s,R}$, and left circular, $I_{s,L}$. For the unpolarized incident light, which refers to the detection of the total scattered intensity, the polarizer before the particle would not be present.

In the absence of any geometric symmetry in the structure, whether it is a single asymmetric particle or an asymmetric group of particles, the 16 elements are independent. For a group of particles where the scattering is fully incoherent, the 4x4 matrix is equivalent to the sum of the individual particle scattering matrices. However, if the structure contains any symmetry, then the number of independent elements is reduced. All polarization characteristics of a scattered wave can therefore be obtained by the information encoded in the 16 scattering matrix elements. A complete set of tables for the combinations of scattering matrix elements is given in Appendix B.
Table 1.5 Combination of scattering matrix elements to give the intensity of different measured transmitted polarizations for parallel and perpendicular incident polarizations.

<table>
<thead>
<tr>
<th>Measured Transmitted Polarization</th>
<th>Incident Polarization</th>
<th>(I_{i,\parallel})</th>
<th>(I_{i,\perp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_{s,u})</td>
<td>(\frac{1}{2}(S_{11} + S_{12}))</td>
<td>(\frac{1}{2}(S_{11} - S_{12}))</td>
<td></td>
</tr>
<tr>
<td>(I_{s,\parallel})</td>
<td>(\frac{1}{4}(S_{11} + S_{12} + S_{21} + S_{22}))</td>
<td>(\frac{1}{4}(S_{11} - S_{12} + S_{21} - S_{22}))</td>
<td></td>
</tr>
<tr>
<td>(I_{s,\perp})</td>
<td>(\frac{1}{4}(S_{11} + S_{12} - S_{21} + S_{22}))</td>
<td>(\frac{1}{4}(S_{11} - S_{12} - S_{21} + S_{22}))</td>
<td></td>
</tr>
<tr>
<td>(I_{s,R})</td>
<td>(\frac{1}{4}(S_{11} + S_{12} - S_{41} - S_{42}))</td>
<td>(\frac{1}{4}(S_{11} - S_{12} - S_{41} + S_{42}))</td>
<td></td>
</tr>
<tr>
<td>(I_{s,L})</td>
<td>(\frac{1}{4}(S_{11} + S_{12} + S_{41} + S_{42}))</td>
<td>(\frac{1}{4}(S_{11} - S_{12} + S_{41} - S_{42}))</td>
<td></td>
</tr>
</tbody>
</table>
1.2 Electromagnetic Wave Interactions with Metals

Up until this point, the discussion on electromagnetic waves has been limited to the propagation of waves and interactions with simple structures composed of arbitrary media. In the following section, two different models for describing metals will be discussed: the Lorentz model and the Drude model. Both models approximately describe the optical properties of metallic structures and the plasmonic properties that arise when the structures have dimensions on the order of nanometers. Specifically, the manifestation of surface plasmons in bulk metals, discrete particles, and metal films will be discussed. The section will conclude with a brief description of different methods of exciting surface plasmon polaritons.

1.2.1 Lorentz Model

A plasma model is used to describe the optical properties of metals due to the free electron movement of the conduction electrons through a fixed positive, ionic background. The model was developed by H. A. Lorentz as a classical approach to describe optical properties of materials by assuming that electrons and ions of a medium are simple harmonic oscillators and neglecting material properties such as the lattice potential and electron-electron interactions. The simple oscillator model is of great use in determining optical properties of a material because it can describe a variety of optical excitations. The microscopic model of a polarizable material becomes a macroscopic system of independent, isotropic, and identical harmonic oscillators which are subjected to an applied electric field, $E$, which acts as a driving force. The oscillation response to an applied local electric field, $E_{local}$, for an electron with an effective mass, $m$, and a charge, $e$, is given by
\[ m\ddot{x} + m\gamma \dot{x} + Kx = -eE_{\text{local}}, \]  
(1.127)

where \( x \) is the distance displaced from equilibrium, \( Kx \) is the restoring force for an electron with a spring constant, \( K \). The oscillation of electrons is damped as a result of collisions, which adds a damping term to the equation, \( m\gamma \), where the collision frequency, \( \gamma = 1/\tau \), and \( \tau \) is the relaxation time for a free electron plasma which at room temperature is typically on the order of \( 10^{-14} \) making \( \gamma = 100 \) THz. Since the electric field has a harmonic time dependence,

\[ E(t) = E_0 e^{-i\omega t}, \]  
(1.128)

with a frequency, \( \omega \), and time, \( t \), the solution to the equation for an electron becomes

\[ x(t) = x_0 e^{-i\omega t}, \]  
(1.129)

where phase shifts between the driving force of the electric field and the electron response is contained in the complex amplitude, \( x_0 \). The oscillatory solution to equation (1.127) becomes

\[ x(t) = \frac{e}{m(\omega_0^2 - \omega^2 - i\gamma\omega)} E(t), \]  
(1.130)

with \( \omega_0^2 = K/m \). A schematic of a Lorentz harmonic is shown in Figure 1.10.
In most systems, there is a certain degree of collisions that occur which means $\gamma \neq 0$ and the phase of the driving field and oscillating electrons have a displacement, $D$,

$$D = Ae^{i\Theta} \left(\frac{eE}{m}\right),$$  \hspace{1cm} (1.131)

with a phase angle, $\Theta$,

$$\Theta = \tan^{-1} \left(\frac{\omega \gamma}{\omega_0^2 - \omega^2}\right),$$  \hspace{1cm} (1.132)

and amplitude, $A$,

$$A = \frac{1}{\left[(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2\right]^\frac{1}{2}}.$$  \hspace{1cm} (1.133)
The consequence of the phase difference results in the maximum amplitude occurring when the frequencies $\omega_0 \cong \omega$. If $\gamma \ll \omega_0$, the height of the maximum amplitude is inversely proportional to $\gamma$ and the full width at half maximum (FWHM) is proportional to $\gamma$. Figure 1.11 shows a plot for the amplitude and phase relation for a hypothetical oscillator. At low frequencies, the oscillator response is in phase with the driving force where $\Theta \cong 0^\circ$ and $\omega \ll \omega_0$ as shown in Figure 1.11 (a). At the resonance frequency, the amplitude is at a maximum and the phase lag is $\Theta = 90^\circ$ as shown in Figure 1.11 (b). Near $\omega_0$, a $180^\circ$ phase change occurs. As a result, at high frequencies, $\omega >> \omega_0$, the oscillator response and the driving force are $180^\circ$ out of phase as shown in Figure 1.11 (c).

Figure 1.11 Hypothetical oscillator response to a driving force at (a) low frequencies, (b) resonance frequency, $\omega_0$, and (c) high frequencies.
For a single oscillator, the induced dipole moment is $p = ex$. For a large number of oscillators, $n$, the dipole moment per unit volume becomes

$$P = -nex,$$  \hspace{1cm} (1.134)

and when combined with equation (1.130) becomes

$$P = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} E\varepsilon_0,$$  \hspace{1cm} (1.135)

where the plasma frequency, $\omega_p$, is given by

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m}. \hspace{1cm} (1.136)$$

The optical constants for the collection of oscillators can then be derived out, where the dielectric function for the bulk material is given by

$$\varepsilon(\omega) = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega},$$  \hspace{1cm} (1.137)

which can be decomposed into the real, $\varepsilon_1$, and imaginary, $\varepsilon_2$, components of the complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, as

$$\varepsilon_1(\omega) = 1 + \chi' = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2},$$  \hspace{1cm} (1.138)
\[
\varepsilon_2(\omega) = \chi'' = \frac{\omega_p^2 \gamma \omega}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2}.
\] (1.139)

At the plasma frequency, \(\omega_0\), the imaginary part of the dielectric constant is at a maximum as shown in Figure 1.12 for silver.

Figure 1.12 Frequency dependence of the real and imaginary parts of the dielectric constant of silver.

1.2.2 Drude Model

In metals, the conduction and valence band overlap allowing for electrons near the Fermi level to be excited to different energy and momentum states by the absorption of photons with very little energy. These intraband transitions give rise to free electrons which can be taken into
account by modification of the Lorentz model. When the spring constant in equation (1.127) is set to zero, it essentially clips the springs of the harmonic oscillators with $K = 0$ and $\omega_b = 0$ to transform equation (1.130) into

$$x(t) = \frac{e}{m(\omega^2 + i\gamma \omega)} E(t). \quad (1.140)$$

When the polarization in equation (1.134) is combined with equation (1.140), it becomes

$$P = -\frac{ne^2}{m(\omega^2 + i\gamma \omega)} E. \quad (1.141)$$

Equation (1.141) substituted into equation (1.29) gives the relation between $D$ and $E$ in terms of frequency and electric permittivity as

$$D = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} \right) E. \quad (1.142)$$

The new dielectric function for the free electrons becomes

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}, \quad (1.143)$$

which can be decomposed into the real, $\varepsilon_1$, and imaginary, $\varepsilon_2$, components of the complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, as
Equation (1.143) demonstrates that the dielectric constant can become zero near the plasma frequency where the material can support collective modes of oscillating electrons in phase with each other. By tuning the geometry of the structure, the oscillation can occur at negative values of the dielectric constant.

### 1.2.3 Surface Plasmons

An interesting phenomenon results from the negative dielectric constant of metals, which is the coherent charge oscillation of the conduction electrons at the interface of a bulk metal and a dielectric, called volume surface plasmons, or just plainly, surface plasmons (SPs) shown in Figure 1.13 (a). The conduction electrons are taken as a free electron plasma with a high density of charged species on the order of $n \approx 10^{23} \text{ cm}^{-3}$. They have longitudinal density fluctuations at a specific eigenfrequency, $\omega_p$, called the plasma frequency. A quanta of volume plasmons have an energy of approximately 10eV, given by

$$\hbar \omega_p = \hbar \sqrt{\frac{ne^2}{m_0 \epsilon_0}},$$  \hspace{1cm} (1.146)
where \( n \) is the number of electrons, \( e \) is the charge of the electron, \( m_0 \) is the mass, and \( \varepsilon_0 \) is the electric permittivity of free space.

In addition to bulk metals, metallic nanostructures can support the same SP modes of collectively oscillating waves of the electron plasma when \( \varepsilon_I = 0 \). SPs waves have magnetic fields parallel to the surface of the metal and normal to the oscillation of the charges. They either can exist as localized excitation modes on a particle, called localized surface plasmons (LSPs), or as propagating transverse magnetic (TM) plane waves along the interface of a metal film, called surface plasmon polaritons (SPPs) shown in Figure 1.13 (b) and (c), respectively.
At the resonance frequency, a small driving force will produce a coherent oscillation of the conduction electrons which oscillate with greater amplitude than other frequencies. The oscillation is strongest near the plasmon resonance frequency. In addition, absorption from electronic collisions and optical scattering as the dipole radiation is strongest near the resonance. A sharp resonance peak is seen for high AC conductive materials, such as silver and gold. The size of the particle affects the peak sharpness, where the sharpest peaks are seen for particles much smaller than the wavelength of excitation prevents the excitation of multipolar modes and particles larger than approximately 5 nm prevents surface damping.
SPs can be excited under resonance conditions at a frequency corresponding to one of the eigenfrequencies specific to the nanostructure. These conditions are defined by intrinsic properties of the nanostructure as a result of its size, the dielectric response of the metal, and the dielectric environment surrounding the nanostructure. Electrodynamic properties of nanoparticles are of interest because of the resulting surface plasmon modes that the particles support. These unique properties of metal nanoparticles are important for use in applications such as biosensors\(^1\), surface enhanced Raman spectroscopy (SERS)\(^2\), light trapping in solar cells\(^3,4\), and novel metamaterials\(^5\).

1.2.3.1 Localized surface plasmons

Illumination of a single particle induces polarization in the material resulting in a displacement of the electron density from the center of the particle and the resulting oscillation is the localized surface plasmons (LSPs). Excitation of LSP modes of a metallic particle can only occur when the size of the particle is much smaller than the wavelength of incident light. At the resonance frequency, the oscillation amplitude of the plasmonic particle surpasses the excitation amplitude of the incident wave. This difference in amplitude results in a strong enhancement of the scattered field compared to the excitation wave at the resonance frequency. At this frequency, the surface charge density for very small particles is generally dipolar, with all the conduction electrons excited in phase. As the particle size is increased, the electric field distribution inside the particle can become uneven resulting in the excitation of higher polarity modes called multipolar modes. For spheres, the collective dipolar resonance occurs below the plasma frequency of the metal at the Fröhlich mode.
When the diameter of a sufficiently small particle, which acts as a single scattering dipole, is significantly less than the wavelength of incident light, an oscillating dipole is produced from the induced polarization from the incident wave. The total field that results is the sum of both the incident field and the radiation from the single dipole. The efficiency, $Q$, is defined the same as in equation (1.80), where the optical cross-section, $\sigma$, is divided by the physical cross-sectional area, $\pi a^2$,

$$\sigma = Q \times \pi a^2.$$ \hfill (1.147)

Absorption efficiency for a small metal sphere is given by

$$Q_{abs} = 12x \frac{\varepsilon_m \varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2},$$ \hfill (1.148)

where $x$ is the size parameter defined as the $k$-vector multiplied by the area, $a$,

$$x = ka = \frac{2\pi n a}{\lambda},$$ \hfill (1.149)

with $n$ representing the refractive index. The peak absorption efficiency occurs at the Fröhlich frequency,

$$Q_{abs}(\omega_F) = \frac{12x \varepsilon_m}{\varepsilon_2(\omega_F)}.$$ \hfill (1.150)
and the physical cross-section, $\sigma_{\text{abs}}$, is proportional to the volume and $a^2$. The scattering efficiency for a small metal particle is

$$Q_{\text{sca}} = \frac{8}{3} x^4 \left| \frac{\epsilon_1 + i \epsilon_2 - \epsilon_m}{\epsilon_1 + i \epsilon_2 + 2 \epsilon_m} \right|^2,$$

(1.151)

with the peak scattering efficiency occurring at the Fröhlich frequency,

$$Q_{\text{sca}}(\omega_F) = \frac{8}{3} x^4 \frac{9 \epsilon_m^2 + \epsilon_2^2(\omega_F)}{\epsilon_2^2(\omega_F)},$$

(1.152)

where $\sigma_{\text{sca}}$ is proportional to the volume squared and $a^6$, which shows that the size of the particle has a larger influence on the scattering than on the absorption for larger particles. If the volume is doubled, the absorption approximately doubles, however, the scattering increases by an exponential factor of two. Therefore, the optical cross-section of a nanoparticle can be greater than the physical cross-section.

The resonantly enhanced absorption has an efficiency with a value of $Q > 1$. Below the resonance frequency, the particle is polarized in phase with the incident polarization and the electric field inside the particle is reduced, which only slightly enhances the electric field outside of the particle. The energy flux, $S$, of the incident light is pushed around the particle along a path that is only slightly larger than the particle diameter, $d$. At the resonance frequency, the strong polarization of the nanoparticle draws energy into the particle which significantly enhances the scattering cross-section. In addition to the enhanced polarization of the particle, there is a large
change in the oscillation amplitude of the conduction electrons which induces enhanced absorption resulting in a phenomenon known as resistive heating. The energy flux of the incident light is now drawn in with an effective diameter, $d_{\text{eff}}$, much greater than the actual diameter of the particle, $d$. Finally, when the frequency of light is much higher than the resonance of the nanoparticle, the energy flow around the particle is only slightly perturbed.

(a) $\omega_{\text{incident}} \gg \omega_{\text{sp}}$ or $\omega_{\text{incident}} \ll \omega_{\text{sp}}$  
(b) $\omega_{\text{incident}} \approx \omega_{\text{sp}}$

Figure 1.14 Energy flux around a particle for a wavelength (a) much higher or lower than the resonance frequency and (b) at the resonance frequency.

The shape of the extinction and scattering spectra of a nanoparticle is affected by the particle composition, dielectric environment, shape and size of the particle, and the polarization of incident radiation. For an individual particle, increasing the refractive index of the dielectric environment red shifts the surface plasmon resonance peak. This is due to a buildup of surface charges in the dielectric which results in a decrease of the restoring force. When nanoparticles are arranged into a one dimensional linear array or a two dimensional planar array, neighboring nanoparticles can interact and thus change the optical response of the individual particles. In a linear particle array with an interparticle distance comparable to the particle diameter, excitation
with polarization parallel to the particle chain results in the near field of one dipole adding constructively to the adjacent dipole. The field lines of adjacent particles point in the same direction which strengthens the exciting field and red shifting the resonance to a lower frequency. This is called the longitudinal excitation mode which decreases the restoring force of neighboring dipoles due to the charge distribution on adjacent spheres which attracts the displaced charge density, lowering the natural oscillation frequency of the particle.

![Diagram](image)

(a) Longitudinal Mode  
(b) Transverse Mode

Figure 1.15 (a) Parallel (longitudinal mode) and (b) perpendicular (transverse mode) polarization of linear arrays of spheres when $k = 0$.

When the linear array is excited with polarization perpendicular to the particle chain, the near fields of adjacent dipoles add destructively, with field lines pointing in opposite directions. The exciting field is weakened around the adjacent dipole, blue shifting the resonance to a higher frequency. This is called the transverse excitation mode which increases the restoring force of the neighboring dipoles. The collective longitudinal and transverse modes can be seen in Figure 1.15 (a) and (b), respectively.
Two dimensional arrays of nanoparticles can act as a grating depending on the diameter of the particles and the interparticle spacing. When the diameter of the particle is greater than the wavelength of incident light, coherent excitation of the particles scatters light at defined angles, like that of a grating. When the diameter of the particle is comparable to the wavelength of incident light, scattering occurs along an order that is parallel to the plane of the particle grating forming singularities in the scattering intensity for particles with large scattering cross-sections, called Wood’s anomalies. For an array of particles with diameters less than the wavelength of incident light, scattering occurs along the zeroth order, which is transmission. Two types of electromagnetic interactions are present when the diameter is less than the wavelength of incident light for these arrays. The first is far field dipolar interactions that occur when the interparticle spacing is approximately equal to $\lambda_{\text{inc}}$ and has a distance dependence of $d^{-1}$, where $d$ is the diameter of the particle. The second is when the interparticle spacing $\ll \lambda_{\text{inc}}$ and near field dipolar interactions dominate with a distance dependence of $d^{-3}$.

