Optical Properties of Single Nanoparticles and Two-dimensional Arrays of Plasmonic Nanostructures

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OPTICAL PROPERTIES OF SINGLE NANOPARTICLES AND TWO-DIMENSIONAL ARRAYS OF PLASMONIC NANOSTRUCTURES

by

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ABSTRACT

The tunability of plasmonic properties of nanomaterials makes them promising in many applications such as molecular detection, spectroscopy techniques, solar energy materials, etc. In the thesis, we mainly focus on the interaction between light with single nanoparticles and two-dimensional plasmonic nanostructures using electrodynamic methods. The fundamental equations of electromagnetic theory: Maxwell’s equations are revisited to solve the problems of light-matter interaction, particularly the interaction of light and noble nanomaterials, such as gold and silver. In Chapter 1, Stokes parameters that describe the polarization states of electromagnetic wave are presented. The scattering and absorption of a particle with an arbitrary shape are discussed. In Chapter 2, several computational methods for solving the optical response of nanomaterials when they are illuminated by incident light are studied, which include the Discrete Dipole Approximation (DDA) method, the coupled dipole (CD) method, etc. In Chapter 3, the failure and reexamination of the relation between the Raman enhancement factor and local enhanced electric field intensity is investigated by placing a molecular dipole in the vicinity of a silver rod. Using a silver rod and a molecular dipole, we demonstrate that the relation generated using a spherical nanoparticle cannot simply be applied to systems with particles of different shapes. In Chapter 4, a silver film with switchable total transmission/reflection is discussed. The film is composed of two-dimensional rectangular prisms. The factors affecting the transmission (reflection) as well as the mechanisms leading to the phenomena are studied. Later, in Chapter 5 and 6, the sandwiched nano-film composed of two 2D rectangular prisms arrays and two glass substrates with a continuous film in between is examined to enhance the transmission of the continuous silver film.
**Key Words:** Plasmonic materials, Discrete Dipole Approximation, Fano Resonance, SERS, Plasmons, Coupling mode, Interaction, Optical properties, Continuous metal film, Transmission, Scattering, Reflection, Enhanced electric fields.
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# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................ x

LIST OF TABLES .......................................................................................................................... xvi

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

1.1 Basic Theory of Light ................................................................................................... 1

1.1.1 Polarization Characteristics of Electromagnetic Radiation ................................. 8

1.1.2 Maxwell’s Equations ........................................................................................... 11

1.1.3 Time-harmonic Fields ....................................................................................... 14

1.1.4 Stokes Parameters and Jones Calculus ............................................................... 15

1.1.4.1 Rotation Transformation Rule for Stokes Parameters ................................. 24

1.2 Reflection and Transmission at a Plane Boundary and a film ................................... 27

1.2.1 Normal Incidence ................................................................................................. 28

1.2.2 Oblique Incidence ................................................................................................. 30

1.2.3 Reflection and Transmission by a Film ............................................................... 34

1.3 Scattering, Absorption of an Arbitrary Particle ......................................................... 38

1.3.1 Analogy between a Film and a Particle ............................................................... 41

1.3.2 Boundary Condition ............................................................................................. 41

1.3.3 Light Propagation in Dielectric Medium ............................................................. 45

1.3.4 Light Propagation in Conducting Medium .......................................................... 49

1.3.5 Amplitude Scattering Matrix ............................................................................... 54

1.3.6 Scattering Matrix ................................................................................................. 59

1.3.7 Extinction of an Arbitrary Nanoparticle .............................................................. 63
1.4 The Interaction between Light and Noble Metals .......................................................... 67
  1.4.1 Surface Plasmons ..................................................................................................... 68

CHAPTER 2: METHODS .......................................................................................................... 72
  2.1 Introduction .................................................................................................................. 72
  2.2 Mie Theory .................................................................................................................. 72
  2.3 Discrete Dipole Approximation Method ...................................................................... 78
  2.4 Coupled Dipole Method .............................................................................................. 81

CHAPTER 3: RELATION BETWEEN THE INTENSITY OF THE ENHANCED ELECTRIC
FIELD NEAR A SINGLE ROD AND THE ENHANCED RAMAN SCATTERING FACTOR 84
  3.1 General Introduction ................................................................................................... 84
  3.2 Results and Discussion ............................................................................................... 87
    3.2.1 Raman Scattering Enhancement Factor ............................................................... 87
    3.2.2 System with a Spherical Particle ......................................................................... 88
    3.2.3 Scattering Spectra of Rods along Different Axes ................................................. 89
    3.2.4 Electric Field Vector Plots of Rods ..................................................................... 90
    3.2.5 Rod along the Y-axis with a Molecule ................................................................ 92
    3.2.6 Electric Field Vector Plots of Rods along the Y-axis .......................................... 94
    3.2.7 Rod along the X-axis with a Molecule ................................................................ 95
    3.2.8 Electric field Vector Plots of Rod along the X-axis ............................................ 97
  3.3 Conclusions ................................................................................................................. 98

CHAPTER 4: TOTAL TRANSMISSION AND REFLECTION IN A TWO-DIMENSIONAL
RECTANGULAR PRISMS ARRAY .......................................................................................... 99
4.1 General Introduction ................................................................................................... 99
4.2 Results and Discussions ............................................................................................ 102
  4.2.1 TE and TM mode ............................................................................................... 102
  4.2.2 The Effect of Prism Width ................................................................................. 103
  4.2.3 Effect of Prism Height ....................................................................................... 106
  4.2.4 Optimal Conditions ............................................................................................ 108
  4.2.5 Comparisons between the Spectra Calculated by Different Methods .......... 110
  4.2.6 Absorption Spectra for the Array ....................................................................... 112
4.3 Conclusions ............................................................................................................... 113

CHAPTER 5: DIFFERENT TRANSMISSION ENHANCEMENT MECHANISMS IN A
SANDWICHED NANOFILM .................................................................................................... 115
  5.1 General Introduction ................................................................................................. 115
  5.2 Results and Discussions ............................................................................................ 118
    5.2.1 Comparisons of the Transmission of Different Film Systems ......................... 119
    5.2.2 Effect of Neighboring Prism Distance ............................................................... 121
    5.2.3 Effect of Glass Layer Thickness ........................................................................ 123
    5.2.4 Electric Field Contours ...................................................................................... 124
    5.2.5 Other Parameters Affecting Transmission ......................................................... 126
  5.3 Conclusions ............................................................................................................... 127

CHAPTER 6: COMBINING BOTH LOCAL AND PROPAGATING PLASMON
POLARITONS TO ENHANCE THE TRANSMISSION OF NANO-FILM ............................ 128
  6.1 General Introduction ................................................................................................. 128
LIST OF FIGURES

Figure 1. Wave U versus z at times from t to t+Δt. ................................................................. 3

Figure 2. Vibration ellipse. ...................................................................................................... 9

Figure 3. The device that can measure the irradiance of transmitted light from a polarizer. .... 18

Figure 4. Two sets of basis vectors $\mathbf{e} \perp$ and $\mathbf{e} \parallel$, $\mathbf{e} -$ and $\mathbf{e} +$ ..................................................... 21

Figure 5. Rotation of the $\mathbf{e} \perp$ and $\mathbf{e} \parallel$ vectors with an angle of $\varphi \geq 0$ in a clockwise direction when looking in the direction of light propagation................................................................. 24

Figure 6. Light incident upon a boundary separating two different media, medium 1 and medium 2 ............................................................................................................................................. 28

Figure 7. Reflection and transmission of obliquely incident wave for (a) S-polarized (TE polarization) state and (b) P-polarized (TM polarization) state. In TE polarization state, all electric vectors are normal to the plane of incidence, while in TM polarization state, all magnetic vectors are normal to the plane of incidence........................................................ 31

Figure 8. Reflection and transmission of a planar film............................................................ 35

Figure 9. (a) An arbitrary individual particle (b) particle cluster and (c) a layer of randomly and sparsely distributed particles illuminated by a parallel beam of light. (d) is a particle taken from (c), each particle in the layer is illuminated by the incident beam and also scatters light, same as other particles in the layer................................................................. 40

Figure 10 Analogy between reflection-transmission by a thin film and scattering by an isolated particle......................................................................................................................... 41

Figure 11 Closed surface A between particle 1 and medium 2. ............................................ 43
Figure 12 Dependence of real $n_r$ and imaginary $n_{im}$ parts of refractive index on the angular frequency near a resonance line. ................................................................. 49

Figure 13 Real and imagery parts of refractive index versus frequency for a conducting medium. ........................................................................................................ 54

Figure 14 Scattering by an arbitrary isolated particle, the light propagates along the Z-axis, which is defined as the forward direction. The particle is placed at the origin of the coordinate... 56

Figure 15 Extinction by a single particle. ............................................................................................. 64