1.2.4 Wavevectors at a Surface

1.2.4.1 Surface plasmon polaritons

Maxwell’s equations allow for propagating charge oscillations at metal interfaces as EM surface waves for a wide range of eigenfrequencies which occur below the plasma frequency and as a result, light cannot travel in the metal. The resulting excitation of a coupled state between incident photons and the plasma oscillations of the conduction electrons at the metal dielectric interface are called surface plasmon polariton (SPP) modes. The $k$-vector for the surface waves is high which results in the waves not coupling to the incident radiation and thus, the modes are
bound modes. SPPs are transverse magnetic (TM) polarized modes that exist at the interface of two materials when the real part of the electric permittivity, $\varepsilon(\omega)$, changes sign across the interface. The most common example of such a system is the boundary between a metal and a dielectric at optical frequencies. When $\varepsilon(\omega)$ changes sign across an interface, the continuity of the normal component of the displacement vector implies a solution with evanescent fields on both sides of the interface.

**1.2.4.2 Dispersion relation boundary conditions**

SPP modes are dispersive electromagnetic waves which are naturally confined in two dimensions by the collective oscillations of the conduction electrons. Solutions to the SPP modes are found by assuming a wave exists at the metal dielectric interface and solve the wave equation using appropriate boundary conditions. The derivation of these boundary conditions can be found in Appendix A. The wavevector in air is given by

$$k_0 = \frac{2\pi}{\lambda} = \frac{\omega}{c}, \quad (1.153)$$

however, in a dielectric the wavevector becomes

$$k_d = \frac{\omega}{c} \sqrt{\varepsilon \omega}, \quad (1.154)$$

and on a surface of the metal the wavevector is given by

$$k_x = \frac{2\pi}{\lambda_x} = k_0 \sin \theta, \quad (1.155)$$
where $\theta$ is the angle of displacement from normal of the incident light.

![Figure 1.16 Illumination of a metal-dielectric interface at an angle, $\theta$, produces polarization along the boundary with $k_x < k_0$.](image)

For a wave incident on a metal film, the wave equation for the surface modes inside the dielectric and inside the metal must be satisfied. The assumptions for the surface modes that are there are no free charges and no free current, resulting in the frequency dependent dielectric constant of the metal fully describing its optical response. In addition to the surface modes, boundary conditions at the interface of the metal and dielectric must be satisfied. The boundary conditions for Maxwell’s equations state that the lateral fields across the interface must be continuous,

$$E_{x,metal} = E_{x,dielectric} = E_0,$$  \hspace{1cm} (1.156)
and the parallel component of the magnetic field intensity must also be continuous across the interface,

\[ H_{y,\text{metal}} = H_{y,\text{dielectric}} = H_0. \] (1.157)

The normal displacement must be continuous across the interface,

\[ \varepsilon_{\text{metal}} E_{z,\text{metal}} = \varepsilon_{\text{dielectric}} E_{z,\text{dielectric}}, \] (1.158)

where differences in the normal electric field are allowed due to surface charges associated with the difference in dielectric constants of the material. Phase matching must occur between the wavevectors along the \( X \) axis, with

\[ k_{x,\text{metal}} = k_{x,\text{dielectric}} = k_x. \] (1.159)

If \( \varepsilon_m \) is sufficiently negative, allowed surface and interface modes can occur when Maxwell’s equations and the boundary conditions are all met.

### 1.2.4.3 Oscillatory solutions for a single wavevector

To find the oscillatory solutions for a single wavevector in the metal and dielectric, the wavevector length needs to satisfy

\[ |k_z| = \frac{n_i \omega}{c}, \] (1.160)
where \( i \) represents either the dielectric or the metal. Applying boundary conditions to the system allows for a single \( k \)-vector value for a specific combination of \( \epsilon_d \) and \( \epsilon_m \). Since bound modes do not exist for TE modes, only TM modes in the \( XZ \) plane need to be constructed. In the dielectric, \( z > 0 \), whereas in the metal, \( z < 0 \), and the electric and magnetic fields given by

\[
E_i = (E_0, 0, E_{z,i})e^{i(k_x x + k_z,i z - \omega t)},
\]

\[
H_i = (0, H_0, 0)e^{i(k_x x + k_z,i z - \omega t)},
\]

where, again, the subscript \( i \) (not to be confused with the exponential imaginary number, \( i \)) represents either the dielectric or the metal. For a wave along the \( x \)-axis, the \( k \)-vector of the mode, \( k_x \), should have a real component and for a wave confined vertically, the imaginary component of \( k_z \) should predominate.

By substituting equation (1.162) into Maxwell’s equation (1.9) relating the rotation of \( H \) to the time derivative of \( E \) gives

\[
\nabla \times H_i = e^{i(k_x x + k_z,i z - \omega t)} \left( \frac{\partial H_{z,i}}{\partial y} - \frac{\partial H_{y,i}}{\partial z}, \frac{\partial H_{x,i}}{\partial z} - \frac{\partial H_{z,i}}{\partial x}, \frac{\partial H_{y,i}}{\partial x} - \frac{\partial H_{x,i}}{\partial y} \right).
\]

However, the only component not equal to 0 is \( H_y \), so all partial derivatives without \( H_y \) cancel out leaving

\[
\nabla \times H_i = e^{i(k_x x + k_z,i z - \omega t)} \left( -\frac{\partial H_{y,i}}{\partial z}, 0, \frac{\partial H_{y,i}}{\partial x} \right),
\]

(1.164)
to give the rotating field vector
\[ \nabla \times \mathbf{H}_i = e^{i(k_x x + k_z z - \omega t)} (-i k_z H_0 - i k_x H_0, 0, 0). \] (1.165)

Following the same steps with the electric field and substituting equation (1.161) into equation (1.9) yields
\[ \varepsilon_i \frac{\partial E_i}{\partial t} = e^{i(k_x x + k_z z - \omega t)} (-i \omega \varepsilon_i E_0, 0, -i \omega \varepsilon_i E_{z,i}). \] (1.166)

Combining equations (1.165) and (1.166) gives
\[ (-i k_z H_0 - i k_x H_0) = (-i \omega \varepsilon_i E_0, 0, -i \omega \varepsilon_i E_{z,i}). \] (1.167)

For both the metal and dielectric, \( i = m \) or \( d \), the \( x \) component gives
\[ k_{z,i} H_0 = \omega \varepsilon_i E_0, \] (1.168)

and rearranging it to solve for \( E_0 \),
\[ E_0 = \frac{k_{z,i} H_0}{\omega \varepsilon_i}. \] (1.169)

From the boundary condition in equation (1.156), which demands for continuous lateral fields and further substituting in for \( E_0 \) with \( i = m \) and \( d \) gives
\[
\frac{k_{z,m}H_0}{\omega \varepsilon_m} = \frac{k_{z,d}H_0}{\omega \varepsilon_d}, \tag{1.170}
\]

which simplifies to an elegant relation between the normal, and approximately imaginary, \(k\)-vector in the metal and dielectric for a fixed \(k_x\), and single \(E_{x,i}\) and \(H_{y,i}\), as

\[
\frac{k_{z,m}}{\varepsilon_m} = \frac{k_{z,d}}{\varepsilon_d}. \tag{1.171}
\]

The same derivation can be done with the \(z\)-component to yield

\[
\varepsilon_d E_{z,d} = \varepsilon_m E_{z,m}, \tag{1.172}
\]

which demonstrates that matching \(k_{x,m} = k_{x,d}\), \(E_{x,m} = E_{x,d}\), and \(H_{y,m} = H_{y,d}\), satisfies \(E_z\).

The spatial periodicity, \(k\), and temporal periodicity, \(\omega\), are linked via the wave equation where fast oscillations, which are high frequencies, correspond to short wavelengths by

\[
|k_{x,y,z}| = n \left(\frac{\omega}{c}\right) = \sqrt{\varepsilon \mu} \left(\frac{\omega}{c}\right), \tag{1.173}
\]

With the \(k_y\) component equal to 0 and assuming that the permeability, \(\mu\), is equal to 1, the total length of the wavevector is now given by

\[
k_x^2 + k_z^2 = \varepsilon \left(\frac{\omega}{c}\right)^2, \tag{1.174}
\]

where \(k_x\) in both the metal and dielectric is
\[ k_x^2 = \varepsilon_i \left( \frac{\omega}{c} \right)^2 - k_{z,i}^2, \quad (1.175) \]

and the wavevector normal to the surface, which gives the size of the plasmonic mode, is

\[ k_{z,i} = \left( \frac{\omega}{c} \right) \sqrt{\varepsilon_i \left( \frac{\omega}{c} \right)^2 - k_x^2}. \quad (1.176) \]

Applying the boundary condition for phase matching across the interface given in equation (1.159) and solving equation (1.171) for \( k_{z,m} \), equation (1.175) can be solved for the complex wavevector, \( k_x \), giving the surface plasmon dispersion relation,

\[ k_x = \left( \frac{\omega}{c} \right) \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}, \quad (1.177) \]

which demonstrates that the increase in momentum of the surface plasmon wavevector, \( k_{sp} \), which is associated with the binding of the SPs to the surface, results in a momentum mismatch between the incident wave and the SP wave at the interface,

\[ \hbar k_{sp} > \hbar k_0, \quad (1.178) \]

which gives rise to the dispersion relation between the two wavevectors.

From the amplitude continuity for \( H_y(0,z) \) and \( E_z(0,z) \) gives
\[ \frac{k_{dx}}{\varepsilon_d} H_{dy} - \frac{k_{mx}}{\varepsilon_m} H_{my} = 0, \quad (1.179) \]

which reduces to

\[ \frac{k_{dx}}{\varepsilon_d} - \frac{k_{mx}}{\varepsilon_m} = 0, \quad (1.180) \]

after taking \( H_{dy} - H_{my} = 0 \). Combined with the propagation constant, \( \beta = k_{dz} = k_{mz} \), the propagation constant of a plane wave in a medium, \( i = m \) or \( d \), becomes

\[ \varepsilon_i k_0^2 - k_{dx}^2 = \beta^2. \quad (1.181) \]

Solving for \( \beta \) gives

\[ \beta^2 = k_0^2 \left( \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right), \quad (1.182) \]

which can be rearranged to give the \( k \)-vector in the dielectric

\[ k_{dx}^2 = k_0^2 \left( \frac{\varepsilon_d^2}{\varepsilon_m + \varepsilon_d} \right), \quad (1.183) \]

and metal,
The plane wave solutions to the wave equation, the SP resonances, are damped oscillations of the electromagnetic field which have an exponential decay perpendicular to the metal-dielectric interface. The decay occurs in both the metal and the surrounding dielectric medium. The length at which the intensity of the electric field inside a medium decreases to $1/e$ is called the penetration depth. The equation is obtained by squaring $k = k' + k''$ and inserting it into equation (1.16) to give the penetration depth in the metal as

$$\delta_m = \frac{1}{k_{x,m}},$$

(1.185)

and dielectric as

$$\delta_d = \frac{1}{k_{x,d}}.$$  

(1.186)

The propagation distance of the SPP mode is the distance when the electric field drops to $1/e$ of the intensity and is given by

$$L_p = \frac{1}{|2k_x|} = \frac{c}{\omega} \left(\frac{\varepsilon_m' + \varepsilon_d'}{\varepsilon_m'\varepsilon_d} \right)^{3/2} \frac{\varepsilon_m'^2}{\varepsilon_m}.$$  

(1.187)
As shown in the previous section, metals have a frequency dependent dielectric constant, \( \varepsilon(\omega) \), and are therefore dispersive materials. It is a consequence of the non-instantaneous polarization response of the material to a time varying electric field. The dispersion relation between the incident light and SPP modes can be demonstrated by plotting the angular frequency against the \( k \)-vector as shown in Figure 1.17, where the angular frequency of the SPP mode diverges as it approaches the plasma resonance at large values of \( k_c \).

![Figure 1.17 Surface plasmon dispersion relation.](image)

It can be seen that there is a resonance condition that arises at the divergence where \( \varepsilon_m = -\varepsilon_d \), defining the surface plasma frequency. From the approximation of \( \varepsilon_m \) in the Drude model, the surface plasma frequency is seen as
\[ \omega_{sp} = \sqrt{\frac{\omega_p^2}{1 + \varepsilon_d}}, \quad (1.188) \]

which reduces to

\[ \omega_{sp} = \frac{\omega_p}{\sqrt{2}}, \quad (1.189) \]

in vacuo or in air.

### 1.2.4.4 Excitation of SPP modes

The dispersion relation in equation (1.177) is useful for describing surface plasmon excitation and propagation. Excitation of SPP modes cannot be done by normal incident light. The \( k \)-vector of a photon in air is always less than the \( k \)-vector of the excited SPP mode, therefore excitation of SPP modes cannot be done directly. It can only be achieved when the wavevector of incident light is increased beyond its free space value. To excite the SPP modes, both energy and momentum need to be conserved which can be achieved through a variety of methods. When the photon is in a dielectric with a larger refractive index than air, the \( k \)-vector is increased. As the refractive index is increased, the \( k \)-vector of the photon can be increased sufficiently enough so that it reaches that of the SPP mode, thus effectively exciting the SPP mode. Several methods for exciting SPP modes include prism coupling to increase \( k_0 \), scattering from a topological defect such as a hole or surface structure which locally generates SPs, and periodic corrugation such as a grating in which the diffracted light allows for momentum matching.
The first method of excitation is via prism coupling by using the Kretschmann configuration as shown in Figure 1.18. For an incident photon in air, $\omega_0 = c k_0$, the photon upon entering the dielectric becomes

$$k_d = \frac{\omega_0}{c} \sqrt{\varepsilon_0}. \tag{1.190}$$

The excitation can be achieved for a given angle, $\theta_0$, to obtain the $k$-vector for the SPP mode by

Figure 1.18 Schematic of the Kretschmann configuration for the excitation of SPPs on a metal film.
$$k_x = \frac{\omega_0}{c} \sqrt{\frac{\varepsilon_m}{\varepsilon_m + 1}} = \frac{\omega_0}{c} \left(\sqrt{\varepsilon_0}\right) \sin \theta_0.$$  

(1.191)

Excitation by a surface structure can be done using a confined light source such as that of a subwavelength aperture probe (SNOM), irradiation of a nanoparticle, or excitation of fluorescent molecules. Each method produces SPP modes from the confined light source, such as the excited localized surface plasmons on a nanoparticle, by locally inducing a separation of charges and the subsequent excitation of evanescent field components which match that of the $k$-vector of the SPP mode. A schematic depicting the excitation of LSP modes on a nanoparticle to excite SPP modes on a metal film is shown in Figure 1.19.
Figure 1.19 Excitation of SPs on a nanoparticle placed on the surface of a metallic film which locally induces charge separation in the film and excites SPP modes travelling along the metal-dielectric boundary.

SPP modes can also be excited using a grating coupler, which is also referred to as the attenuated reflection method. The incident wavevector is increased to momentum match with the SPP mode by the addition of a reciprocal lattice vector of the grating to the wavevector of free space. The surface must have a periodic structure with a periodicity, $a$, resulting in a new wavevector,

$$k_{spp} = k_x \sin \theta_i + \frac{2\pi n}{a},$$  \hspace{1cm} (1.192)

where the second term is the reciprocal lattice vector for $n = 1, 2, \ldots$, shown in Figure 1.20.
In this chapter, the origin of surface plasmons based on electrodynamic theory was discussed. The next chapter will elaborate on different methods employed in the computational work presented in this thesis. The following chapters will discuss applications of surface plasmons for light manipulation at optical frequencies in the nanoscale regime.
CHAPTER 2: METHODS

2.1 Introduction

The origin of electrodynamics began on 21 April 1820 when Hans Christian Ørsted observed a compass needle being deflected from magnetic north while an electric current from a battery nearby was switched on. He became the first to recognize that electric currents create magnetic fields, therefore inextricably linking the two previously independent subjects. Inspired by Ørsted’s work, André-Marie Ampère demonstrated that a set of wires carrying an electric current oriented parallel to each other will attract the other when the currents are flowing in opposite directions, but when the direction of the current in one of the wires is reversed so that the current flow is in the same direction, the wires repelled each other. From this observation, Ampère hypothesized that all magnetic phenomenon are a result of the movement of electric charges.

On 29 August 1831, Michael Faraday used an iron torus with two wires wrapped around opposing sides, with one wire connected to a battery and the other wire connected to a galvanometer to observe the effects of the electric current on the adjacent wire, thus demonstrating magnetic induction. Additional work by Faraday demonstrated that a moving magnet produces an electric current, further building the relationship between electric currents and magnetic fields. On 1 January 1865, James Clerk Maxwell published *A Dynamical Theory of the Electromagnetic Field*, establishing that electric and magnetic fields propagate at the speed of light as waves through space. Contained in his manuscript were a set of 4 equations which...
classically described electromagnetic phenomena relating electric charges and currents to electric and magnetic fields, and thus Maxwell’s Equations were born.

Maxwell’s equations are the foundation of classical electrodynamics theory. The optical properties of metal nanostructures can be calculated out utilizing Maxwell’s electromagnetic theory. In this chapter I will discuss various computational methods utilized in the research contained in this thesis. The methods are the general Mie theory, T-Matrix method, Discrete Dipole Approximation method, and Coupled-Dipole Approximation method.

2.2 Mie Theory

For the first time, light scattering by small spherical particles using Maxwell’s theory of electromagnetic waves was demonstrated in 1908 by Gustav Mie. Mie theory successfully explains the color changing phenomenon observed in gold colloidal solutions with variation of the size of gold particles. The optical properties of a single spherical particle are analytically solved using the general Mie theory. The electromagnetic fields in and around a spherical particle with a core-shell structure generated by illumination with a plane electromagnetic wave can be obtained by using the vector spherical harmonics to describe the electromagnetic fields both in the shell and core, along with the fields outside of the particle and the incident light.

In Mie theory, the incident plane wave is expressed as
\[ E_i = E_0 \sum_{n=1}^{\infty} i^n \frac{2n + 1}{n(n + 1)} (M_{o1n}^{(1)} - iN_{e1n}^{(1)}) , \]  
(2.1)

\[ H_i = \frac{-k}{\omega \mu} E_0 \sum_{n=1}^{\infty} i^n \frac{2n + 1}{n(n + 1)} (M_{e1n}^{(1)} + iN_{o1n}^{(1)}) , \]  
(2.2)

where the electric and magnetic fields within the core, shell and outside of the particle are obtained from

\[ E_1 = \sum_{n=1}^{\infty} E_n (c_n M_{o1n}^{(1)} - id_n N_{e1n}^{(1)}) , \]  
(2.3)

\[ H_1 = \frac{-k_1}{\omega \mu_1} \sum_{n=1}^{\infty} E_n (d_n M_{e1n}^{(1)} + ic_n N_{o1n}^{(1)}) , \]  
(2.4)

\[ E_{sh,j} = \sum_{n=1}^{\infty} E_n (f_{n,j} M_{o1n}^{(1)} - ig_{n,j} N_{e1n}^{(1)} + \nu_{n,j} M_{o1n}^{(2)} - iw_{n,j} N_{e1n}^{(2)}) , \]  
(2.5)

\[ H_{sh,j} = \frac{-k_j}{\omega \mu_j} \sum_{n=1}^{\infty} E_n (g_{n,j} M_{e1n}^{(1)} + if_{n,j} N_{o1n}^{(1)} + w_{n,j} M_{e1n}^{(2)} + iv_{n,j} N_{o1n}^{(2)}) , \]  
(2.6)

\[ E_s = \sum_{n=1}^{\infty} E_n (ia_n N_{e1n}^{(3)} - b_n M_{o1n}^{(3)}) , \]  
(2.7)
\[ H_s = \frac{k}{\omega \mu} \sum_{n=1}^{\infty} E_n \left( i b_n M_{e1n}^{(3)} + a_n N_{o1n}^{(3)} \right), \]  

(2.8)

where the wavevectors in the surrounding environment and in the \( j \)th shell are given by \( k \) and \( k_j \), respectively, and the angular frequency of the light is given by \( \omega \). The permeabilities of the environment and \( j \)th shell, are given by \( \mu \) and \( \mu_j \), respectively, \( n \) represents the degree of the functions, and \( a, b, c, d, g, f, w, v \), are expansion coefficients. \( E_1, H_1 \), are the electric and magnetic fields in the core and \( E_s, H_s \) are the scattered electric and magnetic fields, respectively. \( E_{sh,j} \) and \( H_{sh,j} \) denote the fields within the \( j \)th shell and \( E_\theta \) represents the magnitude of incident electric field, with \( E_n \) expressed as

\[ E_n = i^n \frac{E_\theta(2n+1)}{n(n+1)}. \]  

(2.9)

The vector functions \( M \) and \( N \) are given by

\[ M_{o1n} = \cos \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\theta - \sin \phi \tau_n (\cos \theta) z_n (\rho) \hat{e}_\phi, \]  

(2.10)

\[ M_{e1n} = -\sin \phi \pi_n (\cos \theta) z_n (\rho) \hat{e}_\theta - \cos \phi \tau_n (\cos \theta) z_n (\rho) \hat{e}_\phi, \]  

(2.11)
\[ N_{o1n} = \sin \phi n(n + 1) \sin \theta \pi_n \cos \theta \frac{z_n(\rho)}{\rho} \hat{e}_r \]
\[ + \sin \phi \tau_n (\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\rho + \cos \phi \pi_n (\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\phi, \tag{2.12} \]

\[ N_{e1n} = \cos \phi n(n + 1) \sin \theta \pi_n (\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_r \]
\[ + \cos \phi \tau_n (\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\rho - \sin \phi \pi_n (\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\phi. \tag{2.13} \]

The superscripts appended to the functions \( M \) and \( N \) are the types of spherical Bessel functions \( Z_n \) where (1) represents the power series expansion, \( j_n(\rho) \), and (3) refers to the first kinds of \( h_n(\rho) \). (2) represents the power series, \( j_n(\rho) \), for \( N \) functions and the power series, \( y_n(\rho) \), for \( M \) functions. \( \rho = kr \) is a dimensionless term where \( r \) is the radius of the shell and \( k \) is the wavevector. The spherical polar angles are given by \( \theta \) and \( \phi \). The functions that give \( \pi_n \) and \( \tau_n \) are

\[ \pi_n = \frac{P_n^1}{\sin \theta}, \tag{2.14} \]
\[ \tau_n = \frac{dP_n^1}{d\theta}. \tag{2.15} \]
where \( P_n^1 \) designates the associated Legendre functions of the first kind with an order = \( l \) and degree = \( n \). Applying boundary conditions at every interface, the expansion coefficients are then expressed as

\[
E^{\text{in}}_\theta = E^{\text{out}}_\theta , \quad (2.16)
\]

\[
E^{\text{in}}_\phi = E^{\text{out}}_\phi , \quad (2.17)
\]

\[
H^{\text{in}}_\theta = H^{\text{out}}_\theta , \quad (2.18)
\]

\[
H^{\text{in}}_\phi = H^{\text{out}}_\phi , \quad (2.19)
\]

where the superscripts \( \text{in} \) and \( \text{out} \) symbolize the electromagnetic fields inside, \( \text{in} \), and outside, \( \text{out} \), of the interface surface, and \( P_n^1 \) is the associated Legendre functions of the first kind with order = \( l \) and degree = \( n \).

The extinction and scattering cross-sections can be calculated by

\[
C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) , \quad (2.20)
\]
The absorption cross section, $C_{abs}$, can be obtained from $C_{ext} - C_{sca} = C_{abs}$. The extinction, scattering, and absorption efficiencies are obtained by dividing the optical cross-section obtained from equations (2.20) and (2.21) with the physical cross-section of the spherical particle.

### 2.3 Kramers-Kronig Relations

The Kramers-Kronig relations, also referred to as dispersion relations, are a set of equations that relate the real and imaginary parts of the susceptibility to each other. Combined with the absorption spectrum calculated out from the Mie theory, the Kramers-Kronig relations enable the entire susceptibility to be determined for all frequencies. They allow for the extraction of physical properties, however, they are derived and founded on three principles being linearity, causality, and the inability for a system to respond to infinitely high frequencies.

The polarization, $P(t)$, at time $t$ is dependent on $E(t)$ at all other given times, $t'$ by way of a linear functional relationship,

$$P(t) = \int_{-\infty}^{\infty} G(t, t')E(t')dt'.$$  

The response function, $G$, is given by

$$C_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2).$$  

(2.21)
\[ G(t) = P(t), \quad (2.23) \]

if

\[ E(t) = \delta(t). \quad (2.24) \]

The electric field then is a \( \delta \) function applied at \( t_0 = 0 \)

\[ E(t) = \delta(t - t_0)E_0, \quad (2.25) \]

and the polarization that corresponds to the function is

\[ P(t) = G(t, t_0)E_0. \quad (2.26) \]

where the polarization resulting from the unit amplitude \( \delta \) function is given by \( G \). The polarization is dependent on the time between \( t \) and \( t_0 \), assuming there is no variation in the properties of the medium over time,

\[ G(t - t_0) = G(t, t_0). \quad (2.27) \]

By way of the convolution theorem, which states
\[ P(t) = \int_{-\infty}^{\infty} G(t - t')E(t')dt', \quad (2.28) \]

where

\[ G(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \epsilon_0 \chi(\omega)e^{-i\omega t}d\omega, \quad (2.29) \]

showing that the susceptibility \( \chi(\omega) \) dependent on the frequency indicates the polarization at a given time, \( t \), will depend on the electric field at all other times, \( t' \).

The Fourier transformation of the equations from the time domain to the frequency domain are related via the convolution theorem by

\[ P(t) = G(t)E(t). \quad (2.30) \]

The functions \( P(t) \) and \( E(t) \) need to be real, therefore, via the crossing condition,

\[ P(t) = P^*(-t), \quad (2.31) \]

\[ G(t) = G^*(-t), \quad (2.32) \]

\[ E(t) = E^*(-t). \quad (2.33) \]
Causality, where the present is determined by the past and not the future, requires

\[ G(t - t') = 0 \quad \text{for} \quad t' \geq t. \quad (2.34) \]

Taking the Fourier transform of \( G(t) \) yields the complex susceptibility, \( \chi(\omega) \), for a real value of \( \omega \),

\[ \varepsilon_0 \chi(\omega) = \int_{-\infty}^{\infty} G(t) e^{i\omega t} \, dt = \int_{0}^{\infty} G(t) e^{i\omega t} \, dt. \quad (2.35) \]

For a function of the complex variable \( \tilde{\omega} = \omega' + i\omega'' \)

\[ \varepsilon_0 \chi(\tilde{\omega}) = \int_{0}^{\infty} G(t) e^{i\tilde{\omega} t} \, dt. \quad (2.36) \]

When \( \tilde{\omega} \) is a point on a real axis, \( \chi(\tilde{\omega}) \) coincides with \( \chi(\omega) \). An analytic function of \( \tilde{\omega} \) is

\[ G(t)e^{t\tilde{\omega} t} \quad \text{for} \quad t \geq 0, \quad (2.37) \]

and if \( \omega'' > 0 \), then

\[ |G(t)e^{t\tilde{\omega} t}| \leq |G(t)|. \quad (2.38) \]

The convergence of the integral
occurs when \( \chi(0) \) is finite, then

\[
\int_0^\infty |G(t)| dt, \tag{2.39}
\]

\[
\int_0^\infty G(t)e^{i\omega t} dt, \tag{2.40}
\]

converges to an analytic function in the upper half of the complex plane, \( \tilde{\omega} \). Given an analytic \( \chi(\tilde{\omega}) \), then, with the exception when \( \tilde{\omega} = \omega \),

\[
\frac{\chi(\tilde{\omega})}{(\tilde{\omega} - \omega)}. \tag{2.41}
\]

For a closed contour, \( C \), containing no pole of an analytic function, \( f(\tilde{\omega}) \), Cauchy’s theorem can be stated as

\[
\int_C f(\tilde{\omega}) d\tilde{\omega} = 0, \tag{2.42}
\]

which can be applied to equation (2.41), with \( \omega \) representing a point on the real axis with the contour \( C \), shown in Figure 2.1.
Figure 2.1 Cauchy’s contour of integration.

The contour of integration is comprised of four curves with parametric representations shown in Table 2.1.

Table 2.1 Parametric representations of the four curves in Cauchy’s contour of integration.

<table>
<thead>
<tr>
<th>( C_i )</th>
<th>( \tilde{\omega} = \Omega )</th>
<th>((-A \leq \Omega \leq \omega - a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>( \tilde{\omega} = \omega - ae^{-i\Omega} )</td>
<td>((0 \leq \Omega \leq \pi))</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>( \tilde{\omega} = \Omega )</td>
<td>((\omega + a \leq \Omega \leq A))</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>( \tilde{\omega} = Ae^{i\Omega} )</td>
<td>((0 \leq \Omega \leq \pi))</td>
</tr>
</tbody>
</table>

It can be obtained from Cauchy’s theorem that
\[
\int_{-A}^{\omega-a} \frac{\chi(\Omega)}{\Omega - \omega} d\Omega + \int_{\omega+a}^{A} \frac{\chi(\Omega)}{\Omega - \omega} d\Omega + \int_{0}^{\pi} \frac{iAe^{i\Omega}\chi(Ae^{i\Omega})}{Ae^{i\Omega} - \omega} d\Omega
\]
\[
= \int_{0}^{\pi} i\chi(\omega - ae^{i\Omega}) d\Omega. \tag{2.43}
\]

As \(A\) tends towards infinity when \(\lim_{|\tilde{\omega}| \to \infty} \chi(\tilde{\omega}) = 0\), the integral over \(C_4\) vanishes, giving

\[
i\pi\chi(\omega) = P \int_{\omega+a}^{\infty} \frac{\chi(\Omega)}{\Omega - \omega} d\Omega \tag{2.44}
\]

if \(\chi(\tilde{\omega})\) is continuous, with \(P\) representing the Cauchy principal value of the integral,

\[
\lim_{a \to 0} \int_{-\infty}^{\omega-a} \frac{\chi(\Omega)}{\Omega - \omega} d\Omega + \int_{\omega+a}^{\infty} \frac{\chi(\Omega)}{\Omega - \omega} d\Omega. \tag{2.45}
\]

In the case of the electric susceptibility, \(\chi' + i\chi''\), for a medium which is linear, isotropic, achiral, and homogeneous, the real part of \(\chi(\omega)\) is \(\chi'(\omega)\) and the imaginary part is \(\chi''(\omega)\) as \(\lim_{\omega \to \infty}(\omega) = 0\). The real and imaginary parts of \(\chi\) are related by

\[
\chi'(\Omega) = \frac{2}{\pi} P \int_{0}^{\infty} \frac{\Omega\chi''(\Omega)}{\Omega^2 - \omega^2} d\Omega, \tag{2.46}
\]

\[
\chi''(\omega) = -\frac{2\omega}{\pi} P \int_{0}^{\infty} \frac{\chi'(\Omega)}{\Omega^2 - \omega^2} d\Omega. \tag{2.47}
\]
The susceptibility is related to the refractive index by

\[ n(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\Omega \kappa(\Omega)}{\Omega^2 - \omega^2} d\Omega = \frac{c}{\pi} P \int_0^\infty \frac{\alpha(\Omega)}{\Omega^2 - \omega^2} d\Omega, \quad (2.48) \]

\[ \kappa(\omega) = \frac{\alpha(\omega)c}{2\omega} = -\frac{2\omega}{\pi} P \int_0^\infty \frac{n(\Omega)}{\Omega^2 - \omega^2} d\Omega. \quad (2.49) \]

The integrals are sufficient for most frequencies except for the extreme upper limits where the wavelength of incident light is so small compared to the dimensions of the particle. These relations demonstrate the physical phenomenon that the response time of an oscillator is not instantaneous due to damping and inertia. Physically, it can be interpreted more readily as a sample which has a steady electric field applied to it for an extended period of time will have a steady induced polarization in the medium. If the electric field is instantly removed, the polarization would not become instantaneously zero, but instead would decay on a time scale dependent on the material properties.

\section*{2.4 T-Matrix Method}

The T-matrix method, also called the null field method or extended boundary condition method, was proposed by Waterman\textsuperscript{9} in 1971 and further developed by Mishchenko, Mackowski and coworkers, which calculates the extinction, scattering, and absorption spectra for an array of spherical nanoparticles.\textsuperscript{10-15} It is based on an expansion of the incident, scattered, and transmitted fields into a series of spherical vector wave functions. The method only depends on the incident wavelength, shape of the particle, refractive index of the particle, and the relative position in the
coordinate system. The name of the method arises from the transition matrix which is computed relating the incident and scattered field coefficients.

The scattered electric field, \( E_s \), from an array of spherical particles is obtained by summing the electric field from each sphere, \( E_{s,i} \), by

\[
E_s = \sum_{i=1}^{N_s} E_{s,i} ,
\]

where \( N_s \) is the sphere number and \( E_{s,i} \) is represented by vector spherical harmonics as

\[
E_{s,i} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \sum_{p=1}^{2} a_{mnp}^i H_{mnp}^i (r_i) ,
\]

where \( m \) is the degree and \( n \) is the order for the spherical harmonics, \( H_{mnp}^i \), \( a_{mnp}^i \) is the expansion coefficient for particle \( i \). The mode of scattered electric field is given by \( p \), with \( p = 1 \) denoting the transverse magnetic mode (TM) and \( p = 2 \) denoting the transverse electric mode (TE). The expansion coefficient can be truncated to \( n = N_t^i \) giving

\[
a_{mnp}^i + a_{np} \sum_{j=1}^{N_s} \sum_{l=1}^{N_t^j} \sum_{k=-l}^{l} H_{mnpklq}^j a_{klq}^j = a_{np} p_{mnp}^i ,
\]
where $H_{mnpklq}^{ij}$ is the Hankel-function based addition coefficients, $a_{k}\text{}_{lq}^{j}$ is the TM and TE Mie coefficients, and $p_{mnp}^{l}$ denotes the coefficients of the incident wave at the origin of the $i^{th}$ sphere. From equation (2.52), $a_{mnp}^{l}$ can be transferred to a transition matrix, the T-matrix,

$$a_{mnp}^{l} = \sum_{j=1}^{N_{s}} \sum_{l=1}^{N_{l}} \sum_{k=-l}^{l} \sum_{q=-l}^{l} T_{mnpklq}^{ij} p_{k}^{l}, \quad (2.53)$$

To describe all of the individual spheres in the array as a whole, the electric field based on a single coordinate origin must be constructed. The expansion coefficient for the scattered field is given by

$$a_{mnp}^{0} = \sum_{i=1}^{N_{s}} \sum_{l=1}^{N_{l}} \sum_{k=-l}^{l} \sum_{q=-l}^{l} J_{mnpklq}^{0i} a_{k}^{l}, \quad (2.54)$$

where $J_{mnpklq}^{0i}$ is addition coefficient, yielding

$$a_{mnp}^{0} = \sum_{l=1}^{N_{l}} \sum_{k=-l}^{l} \sum_{q=-l}^{l} T_{mnpklq}^{0} p_{k}^{0}. \quad (2.55)$$

The orientation-averaged extinction cross section of the array of particles is then calculated by
\[ C_{\text{ext}} = \frac{2\pi}{k^2} \text{Re} \left( \sum_{n=1}^{N} \sum_{m=-n}^{n} \sum_{p=1}^{2} T_{nmnp}^{0} \right). \] (2.56)

### 2.5 Discrete Dipole Approximation Method

While the Mie theory and T-matrix method are fast methods of obtaining extinction, scattering, and absorption spectra, they are limited to calculating optical properties of a single or array of spherical particles. To extend electrodynamic calculations to more complex systems containing particles with arbitrary shapes, new calculation methods have been developed to obtain the optical properties of these systems.\(^{20-22}\) The methods include the Discrete Dipole Approximation (DDA).\(^{16-18,23-28}\) Finite Difference Time Domain (FDTD),\(^{29-32}\) and Extended Boundary Condition (EBCM)\(^{33-35}\) methods. In a review article by Wriedt \textit{et al.} these different methods are thoroughly compared.\(^{36}\) Of these methods, it is shown that the DDA method requires less computation time while generating more accurate results.

The DDA method was first proposed by Purcell and Pennypacker,\(^{16}\) and further developed with significant improves by Draine and Flatau.\(^{17,19}\) There are many independently available computational codes which utilize the DDA method, such as DDSCAT,\(^{16-18}\) ZDD,\(^{23-25}\) and ADDA.\(^{26-28}\) A comparison of these various DDA codes is reported by Antti Penttila \textit{et al.}\(^{37}\)

In this section, a modified version of the DDSCAT computational code developed by Draine \textit{et al.}\(^{17,19}\) is overviewed. A more detailed account of the DDSCAT code can be found in Draine’s papers.\(^{17,18}\)
In the DDA method, a target particle with an arbitrary shape is divided into \( N \) polarizable cubes which are effectively individual dipoles. The position and polarizability of each cube is given by \( r_i \) and \( \alpha_i \), respectively. The optical properties of the dipole array comprised of polarizable cubes are solved electrodynamically. Incident light is applied to the target particle, and polarization of each cube position and the localized electric field are calculated.