Figure 16 Schematic of (a) Localized surface plasmons (LSPs) and (b) Surface plasmon polaritons (SPPs). ........................................................................................................ 69

Figure 17 (top) longitudinal mode coupling, (bottom) transverse mode coupling supported in a linear array of particles. ................................................................. 70

Figure 18 Schematic of two kinds of Raman scatterings: Stokes scattering and Anti-stokes scattering. ........................................................................................................ 85

Figure 19 Schematic of spherical nanoparticle with a molecule in its vicinity where the incident light is along the X-axis. $d$ represents the distance between the molecule and the spherical nanoparticle. $r = 50$ nm. (b) The relation between the Raman enhancement factor and the enhanced electric field intensity when $d$ is varied from 2 to 16 nm. ................................. 88

Figure 20 Scattering spectra for a rod with a diameter of 40 nm and a length of 100 nm when its long axis is along the (black) X-, (red) Y- and (green) Z-axes, respectively. The incident light is along the X-axis; the polarization is along the Y-axis. The inset is the zoom in scattering spectra in the wavelengths from 300 to 500 nm................................................. 89
Figure 21 Electric field vector plots in the XY plane when the rod is oriented along the (a) Y-axis and (b) X-axis at the wavelength of 580 nm and illuminated by an incident light of a plane wave. The electric field vector plots are through the rod center................................. 90

Figure 22 Schematic of the silver rod that oriented along the Y-axis with a molecule in its vicinity (b) Scattering spectra for the system when the position of the molecule relative to the end of the rod is varied from $p_1 = 0$ nm to 50 nm and for the isolated molecular dipole. (c,d) The relations between Raman enhancement factor (red curve) and the enhanced electric field intensity (blue curve) at the wavelengths of 400 and 580 nm, respectively. The diameter of the rod is 40 nm, the length is 100 nm. $d_1 = 4$ nm. ........................................... 92

Figure 23 Electric field vector plots of the rods at the wavelength of 580 nm when the rods are illuminated by the molecular dipole at (a) $p_1 = 10$ nm and (b) $p_1 = 50$ nm and oriented along the Y axis. All the electric field vector plots are through the rod center. ................... 94

Figure 24 (a) Schematic of the silver rod that oriented along the X-axis with a molecule in its vicinity (b) Scattering spectra for the system when the position of the molecule relative to the end of the rod is varied from $p_2 = 0$ nm to 50 nm and for the isolated molecular dipole. (c, d) The relations between Raman enhancement factor (red curve) and the enhanced electric field intensity (blue curve) at the wavelengths of 400 and 580 nm, respectively. The diameter of the rod is 40 nm, the length is 100 nm. $d_2 = 4$ nm. ........................................... 95

Figure 25 Electric field vector plots of the rods at the wavelength of 580 nm when the rods are illuminated by the molecular dipole at (a) $p_2 = 10$ nm and (b) $p_2 = 50$ nm and orient along the X- axis. All the electric field vector plots are through the rod center......................... 97
Figure 26 Schematic of two Fano resonance shapes. (red) Usual spectral line shape (blue), Asymmetrical Fano shape and (green) Symmetrical Fano shape. ...................................... 101

Figure 27 Schematic of (a) a free-standing two-dimensional prisms array in the YZ plane where the incident light is along the X-axis and the incident polarization can be either along the Y-axis or the Z-axis. The neighboring prisms distance along the Y and Z axes are expressed as dy and dz, respectively. (b) An individual rectangular prism in the array with width w and height h. ................................................................................................................................ 102

Figure 28 Transmission spectra for the silver rectangular prims arrays when the incident polarization is along the (a, b) the Y-axis and (c, d) the Z-axis. (a, c) w = 100 nm and (b, d) w = 300 nm. h = 150 nm. dy = 500 nm, dz is varied from 500 to 900 nm. ......................... 105

Figure 29 Transmission spectra for the silver rectangular prims arrays when the incident polarization is along the (a, b) the Y-axis and (c, d) the Z-axis. (a, c) h = 150 nm and (b, d) h = 200 nm. w = 200 nm. dy = 500 nm, dz is varied from 500 to 900 nm. ......................... 107

Figure 30 Transmission spectra for the silver rectangular prisms array when the incident polarization is along (a) the Y-axis and (b) the Z-axis. h = 200 nm, w = 300 nm, dy = 500 nm, dz is varied from 500 to 900 nm. .................................................................................. 108

Figure 31 Transmission spectra calculated using the DDA (solid lines) method and CD (dashed lines) method where the incident polarization is along (a) the Y-axis and (b) the Z-axis. The parameters of the prism is as follows: h = 150 nm, w = 300 nm. dy = 500 nm, dz= 800 nm. ............................................................................................................................................. 110
Figure 32 Absorption spectra for the silver rectangular prisms array from contributions of excited dipoles along the (black) X-, (red) Y- and (green) Z-axis only and also the (blue) total absorption when the incident polarization is along the (a) Y-axis and (b) Z-axis. h = 150 nm, w = 300 nm, d_y = 500 nm, d_z = 800 nm.

Figure 33 Schematic of sandwiched nano-film. The thickness of silver film is t, the thickness of glass layers is d. The neighboring prism distances are expressed as D_y and D_z along the Y- and Z-axes, respectively. The parameters of the rectangular prism: height is h, width is w. The incident light is along the X-axis, the polarization is either along the Y- or Z-axis.

Figure 34 Comparisons of the transmission spectra for several different nano-film systems. Black solid curve: The isolated continuous silver film with a thickness of 50 nm. Green curves: The silver film sandwiched by glass substrates and one nanoprisms array lying above and below it. Solid and dashed lines represent the conditions when the incident polarization is along the Y- and Z-axes, respectively. D_y = 300 nm, D_z = 600 nm. The transmission spectra are overlapped whether the incident polarization is along the Y- or the Z-axis.

Figure 35 Transmission spectra for the sandwiched nanofilm when the incident polarization is parallel to (a) the Y-axis and (b) the Z-axis. w = 150 nm, h = 50 nm, D_y = 300 nm, D_z is varied from 400 to 800 nm.

Figure 36 Transmission spectra for the sandwiched nanofilm when the incident polarization is along (a) the Y axis and (b) the Z axis. w = 150 nm, h = 50 nm, D_y = 300 nm, D_z = 600 nm. d is increased from 20 to 60 nm.
Figure 37 Electric field distribution contours in the (a, c) XY-plane and (b, d) XZ-plane when the incident polarization is along the Z axis at the wavelengths of (a, b) 640 nm and (c, d) 1030 nm. The monitor is placed in the center of nano-film system at all the conditions. h = 50 nm, w = 150 nm, D_y = 300 nm, D_z = 600 nm, d = 20 nm.

Figure 38 Transmission spectra of the sandwiched films when the incident polarization is along (a, c) the Y-axis and (b, d) the Z-axis. The prisms lying below the above the film are shifted with respect to each other along (a, b) the Y-axis and (c, d) the Z-axis.

Figure 39 (a) Transmission spectra for the sandwiched nano-film when the incident polarization is along the Z-axis where the thickness of the glass substrate, d, is increased from 50 to 150 nm. (b) The evolvement of the transmission spectra with the thickness of glass substrate. Black lines: the relation between peak wavelength and d. Blue lines: the relation between peak transmission efficiency and d. The parameters of the sandwiched nano-film are as follows: h = 50 nm, w = 150 nm, D_y = 300 nm, D_z = 600 nm.

Figure 40 Transmission spectra for the continuous nano-film with varying thickness where d = 110 nm, D_y = 300 nm, D_z = 600 nm, h = 50 nm, w = 150 nm. The incident polarization is along the Z axis.

Figure 41 Transmission spectra for the continuous nano-film when the incident polarization is along (a) the Y-axis and (b) the Z-axis. D_y = 300 nm, D_z is varied from 300 to 900 nm, h = 50 nm, w = 150 nm.

Figure 42 Transmission spectra for the nano-film when the incident polarization is along (a) the X-axis and (b) the Z-axis. D_y = 300 nm, D_z is varied from 300 to 900 nm, h = 50 nm, w = 150 nm.
LIST OF TABLES

Table 1. Jones Matrices for some linear optical elements ............................................................ 17

Table 2. Stokes parameters for corresponding polarization states of light ................................. 26

Table 3. Scattering matrix elements ............................................................................................. 62
CHAPTER 1: INTRODUCTION

Optics studies the interaction between light and materials, among them the most attractive field might be the interaction between light and nanosized particles and structures, since the interaction will generate more phenomena than the bulk counterparts. Before studying the interaction between light and nanomaterials, we must be familiar with the nature of light. It is well-known that light is merely a kind of electromagnetic energy. When a beam of light propagates in a medium, usually the intensity of the beam will be attenuated, this attenuation is because of the scattering and absorption by the particles in the medium. The total of absorption and scattering is called extinction. To quantitatively understand the interaction between light and nanomaterials, in addition to Maxwell’s electromagnetic theory, the quantum theory need also to be used. However, in the thesis, we only focus on classical electromagnetic theory and linear optics. And the medium is considered as homogenous and non-absorbing. The basic concepts and equations in electromagnetic theory will be presented. We will also briefly introduce the interaction between a plane harmonic wave with an arbitrary particle and a film.

1.1 Basic Theory of Light

Nowadays, we know that visible light is a form of electromagnetic energy, the finding is mainly because of the pioneering work of Clerk Maxwell (1831-1879). In the thesis, we only focus on Maxwell’s electromagnetic theory and mainly visible to near infrared wavelengths range. The detailed introduction of quantum theory describing the interaction of light and matter can be found in reference 1.¹
In this section, we show the phase relations in a plane wave travelling in vacuum. Before we start, an important partial differential equation needs to be introduced.

\[ \nabla^2 (\ ) = \frac{1}{c^2} \frac{\partial^2 (\ )}{\partial t^2} \]  

(1.1)

The Equation (1.1) is called the wave equation, it can be used to describe many physical phenomena such as the oscillations of string, sound waves, and wave of water, etc. More importantly, it can be applied to electromagnetic wave.

For an electromagnetic wave that consists of electric field \( E \) and magnetic field \( H \), we can obtain:

\[ \nabla^2 (E) = \frac{1}{c^2} \frac{\partial^2 (E)}{\partial t^2} \]  

(1.2)

\[ \nabla^2 (H) = \frac{1}{c^2} \frac{\partial^2 (H)}{\partial t^2} \]  

(1.3)

where

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

(1.4)

Where \( \mu_0 \) is the permeability of the vacuum, which is a constant. The other constant, \( \varepsilon_0 \) is the permittivity of the vacuum.
When light is travelling in an isotropic nonconducting medium, the equations above are same as these in vacuum, while the constants need to be modified to the corresponding constants of the medium, $\mu$ and $\varepsilon$. Thus, the speed of the electromagnetic wave in the medium will be changed to

$$v = \frac{1}{\sqrt{\mu \varepsilon}} \quad (1.5)$$

If we introduce two more ratios, $K_m = \frac{\mu}{\mu_0}$ and $K = \frac{\varepsilon}{\varepsilon_0}$, Equation (1.5) can be simplified to a new form.

$$v = \frac{1}{\sqrt{\mu_0 \varepsilon_0 K_m K}} = \frac{c}{\sqrt{K_m K}} \quad (1.6)$$

Figure 1. Wave $U$ versus $z$ at times from $t$ to $t+\Delta t$. 

3
The refractive index, \( n \), which is defined as the ratio of the speed of light in vacuum to the phase velocity of light in the medium, can be expressed as

\[
n = \frac{c}{v} = \sqrt{\frac{K}{K_m}} \quad (1.7)
\]

Equation (1.7) shows that the \( n \) is a constant number in the chosen medium, while later we will find out that the \( n \) varies with the change of frequency (or wavelength) of the radiation.

For a light wave, \( U \), propagates in an arbitrary direction, \( z \), the operator \( \nabla^2 \) in Equation (1.1) is reduced to \( \frac{\partial^2}{\partial z^2} \), the new form will be

\[
\frac{\partial^2 U}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 U}{\partial t^2} \quad (1.8)
\]

The graph of \( U \) verse \( z \) is shown in Figure 1.

It can be easily verified that

\[
U(z, t) = U_0 \cos(kz - \omega t) \quad (1.9)
\]

is the solution to Equation (1.8) provided the relation \( v = \omega / k \) exists. The Equation (1.9) represents a fundamental wave, which is named as a plane harmonic wave. The detailed
The introduction of the plane harmonic wave will be presented in Section 1.1.3. The constants $k$ and \( \omega \) in Equation (1.9) are known as angular wavenumber and angular frequency, respectively.

Note that the propagation of wave is not just limited to one dimension, for a wave propagating in three dimensions, the new wave equation will be

\[
U(x, y, z, t) = U_o \cos(\vec{k} \cdot \vec{r} - \omega t) \tag{1.10}
\]

where the term \( \vec{k} \cdot \vec{r} - \omega t \) is the wave phase and the position of wave \( \vec{r} \) is defined as

\[
\vec{r} = ix + jy + kz \tag{1.11}
\]

The wave vector \( \vec{k} \) is defined as

\[
\vec{k} = ik_x + jk_y + kk_z \tag{1.12}
\]

Till now we have learned that the wave equation for a three-dimensional plane harmonic wave can be expressed as

\[
U = U(x, y, z, t) = U_o \cos(\vec{k} \cdot \vec{r} - \omega t) \tag{1.13}
\]

The complex form of Equation (1.13) can be written as
\[ U = U_0 e^{i(k\vec{r} - \omega t)} \]  

(1.14)

The mathematical relation that we used in the transformation from Equation (1.13) to (1.14) is

\[ e^{i\alpha} = \cos \alpha + i \sin \alpha \]  

(1.15)

In the field of electrodynamics, we always assume that the physical quantity represented by a complex expression equals to the real part of that expression. For the wave \( U \), its intensity or irradiance is proportional to the square of the amplitude, which may be written as

\[ |U|^2 = U \cdot U^* = (U_0 \cos \alpha + iU_0 \sin \alpha)(U_0 \cos \alpha - iU_0 \sin \alpha) = U_0^2 \]  

(1.17)

where the asterisk denotes the complex conjugate value. The intensity of a plane wave is usually marked as \( I \) The detailed derivation of wave intensity is presented as follows. The electric field \( E \) and the magnetic field \( H \) of a plane harmonic wave can be given by

\[ E = E_0 \cos(k \cdot \vec{r} - \omega t) \]

\[ H = H_0 \cos(k \cdot \vec{r} - \omega t). \]  

(1.18)

Poynting vector, \( S \), shows the time rate of flow of electromagnetic energy per unit area, which is defined as the cross product of the electric and magnetic fields
Thus, the average value of the Poynting vector will be

\[
\langle S \rangle = \frac{1}{2} E_0 \times H_0, \tag{1.20}
\]

because the average value of cosine squared is 1/2. We know that unit vector of \( \vec{k} \) is also perpendicular to the plane composed of electric field \( E \) and magnetic field \( H \). So the Poynting vector can also be written as

\[
\langle S \rangle = \frac{\vec{k}}{k} \tag{1.21}
\]

Both Equations (1.20) and (1.21) indicate the energy flow of an electromagnetic wave has the same direction as that of wave vector \( \vec{k} \) and can be specified by \( S \).

The irradiance of an incident wave will be exponentially attenuated when it travels through an absorbing medium. The relation between the irradiance \( I \) and initial irradiance \( I_0 \) can be given by

\[
I = I_0 e^{-\beta z} \tag{1.22}
\]

where \( z \) is the distance that the wave travels and the coefficient \( \beta \) can be expressed as
\[ \beta = \frac{4\pi k}{\lambda} \] (1.23)

1.1.1 Polarization Characteristics of Electromagnetic Radiation

In this section, we focus on the study of the polarization states of a plane wave. In addition to its irradiance and frequency, the plane harmonic electromagnetic wave also has a property named its state of polarization. Polarization state is an important factor when we study the interaction of light and nanomaterials, since different polarization states might behave quite differently, thus leading totally distinct optical response. Researchers mainly focus on electric field \( E \) in discussions of polarization or polarization state of a wave.

A more general form of time-harmonic electromagnetic wave can be written as

\[
E_c = (A + iB)e^{(ikz - i\omega t)},
\] (1.24)

it propagates in the \( z \) direction in a nonabsorbing medium. The two arbitrary component fields \( A \) and \( B \) are independent of time.

Its electric field \( E \) can be expressed as

\[
E = Re\{E_c\} = Re((A + iB)e^{(ikz - i\omega t)})
= A\cos(kz - \omega t) - B\sin(kz - \omega t)
\] (1.25)
The electric field vector at any point is perpendicular to the direction of propagation, which is $\vec{k}$.

For the condition when $z = 0$, Equation (1.25) becomes its simplest form

\[ E(z = 0) = A \cos \omega t + B \sin \omega t \quad (1.26) \]

Equation (1.26) can be represented by an ellipse, as shown in Figure 2, named vibration ellipse.