The polarization, \( P_i \), of each dipole is a result of the incident field and the summation of the retarded fields resulting from all of the surrounding dipoles in the dipole array and is given by

\[
P_i = \alpha_i E_{\text{loc},i},
\]

with \( i = 1, 2, \ldots, N \), where \( E_{\text{loc},i} \) is the localized electric field which comes from the sum of the retarded and incident electric fields. The retarded electric field component comes from all of the surrounding dipoles. For a given wavelength of incident light, \( \lambda \), the local electric field can be expressed as

\[
E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{retard},i} = E_0 \exp(ik \cdot r_i) - \sum_{j=1}^{N} A_{ij} \cdot P_j,
\]

with \( i = 1, 2, \ldots, N \), where \( E_0 \) denotes the amplitude of the incident light with a wavelength, \( \lambda \), and a wavevector, \( k = 2\pi/\lambda \). \( A \) is the interaction matrix given by
\[ A_{ij} \cdot P_j = k^2 \exp(ikr_{ij}) \frac{r_{ij} \times (r_{ij} \times P_j)}{r_{ij}^3} + \exp(ikr_{ij})(1 - ikr_{ij}) \left[ \frac{r_{ij}^2 P_j - 3r_{ij}^2 (P_j \cdot P_j)}{r_{ij}^5} \right], \quad (2.59) \]

with \( i = 1, 2, ..., N, \) and \( j = 1, 2, ..., N, \) where \( j \neq i.\) Then, distance between the two dipoles \( i \) and \( j, \) is given by the vector \( r_{ij} = r_i - r_j. \) Combining equations (2.57), (2.58), and (2.59) gives

\[ (\alpha_i^{-1})P_i + \sum_{j \neq i} A_{ij} \cdot P_j = E_{inc,i}, \quad (2.60) \]

with \( i = 1, 2, ..., N, \) which can be expressed as a \( 3N \) linear equation in the form of

\[ A'P = E. \quad (2.61) \]

The diagonal elements of the matrix, \( \alpha_i^{-1}, \) comes from the polarizability and the off-diagonal elements are symmetric. After solving equation (2.61), the polarization and local electric field of each cube is obtained. From the dipole polarization and local electric field, the extinction and scattering cross-sections can be obtained via

\[ C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{inc,j}^* \cdot P_j), \quad (2.62) \]
\[ C_{\text{sca}} = \frac{k^4}{|E_0|^2} \int d\Omega \left| \sum_{j=1}^{N} [P_j - \hat{n}(\hat{n} \cdot P_j)] \exp(-ik\hat{n} \cdot r_j) \right|^2, \tag{2.63} \]

where \( \hat{n} \) is the unit vector along each scattering direction and \( \Omega \) is the integration angle in space.

The absorption cross-section, \( C_{\text{abs}} \), is calculated by \( C_{\text{ext}} - C_{\text{sca}} = C_{\text{abs}} \). The extinction, scattering and absorption cross-sections obtained here have units of area, where the corresponding efficiencies, \( Q \), of the overall structure are obtained by dividing the cross-sections by physical areas of the particles or films.

### 2.6 Coupled Dipole Approximation Method

A simplification of the DDA method can be used for spherical nanoparticles or nanoparticle arrays, called the Coupled-Dipole Approximation method.\(^{38}\) In this method, the wavevector of incident light is oriented vertical to the long axis of a nanoparticle array. Assuming that the induced polarization for every particle has same value, a simple analytical solution can be obtained for equation (2.61). The polarization, \( P \), of each particle can be expressed from the polarizability, \( \alpha \), as

\[ P = \frac{\alpha_s E_0}{1 - \alpha_s S} = \frac{E_0}{1/\alpha_s - S}, \tag{2.64} \]

where the extinction cross section of each individual particle is calculated as
\[ C_{\text{ext}} = 4\pi k \text{Im} \left( \frac{P}{E_0} \right) = 4\pi k \text{Im} \left( \frac{1}{1/\alpha_s - S} \right), \] (2.65)

where \( S \) denotes the sum of retarded dipoles given by

\[ S = \sum_{j \neq l} \left[ \left( 1 - ikr_{ij} \right) \left( 3\cos^2 \theta_{ij} - 1 \right) e^{ikr_{ij}} \frac{k^2 \sin^2 \theta_{ij} e^{ikr_{ij}}}{r_{ij}} \right], \] (2.66)

The polarizability in Equation (2.32) is

\[ \alpha_s = \frac{3a_1}{2k^3}, \] (2.67)

where \( k \) is the wavevector of the incident light and \( a_1 \) represents the expansion coefficients from the Mie theory given by

\[ a_1 = \frac{\mu m^2 j_1(mp)[\rho j_1(\rho)]' - \mu_s j_1(\rho)[mpj_1(mp)]'}{\mu m^2 j_1(mp)[\rho h_1(\rho)]' - \mu_s h_1(\rho)[mpj_1(mp)]'}, \] (2.68)

where \( \mu_i \) is the magnetic permeability inside the particle, \( \mu_o \) is the magnetic permeability outside of the particle, \( m \) is the ratio of the refractive index of the particle to the refractive index of the surrounding medium, \( \rho = kr \), where \( r \) is particle radius, and \( j_1, h_1 \) denote the usual spherical Bessel functions described previously.
CHAPTER 3: FANO RESONANCE AND DARK MODES IN NANORODS

3.1 General Introduction

Metal nanorods, when illuminated, support localized surface plasmon (LSP) modes. These plasmonic excitations have two pathways through which they can decay, occurring on the timescale of several femtoseconds. The first pathway is the radiative emission of photons into the far field and the second is a non-radiative pathway via electron-hole excitations. The radiative decay of the excited mode, which is efficiently coupled to the far field as a result of a strong dipole moment, is referred to as a bright mode. The radiative decay pathway can be suppressed if the excited mode demonstrates a weak dipole and thus does not couple with the far field. Therefore it is solely a near field mode, referred to as a dark mode. Consequently, the interaction of light with the LSP modes of the nanorods affects the optical properties of the structure.

Understanding the fundamental mechanisms of LSPs is paramount to further development of novel plasmonic technology which has expanded research in photonic and plasmonics fields for applications such as electricity transmission,\textsuperscript{39} molecular sensing,\textsuperscript{40-42} optical data storage,\textsuperscript{43} and waveguiding.\textsuperscript{44-47} Furthermore, a new group of photonic devices emerge which use light as the information carriers instead of the electrons used in current electronic devices. Curiously, reports have shown that the interaction of incident photons with different LSP resonance modes affects the optical properties of a nanostructure, where this interaction relies on the symmetry of the external fields of nanostructure and the geometry of the nanostructure itself. For interaction purposes, the external fields can be either incident or scattered.\textsuperscript{48-50} Understanding how the optical properties of nanorods are affected by changing the
structure aids in understanding plasmonic phenomena to facilitate the development of next generation photonic devices.

### 3.2 Dark Modes in Nanorods

#### 3.2.1 Introduction

The strength of coupling between a plasmonic mode and free space incident light determines the type of plasmonic mode produced.\(^5\) For nanorods and nanowires, the fundamental dipolar mode, \(m = 1\), along with higher order, multipolar modes with an odd numbered mode index, \(m = 3, 5, \text{ etc.}\), can be excited by incident light. Excitation of SPP modes by incident light occurs when there is an asymmetric charge distribution for the mode where the overall dipole moment of the rod does not vanish. These modes are radiative, bright modes that can couple strongly to incident light and have a large scattering cross-section. On the other hand, modes which have a centro-symmetric charge distribution with an even numbered mode index, corresponding to an even number of nodes, are subradiant dark modes which have a low scattering cross-section with poor light scattering efficiency.

Dark modes have been reported in both experimental and theoretical studies for a variety of different nanostructures.\(^4\)\(^4\),\(^5\)\(^2\)\(^-\)\(^5\)\(^8\) The destructive interference between different modes of the nanostructure results in a reduced scattering cross-section of the dark mode.\(^5\)\(^9\),\(^6\)\(^0\) Despite the reduced radiative loss of the dark mode, it has the ability for longer propagation on subwavelength scales.\(^5\)\(^6\) Lengthy propagation distances due to dark modes have been experimentally reported for nanorods and other structures.\(^4\)\(^4\),\(^5\)\(^6\),\(^6\)\(^1\)-\(^6\)\(^4\)
3.2.2 Results and Discussion

To model the optical properties of partially illuminated rods, the discrete dipole approximation (DDA) method was revised. In the DDA method, a target particle is divided into an array of polarizable cubes. By allowing the incident light to illuminate on a select number of cubes, the extinction, absorption, and the scattering spectra can be calculated as well as the electric field distribution of a partially illuminated silver nanorod.

3.2.2.1 Scattering of a fully versus partially illuminated rod

First, to focus on the different mode excitations of a silver rod, the scattering spectra are calculated when the rod is fully illuminated and when it is partially illuminated. Figure 3.1 (a) and (b) show the schematic of the rods which are oriented along the $Y$ axis with a square cross-section of 50 nm × 50 nm, where the total length of the rod for a fully illuminated structure, shown in Figure 3.1 (a), is 250 nm. For a partially illuminated rod, shown in Figure 3.1 (b), the length of the illuminated region is 50 nm and the length of the region in the dark is 200 nm to give a total length of 250 nm. The notation, 50+200 nm, is used to represent the extent of the illuminated region of the structure, where the first number represents the length in the illumination region while the second number indicates the length in dark. For both structures, the $k$-vector of the incident light is along the $X$ axis and the polarization is along the $Y$ axis.
The scattering spectra for a rod are shown in Figure 3.2, where a fully illuminated rod has the total length of 250 nm illuminated and a partially illuminated rod has a 50 nm illuminated region with a 200 nm dark region. The two spectra are normalized for the convenience of comparison. The fully illuminated rod shows one main resonance peak at a wavelength of 1000 nm and a small peak at a wavelength of 410 nm. However, when the rod is partially illuminated, a new bright mode peak that is forbidden in the fully illuminated rod appears at a wavelength of 540 nm, coupling more strongly to the incident light than the bright mode at a wavelength of 1000 nm. The peak shows the characteristic narrow line width of a quadrupolar, asymmetric mode in comparison with the broader line shape of the dipolar, symmetric mode at a wavelength of 1000 nm.
of 1000 nm seen in both structures. By partially illuminating the rod, the symmetry of the rod is effectively broken and new forbidden bright resonance modes can arise as a result of the new coupling that can occur.

Figure 3.2 Scattering spectra of a 50+200 nm partially illuminated silver rod (red) and scattering spectra of a 250 nm fully illuminated rod (black).

### 3.2.2.2 Electric field contour plots

To characterize the new mode observed in the partially illuminated rod spectrum, the real part of the scattered electric field, $|E_r|^2$, is plotted in the $YZ$ is plotted at a wavelength of 410 nm and 540 nm as shown in Figure 3.3 (a) and (b), respectively, with incident polarization along the $Y$ axis. At 410 nm, the mode is symmetric which produces a dipolar like field distribution inside the rod. At 540 nm, the dipolar forbidden mode is asymmetric. The forbidden mode is
characterized by the quadrupole pattern of the scattered light, seen in Figure 3.3 (b), demonstrating that the narrow line width peak is definitively an asymmetric, quadrupolar mode.

![Symmetric mode](image1.png) ![Asymmetric mode](image2.png)

Figure 3.3 The electric field distribution in the YZ plane is shown for a partially illuminated 50+200 nm rod at wavelengths of (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis.

The corresponding electric field, |E|^2, distribution in the XZ plane is shown in Figure 3.4 (a) for 410 nm and (b) 540 nm, with incident polarization parallel to the rod axis along the Y axis. The multipolar, symmetric mode in Figure 3.3 (a) displays an odd number of nodes, m = 3, with dipolar characteristics. The near field distribution of a second-order mode, m = 2, along the rod in Figure 3.4 (b) at 540 nm displays an even number of nodes at -80 and 80 nm, respectively. The asymmetric shape of the field distribution at 410 nm is due to the partial illumination of the rod. While the 3 nodes are not very clear in a short rod, when the rod length is extended, the
nodes become much easier to identify. This will be discussed later in the chapter and is shown in Figure 3.7.

Figure 3.4 The electric field distribution in the XZ plane for the rod at (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis.

The wavelength of the SPP mode, \( \lambda_{spp} \), can be related to the length of the rod, \( L \), and mode index, \( m \), by

\[
\lambda_{spp} = \frac{2L}{m}.
\]

Equation (3.1) gives \( \lambda_{spp} = 250 \text{ nm} \) for the dipole forbidden bright mode at 540 nm with \( m = 2 \) and \( \lambda_{spp} = 167 \text{ nm} \) with \( m = 3 \) for the dipole allowed bright mode at 410 nm. The partial illumination of the rod effectively breaks the symmetry by introducing a phase difference at each end of the nanorod for the incoming wave resulting in a centro-symmetric charge distribution and excitation of the dipole forbidden second-order asymmetric mode, \( m = 2 \).

To further characterize the symmetric mode at 410 nm and the asymmetric mode at 540 nm, the electric field vector plots are shown in Figure 3.5 (a) and (b), respectively. The electric
field vector plot for the symmetric mode, shown in Figure 3.5 (a), reveals that the electric field distribution pattern is generated by the parallel field distribution inside the rod. Compared to the resonance wavelength at 410 nm, the electric field vector plot for the asymmetric mode at 540 nm displayed in Figure 3.5 (b), reveals an antiparallel field distribution inside the rod, leading to the quadrupolar electric field distribution.

Figure 3.5 The electric field vector plot inside the rod in the XZ plane for wavelengths at (a) 410 nm and (b) 540 nm. The incident polarization is parallel to the rod axis.

3.2.2.3 Propagation of dark modes

To demonstrate the waveguide applications of different excited modes, the length of the rod in the dark region is extended to 1000 nm as shown in the schematic in Figure 3.6 (a). The illuminated length is kept at 50 nm. To differentiate the excited forbidden mode from those allowed in the fully illuminated rod, Figure 3.6 (b) displays both the total scattering spectrum of the rod and the scattering spectrum along the Z direction, which is perpendicular both to the \( k \)-vector and the polarization direction. The even-ordered, dipole forbidden modes appear around wavelengths of 540 nm, 600 nm, 810 nm, and 1600 nm.
Figure 3.6 (a) A schematic of the partially illuminated 1050 nm rod. (b) The total scattering spectrum and the scattering spectrum along the Z axis, perpendicular to the incident wave and polarization directions, of a 50+1000 nm long rod when the polarization is parallel to the rod axis. (b) The extinction, scattering, and absorption spectra of the rod when the incident polarization is perpendicular to the rod axis.

By changing the incident polarization direction relative to the rod axis, it is found that super dark modes with extremely small scattering can be obtained in a partially illuminated silver rod when the incident polarization is perpendicular to the rod axis. Figure 3.6 (c) shows the extinction, scattering, and absorption spectra of the partially illuminated 50+1000 nm long rod when the incident polarization is perpendicular to the rod axis. At the resonance peak around
2800 nm, there is no scattering, indicating a dark mode is present. Since dark modes typically have low scattering, not zero scattering, the zero scattering dark mode is deemed to be a, “super dark mode,” to differentiate it from low scattering dark modes.

Since dark modes have low radiative loss, they may appear to be choice modes which offer low loss propagation for efficient waveguide applications. With the hope of demonstrating the efficient waveguide applications of those excited dark modes, the electric field distribution near the rod at a wavelength of 2800 nm is calculated. Quite interestingly, the efficient absorption of the super dark mode hinders light propagation and the light intensity drops quickly after a distance of approximately 400 nm as shown in Figure 3.7 (a).

Due to the unexpected result of poor propagation from the super dark mode, a mode which shows some scattering is investigated. The electric field $|E|^2$ distribution near the rod at a moderately scattering resonance wavelength of 1060 nm is shown in Figure 3.7 (b). Interestingly, it reveals that light may efficiently propagate over one micron with only a slight drop in the intensity with a $\lambda_{spp} = 667$ nm and $m = 3$.

To investigate the extent of SPP propagation, the length of the rod in the dark region is extended to 5 microns, while maintaining the 50 nm illuminated region, to give a total rod length of 5050 nm. Figure 3.7 (c) shows the electric field distribution at the resonance wavelength of 1230 nm with a $\lambda_{spp} = 842$ nm for a 5050 nm long rod with 12 nodes. The light intensity only drops about 5% after the 5 micron propagation, demonstrating the efficient wave propagation.
Figure 3.7 (a) The electric field distribution at a wavelength of 2800 nm when the incident polarization is perpendicular to the rod axis, (b) the electric field distribution at a wavelength of 1060 nm when the incident polarization is parallel to the rod axis, and (c) the electric field distribution for a 50+5000 nm rod at a wavelength of 1230 nm.

To investigate the results from the electric field contour plots, the surface plasmon dispersion relation curve for a single Ag-air interface is plotted in Figure 3.8 along with the modes for the rods with lengths of 250 nm, 1000 nm, and 5050 nm. The 250 nm rod modes are designated by a navy square for a resonance wavelength of 410 nm and a purple square for a resonance wavelength of 540 nm, corresponding to Figure 3.4 (a) and (b), respectively.
Figure 3.8 Surface plasmon dispersion relation curves for a single Ag-air interface (green) and nanorods with varied length. Wavevector (square) for 250 nm rods, (diamond) for long nanorods (red, orange = 1000 nm; blue = 5050 nm) calculated using the DDA method are plotted. The free space wavevector, $k_0$ (navy), and the plasma frequency of bulk Ag (dark grey) is also plotted for comparison.

The modes for a 1000 nm rod are designated by the red diamond for a resonance wavelength of 1060 nm and an orange diamond for a resonance wavelength of 2800 nm. The mode for the 5050 nm rod is designated by the blue diamond for a resonance wavelength of 1230 nm. The super dark mode, shown as the orange diamond in Figure 3.8, is a very poor propagating mode compared to the other rod modes which lie significantly closer to the Ag-air dispersion curve. The calculations and electric field contour plots indicate that dark modes which
have moderate scattering are desirable for efficient light propagation, despite the radiative loss due to the scattering.

3.2.3 Summary

In conclusion, newly excited dark modes were demonstrated, which are forbidden in a fully illuminated rod, appear when the incident light polarization is parallel to the rod axis and the rod is partially illuminated. The previously forbidden, quadrupolar modes are excited by generating a centro-symmetric, antiparallel electric field distribution within the rod by breaking the symmetry of the rod via partial illumination. Super dark modes were able to be obtained when the incident light polarization is perpendicular to the rod axis. Unexpectedly, these super dark modes display poor propagation efficiency. Therefore, waveguide modes with moderate scattering will be desirable for efficient waveguide applications.