Figure 2. Vibration ellipse.
Vibration ellipse is characterized by its ellipticity, the ratio between $B$ and $A$ and also its azimuth, the angle between the semimajor axis and an arbitrary reference direction. $B$ is the length of the semiminor axis and $A$ is that of the semimajor axis, as shown in Figure 2. Using the vibration ellipse, all the polarization states of light can be displayed. For natural (or unpolarized) light, the instantaneous polarization fluctuates rapidly in a random manner. In the case of linearly polarized light, the electric field $E_0$ and the magnetic field $H_0$ are real constant vectors, which means $A = 0$ (or $B = 0$) if we show it using the vibration ellipse. The vibration ellipse is just a straight line, while its azimuth angle can be different. For circularly polarized light, $|A| = |B|$ and $A \cdot B = 0$, the vibration ellipse becomes a circle. Circularly polarized light can also be treated as the superposition of two linearly polarized light of same amplitude polarized orthogonally to each other with a phase difference of $\pi/2$. Suppose we have two component electric fields and the electric vectors of these two fields are in $A$ and $B$ directions, respectively. The two fields are

$$
\hat{i}E_0 \cos(kz - \omega t) \\
\hat{j}E_0 \sin(kz - \omega t)
$$

(1.27)

where $\hat{i}$ is the unit vector in $A$ direction, $\hat{j}$ is the unit vector in $B$ direction. Thus, the total electric field $E$ will be the sum of the two component fields, which can be given by
The complex form for the circularly polarized light can be written as

$$E = E_0[i \cos(kz - \omega t) + j \sin(kz - \omega t)] \quad (1.28)$$

The vibration ellipse is also useful in assigning the handedness for light. It is customary to say the vibration ellipse is right-handed if the vector $A \times B$ is opposite to the direction of propagation.

In the case of elliptically polarized light, $|A| \neq |B|$ and $A \cdot B = 0$, the vibration ellipse becomes a real ellipse. Under this condition, a complex vector amplitude $E_0$ can be defined as follows

$$E = iE_0 \exp i(kz - \omega t) + jE_0 \exp i(kz - \omega t \pm \pi/2) \quad (1.29)$$

where $E_0 \neq E'_0$. At any given point in space, the resultant electric vector rotates and changes in amplitude.

1.1.2 Maxwell’s Equations

As we mentioned before, Maxwell’s equations are fundamental in solving electromagnetic wave problems. The two component fields of the electromagnetic wave, $E$ and $H$, are independent of each other and are determined by the distribution of charge and current in all space, respectively. All the classical optical phenomena can be solved using a set of Maxwell’s
equations for the macroscopic electromagnetic field at interior points in material. The simple forms of Maxwell’s equations are as follows:

\[ \nabla \cdot \mathbf{D} = \rho \]  
(1.31)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  
(1.32)

\[ \nabla \cdot \mathbf{B} = 0 \]  
(1.33)

\[ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]  
(1.34)

Where \( t \) is time, \( \mathbf{B} \) is the magnetic induction, \( \mathbf{D} \) the electric displacement, \( \rho \) the macroscopic free charge density and \( \mathbf{J} \) the current density. One should be noted that all the entering in Equations (1.31) – (1.34) are functions of time and spatial coordinates.

\( \mathbf{D} \) and \( \mathbf{H} \) are defined by

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \]  
(1.35)

\[ \mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \]  
(1.36)
where $P$ is the electric polarization, which is defined as average electric dipole moment per unit volume, $M$ the magnetization (average magnetic dipole moment per unit volume), and $\varepsilon_0$ and $\mu_0$ are the electric permittivity and magnetic permeability of the free space, respectively. The underlying relation in the Maxwell’s equations is

$$\frac{\partial D}{\partial t} + \nabla \cdot J = 0$$  \hspace{1cm}(1.37)$$

However, Equations (1.33) – (1.36) are insufficient in determining the electric and magnetic fields from a given distribution of charges and currents; they must be supplemented with so-called constitutive relations, the forms are as follows

$$J = \sigma E$$  \hspace{1cm}(1.38)$$

$$B = \mu H$$

$$P = \varepsilon_0 \chi E$$

where $\sigma$ is the conductivity, $\mu$ the permeability, and $\chi$ the electric susceptibility, which indicates the degree of polarization of a material in response to an applied electric field. The coefficients, $\sigma, \mu$ and $\chi$ are assumed to be independent of the fields, position and direction, since the medium we considered is linear, homogenous and isotropic. The detailed introduction of Maxwell’s equations can be found in reference 2.²
1.1.3 Time-harmonic Fields

In this work, we treat all the fields and sources as time-harmonic and the real time-dependent fields are treated as real parts of the respective complex fields. For a simple time-harmonic field, \( E \), its the simplest form can be described by Equation (1.26). We have learned that the \( E \) can be written as the real part of a complex vector: \( E = Re\{E_c\} \), where

\[
E_c = (A + iB)e^{-i\omega t}
\]  
(1.39)

The time-dependent factor has two choices: \( e^{i\omega t} \) and \( e^{-i\omega t} \), the quantities of physical meaning are always the same no matter which choice is made. In this thesis, we choose \( e^{-i\omega t} \). If the constitutive relations are substituted into the set of Maxwell’s equations, the following equations can be obtained

\[
\nabla \cdot (\varepsilon E_c) = 0
\]  
(1.40)

\[
\nabla \times E_c = i\omega \mu H_c
\]  
(1.41)

\[
\nabla \cdot H_c = 0
\]  
(1.42)

\[
\nabla \times H_c = -i\omega \varepsilon E_c
\]  
(1.43)

where the permittivity \( \varepsilon \) is a complex number, which can be denoted as
\[ \varepsilon = \varepsilon_0(1 + \chi) + i \frac{\sigma}{\omega} \] (1.44)

From this standing point, we know that the constitutive coefficient \( \sigma, \mu \) and \( \chi \) are not restricted to real numbers. Take \( \mu \) as an example, a complex \( \mu \) means that a phase difference between real time-harmonic magnetic field \( H \) and the corresponding real time-harmonic magnetic induction \( B \) exists. In the later section, we will show complex \( \varepsilon \) or/and \( \mu \) generates an imaginary part of the refractive index, \( n \), which causes the absorption of electromagnetic energy. Equations (1.40)-(1.43) are usually used in solving scattering problems when a nanomaterial is placed in the field of an electromagnetic wave.

1.1.4 Stokes Parameters and Jones Calculus

Vibration ellipse is an important way to understand the polarization state of an electromagnetic wave, while its downside is also evident, since the transformation of the polarized light is not readily visualized and measured when light interacts with materials. An easier way to describe the polarization state of an electromagnetic wave is using matrix, which includes both Stokes parameters and Jones calculus. In this section, Jones calculus will be briefly introduced and also the Stokes parameters.

The complex amplitude of a plane harmonic wave can be expressed as

\[ E_0 = iE_{0x} + jE_{0y} \] (1.45)
where both $E_{0x}$ and $E_{0y}$ can be complex. Thus, they can be written as follows

\[
E_{0x} = |E_{0x}|e^{i\theta_x} \\
E_{0y} = |E_{0y}|e^{i\theta_y}
\]  

(1.46)

or using matrix

\[
\begin{bmatrix}
E_{0x} \\
E_{0y}
\end{bmatrix} = \begin{bmatrix}
|E_{0x}|e^{i\theta_x} \\
|E_{0y}|e^{i\theta_y}
\end{bmatrix} 
\]  

(1.47)

The normalized form of the Jones vector can be obtained by dividing $\left(|E_{0x}|^2 + |E_{0y}|^2\right)^{1/2}$ at both sides of Equation (1.47), since the normalized form is more useful in solving real-world problems. For example, $\begin{bmatrix} A \\ 0 \end{bmatrix} = A \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ shows a linearly polarized wave in the $X$ direction, which means one of the electric fields does not exist. $\begin{bmatrix} A \\ A \end{bmatrix} = A \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ represents a linearly polarized at $45^\circ$ relative to the $X$-axis. Some Jones matrices for optical elements are summarized in Table 1.
Table 1. Jones Matrices for some linear optical elements

<table>
<thead>
<tr>
<th>Optical elements</th>
<th>Jones matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear polarizer</td>
<td></td>
</tr>
</tbody>
</table>
| Transmission axis horizontal | \[
\begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\] |
| Transmission axis vertical | \[
\begin{bmatrix}
0 & 0 \\
0 & 1
\end{bmatrix}
\] |
| Transmission axis at ±45° | \[
\frac{1}{2} \begin{bmatrix}
1 & 1 & ±1 \\
±1 & 1 & 1
\end{bmatrix}
\] |
| Quarter-wave plate |             |
| Fast axis vertical | \[
\begin{bmatrix}
1 & 0 \\
0 & -i
\end{bmatrix}
\] |
| Fast axis horizontal | \[
\begin{bmatrix}
1 & 0 \\
0 & i
\end{bmatrix}
\] |
| Fast axis at ±45° | \[
\frac{1}{\sqrt{2}} \begin{bmatrix}
1 & ±i \\
±i & 1
\end{bmatrix}
\] |
| Half-wave plate |             |
| Fast axis either vertical | \[
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\] |
| Or horizontal | \[
\begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}
\] |
| Isotropic phase retarder | \[
\begin{bmatrix}
e^{i\theta} & 0 \\
0 & e^{i\theta}
\end{bmatrix}
\] |
| Relative phase changer | \[
\begin{bmatrix}
e^{i\theta x} & 0 \\
0 & e^{i\theta y}
\end{bmatrix}
\] |
| Circular polarizer |             |
| Right | \[
\begin{bmatrix}
1 & 0 & i \\
2 & -i & 1
\end{bmatrix}
\] |
| Left | \[
\begin{bmatrix}
1 & 1 & -i \\
2 & i & 1
\end{bmatrix}
\] |

Note that the 2 x 2 Jones calculus only works for light that is initially polarized.
From Section 1.1.1, we know that any monochromatic wave (wave of a single wavelength) can be expressed as a superposition of two orthogonal component fields, horizontal and vertical; right- and left-circular; and so on. Suppose we have a device that is composed of an arbitrary monochromatic beam as a light source, a polarizer $P$, a detector that can detect the irradiance of the emission light and omit the polarization state. A polarizer is an optical device that can filter the polarization state of a wave, it allows light with a specific polarization to pass and blocks other polarizations. The schematic of the device is shown in Figure 3.