3.3 Fano Resonance in Nanorods

3.3.1 Introduction

Dark modes are accompanied by a Fano resonance peak, which is an asymmetric line shape in the optical spectrum that arises from the constructive and destructive interference between a narrow, dark mode and a broad, bright mode. It is named after the Italian physicist Ugo Fano who was the first to theoretically explain the phenomenon initially for photoionization and the inelastic electron scattering of helium. Fano resonance is the atomic counterpart to Feshbach resonance in nuclear physics, resulting in a combined term Fano-Feshbach resonance,
where they all refer to the asymmetric resonance peak which is produced from the coupling of discrete, or bound, states and the continuum in a many-body system.

The Fano line shape has been observed in many other systems aside from the atomic spectra\textsuperscript{31,71-76} including metallic nanostructures of a spherical particle\textsuperscript{77} assembled symmetric structures\textsuperscript{54,78-80} and numerous structures with broken symmetries\textsuperscript{55,81,82} Recent review papers by Luk’yanchuk et al.\textsuperscript{83} and Miroshnichenko et al. further detail out more systems of Fano resonance.\textsuperscript{84} Silver rod structures have been studied extensively\textsuperscript{85-87} however, no spectra containing a Fano line shape were reported. Due to the dark state nature of Fano resonance\textsuperscript{54-56} with the sharp line shape, holds promise in applications such as sensing, waveguide, and enhanced transmission.

### 3.3.2 Results and Discussion

Different mechanisms are discussed which lead to Fano line shapes in the scattering spectra of silver rods by breaking the symmetry of the rod.\textsuperscript{88} The dielectric constants of silver were taken from Palik's handbook.\textsuperscript{89} The calculations of the rod structures were carried out using the discrete dipole approximation method.\textsuperscript{90} The spherical particles are modeled using the T-matrix method.\textsuperscript{91} The scattering spectra of linearly polarized and circularly polarized incident light are obtained using Stokes parameters in a scattering matrix.

#### 3.3.2.1 Fano line shape of cylindrical nanorods

First, the Fano line shape due to the interference of scattered light from different excitation modes is examined. To avoid the interference of the scattered light with the incident
wave, the scattering spectra obtained along the direction perpendicular both to the incident light propagation and the incident polarization directions is discussed. In all the simulations, the incident light is propagating along the $X$ axis and the incident polarization is along the $Y$ axis. The incident polarization is also parallel to the rod symmetry axis. All the calculated scattering spectra are obtained along the $Z$ axis.

Figure 3.9 (a) Scattering and (b) absorption spectra of silver rods with different lengths.

Figure 3.9 (a) and (b) show the scattering and absorption spectra of cylindrical silver rods, each with a diameter of 40 nm and varying lengths. Figure 3.9 (a) shows that when the rod length is 100 nm, only the dipole peak is obvious. When the rod length is extended to 200 nm, a peak with an asymmetric line shape appears at a wavelength of 400 nm. As the rod length is increased to 300 nm, the peak becomes sharper and is red shifted to 460 nm.

The absorption spectra in Figure 3.9 (b) show similar length dependence of the resonance wavelength as that of the scattering spectra but are symmetric in shape. The enhanced absorption
and reduced scattering lead to a dark state which has been discussed previously in literature.\textsuperscript{54,55}

Figure 3.10 displays the electric field vector plot for the 300 nm long rod taken at the resonance dip seen in the scattering spectrum at a wavelength of 480 nm.

![Electric field vector plot inside a rod with a length of 300 nm at a resonance wavelength of 480 nm, where the plane is in the XY plane and through the rod center.](image)

Two nodes can be observed in Figure 3.10. Both nodes are located at a quarter of the rod length from the two ends. The electric fields at the two ends of the rods are parallel to each other, but both are anti-parallel to the electric fields at the center. The resonance dip at the wavelength of 480 nm in the scattering spectrum, as shown in Figure 3.9 (a), occurs as a result of the destructive interference of oppositely oriented dipoles, with two being induced at the two ends, from -150 to -80 nm and from 80 to 150 nm, and one being induced at the center, from -80 to 80 nm, of the rod.
3.3.2.2 Symmetry breaking in the nanorod

To further understand the mechanism leading to the observed resonance peaks, the symmetry of the rod is broken by cutting a 300 nm long rod perpendicular to the rod axis into two individual rod segments separated by a 20 nm gap.

Figure 3.11 Scattering spectra of a rod with a 20 nm cut at different distances ($lc$) from one end.

Figure 3.11 shows the scattering spectra for the rod of different cutting positions. The numbers in the figure indicate the distance ($lc$) of the cut to the rod end. Figure 3.11 shows that when $lc = 150$ nm or when the cut is taken at the center of the rod, the resonance peak observed around a wavelength of 480 nm weakens but is still present. When the cut is moved towards one end, the overall symmetry of the rod is broken. This asymmetric structure leads to a new dip observed in the scattering spectra at a wavelength near 620 nm when $lc = 130$ nm. The resonance
wavelength of the asymmetric structure blue shifts as the cut is taken further towards one end. The blue shift is reasonable since the new resonance dip is due to the destructive interference of the excited dipoles between the short and long segments of the separated rod. The resonance wavelength is determined by the shorter rod segment, which gives a line shape that is sharp and blue shifts when the length is decreased. To support the argument, the electric field vector plot is calculated at two resonance wavelengths located at 480 and 570 nm when $l_c = 100$ nm.

Figure 3.12 Electric field contour plots at (a) 450, (b) 480 and (c) 570 nm wavelength for rods of a cut at $l_c = 100$ nm and (d) for $l_c = 150$ nm rods at 620 nm wavelength.
Figure 3.12 (b) shows the electric field vector plot at a wavelength of 480 nm which indicates that the resonance dip observed in the scattering spectra is due to the coupling between the excited dipole of the shorter rod segment and the excited quadrupole of the longer segment. Figure 3.12 (c) shows the resonance dip at a wavelength of 570 nm is due to the coupling of the oppositely oriented dipoles of both segments. The electric field vector plots in Figure 3.12 (b) and (c) indicate that a Fano resonance can be obtained by either the coupling between the excited dipoles and in-plane quadrupoles of the rods or the coupling between the two oppositely oriented dipoles. The electric field vector plot calculated at a local peak wavelength of 450 nm, which is less destructive in comparison to those of 570 and 480 nm, is given in Figure 3.12 (a). The electric field vector plot calculated at a wavelength of 620 nm for the rod of \( lc = 150 \) nm is displayed in Figure 3.12 (d). Since the two induced dipoles are parallel to each other, there is no Fano resonance peak present at a wavelength of 620 nm in Figure 3.11 for the rod with a \( lc = 150 \) nm.

### 3.3.2.3 The influence of the node position on resonance peaks

The effect of the nodes on the resonance peak was further explored by comparing the scattering spectra of a single 300 nm long rod, rods with either one or two cuts taken at the nodal positions, and a rod with a cut at the center. The schematic of the rod structures is shown in Figure 3.13 (a) and the spectra in (b). The cut results in a 20 nm gap between rod segments. As discussed in the previous paragraphs, for a rod with a cut taken at the center, the resonance dip observed around 480 nm weakens and no additional Fano resonance peaks appear.
Figure 3.13 (a) Schematic of cutting positions on the nanorod. (b) Scattering spectra of a single rod, a rod with one or two cuts at nodal positions and the rod center.

When the position of the cut corresponds to the position of one of the nodes observed in the single rod, the sharp change in the scattering spectrum of the segmented rod at a wavelength of 480 nm becomes more prominent. The resonance peak due to the coupling between the excited dipoles of the longer and shorter segments at a wavelength of 550 nm can still be observed. When the two cuts correspond to the positions of both of the nodes of a single rod, the sharp change of the resonance peak at a wavelength of 480 nm becomes stronger. Since the structure becomes symmetric again, the resonance peak at a longer wavelength around 550 nm due to the anti-symmetric coupling of the structure disappears.
3.3.2.4 The influence of circular polarized light on the resonance peaks

Figure 3.14 Scattering spectra of the left and right circularly polarized light along the direction perpendicular to the incident wave and polarization directions for (a) a 300 nm long rod and (b) a 100 nm radius spherical particle when the incident light is left circularly polarized. Equal magnitude indicates a linearly polarized light.

The scattering spectra of rods with a length of 300 nm was examined when the incident light is left circularly polarized. At the dipole resonance wavelength of 1200 nm, regardless of the polarization of the incident light, the scattered light is always linearly polarized as shown in Figure 3.14 (a), where the same magnitude of right and left circularly polarized components indicates linearly polarized light. Near the Fano resonance wavelength, the scattered light is not purely linear polarized light but is very close to it. This supports the previous conclusion that the Fano resonance is a result of the coupling between the excited dipole and the in plane quadrupole. For comparison, in Figure 3.14 (b), the scattering spectrum of a spherical silver particle with a radius of 100 nm is shown when the incident light is left circularly polarized. For the 300 nm
long rod, an in plane quadrupole excitation is observed, whereas, an out-of-plane quadrupole is excited near 420 nm for the 100 nm radius spherical silver particle. Figure 3.14 (b) shows that the scattered light along the perpendicular direction becomes right circularly polarized due to the excited out-of-plane quadrupole.

3.3.3 Summary

The line shape of the Fano resonance in the scattering spectra of silver nanorods was numerically examined using theoretical tools. The studies showed that the Fano line shape can be obtained by either coupling a dipole and an in-plane quadrupole or by coupling two dipoles of antiparallel orientations. By segmenting the rod, the symmetry of the rod is broken which facilitates the generation of the Fano line shape spectra. It was shown that when a gap is introduced at the electric field nodal positions of a single rod to form a segmented structure, it will strengthen the Fano line shape in the resulting scattering spectra.

3.4 Conclusion

In conclusion, dark modes within a nanorod structure were demonstrated where, due to the symmetry of a nanorod, only certain modes could be excited. The excitation of the forbidden modes of a rod was validated by breaking the symmetry via partially illuminating it instead of changing the actual structure. Dark mode excitation was also revealed and was shown to propagate only a short distance, making it a poor candidate for waveguide applications when compared to that of a bright mode.
Fano line shapes in the scattering spectra of silver rods were numerically demonstrated and where shown to be a result of different mechanisms. One of the line shapes is due to the coupling of an in plane quadrupole mode and a dipole mode in a single rod. Two nodes located at a quarter of rod length from the two ends were observed at the resonance wavelength. Cutting at the two nodal positions strengthens the Fano resonance. Breaking the rod symmetry introduces a new Fano resonance peak due to the asymmetric coupling between the two excited dipoles. When the Fano resonances due to the asymmetric coupling of the two dipoles and the coupling between the in plane quadrupole and the dipole overlap, the resonance peak becomes stronger. These findings facilitate the understanding of plasmonic phenomena for applications in optical waveguides and photonic devices.
CHAPTER 4: PLASMONIC MIM STRUCTURES FOR WAVEGUIDING

4.1 General Introduction

Advancement in modern electronics is characterized by the continual decreasing of device size and increasing of device processing speed. However, it is limited by the speed of electron transport in the components of the device.\textsuperscript{92} The utilization of electromagnetic waves, instead of electrons, as information carriers circumvents this problem. In a photonic device, electromagnetic waves travel via waveguides that confine and guide wave propagation, which is analogous to conductive wires in an electronic device channeling electrons. Still, with the use of optical information carriers in nanoscale waveguides, a new challenge arises: localizing and propagating the electromagnetic waves beyond the diffraction limit. Yet, at optical wavelengths, metals such as gold and silver exhibit a collective oscillation of conduction electrons, called surface plasmons (SPs). Metal interfaces can support evanescent surface waves called surface plasmon polaritons (SPPs). Since the SPP wavelength is smaller than the wavelength of light in a vacuum, the diffraction limit can be diminished in device design. Various methods have shown that the size of the waveguide and other nanostructured devices can be reduced beyond the diffraction limit of light using surface plasmons.\textsuperscript{93-98} Furthermore, integrating of nanoscale waveguide components into a functional system has shown that the realization of subwavelength photonic devices is attainable.\textsuperscript{99}

In this chapter, MIM structures will be discussed. First, the optical properties of a simple two layer silver film are investigated using an analytical model. In the second half of the chapter, the light trapping, confinement, and propagation of light a MIM silver film is investigated.
4.2 Multilayer Film

In the first of two sections on MIM waveguides, a simple model of a multilayer film structure is discussed. To start off, the effect of the surrounding medium on the optical properties of a two layer silver film is investigated using an analytical model. The media was varied before the first layer, between the two layers, and after the second layer. The optical properties of the film were found to be dominantly determined by the medium between the two layers. The resonance wavelength red shifts when the medium between the two layers is changed from vacuum to water and then glass. The media before the first layer and after the second layer have little effect on the spectra of the film when the thicknesses of the layers are larger than 40 nm.

4.2.1 Introduction

A multilayer film, a simple structure which can be fabricated using relatively matured techniques,\textsuperscript{100-102} has many interesting optical properties which are attractive to researchers from different disciplines. The multilayer film, such as a Fabry-Pérot (FP) interferometer consisting of a transparent plate with two parallel mirrors, may achieve high-resolution spectra\textsuperscript{103,104} and has been utilized as optical sensors,\textsuperscript{105-113} lasers,\textsuperscript{114,115} and waveguide devices.\textsuperscript{116-121} In a previous study, Yu et al.\textsuperscript{122} studied the scattering, absorption, and extinction spectra as well as the enhanced electric field of a two layer silver film, which is similar to a FP interferometer. In the paper by Yu etc, the film is placed in a vacuum environment. In this manuscript, the medium influence on the optical properties of the two layer film is discussed. The spectrum evolution of the film is studied when the media is varied between vacuum, water, and glass. The media is varied first before the film, then after the film, and finally, in between the two layers of the film.
For a flat multilayer film with different compositions and environments, its optical properties can be analytically obtained by matching the electromagnetic boundary conditions in which the tangential components of the electric and magnetic fields are continuous across a boundary between two different media. In a multilayer film, once the amplitudes of the electric fields in different layers are achieved, the scattering, absorption, extinction, and transmission spectra can be calculated using the equations described in section 1.1.3.123 The schematic of the studied film, a two layer silver film, is shown in Figure 4.1.

4.2.2 Results and Discussion

In Figure 4.1, \(d_1\) and \(d_2\) represent the thicknesses of the two silver layers, \(L\) denotes the distance between the two layers, \(N_{1-5}\) refer to the indices of refraction of the media, \(E_j^+\) and \(E_j^-\), where \(j = 1, 2, 3, 4,\) and \(5\), are the amplitudes of the wave propagating along the \(+x\) and \(–x\) directions in medium \(N_j\). When a ray of light normally incidents on a flat slab as shown in Figure 4.1, the incident, reflected, and transmitted waves are expressed as \(E_1^+ \exp(ikN_1x)\), \(E_1^- \exp(–ikN_1x)\), and \(E_5^+ \exp(ikN_5x)\), respectively. Here \(k = 2\pi/\lambda\) is the wavenumber of the incident light, \(x\) denotes the coordinate along the \(X\) axis. The waves inside medium \(N_j\) propagating along \(+x\) and \(–x\) directions are expressed as \(E_j^+ \exp(ikN_jx)\) and \(E_j^- \exp(–ikN_jx)\), respectively.
Figure 4.1 Schematic of a two layer film made up of two parallel infinite silver layers. $L$ refers to the distance between the two layers; $d_1$ and $d_2$ are the thicknesses of the first and the second layer, respectively; $N_1$, $N_2$, $N_3$, $N_4$, and $N_5$ represent the index of refraction of each layer and surrounding medium. $N_2$ equals $N_4$ in the current studies.

At the first boundary, where $x = 0$, the boundary conditions satisfy the following equations.

\begin{align}
E_1^+ + E_1^- &= E_2^+ + E_2^-,
\tag{4.1}
\end{align}

\begin{align}
E_1^+ - E_1^- &= \frac{N_2}{N_1}(E_2^+ - E_2^-).
\tag{4.2}
\end{align}

At the $j$th boundary where $x = h_j$, the boundary conditions satisfy the following equations.
\[ E_j^+ \exp(ikN_jh_j) + E_j^- \exp(-ikN_jh_j) = E_{j+1}^+ \exp(ikN_{j+1}h_j) + E_{j+1}^- \exp(-ikN_{j+1}h_j), \]  

(4.3)

\[ E_j^+ \exp(ikN_jh_j) - E_j^- \exp(-ikN_jh_j) = \frac{N_{j+1}}{N_j} [E_{j+1}^+ \exp(ikN_{j+1}h_j) - E_{j+1}^- \exp(-ikN_{j+1}h_j)], \]  

(4.4)

The reflectance, \( R \), and the transmittance, \( T \), of the two layer film can be calculated with the following equations:

\[ R = \left| \frac{E_1^-}{E_1^+} \right|^2, \]  

(4.5)

\[ T = \text{Re}\left(\frac{N_5}{N_1}\right) \left| \frac{E_5^+}{E_1^+} \right|^2. \]  

(4.6)

The scattering efficiency of the film equals the reflectance \( R \). The extinction efficiency is obtained through \( 1 - T \) and the absorption efficiency is given by \( 1 - T - R \). The validity of the analytical model had been checked in a previous paper\(^{122} \) by comparing the results from the analytical model with those obtained using the discrete dipole approximation method.\(^{124} \)

In the simulations, incident light propagates along the \( X \) axis and the film is placed in the \( YZ \) plane perpendicular to the incident light. The thicknesses of the first and the second layers are
taken to be 40 and 60 nm, respectively. First, $N_1$ and $N_5$, the media before and after the film, are held constant as a vacuum. The absorption, scattering, and extinction spectra of the two layer film are displayed in Figure 4.2 (a), (b), and (c), respectively. The solid line shows the spectrum when $N_3$, the medium between the two layer is a vacuum. The dotted and dashed lines represent the spectra when $N_3$ is changed to water, with a refractive index of $n = 1.33$, and glass with an index of refraction $n = 1.52$. The resonance wavelengths redshift with increasing index of refraction, $N_3$. Both absorption and scattering efficiencies decrease with increasing $N_3$. Figure 4.2 (d) demonstrates the electric field, $|E|^2$, along the $X$ axis.
Figure 4.2 (a) Absorption, (b) scattering, and (c) extinction spectra of a two-layer silver film with 40($d_1$) and 60($d_2$) nm thickness and $L = 150$ nm separation. (d) Enhanced electric field, $|E|^2$, along the $X$ axis at corresponding resonance wavelength.