![Figure 3](image)

Figure 3. The device that can measure the irradiance of transmitted light from a polarizer.

The polarizer of the device will not change the amplitude of the transmitted component, and the electric field is composed of two orthogonal components fields $\hat{e}_\perp$ and $\hat{e}_\parallel$, which we name as “vertical” and “horizontal”, respectively. The relations between them are

$$E = E_0 \exp(ikz - i\omega t)$$  \hspace{1cm} (1.48)
\[ E_0 = E_\parallel \hat{e}_\parallel + E_\perp \hat{e}_\perp \]  

(1.49)

\[ E_\parallel = a_\parallel e^{-i\delta_\parallel} \]  

(1.50)

\[ E_\perp = a_\perp e^{-i\delta_\perp} \]  

(1.51)

If there is no polarizer exists between the beam and detector, the irradiance or intensity detected by the detector is

\[ I = E_\parallel E_\parallel^* + E_\perp E_\perp^* = a_\parallel^2 + a_\perp^2 \]  

(1.52)

If \( P \) is a horizontal polarizer, the irradiance recorded by detector will be \( I_\parallel = E_\parallel E_\parallel^* \); If \( P \) is a vertical polarizer, the irradiance will be \( I_\perp = E_\perp E_\perp^* \), the difference will be

\[ I_\parallel - I_\perp = E_\parallel E_\parallel^* - E_\perp E_\perp^*. \]  

(1.53)

When we consider \( \pm 45^\circ \) linear polarization states, another orthonormal set of basis vectors \( \hat{e}_+ \) and \( \hat{e}_- \) need to be defined, as shown in Figure 4.

\[ \hat{e}_+ = \frac{1}{\sqrt{2}} (\hat{e}_\parallel + \hat{e}_\perp) \]  

(1.54)
\( \hat{e}_- = \frac{1}{\sqrt{2}} (\hat{e}_\parallel - \hat{e}_\perp) \)  

(1.55)

Thus, the electric field can be written as

\[ E_0 = E_+ \hat{e}_+ + E_- \hat{e}_- \]  

(1.56)

where \( E_+ \) and \( E_- \) can be given by

\[ E_+ = \frac{1}{\sqrt{2}} (E_\parallel + E_\perp) \]  

(1.57)

\[ E_- = \frac{1}{\sqrt{2}} (E_\parallel - E_\perp) \]  

(1.58)

If \( P \) is a +45° polarizer, its irradiance \( I_+ = \left( E_\parallel E_\parallel^* + E_\parallel E_\perp^* + E_\perp E_\parallel^* + E_\perp E_\perp^* \right)/2 \); If \( P \) is a −45° polarizer, its irradiance \( I_- = \left( E_\parallel E_\parallel^* - E_\parallel E_\perp^* - E_\perp E_\parallel^* + E_\perp E_\perp^* \right)/2 \). The irradiance difference between the two polarization states is given by

\[ I_+ - I_- = E_\parallel E_\perp^* + E_\perp E_\parallel^* \]  

(1.59)
Figure 4. Two sets of basis vectors $\hat{e}_\perp$ and $\hat{e}_\parallel$, $\hat{e}_-\!$ and $\hat{e}_+\!$.

Same as the situation when we study $\pm 45^\circ$ linear polarization states, a set of basis vector $\hat{e}_R$ and $\hat{e}_L$ also needs to be introduced when examining circular polarization, where $\hat{e}_R$ and $\hat{e}_L$ correspond to right and left circular polarization states, respectively

$$\hat{e}_R = \frac{1}{\sqrt{2}} (\hat{e}_\parallel + i\hat{e}_\perp)$$  \hfill (1.60)
\( \hat{e}_L = \frac{1}{\sqrt{2}} (\hat{e}_\parallel - i\hat{e}_\perp) \) \hspace{1cm} (1.61)

The basis vectors have the following relations

\( \hat{e}_R \cdot \hat{e}_R = 1 \) \hspace{1cm} (1.62)

\( \hat{e}_R \cdot \hat{e}_R = 1 \) \hspace{1cm} (1.63)

\( \hat{e}_R \cdot \hat{e}_R = 1 \) \hspace{1cm} (1.64)

The incident field can be written as

\[ E_0 = E_R \hat{e}_R^* + E_L \hat{e}_L^* \] \hspace{1cm} (1.65)

where \( E_R = \frac{1}{\sqrt{2}} (E_\parallel - iE_\perp) \), \( E_L = \frac{1}{\sqrt{2}} (E_\parallel + iE_\perp) \)

If \( P \) is a right-handed polarizer, the \( I_R = (E_\parallel^* E_\parallel - iE_\parallel^* E_\perp + iE_\perp^* E_\parallel + E_\perp^* E_\perp) / 2 \); If \( P \) is a right-handed polarizer, the \( I_L = (E_\parallel^* E_\parallel + iE_\perp^* E_\parallel - iE_\parallel^* E_\perp + E_\perp^* E_\perp) / 2 \). The difference between these two irradiances can be given by

\[ I_R - I_L = i(E_\perp^* E_\parallel - E_\parallel^* E_\perp) \] \hspace{1cm} (1.66)
Now, we can easily describe any polarization states of a wave using the above factors. The

*Stokes parameters* $I, Q, U, V$ can be summarized as follows

\begin{align*}
I &= E_\parallel E_\parallel^* + E_\perp E_\perp^* = a_\parallel^2 + a_\perp^2 \quad (1.67) \\
Q &= E_\parallel E_\parallel^* - E_\perp E_\perp^* = a_\parallel^2 - a_\perp^2 \quad (1.68) \\
U &= E_\parallel E_\perp^* + E_\perp E_\parallel^* = 2a_\parallel a_\perp \cos \delta \quad (1.69) \\
V &= i(E_\parallel E_\perp^* - E_\perp E_\parallel^*) = 2a_\parallel a_\perp \sin \delta \quad (1.70)
\end{align*}

where $\delta = \delta_\parallel - \delta_\perp$.

Since it is the relative irradiance value rather than absolute one that we usually deal with, the factor $k/2\omega\mu_0$ has been omitted in the above calculations. The experimental determination of Stokes parameters shows that $I, Q, U, V$ are all real-valued and have the dimension of monochromatic energy flux. $Q, U, V$ can be used to describe the polarization state of the wave, and $I^2 \equiv Q^2 + U^2 + V^2$, which indicates the Stokes parameters of a plane monochromatic wave are not completely independent.
Figure 5. Rotation of the $\hat{e}_{\perp}$ and $\hat{e}_{\parallel}$ vectors with an angle of $\varphi \geq 0$ in a clockwise direction when looking in the direction of light propagation.

Note that the Stokes parameters are defined concerning a reference plane involving the wave propagation direction. Once the basis vectors $\hat{e}_{\perp}$ and $\hat{e}_{\parallel}$ are chosen, the values of $Q$ and $V$ can be correspondingly determined. If the definition of horizontal and vertical directions is changed, the Stokes parameters will also need to be modified. As the schematic shown in Figure 5, the basis vectors $\hat{e}_{\perp}$ and $\hat{e}_{\parallel}$ are rotated in a clockwise direction with an angle of $\varphi$ when viewing in the direction of light propagation, $\hat{k}$. The new Stokes parameters $[I', Q', U', V']$ are relative to the
new rotated basis vectors $\hat{e}_\perp'$ and $\hat{e}_\parallel'$, while the relation between the new Stokes parameters and the original parameters $[I, Q, U, V]$ can be calculated using the following equation

$$S' = \begin{bmatrix} I' \\ Q' \\ U' \\ V' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos 2\varphi & -\sin 2\varphi & 0 \\ 0 & \sin 2\varphi & \cos 2\varphi & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix}. \quad (1.71)$$

The new electric field vectors set $E_\perp'$ and $E_\parallel'$ will be

$$E_\perp' = E_\perp \cos \varphi + E_\parallel \sin \varphi \quad (1.72)$$

$$E_\parallel' = -E_\perp \cos \varphi + E_\parallel \sin \varphi \quad (1.73)$$

The 4 x 4 matrix on the right side of Equation (1.71) is defined as Stokes rotation matrix for angle $\varphi$. We can also learn from Equation (1.71) that the quantities: $I$, $Q^2 + U^2$, $V$ will not change when the basis vectors are modified. Table 2 shows some examples of Stokes parameters for different polarized-light.
Table 2. Stokes parameters for the corresponding polarization states of light.