Regardless of the composition of the inner medium, the highest enhanced electric field is located exactly in the middle of the two layers, namely, 75 nm from the surface of each layer. Additionally, the electric field is more intense when the middle layer, $N_3$, is water than when the middle layer, $N_3$, is vacuum or glass.
Figure 4.3 (a) Absorption spectra of the two layer film when the media, $N_3$ and $N_5$, are fixed as water and the medium $N_1$ is changed from vacuum (solid line), water (dotted line), to glass (dashed line); (b) absorption spectra of the two layer film when the media, $N_1$ and $N_3$, are fixed as water and the medium, $N_5$, is changed from vacuum, water, to glass.

The influence of the media, $N_1$ and $N_5$, on the spectrum of the film is investigated. The thicknesses of the two layers were fixed at 40 ($d_1$), 60 ($d_2$) nm and the layer distance, $L$ was taken to be 150 nm. The medium $N_3$ was held constant as water. Figure 4.3 (a) shows the absorption spectra when the medium $N_3$ is taken as water and the medium $N_1$ is changed from vacuum (solid line) to water (dotted line) and glass (dashed line). Figure 4.3 (b) shows the absorption spectra when the medium $N_1$ is taken as water and the medium $N_5$ is changed from vacuum (solid line) to water (dotted line) followed by glass (dashed line). The lines almost overlap with each other, demonstrating that the variation of $N_1$ and $N_5$ has minimal effect on the absorption efficiency of the film when the thicknesses of two layers are 40 and 60 nm, respectively.
Figure 4.4 Absorption spectra of the film when the second layer is 60 nm, as $N_5$ is water and varying $N_1$ from vacuum (solid line) to water (dotted line) and finally, to glass (dashed line). (a) The first layer is 10 nm, (b) the first layer is 20 nm, and (c) the first layer is 30 nm. (d) Schematic of the film structure with the varied parameters highlighted in red.

The influence of the media was also examined for $N_1$ and $N_5$ on the spectrum of the two layer film when the thicknesses of the two layers were varied. Absorption spectra of the film are displayed in Figure 4.4 (a) which was obtained when fixed the thickness of the second layer at 60
nm, the first layer at 10 nm, the medium, $N_3$, as water and changed $N_f$ to vacuum, water and glass, respectively. The absorption spectra displayed in Figure 4.4 (b) and (c) were obtained when the first layer is 20 and 30 nm, respectively, and the other parameters are the same as those in Figure 4.4 (a). From comparing the absorption spectra, it was discovered that the medium before the first layer has some influences on the optical properties of the film when the thickness of first layer is small enough. However, the influences are minimal as the medium, $N_f$ is changed from vacuum, water, and then to glass, where it has very little effect on the optical properties of the film within scale of this study.
Figure 4.5 Absorption spectra when the first layer is 40 nm, $N_1$ is water and varying $N_5$ from vacuum (solid line) to water (dotted line) then glass (dashed line). (a) The second layer is 30 nm; (b) the second layer is 40 nm, (c) the second layer is 50 nm. (d) Schematic of the film structure with the varied parameters highlighted in red.

Absorption spectra displayed in Figure 4.5 (a) was obtained when the first layer was fixed at 40 nm and the second layer was fixed at 30nm, the medium $N_1$ was fixed as water and $N_5$ was
varied from vacuum to water and then to glass, respectively. The absorption spectra displayed in Figure 4.5 (b) and (c) were obtained when the second layer is 40 nm and 50 nm, respectively, and the other parameters are the same as those in Figure 4.5 (a). It is concluded that the influences of the medium, $N_5$, increase with decreasing thickness of the second layer. However, the influences are minimal, even though the thickness of second layer is 30 nm. It mainly results from the fact that there is too little light going through the two layer film and the electromagnetic wave bouncing back and forth between the two layers is dominant in influencing the optical properties of the film.

### 4.2.3 Summary

The optical properties of a two layer silver film were investigated using an analytical model. The influences of different media on the spectra of the film were discussed. It can be concluded that the resonance wavelength red shifts as the middle layer ($N_3$) is varied from vacuum to water and then to glass. The medium ($N_1$) before the first silver layer and the medium ($N_5$) after the second silver layer were shown to have very little influences on the spectra of the two layer film when the thickness of the first layer is greater than 40 nm and that of the second layer is larger than 60 nm. These results aid in the understanding of light propagation in extended metal-insulator-metal (MIM) structures for applications such as waveguides, optical components, and other photonic devices.

### 4.3 Periodic Hole Array Waveguide

In this section, the light trapping, confinement, and propagation of a two layer silver film with periodically perforated holes is investigated. Further discussion on the effects of the
dielectric constants of the media is elaborated. Extreme subwavelength confinement and propagation is demonstrated for a metal-insulator-metal (MIM) waveguide.

4.3.1 Introduction

A subwavelength photonic waveguide is proposed which consists of a two layer, MIM film structure with perforated holes to meet three main goals of waveguide design: (1) trapping, (2) confining, and (3) propagating light. From our previous work, the focus was on the first goal of waveguide design using conical frustum shaped holes in a two layer silver film. It was concluded that a 1 to 3 critical ratio of the upper and lower diameters of the holes was necessary to achieve high absorption due to the reduced reflection of incident light perpendicular to the layers.\textsuperscript{125,126} In the current work, the focus is on confining and propagating the light, therefore the upper and lower diameters of the holes are kept the same so as to take advantage of the light trapping properties without sacrificing other waveguide design goals. It is demonstrated that the light propagation is related to the electric field confinement in the narrow region between the two layers and that the light from a single hole can propagate in an enclosed channel. The structure can be tuned so that propagation can be achieved for a variety of wavelengths, regardless of the resonance frequency, making it more versatile than resonance dependent structures. The effective index is calculated out theoretically so as to explain such phenomenon, which agrees well with the simulations. The results have potential applications for subwavelength waveguide design.
4.3.2 Results and Discussion

Using the Discrete Dipole Approximation (DDA) method, the study begins by first investigating the effects of varying the different structural components of the waveguide: the hole diameter and the distance between the two silver layers. The DDA method, which was first proposed by Purcell and Pennypacker\textsuperscript{127} and developed by Draine\textsuperscript{18}, is a commonly used program which calculates the optical properties of films or particles with arbitrary shapes and dielectric properties of the materials. The dielectric constants of silver are taken from Palik’s handbook.\textsuperscript{128} In the DDA method, the target is divided into $N$ small cubes which are considered polarizable dipoles. After solving $3N$ linear equations, the induced dipole and local electric field of each cube are obtained, followed by the calculation of the amplitude scattering matrix, which relates the incident and scattered light. The Mueller matrix, which relates the incident and scattered waves, is calculated from the amplitude scattering matrix and gives the scattering and transmission spectra of the target.\textsuperscript{129}

4.3.2.1 Open hole array in a silver film

To begin investigating the light trapping the absorption, scattering and extinction spectra, shown in Figure 4.6 for a 10 nm distance between films, are calculated when the distance is varied between the films, $L$ as shown in the schematic in Figure 4.7 (a). Additionally, the hole diameter, $d$, is varied and in both cases the holes are periodic every 400 nm along the $Y$ axis and every 10 microns along the $Z$ axis. The thickness of the silver layers, $t_1$ and $t_2$, is fixed at 100 nm so that the layers are optically thick enough to prevent transmission. The incident light propagates along the $X$ axis and the polarization is along the $Z$ axis. The absorption, scattering,
and transmission spectra for a film with a distance between layers of 10 nm are shown in Figure 4.6. Due to the significantly larger area of the silver film compared to the area taken up by the holes, the spectra for films with different distances between layers did not vary significantly, therefore only the spectra for the 10 nm film spacing is shown.

![Figure 4.6 Absorption (blue), scattering (green), and transmission (red) for a periodically perforated film with a distance between layers of 10 nm.](image)

Figure 4.6 Absorption (blue), scattering (green), and transmission (red) for a periodically perforated film with a distance between layers of 10 nm.

Initial electric field contour plots were calculated for hole diameters of 200 nm, 300 nm, and 400 nm for film distances of 50 nm, 40 nm, 30 nm, 20 nm, and 10 nm. It is found that holes with 300 nm diameters showed the highest efficiency for light trapping between the two layers. For the purpose of this paper, only the optimized results from the diameter tests of 300 nm are shown.
Figure 4.7 (a) Schematic of an open array of holes periodic at 10 microns along the Z axis and 400 nm along the Y axis. Electric field contour plots between the two layers in the YZ plane with a distance between films of (b) 40 nm and (c) 30 nm at a wavelength of 800 nm and (d) 10 nm at a wavelength of 1300 nm.

Figure 4.7 (b)-(c) shows the electric field contour plots, $|E|^2$, for $Z$ polarized incident light at a wavelength of 800 nm with varied inter film distance, $L$, and fixed diameter, $d = 300$ nm. Efficient light propagation is observed as alternating bright and dark fringes which result from the interference between the holes along the Z axis, where the distance between bright fringes is half of the wavelength of the SPP mode excited at the interface of the top and bottom metal films.
4.3.2.2 SPP dispersion relation of MIM

For a single metal-dielectric interface, the wavelength of the SPP mode, \( \lambda_{\text{SPP}} = \frac{2 \pi}{k_{\text{SPP}}} \), where \( k_{\text{SPP}} \) is the wavevector of the SPP mode and is related to the dielectric constant of the dielectric material, \( \varepsilon_d \), through the surface plasmon dispersion relation:

\[
k_{\text{SPP}} = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}},
\]

(4.7)

where \( k_0 = \frac{2 \pi}{\lambda_0} \) is the free space wavevector with a wavelength of \( \lambda_0 \), and \( \varepsilon_m \) is the dielectric constant of the metal. The dispersion relation gives the factor needed to increase the momentum of a free space photon, \( \hbar k_0 \), to match that of an excited SPP mode wavevector, \( \hbar k_{\text{SPP}} \), at a metal-dielectric interface. However, due to the presence of the second film, \( \varepsilon_d \) inside the waveguide is increased resulting in a new “effective” dielectric constant, \( \varepsilon_{d,\text{eff}} \). Therefore, \( \lambda_{\text{SPP}} \) in a MIM system is what is referred to as the “effective” wavelength, and \( \varepsilon_d \) in equation (4.7) becomes \( \varepsilon_{d,\text{eff}} \).

To confine the light and demonstrate the dependency of the SPP mode on \( \varepsilon_{d,\text{eff}} \), \( L \) is decreased from 40 nm to 30 nm at a fixed \( \lambda_0 = 800 \text{ nm} \). A schematic of the structure is shown in Figure 4.7 (a). The intensity of the electric field between the two layers increases while at the same time maintaining efficient light propagation as shown in Figure 4.7 (b) and (c), respectively. In conjunction with the increased intensity, a decreased \( \lambda_{\text{SPP}} \) is observed from \( \lambda_{\text{SPP}} = 556 \text{ nm} \) for \( L = 40 \text{ nm} \) to \( \lambda_{\text{SPP}} = 500 \text{ nm} \) for \( L = 30 \text{ nm} \). \( L \) is decreased to an incredibly small channel height of 10 nm at \( \lambda_0 = 1300 \text{ nm} \) to demonstrate that efficient light propagation with different distances
between films, while preserving the SPP wavelength, is still achievable, as shown in Figure 4.7 (d). The resulting SPP wavelength, for \( L = 10 \) nm is \( \lambda_{spp} = 556 \) nm for \( \lambda_0 = 1300 \) nm, which is the same as that of the \( L = 40 \) nm structure with \( \lambda_0 = 800 \) nm. Therefore, tuning of the waveguide device can be done by decreasing the film spacing to decrease the resulting SPP wavelength and the propagation efficiency of the waveguide has little dependency on the resonance frequency of the structure.

The change of the effective wavelength versus the film distance can be explained by replacing \( \varepsilon_d \) in equation (4.7), with \( \varepsilon_{d,eff} \), and thus returning the “effective” wavelength in the waveguide. From Figure 4.7 (b)-(d), it is seen that decreasing \( L \) increases \( k_{spp} \), which means there must be an increase in the effective refractive index,

\[
n_{eff} = \sqrt{\varepsilon_d}, \tag{4.8}
\]

in the channel to satisfy the momentum matching criteria of the dispersion relation. Neglecting the effects of the holes in the film and treating the system as a MIM layer structure, \( n_{eff} \) can be solely approximated from \( \varepsilon_d, \varepsilon_m, \) and \( L \), through the free space wavevector, \( k_0 \), and propagation constant, \( \beta \), \(^{130}\):

\[
n_{eff}^2 = \left( \frac{\beta}{k_0} \right)^2 = \varepsilon_{d,eff}, \tag{4.9}
\]

where \( \beta \) comes from:

133
\[- \frac{\varepsilon_d \sqrt{\beta^2 - k_0^2 \varepsilon_m}}{\varepsilon_m \sqrt{\beta^2 - k_0^2 \varepsilon_d}} = \tanh \left( \frac{L}{2} \sqrt{\beta^2 - k_0^2 \varepsilon_d} \right). \quad (4.10)\]

Figure 4.8 shows the plasma frequency of Ag, $\omega_p$, (dark grey line) and $k_0$ (navy line) plotted with the dispersion curves calculated from equations (4.7)-(4.9) for the dispersion relation of a single Ag-air interface (green) and the two layers, MIM structures for $L = 40_{(\text{MIM})}$ (teal), $L = 30_{(\text{MIM})}$ (maroon), and $L = 10_{(\text{MIM})}$ (indigo). All of the modes lie at higher wavevectors to the right of the light line, $k_0$ and at lower frequencies than $\omega_p$, indicating they are all propagating modes. When the second Ag layer is added, the dispersion curve shifts to the right and diverges at a lower frequency than the single interface. As $L$ is decreased, the modes further shift to larger wavevectors and diverge at even lower frequencies due to the increase of $n_{\text{eff}}$ in the region. The shift of the dispersion curve in relation to $k_0$ corresponds with the momentum mismatch between $\hbar k_0$ and $\hbar k_{\text{app}}$. 
Figure 4.8 Surface plasmon dispersion relation curves for a single Ag-air interface (green) calculated from equation (4.7) and MIM structures with varied $L$ (teal, maroon, indigo) calculated from equations (4.8)-(4.10). Wavevector (diamond) for each of the periodic hole array structures from Figure 4.7 (b)-(d) calculated using the DDA method are plotted with corresponding colors to the MIM counterparts. The free space wavevector, $k_0$ (navy), and the plasma frequency of bulk Ag (dark grey) is also plotted for comparison.

For comparison, $k_{spp,DDA}$ (diamonds) from the measured $\lambda_{spp,DDA}$ obtained from the $|E|^2$ plots in Figure 4.7 (b)-(d) are included at corresponding $L_{(MIM)}$ distances. For the periodic hole array with $\lambda_0 = 800$ nm, when $L = 40$ nm, $\lambda_{spp,MIM} = 510$ nm is red shifted to $\lambda_{spp,DDA} = 556$ nm and when $L = 30$, $\lambda_{spp,MIM} = 500$ nm is red shifted to $\lambda_{spp,DDA} = 556$ nm. For $L = 10$ nm with $\lambda_0 = 1300$ nm, $\lambda_{spp,MIM} = 463$ nm is red shifted to $\lambda_{spp,DDA} = 500$ nm, where the $k_{spp,DDA}$ of the $L = 10$ nm is the same as the $k_{spp,DDA}$ for $L = 30$. $k_{spp,DDA}$ correlates with $k_{spp,MIM}$, but are blue shifted to
higher frequencies as a result of the coupling effects in the array. The addition of the periodic hole array results in a smaller momentum mismatch between $\hbar k_{spp}$ and $\hbar k_0$, shifting $k_{spp}$ closer to $k_0$. However, decreasing the film spacing allows for excited SPP modes on the silver interface to exist at optical frequencies and facilitates efficient propagation of light through the waveguide despite the reduced dimensions of the channel.

### 4.3.2.3 SPP confinement in a channel hole array

To test the limits of light confinement, the holes are isolated along the $Z$ axis in 400 nm wide channels with a $Y$ periodicity of 500 nm, by including a 100 nm sidewall barrier between adjacent holes as shown in Figure 4.9 (a). The $|E|^2$ in the $YZ$ plane for $L = 10$ nm with $Z$ polarized incident light with $\lambda_0 = 1020$ nm is shown in Figure 4.9 (b), which demonstrates that light can propagate over a distance of 10 microns when the channels are isolated with a dimension of $10 \times 400$ nm$^2$. 
Figure 4.9 (a) Schematic of an isolated hole array separated by 100 nm walls to form isolated channels along the Z axis. The electric field contour plots between the two layers in the YZ plane at a wavelength of 1020 nm are plotted for channel widths of (b) 400 nm and (c) 300 nm.

To test the limits of light confinement, the holes are isolated along the Z axis in 400 nm wide channels with a Y periodicity of 500 nm, by including a 100 nm sidewall barrier between adjacent holes as shown in Figure 4.9 (a). The $|E|^2$ in the YZ plane for $L = 10$ nm with Z polarized incident light with $\lambda_0 = 1020$ nm is shown in Figure 4.9 (b), which demonstrates that light can propagate over a distance of 10 microns when the channels are isolated with a dimension of $10 \times 400 \text{ nm}^2$. The wavelength of the MIM structure calculated from equation (4.7), $\lambda_{spp,MIM} = 389$ nm, red shifts with the addition of the channel walls to $\lambda_{spp,DDA} = 500$ nm. To further confine the light, the channel width is reduced to equal that of the diameter of a hole, $d = 300$ nm. At the same $\lambda_0$, when the channel width is reduced from 400 nm to 300 nm, $\lambda_{spp,DDA} = 500$ nm red shifts.
to $\lambda_{spp,\text{DDA}} = 556$ nm, achieving a smaller momentum mismatch between the corresponding wavevectors. The calculated $|E|^2$ shown in Figure 4.9 (c) reveals that light at a wavelength of 1020 nm can be trapped by a single hole and propagated along a 10 micron long channel with cross-sectional dimension of $10 \times 300$ nm$^2$.

4.3.2.4 SPP propagation along a ridge hole array

To further test the limits of light confinement in the waveguide, the channel walls are removed and a 20 nm wide ridge is added which extends from the center edges of adjacent holes every 10 microns along the $Z$ axis to form a new waveguide structure as shown in Figure 4.10 (a). The distance between the ridge and the top film layer, $t_2$, is fixed at 10 nm while $L$ is increased from 30 nm to 40 nm. The function of the ridge is different than that of the walls, where the ridge serves to facilitate propagation within the highly confined ridge region compared to the inter film region, while the walls act as barriers to fully confine the holes along the $Z$ axis.
Figure 4.10 (a) Schematic of an open hole array with ridges along the Z axis with 10 micron periodic holes. Electric field contour plots between the two layers in the YZ plane of the ridge structures with a spacing between the coaxial and top film of 10 nm and \( L = (b) \) 30 nm and (c) 40 nm at an incident wavelength of 1300 nm.

Figure 4.10 (b) demonstrates that for \( \lambda_0 = 1300 \) nm and \( L = 30 \) nm with a 20 nm high ridge, light preferentially propagates along the extremely small region between the ridge and the \( t_2 \), rather than in the region between \( t_1 \) and \( t_2 \), with \( \lambda_{spp} = 740 \) nm. Amazingly, when \( L \) is increased to 40 nm with a ridge height of 30 nm, the electric field intensity decreases even further in the inter film region while leaving the ridge region intensity nearly unchanged with a red shifted \( \lambda_{spp} = 769 \) nm as shown in Figure 4.10 (c). The wavelength of the SPPs propagating at the interface of the top metal film is shown to be determined mainly by the spacing between...
the two films and not the spacing between the ridge and top film. Consequently, as the inter film spacing is increased and \( n_{\text{eff}} \) is decreased, the effective wavelength of the SPP modes is red shifted, but light confinement and propagation is preserved along the ridge.

### 4.3.3 Summary

The trapping, confinement, and propagation of light between two silver films at an extremely subwavelength dimension of 10x20 nm\(^2\) has been numerically demonstrated. The wavelength of the SPP modes is dependent on \( n_{d,\text{eff}} \) of the dielectric region in the waveguide which is dictated by the distance between films. The most efficient waveguides have a smaller spacing between films due to the increased coupling of SPP modes at the Ag-air interfaces so that light preferentially propagates in a 10 nm region, despite the drastic mismatch between \( \lambda_0 \) and the waveguide dimensions. The SPP wavelength can be tuned by changing the distance between films with the propagation preservation achieved by including a ridge to confine light. The extreme confinement and propagation of light in a two dimensional region by the two layer film can provide useful information for the future design of waveguides at extreme subwavelength dimensions.

### 4.4 Conclusion

The confinement and propagation of light under the diffraction limit is a substantial challenge for the development of waveguides as components in subwavelength optical devices. In this chapter, light interaction with MIM structures was investigated. First, the effect of the surrounding medium on the optical properties of a two layer silver film was investigated using an analytical model. The media was varied before the first layer, between the two layers, and after
the second layer which yielded that the optical properties of the film are predominantly
determined by the medium between the two layers. The resonance wavelength red shifts when
the medium between the two layers is changed from vacuum to water and then glass, correlating
with the increased refractive index of the medium. However, the media before the first layer and
after the second layer have little effect on the spectra of the film when the thicknesses of the
layers are larger than 40 nm.

Second, light confinement and propagation at optical frequencies in a two layer silver
film with a periodic array of holes is investigated in a numerical study using the discrete dipole
approximation method. Extreme subwavelength confinement and propagation of light can be
obtained along an extremely subwavelength cross-sectional area of a region as small as $10\times20$

nm$^2$ at a distance of over 10 microns. This study provides rational design for photonic
waveguides under subwavelength dimensions.
CHAPTER 5: PLASMONIC METAMATERIALS FOR LIGHT MANIPULATION

5.1 General Introduction

Surface plasmons, the coherent oscillation of conduction electrons, can be observed at an interface between a metal and a dielectric material. Many novel optical properties have been discovered for metals associated with the excitations of surface plasmons. The important applications of surface plasmons include surface enhanced Raman scattering,\textsuperscript{131-138} subwavelength waveguides,\textsuperscript{139-148} and imaging.\textsuperscript{149-158} The frequency dependence of the dielectric constant for metals results in a region of frequencies which typically spans up to optical frequencies where $\varepsilon < 0$ and $\mu > 0$. Since the values of neither $\varepsilon$ or $\mu$ in Maxwell’s equations are prohibited from being negative, it is possible for media to exist with $\varepsilon > 0$ and $\mu < 0$ or $\varepsilon < 0$ and $\mu < 0$. In the latter case, where both quantities are simultaneously negative, the material is termed a negative index media or left handed media. As a result, a variety of new materials with interesting properties can be constructed. These new materials are called metamaterials. To be considered a metamaterial, $\varepsilon_{\text{relative}}$ and $\mu_{\text{relative}}$ of a material must be less than zero and the refractive index, $n^2 = (\varepsilon_{\text{relative}}\mu_{\text{relative}})$ must be defined as

$$n = -\sqrt{\varepsilon_{\text{relative}}\mu_{\text{relative}}},$$  \hspace{1cm} (5.1)

so that the refractive index is also less than zero. Combining the three criteria for a wave yields energy flux in the same direction as the propagation direction of the wave.
Since negative index materials do not exist naturally, different techniques such as utilizing SP properties of metallic nanostructures can be used to realize these artificial materials with a negative index of refraction, or left handed materials (LHM), \(^{159-165}\) which was first proposed by Russian theorist V. G. Veselago in 1968.\(^{159}\) For a left handed material, simultaneous negative permittivity, \(\varepsilon\), and permeability, \(\mu\), are required and negative phase velocity and Doppler effect\(^{159}\) are expected. After the first experimental demonstration of a LHM at microwave frequency,\(^{160}\) tremendous experimental and theoretical efforts have been reported in searching LHMs, especially two dimensional LHMs in the visible wavelengths.

One of the promising applications of LHMs is for superlenses\(^{166-168}\) which was proposed to be perfect theoretically\(^{166}\) and demonstrated experimentally with imperfection. The index of refraction of a LHM is negative indicating that the refracted light ray through an interface between a LHM and a normal medium will propagate along the same side of the interface normal as the incident wave. The abnormal propagation direction of the refracted light rays can also be observed phenomenologically in natural materials when light travels between an isotropic medium and an anisotropic medium\(^{169-171}\) or thin films composed of gain medium.\(^{172,173}\)

In this chapter, the propagation of electromagnetic waves is investigated. The first section combines the Mie theory and the Kramers-Kronig transformation method to investigate a spherical silver nanoparticle. The second section uses the discrete dipole approximation (DDA) method to investigate a nanostructured silver film comprised of silver prisms. These investigations are pertinent to understanding plasmonic light-matter interactions of nanostructures for applications such as waveguides and photonic based devices.
5.2 Light Manipulation by a Spherical Silver Nanoparticle

5.2.1 Introduction

Using electrodynamics tools, the effect of surface plasmons on the propagation direction of electromagnetic wave around a spherical silver nanoparticle is investigated. The studies show that the calculated effective index of refraction of a spherical silver nanoparticle from the Kramers-Kronig transformation method may not represent the index of refraction of the system, but are consistent with the Poynting vector direction which shows the energy flow at the microscopic scale.

For a spherical particle, its absorption cross-section, $C_{\text{abs}}$, can be calculated using the general Mie theory.\textsuperscript{44, 45} Once the absorption cross-section of the particle is obtained, the effective real and imaginary indices of refraction of the particle can be calculated using the Kramers-Kronig transformation method.\textsuperscript{45, 46} For mathematical purposes only, it is assumed that an artificial film has the same optical properties as that of a particle with a radius of $r$. This assumption is physically incorrect, where no such film exist naturally, since the optical properties of the nanoparticles will be changed significantly when their sizes are changed or they are arranged close to each other. The attenuation of incident light, $I$, is obtained by

$$I = I_0 e^{-\frac{C_{\text{abs}}}{\pi r^2}} = I_0 e^{-\alpha h}, \quad (5.2)$$

where $I_0$ is the initial intensity of incident light, $r$ is the radius of the particle, $\alpha$ is the absorption coefficient of the artificial film, and $h$ the effective thickness of the film, which is given by
\[ h = \frac{V}{\pi r^2}, \]  
(5.3)

where \( V \) is the volume of the particle given by

\[ V = \frac{4}{3} \pi r^2. \]  
(5.4)

The absorption coefficient is derived from equation (5.2) as

\[ \alpha = \frac{C_{abs}}{V}. \]  
(5.5)

The effective imaginary index of refraction, \( \kappa \), for a particle at a wavelength, \( \lambda \), is calculated by the Kramers-Kronig transformation method\(^{45,46} \) as

\[ \kappa = \frac{\alpha \lambda}{4\pi}. \]  
(5.6)

and the real index of refraction, \( n \), by

\[ n(\omega) = \frac{c}{\pi} \int_{0}^{\infty} \frac{\Delta \alpha(\omega')}{(\omega')^2 - \omega^2} d\omega' + 1, \]  
(5.7)

where

\[ \omega = \frac{2\pi c}{\lambda}, \]  
(5.8)
is the angular frequency of incident light and \( c \) is the speed of light. Please note that the calculated effective indices of refraction are for an isolated single particle only.

### 5.2.2 Results and Discussion

Using Mie theory, the absorption spectrum of a silver particle with a 10 nm radius is calculated, which is shown in Figure 5.1 (a). The dielectric constants of the bulk silver were taken from Palik’s handbook.\textsuperscript{89} The resonance wavelength of the particle appears at 354 nm. The effective real, \( n \), and imaginary, \( \kappa \), indices of refraction of the particle calculated using the Kramers-Kronig transformation method\textsuperscript{8,174} are shown in Figure 5.1 (b). The imaginary index of refraction exhibits a similar profile as that of the absorption spectrum with a peak at a wavelength of 354 nm. The real index of refraction curve indicates that effective negative indices of refraction can be achieved for wavelengths ranging from 310 to 353 nm. The lowest \( n \) of -2.6 was obtained at a wavelength of 345 nm. The real index of refraction increases and becomes positive when the wavelength is longer than the resonance wavelength of 354 nm. The value reaches 5.0 at a wavelength of 371 nm and drops gradually with further increasing the wavelength.
Figure 5.1 (a) Absorption spectrum of a 10 nm silver particle in a vacuum. (b) Effective indices of refraction of the particle obtained from the Kramers-Kronig transformation method.

The polarizability of the spherical particle is evaluated at various wavelengths. For a small particle with a radius less than 10 nm, the excited particle can be treated as a single dipole and the polarizability of the particle, $\alpha$, can be expressed as,$^{175}$

\[
\alpha = i \frac{3a_1}{2k^3},
\]

where $a_1$ is the expansion coefficient in the Mie theory and $k = 2\pi/\lambda$ refers to the wavenumber at wavelength $\lambda$. The polarizabilities of the particle at different wavelengths are shown in Figure 5.2. The profile of Figure 5.2 looks very similar to that of Figure 5.1 (b). At a wavelength around 345 nm, the real polarizability is negative.
The negative polarizability indicates that the internal electric fields in the silver particle are along the same direction as the incident electric field, which is parallel to the $Z$ axis in this case, as shown in Figure 5.3 (a). In Figure 5.3, all the contour plots are in the $XZ$ plane where the incident electric field is polarized along the $Z$ axis and wavevector direction is along the $X$ axis and through the particle center. Figure 5.3 (b) shows that the internal electric fields at a wavelength of 371 nm are antiparallel to the incident electric field. Figure 5.3 (a) and (b) also reveal an enhancement of the local electric fields at a wavelength of 371 nm near the particle surface along the polarization direction in the $Z$ axis. The electric fields at the same region are reduced at the 345 nm wavelength due to the negative polarizability of the particle.
Figure 5.3 Electric field vector plots for a 10 nm radius silver particle at (a) 345 and (b) 371 nm wavelengths and Poynting vector plot for the silver particle at wavelengths of (c) 345 nm and (d) 371 nm. All the plots are in the $XZ$ plane and through the particle center.

The Poynting vector plot around the 10 nm radius silver nanoparticle at 345 and 371 nm wavelengths are shown in Figure 5.3 (c) and (d). The contour plane is in the $XZ$ plane and through the particle center. Figure 5.3 (c) shows that light propagates along the $X$ axis inside the particle which is consistent with the internal electric field direction as shown in Figure 5.3 (a).
Figure 5.3 (c) also displays that the refracted Poynting vector and the incident light are on the same side of the surface normal which is consistent with the calculated negative effective index of refraction of the particle at 345 nm wavelength. Figure 5.3 (d) exhibits the Poynting vector plot at 371 nm wavelength. Poynting vectors are along the negative $X$ direction inside the particle. The refracted Poynting vector points toward the central symmetry axis of the particle and are on the different side of the surface normal relative to the incident wave.

Even though the calculated effective index of refraction of the silver nanoparticle shows consistency with the Poynting vector plot, the calculations are only mathematically valid since the optical properties of the particle will be varied when the particle size is changed or they are assembled into a three dimensional film. For example, the absorption efficiency, which is defined the absorption cross-section over the physical cross-section of the particle, for a silver nanoparticle can exceed one, however, it can never be obtained by an infinite film.

### 5.2.3 Summary

Using the Mie theory and Kramers-Kronig transformation method, the effective negative indices of refraction were able to be achieved for a silver nanosphere with a radius of 10 nm for wavelengths ranging from 310 to 353 nm. At a wavelength of 345 nm, the lowest $n$ of -2.6 was obtained. As the wavelength is increased beyond the resonance wavelength of 354 nm, real index of refraction increases and becomes positive. The negative polarizability of the silver nanoparticle was also shown to reduce the electric fields inside the particle at the resonance wavelength of 345 nm. The negative polarizability arises from both the internal electric fields in the silver particle and the incident electric field along the $Z$ axis, being parallel to each other.
5.3 Light Manipulation with a Periodic Silver Prism Film

5.3.1 Introduction

Using a silver film composed of periodic triangular prisms, an electromagnetic wave was numerically demonstrated to selectively propagate along different directions depending on the incident polarization direction. When the incident polarization is in the plane of incidence and the surface plasmons are excited, the refracted light ray propagates along the same side of the surface normal as the incident wave. When the incident polarization is perpendicular to the plane of incidence, the refracted light ray always propagates on the opposite side of the surface normal. The results show that a silver film composed of periodic nano-sized triangular prisms may be used as a filter to simultaneously generate two polarized light rays of orthogonal polarizations from one light source.

5.3.2 Results and Discussion

To macroscopically demonstrate the effect of surface plasmons on the light propagation direction, the propagation direction was calculated for light rays through a thin silver film using the DDA method. The silver film was constructed with periodic triangular prisms. The prism was infinitely long along the $Y$ axis. The periodic distance, $d$, is along the $Z$ axis, the height, $h$, is along the $X$ axis. The incident wavevector is parallel to the $X$ axis in all the simulations. Figure 5.4 (a) shows the schematic of reflected, reflection followed with a refraction, and refracted light rays in a right handed film when the incident wavevector is along the $X$ axis and Figure 5.4 (b) displays the corresponding light rays through a left handed film. Figure 5.4 (b) shows that both
the refracted and the reflected light rays propagate along the opposite directions in a left handed film in comparison to a right handed film in (a).

![Sketches of light rays through (a) a right handed and (b) a left handed film comprised of periodic triangular prisms.](image)

Figure 5.4 Sketches of light rays through (a) a right handed and (b) a left handed film comprised of periodic triangular prisms.

Before examining the propagation directions of the refracted and reflected light rays, the scattering, absorption, and extinction spectra are calculated for a silver film with incident polarization direction parallel to the $Y$ or $Z$ axis. The prism height, $h$, was kept at 40 nm considering the skin depth of silver in the visible wavelength region. The periodic distance, $d$, is taken to be 1000 nm. Figure 5.5 shows increasing scattering efficiencies and decreasing absorption efficiencies as the wavelength is increased, similar to that of a flat silver film. Several resonance peaks are observed at wavelengths of 525 nm, 580 nm, and 680 nm when the polarization direction is along the $Z$ axis. The spectra for the $Y$ polarized light shows less structures as displayed in Figure 5.5 (b).
Figure 5.5 Spectra of silver films comprised of periodic triangular prisms for (a) Z polarized incident light and (b) Y polarized incident light.

The propagation directions of the reflected and refracted light rays were examined by calculating the electric field $|E_r|^2$, the square of the real part of the electric field, contour plots at wavelengths between 500 nm and 800 nm. Several wavelengths are randomly selected and it was found that light propagates along the same side of the surface normal relative to the incident wave at most wavelengths when the incident polarization was along the Z axis, which is in the plane of incidence, and surface plasmons were excited. The calculations are consistent with the numerical analysis of Poynting vector displacement in a thin silver film by Dolling et al.\textsuperscript{172}

Figure 5.6 (a) shows the electric field contour plot at a wavelength of 600 nm for the Z polarized light. The contour plane is in the XZ plane. The 40 nm thick silver film is placed at the middle of the plot, though it is difficult to see in a 2000 nm scale plot. The arrangement of the unit prism is similar to the sketches in Figure 5.4.
Figure 5.6 Electric field $|E_r|^2$ contour plots of silver prism films in the $XZ$ plane (a) at 600 nm and (b) 700 nm wavelength for the $Z$ polarized incident light; (c) at 600 nm and (d) 700 nm wavelength for the $Y$ polarized incident light. The incident wave vector is parallel to the $X$ axis.

Since the angle between the upper surface normal and the $X$ axis is only $2.3^\circ$, Figure 5.6 (a) clearly demonstrates that the refracted light propagates toward the left with an angle of $19^\circ$. The reflected light rays also propagate toward the left which looks similar to the schematic in Figure 5.6 (b). Figure 5.6 (b) displays the electric field contour plot at a wavelength of 700 nm
showing the similar phenomenon as that at a wavelength of 600 nm. As discussed by Dolling et al., the Poynting vector displacement in a thin metal film depends on the polarization direction of the incident light. Figure 5.6 (c) and (d) show the electric field contour plot at 600 and 700 nm wavelengths when the incident polarization direction was along the $Y$ axis, which is perpendicular to the plane of incidence. The refracted light propagates along the opposite side of the surface normal relative to the incident wave.

To confirm that the negative diffraction is not due to the coupling between the periodic structures, the diffracted light rays in a single silver prism were also examined. The Poynting vector plots for a single silver prism with a height of 40 nm and a bottom edge length of 1000 nm at wavelengths and polarizations corresponding to Figure 5.6 (a) and (b) are shown in Figure 5.7 (a) and (b), respectively. The prism is highlighted in blue to better illustrate its position and the incident and refracted rays are shown in red. The vector plots verify that the negative diffraction can be observed at wavelengths of 600 nm and 700 nm in a single silver prism, which further demonstrates the increase in refracted angle that is observed when the wavelength is increased with $Z$ polarized incident light.
Figure 5.7 Poynting vector plots of a single silver prism in the XZ plane (a) at 600 nm and (b) 700 nm wavelength for the Z polarized incident light.