<table>
<thead>
<tr>
<th>Polarization states of light</th>
<th>Stokes parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpolarized light</td>
<td></td>
</tr>
</tbody>
</table>
|                             | ![Unpolarized Light Diagram] | \[
[1] \\
[0] \\
[0]
\] |
| Linearly polarized light    |                   |
| 0°                          | ![Linearly Polarized Light 0° Diagram] | \[
[1] \\
[1] \\
[0] \\
[0]
\] |
| 90°                         | ![Linearly Polarized Light 90° Diagram] | \[
[1] \\
[-1] \\
[0] \\
[0]
\] |
| +45°                        | ![Linearly Polarized Light +45° Diagram] | \[
[1] \\
[0] \\
[1] \\
[0]
\] |
| -45°                        | ![Linearly Polarized Light -45° Diagram] | \[
[1] \\
[0] \\
[-1] \\
[1]
\] |
| Circularly polarized light  |                   |
| Right-hand                  | ![Circularly Polarized Light Right-hand Diagram] | \[
[1] \\
[0] \\
[0]
\] |
| Left-hand                   | ![Circularly Polarized Light Left-hand Diagram] | \[
[1] \\
[0] \\
[-1]
\] |
1.2 Reflection and Transmission at a Plane Boundary and a film

In section (1.1), we have learned Maxwell’s equations and the different polarization states for a plane-harmonic wave. In this section, we study the reflection and transmission that happens when a plane harmonic wave incident upon a boundary separating two different optical media, as well as the interaction between light with a film with two boundaries. Consider the situation that a plane wave propagates in a non-absorbing homogenous medium 1 with a real refractive index \( n_1 \) and the second medium has a complex refractive index \( n_2 = n_{2r} + i n_{2im} \). Reflected and transmitted waves will occur when wave is incident upon the boundary, since the two optical media have different refractive indices, as the schematic shown in Figure 6. The amplitude of the incident light is marked as \( E_{inc} \), and these of reflected and transmitted wave are denoted as \( E_{ref} \) and \( E_{trans} \), respectively. It is noted that the incident wave can be normal to the boundary, it can also be with an angle. In section 1.2.1, we first consider the condition when light is normally incident upon the boundary. And the condition when light is incident upon the boundary with an angle will be considered in section 1.2.2.
1.2.1 Normal Incidence

In this section, we study the condition when light is normally incident upon the boundary. In medium 1, the space-time dependence of the incident and reflected waves, can be given by the following complex expressions:

\[ E_{inc} e^{i \omega \left( \frac{n_1 r}{c} + t \right)} , \quad E_{ref} e^{-i \omega \left( \frac{n_1 r}{c} + t \right)} \]

In medium 2, the space-time dependence of the transmitted wave can be expressed as

\[ E_{trans} e^{i \omega \left( \frac{n_2 r}{c} + t \right)} \]

In order to satisfy the requirement that constant relations hold truth for all points of the boundary and for all \( t \), the tangential components of the electric fields need to be continuous when \( r = 0 \), which means the following relation exists at the boundary.
\[ E_{\text{inc}} + E_{\text{ref}} = E_{\text{trans}} \]  \hspace{1cm} (1.74)

It is called boundary condition, and the detailed introduction will be presented in section (1.3.2).

The tangential magnetic field should also be continuous, so

\[ E_{\text{inc}} - E_{\text{ref}} = \frac{n_2}{n_1} E_{\text{trans}} \]  \hspace{1cm} (1.75)

considering \( H = nE/(\mu_0\varepsilon_0)^{1/2} \). We assume the permeabilities of both media are the same.

After solving Equations (1.74) and (1.75), the relations between \( E_{\text{inc}} \) with \( E_{\text{ref}} \) and \( E_{\text{trans}} \) can be calculated, they are given by

\[ E_{\text{ref}} = \frac{1 - m}{1 + m} E_{\text{inc}} = C_{\text{ref}} E_{\text{inc}} \]  \hspace{1cm} (1.76)

\[ E_{\text{trans}} = \frac{2}{1 + m} E_{\text{inc}} = C_{\text{trans}} E_{\text{inc}} \]  \hspace{1cm} (1.77)

Where \( C_{\text{ref}} \) and \( C_{\text{trans}} \) are known as the reflection and transmission coefficients, respectively.

And

\[ m = \frac{n_2}{n_1} = \frac{n_{2r} + n_{2im}}{n_1} \]  \hspace{1cm} (1.78)
is the ratio between the refractive index of medium 2 and that of medium 1.

The square of the absolute value of $C_{\text{ref}}$ is called reflectance, $R$.

$$R = \left| \frac{1 - m}{1 + m} \right|^2$$  \hspace{1cm} (1.79)

From Equation (1.79), we learn that reflectance is close to 1 if either $\frac{n_2}{n_1} \gg 1$ or $\frac{n_2}{n_1} \leq 1$ or $\frac{n_2}{n_1} \gg 1$, this kind of material is highly reflecting.

1.2.2 Oblique Incidence

The incident wave is normal to the boundary plane in section 1.21, the polarization state of incident wave is omitted since the state of polarization has no effect on the transmission or reflection. However, when the plane wave is obliquely incident upon the boundary, the different polarization states of incident wave must be considered. First we need to define a term named as incident plane or plane of incidence, which is a plane containing the surface normal and the wave vector of the incoming wave. The first polarization state is transverse electric or $TE$ polarization where the electric vector of the incident wave is perpendicular to plane of incidence, it is commonly named as $S$-polarized light. The second case is the condition that the magnetic vector of the incident wave is perpendicular (the electric vector of the incident light is parallel) to the plane of incidence, which is named as transverse magnetic or $TM$ polarization, this kind of incident light is commonly known as $P$-polarized light.
Figure 7. Reflection and transmission of obliquely incident wave for (a) $S$-polarized (TE polarization) state and (b) $P$-polarized (TM polarization) state. In TE polarization state, all electric vectors are normal to the plane of incidence, while in TM polarization state, all magnetic vectors are normal to the plane of incidence.

Note that the polarization states of the reflected and transmitted wave are the same as that of the incident wave in any cases. We assume the readers are familiar with Snell’s law and the law of specular reflection. The reflection and transmission of the obliquely incident wave for both TE and TM polarization are shown in Figure 7. For TE polarization, the incident wave, reflected wave and transmitted wave are marked as $\mathbf{E}_{\text{sinc}}$, $\mathbf{E}_{\text{sref}}$ and $\mathbf{E}_{\text{strans}}$, respectively. They are marked individually as $\mathbf{E}_{\text{pinc}}$, $\mathbf{E}_{\text{pref}}$ and $\mathbf{E}_{\text{ptrans}}$ for TM polarization. We first study the condition when the electric vector of incident light is perpendicular to the plane of incidence, which is TE polarization. Same as the requirement in section 1.21, the tangential components of both the electric and magnetic fields need to be continuous, which means
\[ E_{sinc} + E_{sref} = E_{strans} \]  \hspace{1cm} (1.80)

\[-H_{sinc} \cos \theta_i + H_{sref} \cos \theta_r = -H_{strans} \cos \theta_t \]  \hspace{1cm} (1.81)

\[-k_{sinc} E_{sinc} \cos \theta_i + k_{sref} E_{sref} \cos \theta_r = -k_{strans} E_{strans} \cos \theta_t \]  \hspace{1cm} (1.82)

For the second case, \(TM\) polarized light should have following relations:

\[ H_{pinc} - H_{pref} = H_{ptrans} \]  \hspace{1cm} (1.83)

\[ k_{inc} E_{pinc} - k_{ref} E_{pref} = k_{trans} E_{ptrans} \]  \hspace{1cm} (1.84)

\[ E_{pinc} \cos \theta_i + E_{pref} \cos \theta_r = E_{ptrans} \cos \theta_t \]  \hspace{1cm} (1.85)

The underlying relation between \(E\) and \(H\) are as follows:

\[ H = \frac{1}{\mu \omega} k \times E \]  \hspace{1cm} (1.86)