To show a clear magnitude of the effect, the angle of incidence versus the angle of refraction, defined as the angles between the incident and refracted light rays and the upper surface normal, is displayed in Figure 5.8 for prisms of different heights and periodic distances. Only the Z polarized light at three different wavelengths are displayed. Since the angle of refraction is determined by the dielectric constant of the silver at the corresponding wavelength and the configuration of the triangular prism, the absolute value of the angle of refraction did not show a monotonic increase with increasing angle of incidence.
Figure 5.8 The angle of incidence versus the angle of refraction, which are the angles between the incident and refracted light rays and the upper surface normal, at different wavelengths for silver prism films of different heights and periodic distances when the polarization direction is in the plane of incidence.

5.3.3 Summary

Silver prism films have been shown to exhibit an effective negative index of refraction for wavelengths of 500 nm, 600 nm, and 700 nm when the incident light is Z polarized. Since light rays of different polarizations propagate at different angles through the film, the film may be used as a filter to simultaneously generate polarized light rays of orthogonal polarization from a single source. In addition, single silver prisms also demonstrated an effective negative index of refraction which confirmed that the negative diffraction is not due to the coupling between the periodic structures. Investigation of nanostructured films comprised of silver prisms and the
individual silver prisms aids in the understanding and development of photonic waveguides, filters, and other next generation optical devices.

### 5.4 Conclusion

The numerical demonstration of light propagation through a silver film composed of periodic triangular prisms is consistent with the mathematical calculations for the spherical silver particle. For a small silver sphere with a 10 nm radius, the excited surface plasmon modes are dominated by the Transverse Magnetic (TM) modes in which no magnetic field is in the propagation direction. The contribution of the Transverse Electric (TE) mode is negligible. The mathematically calculated effective negative indices of refraction of the nanoparticle are associated with the excitation of the TM modes. For the silver films, the same conclusion was obtained where the refracted light ray was shown to propagate along the opposite side of the surface normal relative to the incident light for the TE mode excitation which when the incident polarization is perpendicular to the plane of incidence in the simulation. When the incident polarization was parallel to the plane of incidence, which is the TM mode, the refracted light ray was shown to propagate along the same side of the surface normal relative to the incident light showing the consistent conclusion as in the particle simulations.

Using the general Mie theory\(^{176}\) and the Kramers-Kronig transformation method,\(^{8,174}\) an effective negative index of refraction of -2.6 was able to be achieved in a spherical silver particle of 10 nm radius at a resonance wavelength of 345 nm. The calculated effective negative index of refraction is only phenomenological and has nothing to do with the negative index of refraction described by Dr. Veselago.\(^{159}\) Nevertheless, the calculated negative index of refraction was
microscopically consistent with the Poynting vector direction around the nanoparticle. The propagation direction of electromagnetic wave was also examined through a silver film composed of periodic nanostructured triangular prisms and numerically demonstrated that the refracted light rays may propagate either on the same side or the opposite side of the surface normal relative to the incident wave at visible wavelengths depending on the polarization direction of the incident light. These studies provide insight into plasmonic light manipulation for photonic applications ranging from subwavelength waveguides to optical filters.
CHAPTER 6: SUMMARY

Light interaction with plasmonic nanostructures was theoretically investigated for photonic applications such as subwavelength waveguides, beam splitters, filters, polarizers, and other optical devices. In Chapter 3, using electrodynamic methods, propagating modes were investigated within a nanorod structure, where due to the symmetry of a nanorod only certain modes were able to be excited. The excitation of the forbidden modes of a rod was validated by breaking the symmetry by partially illuminating one end of the rod instead of changing the physical geometry of the structure. In addition, excitation of super dark modes was revealed and the modes were shown to be poor for waveguide applications compared to that of bright modes.

Fano line shapes were demonstrated in the scattering spectra of silver rods which were found to be a result of the coupling of an in plane quadrupole mode and a dipole mode in a single rod, where two nodes located at a quarter of rod length from the two ends were observed at the resonance wavelength. In addition, cutting at the two nodal positions was shown to strengthen the Fano resonance peak. Breaking the rod symmetry introduced a new Fano resonance peak which is due to the asymmetric coupling between the two excited dipoles. The resonance peak becomes stronger when the Fano resonances due to the asymmetric coupling of the two dipoles and the coupling between the in plane quadrupole and the dipole overlap.

In Chapter 4, the effect of the surrounding medium on the optical properties of a two layer silver film was investigated by varying the media before the first layer, between the two layers, and after the second layer which demonstrated that the optical properties of the film are
predominantly determined by the medium between the two layers. The resonance wavelength was shown to red shift when the medium between the two layers was changed from vacuum to water and then glass, correlating with the increased refractive index of the medium. It was shown that the media before the first layer and after the second layer have little effect on the spectra of the film when the thicknesses of the layers are larger than 40 nm.

Following the investigation of the media surrounding the two films, light confinement and propagation at optical frequencies in a two layer silver film with a periodic array of holes was investigated. Extreme subwavelength confinement and propagation of light can be obtained along an extremely subwavelength cross section of a region as small as $10 \times 20 \text{ nm}^2$ at a distance of over 10 microns. The study on MIMs provides rational design of waveguides under subwavelength dimensions.

Finally, in Chapter 5, an effective negative index of refraction of $-2.6$ was obtained for a spherical silver particle with a radius of 10 nm at a wavelength of 345 nm. While the calculated effective negative index of refraction is only phenomenological, it was microscopically consistent with the Poynting vector direction around the nanoparticle. The propagation of electromagnetic waves through a silver film composed of periodic nanostructured triangular prisms was numerically demonstrated to propagate refracted light rays on either the same side or the opposite side of the surface normal relative to the incident wave at visible wavelengths depending on the polarization direction of the incident light.
The work presented here expands the understanding of plasmonic phenomena which arises from the interaction of light with metallic nanostructures. These studies provide insight into plasmonic mechanisms utilized to overcome the diffraction limit of light. Through better understanding of how light-matter interactions of plasmonic nanostructures occurs, further advancements in nanophotonic technologies for applications such as extremely subwavelength waveguides, sensitive optical detection, optical filters, polarizers, beam splitters, optical data storage devices, high speed data transmission, and integrated subwavelength photonic circuits can be achieved.
APPENDIX A: DERIVATION OF BOUNDARY CONDITIONS
A.1 Electromagnetic Boundary Conditions

Maxwell’s equations are a set of differential equations which describe the relationship between the macroscopic electric and magnetic fields of an electromagnetic wave at any point in space-time, \((x, y, z, t)\). The propagation of the wave through a medium is determined by several parameters of the medium,

\[
\nabla \cdot \mathbf{E} = -
\frac{1}{\varepsilon_0} \nabla \cdot \mathbf{P} + \frac{\rho}{\varepsilon_0},
\]

(A.1)

\[
\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M},
\]

(A.2)

\[
\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} - \mu_0 \frac{\partial \mathbf{M}}{\partial t},
\]

(A.3)

\[
\nabla \times \mathbf{H} = \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{J}.
\]

(A.4)

At an interface, or boundary, the microscopic properties gradually change on the atomic scale which, macroscopically, is seen as a drastic change in the media properties. The equations are valid when the parameters of the medium do not change drastically. For the purpose of treating wave propagation classically, the macroscopically averaged parameters of the medium are sufficient.

By defining the electric displacement as \(\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}\), and magnetic induction as \(\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})\) and rearranging the equations, a more useful way to look at them is given where
\[ \nabla \cdot D = \rho, \]  \hspace{1cm} (A.5)

\[ \nabla \cdot B = 0, \]  \hspace{1cm} (A.6)

\[ \nabla \times E + \frac{\partial B}{\partial t} = 0, \]  \hspace{1cm} (A.7)

\[ \nabla \times H - \frac{\partial D}{\partial t} = j. \]  \hspace{1cm} (A.8)

For mathematical validity, the differential forms of the equations must have partial derivative forms to exist, but as a result of the macroscopically averaged, microscopic properties there are discontinuities at the boundary resulting in a breakdown of the macroscopic approximations. To circumvent the macroscopic breakdown, a boundary value problem must be used, where a differential equation together with an additional set of restraints is called a boundary condition. Boundary conditions must be applied to a system so that the approximate solutions to the electric and magnetic fields can be obtained by meeting the requirements of the system and boundary conditions. The differential forms are transformed into the integral form via the divergence theorem and Stokes theorem.

**A.2 Boundary Conditions for the Electric Field**

The first two of Maxwell’s equations, (A.5) and (A.6), are known as Gauss’s Laws. At a boundary between two mediums, Medium 1 and Medium 2, the electric field of the propagating wave in Medium 1 is given as vector \( E_1 \), which can be broken down into two vector components
which lie in the same plane as $E_1$: $E_{n1}$ for the component normal to the boundary, and $E_{t1}$ for the component tangent to the boundary and perpendicular to $E_{n1}$. The same can be done for $E_2$ in Medium 2. The schematic for the electric field components, shown in blue, and the magnetic field components, shown in green, is displayed in Figure A.1.

![Diagram of electric and magnetic field vectors at a boundary between two media.]

**Medium 1 ($\varepsilon_1, \mu_1, \sigma_1$)**

**Medium 2 ($\varepsilon_2, \mu_2, \sigma_2$)**

Figure A.1 Electric and magnetic field vectors at an interface between two media.

**A.2.1 Normal Component of D**

Strictly looking at the first equation for the electric displacement, the boundary conditions for the normal component of $D$ can be derived. The first boundary condition for the normal part of the electric field can be derived from the Maxwell’s equation known as Gauss’ Flux Law, relating the distribution of charges to the resulting electric field by
\[ \oint D \cdot dS = \int_{V} \rho dV, \quad (A.9) \]

\[ \oint D \cdot dS \rightarrow D_{1} \cdot \hat{n} \Delta s + D_{2} \cdot (-\hat{n}) \Delta s = D_{n1} \Delta s - D_{n2} \Delta s. \quad (A.10) \]

Figure A.2 Gaussian pillbox showing the flux of the electric field out of a surface at the interface between two media.

Equation (A.11) states that the charge, \( \rho \), contained within a given region, \( V \), is equivalent to the total flux of the electric field, \( D \), out of the surface, \( s \), of the region. To determine the boundary condition, Gauss’ Flux Law is applied to an imaginary Gaussian pillbox that is placed across the boundary region as shown in Figure A.2. As the height of the pillbox, \( h \), goes to zero, the electric flux within the region can only enter or leave out of the top or bottom of
the pillbox, with the sides of the pillbox contributing negligibly. Any charges on the surface, \( s \), will affect the amount of charge moving through the region which is derived as

\[
\int_V \rho dV = \rho_s \Delta s, \quad (A.11)
\]

\[
D_{n1}\Delta s - D_{n2}\Delta s = \rho_s \Delta s, \quad (A.12)
\]

\[
D_{n1} - D_{n2} = \rho_s. \quad (A.13)
\]

Equation (A.13) states that any discontinuity in the normal component of \( D \), is equivalent to the charge, \( \rho_s \), at the surface. If no surface charges exist, and \( \rho_s = 0 \), then the normal components of the electric flux in Medium 1 and 2 becomes equal and can be written in terms of the electric field normal components by

\[
D_{n1} = D_{n2}, \quad (A.14)
\]

\[
\varepsilon_1 E_{n1} = \varepsilon_2 E_{n2}, \quad (A.15)
\]

\[
E_{n1} = E_{n2} \left( \frac{\varepsilon_2}{\varepsilon_1} \right). \quad (A.16)
\]
A.2.2 Tangential Component of E

The next boundary condition for the tangential component of the electric field, $E_{t1}$ and $E_{t2}$, is obtained by applying Faraday’s Law of Induction to a rectangular loop intersecting the boundary.

Figure A.3 Application of Faraday’s Law of Induction to a rectangular loop across an interface between two media showing electric field flux across the boundary.

As $h$ perpendicular to the boundary goes to zero, the magnetic flux within the loop also goes to zero as depicted in Figure A.3 and derived as
\[ \oint_{\partial \Sigma} E \cdot dl = - \int_{\Sigma} \frac{\partial B}{\partial t} \cdot dA, \]  
(A.17)

\[ \oint E \cdot dl \rightarrow \int_{a}^{b} E_{1} \cdot dl + \int_{c}^{d} E_{2} \cdot dl = 0, \]  
(A.18)

\[ E_{1} \cdot \Delta l + E_{2} \cdot (-\Delta l) = 0, \]  
(A.19)

\[ E_{t1} \Delta l - E_{t2} \Delta l = 0, \]  
(A.20)

\[ E_{t1} - E_{t2} = 0 \rightarrow E_{t1} = E_{t2}. \]  
(A.21)

Therefore, the tangential components of the electric field are equal on either sides of the boundary.

**A.3 Boundary Conditions for the Magnetic Field**

The boundary conditions for the magnetic field, \( B \), normal and tangential components, \( B_{n} \) and \( B_{t} \), respectively, is derived in the same manner as the electric field components at a boundary between two different media. Gauss’ Flux Law is applied to \( B_{n} \) shown in equation (A.22). When applied to the magnetic field, unlike the electric component which contains a term for charges, the integral is equal to zero because magnetic monopoles are currently non-existent. The two boundary conditions for the magnetic field are
\[ \oint B \cdot dS = 0, \quad \text{(A.22)} \]

\[ \oint H \cdot dl = \int_S J \cdot dS + \int_S \frac{\partial D}{\partial t} \cdot dS. \quad \text{(A.23)} \]

A.3.1 Normal Component of \( B \)

The Ampère-Maxwell Law of Magnetic Fields is shown in equation (A.22). As with \( E_n \), the boundary condition for the normal component can be obtained by applying equation (A.22) to a Gaussian pillbox. Following the same process as \( E_n \), the length of the side is decreased so that \( \Delta h \) goes to zero and any flux of \( B \) must occur through the top or bottom of the pillbox where

\[ \oint B \cdot dS \rightarrow B_1 \cdot \hat{n} \Delta s + B_2 \cdot (-\hat{n}) \Delta s = B_{n1} \Delta s - B_{n2} \Delta s. \quad \text{(A.24)} \]
The schematic for the Gaussian pillbox is shown in Figure A.4.

Figure A.4 Gaussian pillbox showing the flux of the magnetic field out of a surface at the interface between two media.

**A.3.2 Tangential Component of H**

As with the tangential component of $E$, the boundary conditions for the tangential component of $H$, $H_t$, is determined using the fourth of Maxwell’s equations, Ampère’s Law, and applying it to a closed loop circuit that spans a boundary interface shown in Figure A.5.
Figure A.5 Ampère’s Law applied to a rectangular loop across an interface between two media showing magnetic flux across the boundary.

The right side of Ampere’s Law contains two terms, the first of which is the conductivity and the second of which is the displacement current,

\[
\oint H \cdot dl = \int_{S} J \cdot dS + \int_{S} \frac{\partial D}{\partial t} \cdot dS.
\]  

(A.25)

As \( h \) goes to zero, so does the displacement current term on the right side of the equation. From the physical standpoint as seen in most real systems, conductivity is a finite quantity and therefore \( J \) is also finite. As \( h \) goes to zero, it results in the conductivity term also going to zero and \( H_{11} = H_{22} \) where
\[ \int H \cdot dl \rightarrow \int_{a}^{b} H_{1} \cdot dl + \int_{c}^{d} H_{2} \cdot dl = H_{1} \cdot \Delta l + H_{2} \cdot (-\Delta l) = 0, \quad (A.26) \]

\[ H_{t1} = H_{t2}. \quad (A.27) \]

If one of the materials is a perfect conductor and \( J \) is infinite, then a surface current can exist which in many cases can be treated as flowing in an infinitesimally thin layer perpendicular to the plane of \( H_{1} \) and \( H_{2} \). The current term does not go to zero, so then \( J_{s} \), which is the magnitude of the vector describing the surface current density, remains in the equation and the boundary condition becomes

\[ H_{t1} - H_{t2} = J_{s}. \quad (A.28) \]

In summary, the final four boundary conditions are

\[ D_{n1} - D_{n2} = \rho_{s}, \quad (A.29) \]

\[ B_{n1} - B_{n2} = 0, \quad (A.30) \]

\[ E_{t1} - E_{t2} = 0, \quad (A.31) \]

\[ H_{t1} - H_{t2} = J_{s}. \quad (A.32) \]

and in vector form,
\[ D_1 \cdot \mathbf{k} - D_2 \cdot \mathbf{k} = \rho_s, \]  
(A.33)

\[ B_1 \cdot \mathbf{k} - B_2 \cdot \mathbf{k} = 0, \]  
(A.34)

\[ \mathbf{k} \times E_1 - \mathbf{k} \times E_2 = 0, \]  
(A.35)

\[ \mathbf{k} \times (H_1 - H_2) = J_s. \]  
(A.36)
APPENDIX B: SCATTERING MUELLER MATRIX ELEMENTS
B.1 Scattering Mueller Matrix Elements

The scattering Mueller matrix elements can be combined to give the polarization intensity, \( I_s \), for a scattered wave at a specific angle, \( \theta \), for a given incident polarization, \( I_i \). A schematic of the general experimental set up to determine the measurements is shown in Figure B.1. The following tables give the combination of scattering matrix elements for incident light which is unpolarized, \( I_{i,u} \), linear parallel, \( I_{i,\parallel} \), linear perpendicular, \( I_{i,\perp} \), linear +45, \( I_{i,+45} \), linear -45, \( I_{i,-45} \), right circular, \( I_{i,R} \), left circular, \( I_{i,L} \), and the intensity of the scattered light for a given polarization transmitted by a polarizer: unpolarized, \( I_{s,u} \), linear parallel, \( I_{s,\parallel} \), linear perpendicular, \( I_{s,\perp} \), linear +45, \( I_{s,+45} \), linear -45, \( I_{s,-45} \), right circular, \( I_{s,R} \), left circular, \( I_{s,L} \). For the unpolarized incident light, the polarizer before the particle would not be present and for unpolarized scattered light, the polarizer after the particle would not be present.

Figure B.1 Schematic of an experimental setup to measure the intensity of a specific polarization of light scattered by a particle and further transmitted by a polarizer for incident light at various polarizations.
### B.2 Unpolarized Incident Light

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### B.3 Linearly Polarized Incident Light

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### B.4 +45/-45 Linearly Polarized Incident Light

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### B.5 Circularly Polarized Incident Light

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