From Equations (1.83) to (1.86), we can calculate the coefficients of reflection and transmission for both \(S\)-polarized and \(P\)-polarized light.
The relations can be further simplified considering \( n = c/u = ck/\omega \) and Snell's law, which can be written as

\[
rs = \left[ \frac{E_{sref}}{E_{sinc}} \right]_{TE} \quad (1.87)
\]

\[
t_s = \left[ \frac{E_{trans}}{E_{sinc}} \right]_{TE} \quad (1.88)
\]

\[
r_p = \left[ \frac{E_{sref}}{E_{sinc}} \right]_{TM} \quad (1.89)
\]

\[
t_p = \left[ \frac{E_{trans}}{E_{sinc}} \right]_{TM} \quad (1.90)
\]

The relations can be further simplified considering \( n = c/u = ck/\omega \) and Snell’s law, which can be written as

\[
rs = \frac{\cos \theta_i - m \cos \theta_l}{\cos \theta_i + m \cos \theta_l} = -\frac{\sin(\theta_i - \theta_l)}{\sin(\theta_i - \theta_l)} \quad (1.91)
\]

\[
t_s = \frac{2 \cos \theta_i}{\cos \theta_i + m \cos \theta_l} = \frac{2 \cos \theta_i \sin \theta_l}{\sin(\theta_i + \theta_l)} \quad (1.92)
\]

\[
r_p = \frac{\cos \theta_i - m \cos \theta_l}{\cos \theta_i + m \cos \theta_l} = -\frac{\tan(\theta_i - \theta_l)}{\tan(\theta_i + \theta_l)} \quad (1.93)
\]
\[ t_p = \frac{2 \cos \theta_i}{\cos \theta_i + m \cos \theta_i} = \frac{2 \cos \theta_i \sin \theta_i}{\sin(\theta_i + \theta_t) \cos \theta_i - \theta_t} \]  

Equations (1.91) to (1.94) are known as *Fresnel’s equations*.

1.2.3 Reflection and Transmission by a Film

In section 1.2.1 and 1.2.2, we have studied the reflection and transmission when the light is normally and obliquely incident upon a boundary separating two optical media with different refractive indices, respectively. In this section, we consider the reflection and transmission of a plane harmonic wave incident upon a planar film. There are two boundaries we need to study in this case. Note that the underlying mechanism is the same, and the only difference is that we need to do the calculations twice. Figure 8 shows a planar film of arbitrary material with a refractive index of \( n_2 = n_{2r} + n_{2im} \) embedded in a nonabsorbing medium with a refractive index of \( n_1 \).
When a plane wave $E_{inc} \exp[i \omega (n_1 z/c - t)]$ propagates in the $Z$-direction and is incident upon the film, the reflected and transmission waves can be written as

$$E_{ref} \exp[-i \omega \left(\frac{n_1 z}{c} + t\right)]$$

$$E_{trans} \exp[i \omega \left(\frac{n_1 z}{c} - t\right)].$$

To make sure the electric fields are continuous at the two boundaries, we assume the wave propagate in both $+z$ and $-z$ inside the film.
\[ E_2^+ \exp \left[ i \omega \left( \frac{n_2 z}{c} - t \right) \right] \]

\[ E_2^- \exp \left[ -i \omega \left( \frac{n_2 z}{c} + t \right) \right] \]

Since the reflection and transmission are normal to the boundary, they are independent of the polarization state. At the first boundary \( z = 0 \)

\[ E_{\text{inc}} + E_{\text{ref}} = E_2^+ + E_2^- \quad (1.95) \]

\[ E_{\text{inc}} - E_{\text{ref}} = \frac{n_2}{n_1} (E_2^+ - E_2^-) \quad (1.96) \]

At the second boundary \( z = h \)

\[ E_2^+ \exp(ikn_2 h) + E_2^- \exp(-ikn_2 h) = E_{\text{trans}} \exp(ikn_1 h) \quad (1.97) \]

\[ E_2^+ \exp(ikn_2 h) - E_2^- \exp(-ikn_2 h) = \frac{n_1}{n_2} E_{\text{trans}} \exp(ikn_1 h) \quad (1.98) \]

where \( k = \omega / c = 2\pi / \lambda \). From Equations (1.95) to (1.98), we can obtain the reflection and transmission coefficients for the film

\[ r_{\text{film}} = \frac{E_{\text{ref}}}{E_{\text{inc}}} = \frac{C_{\text{ref}} [1 - \exp(i2kn_2 h)]}{1 - C_{\text{ref}} \exp(i2kn_2 h)} \quad (1.99) \]
\[
t_{f_{ilm}} = \frac{E_{\text{trans}}}{E_{\text{inc}}} = \frac{4m}{(m + 1)^2} \frac{\exp(-ikn_1h)}{\left[\exp(-ikn_2h) - c_{ref}^2 \exp(ikn_2h)\right]} \tag{1.100}
\]

where \(c_{ref}\) is the reflection coefficient defined before in Equation (1.76).

The transmittance is defined as the square of transmission coefficient

\[
T_{f_{ilm}} = \left| t_{f_{ilm}} \right|^2 = \frac{(1 - R)^2 + 4R(\sin \psi)^2}{R^2 e^{-\alpha h} + e^{\alpha h} - 2R \cos(\xi + 2\psi)} \tag{1.101}
\]

Where

\[
\psi = \frac{1}{\tan\left(\frac{2n_1k_2}{n_2^2 + k_2^2 - n_1^2}\right)} \quad 0 \leq \psi \leq \pi
\]

\[
\xi = \frac{4\pi n_2h}{\lambda}, \quad \alpha = \frac{4\pi k_2}{\lambda}, \quad R = \left| c_{ref} \right|^2
\]

Usually, the film is embedded in the vacuum \((n_1 \approx 1)\) and in the real experiment we need to make sure a measurable amount of light must be able to transmit, which requires the film is thin enough and \(k_2\) needs to be small enough. An approximation of transmittance can be given with these restrictions.
We have studied the transmission and reflection of a boundary and a film when light is incident upon them in section 1.2. In this section, we mainly focus on the scattering and absorption problems of a particle with an arbitrary shape when it is illuminated by incident light. The electromagnetic fields in a homogenous medium will be altered when an object with a different refractive index with that of the medium is placed inside. The presence of the object will change the field distribution since the object will scatter field. Thus the new filed is the superposition of the original (incident) field and the scattered fields.

When the particle is illuminated by the incident light, the amount and angular distribution of the scattered field, as well as the amount of the absorbed field strongly depend on the polarization state, the directional characteristics of the incident field, and also the shape, size, orientation and composition of the scatterer (particle). Among them, the relative size of the particle to the incident wavelength matters a lot. The scattering and absorption under the situation would be complicated if we consider all the possibilities. First, the oscillating charge will generate secondary waves, which also simulate the oscillations of other charges forming the particle. Second, we need to consider the phase difference between the secondary waves and initial waves when calculating total scattered field. In summary, the total scattered field largely depends on the arrangement of charge composing the particle concerning the incident directions. However, the problem might become simpler if an appropriate mathematical and physical
framework are well established. In real condition, we treat all the charges composing the particle as a macroscopic body with a specific distribution of the refractive index. In another words, the particle is composed of a linear and isotropic materials, which share common features to the scattering and absorption process. Under this condition, the total scattered field can be solved using Maxwell’s equations for the macroscopic electromagnetic field with appropriate boundary conditions.\textsuperscript{3} Figure 9 summarizes the scattering problem we may encounter in real condition, which includes (a) far-field electromagnetic scattering by an isolated particle (b) far-field scattering by a randomly positioned particle cluster with large interparticle distance (c) multiple scattering by a layer of particles.
Figure 9. (a) An arbitrary individual particle (b) particle cluster and (c) a layer of randomly and sparsely distributed particles illuminated by a parallel beam of light. (d) is a particle taken from (c), each particle in the layer is illuminated by the incident beam and also scatters light, same as other particles in the layer.

All the scattering processes lead to polarization. The goal of this section is to present a basic theoretical skeleton for more specific problems.
1.3.1 Analogy between a Film and a Particle

![Analogy between film and particle](image)

Figure 10 Analogy between reflection-transmission by a thin film and scattering by an isolated particle.

In Section 1.2.3, we have studied the reflection and transmission of a film when it is illuminated by an incident light. Many similarities can be found when we compare the condition when light interacts with films and the condition when light interacts with nanoparticles. The analogy is shown in Figure 10. The film has a regular shape (surface), thus the oscillations of the charge (dipole) can be coherently interfere which creates scattered wave in only two directions, reflection and transmission. Similarly, the oscillations of dipoles in a particle scatter radiation in the same way with less coherent interfere, thus leading to scattering with uneven magnitudes.

1.3.2 Boundary Condition

The requirement to use Maxwell’s equations is that $\varepsilon$, $\mu$ and $\chi$ need to be continuous in the studied medium. However, a change in these properties happens at the boundary between particle and medium where the physical properties of the medium become discontinuous, the
region is usually with a thickness of the order of atomic dimensions. To solve this problem, we need to add the following requirements on the electric and magnetic fields:

\[
[E_2(x) - E_1(x)] \times \hat{n} = 0 \quad (1.104)
\]

\[
[H_2(x) - H_1(x)] \times \hat{n} = 0 \quad (1.105)
\]

where \( \hat{n} \) is normal to the boundary surface \( S \) of the particle. Equations (1.104) and (1.105) are a well-known limiting process into the boundary conditions for the tangential components for \( E \) and \( H \). For the normal components, the boundary conditions are as follows:

\[
[n_2^2E_2(x) - n_1^4E_1(x)] \cdot \hat{n} = 0 \quad (1.106)
\]

\[
[H_2(x) - H_2(x)] \cdot \hat{n} = 0 \quad (1.107)
\]

where \( n_1 \) and \( n_2 \) are the refractive index of particle and medium, respectively, as shown in Figure 11. Figure 11 shows an arbitrary surface separating region 1 (particle) and region 2 (medium) with a normal outward \( \hat{n} \).
The transfer rate of the electromagnetic energy across the closed surface $A$ in region 1 can be expressed as

$$\iint_{A_1} \mathbf{S}_1 \cdot \hat{n} \, dA = \iint_{A_1} \hat{n} \cdot (\mathbf{E}_1 \times \mathbf{H}_1) \, dA \quad (1.108)$$

where $\mathbf{E}_1$ and $\mathbf{H}_1$ are not restricted to be time-harmonic. Similarly, the electromagnetic energy transfer rate across the surface $A$ in region 2 can be expressed as

$$\iint_{A_2} \mathbf{S}_2 \cdot \hat{n} \, dA = \iint_{A_2} \hat{n} \cdot (\mathbf{E}_2 \times \mathbf{H}_2) \, dA \quad (1.109)$$
From Equations (1.106) and (1.107), we can get \( E_2 \times \hat{n} = E_1 \times \hat{n}, H_2 \times \hat{n} = H_1 \times \hat{n}, \)
so the above integrals (1.108) and (1.109) can be written in the new forms, respectively

\[
\int_A S_1 \cdot \hat{n} dA = \int_A H_1 \cdot (\hat{n} \times E_1) dA = \int_A H_1 \cdot (\hat{n} \times E_2) dA
\]

\[
\int_A S_2 \cdot \hat{n} dA = \int_A E_2 \cdot (H_2 \times \hat{n}) dA = \int_A H_1 \cdot (\hat{n} \times E_2) dA.
\]

(1.110)

(1.111)

The integrals mean there are no sources or sinks of energy on \( A \):

\[
\int_A S_1 \cdot \hat{n} dA = \int_A S_2 \cdot \hat{n} dA
\]

(1.112)

To satisfy the energy conservation requirement across the boundary, the tangential components of the electromagnetic field must be continuous. We treat the incident light as plane monochromatic wave in constructing the solutions to Maxwell’s equations inside and outside the particle. In the real problem, the incident light is not limited to monochromatic wave, any arbitrarily polarized wave is possible. Thus, we only need to solve the scattering problem twice since any polarized wave can be treated as a superposition of two orthogonal polarization state. The same treatment can also be applied to a sharp boundary between two homogeneous media. The boundary conditions are useful in extending Maxwell’s equations in different adjacent regions with continuous physical properties to determine the fields throughout the whole space.
1.3.3 Light Propagation in Dielectric Medium

The problem is as follows: A particle, with specified size and orientation, is placed in a homogenous electric field (or an arbitrarily polarized monochromatic wave), and the electric field of all the points in the particle and the medium need to be determined. Note that the scattered field of the particle, excited by the electric polarization of the particle, alters the applied field both in and near the particle. In this section, we review the famous Lorentz oscillator model to introduce a factor in solving scattering problem: electric susceptibility, $\chi$. Lorentz oscillator model is useful in solving the problem of an electromagnetic field interacting with a dielectric material. It is fundamental since it shows that the applied electric field will cause the electrons in the material to be displaced resulting the separation between the positive and negative charges, which are known as dipoles.

In the model, materials are composed of atoms and molecules, which can be polarized by the incident light. For the smallest unit of materials, the atom is composed of nucleus and electrons. The nucleus and electrons remain in balanced condition without the applied electric field, while the electrons will be distorted under the electric field. In Lorentz model, the interaction between electric field (or incident light) and materials can be treated as a driven damped mechanical oscillator or string.\(^5\)\(^6\) The forced motion of the electron gas can be expressed as:

$$m_e \frac{\partial^2 x}{\partial t^2} = -k_e x - m_e r \frac{dx}{dt} + eE_0 e^{-i\omega t}$$

(1.113)

where $m_e$ is the mass of electron, $k_e$ is a constant, similar to the spring constant. The term $m_e r (dx/dt)$ is a frictional damping force that is proportional to the velocity of the electron...
movement. The term \( k_e x \) is the restoring force for electrons. The term \( eE_0 e^{-i\omega t} \) represents the applied electric field that varies harmonically with time. The solution to Equation (1.113), which shows the displacement of electron from its equilibrium position, can be written as

\[
\bar{x} = x_0 e^{-i\omega t} = \frac{e}{m(\omega_0^2 - \omega^2 - i\omega x)} \bar{E} \tag{1.114}
\]

The macroscopic polarization (dipole moment) of the medium is given as

\[
\bar{p} = e\bar{x} \tag{1.115}
\]

For \( N \) atoms or molecules, the polarization will be

\[
\bar{P} = N\bar{p} = \frac{Ne^2\bar{E}}{m_e(\omega_0^2 - \omega^2 - i\omega x)} = \chi_e e_0 \bar{E} \tag{1.116}
\]

When \( \omega = 0 \), Equation (1.116) reduces to its static value. The imaginary term \( i\omega x \) in the denominator means the phase of \( P \) depends on the frequency.

\[
\omega_0 = \sqrt{\frac{k_e}{m_e}} \tag{1.117}
\]
is defined as the effective resonance frequency of the bound electron. Note that the plasma frequency is defined as

\[ \omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m_e}} \]  

(1.118)

The dielectric constant (relative permittivity) of the bulk material is

\[ \varepsilon(\omega) = 1 + \chi_e = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega x} \]  

(1.119)

The relative permittivity can be divided into real \( \varepsilon_r \) and imaginary \( \varepsilon_{im} \) parts

\[ \varepsilon_r = 1 + \frac{(\omega_0^2 - \omega^2)\omega_p^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 x^2} \]  

(1.120)

\[ \varepsilon_{im} = \frac{\omega_p^2 \omega x}{(\omega_0^2 - \omega^2)^2 + \omega^2 x^2} \]  

(1.121)

Remember that \( n = \sqrt{1 + \chi_e} \), then \( n \) can be represented by

\[ n = n_r + in_{im} \]  

(1.122)
\[ n^2 = 1 + \chi_e = 1 + (\chi'_e + i\chi''_e) \] (1.123)

The imaginary part \( n_{lm} \) of the complex refractive index is known as *extinction index*, the relation between the imaginary and real parts of complex refractive index can be given by

\[ n_r^2 - n_{lm}^2 = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 x^2} \] (1.124)

\[ 2n_r n_{lm} = \frac{\omega x \omega_p^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 x^2} \] (1.125)

The dependence of \( n_r \) and \( n_{lm} \) on frequency, \( \omega \), is shown in Figure 12.
1.3.4 Light Propagation in Conducting Medium

In most cases, the problem we encountered is light propagation in conducting media, such as in metal. In the case, another classical model, named Drude-Lorentz model, needs to be applied. In the conducting media, the valence electrons are loosely bound to the nucleus and can wander around the entire metal, which are known as conduction electrons. The light propagates in conducting media, where the effects of conduction electrons can be treated as a similar way to the effects of polarization in dielectric media. In conduction media, we need to consider the motion of electrons under the influence of the oscillating electric field.

Figure 12 Dependence of real \( n_r \) and imaginary \( n_{im} \) parts of refractive index on the angular frequency near a resonance line.
Compare with the situation in section 1.3.3, we don’t need to consider elastic restoring force because the conduction electrons in conducting media are not bound. The differential equation for the electron motion can be given by

\[ m_e \frac{dv}{dt} + m_e \tau^{-1}v = -eE \]  \hspace{1cm} (1.126)

where \( v \) is the velocity of the electron. The term \( m_e \tau^{-1}v \) indicates the frictional dissipation of the electron movement. The current density is given by

\[ J = -Nev \]  \hspace{1cm} (1.127)

Where \( N \) is conduction electron density, thus Equation (1.126) can be modified to

\[ \frac{dJ}{dt} + \tau^{-1}J = \frac{Ne^2}{m_e} E \]  \hspace{1cm} (1.128)

For a static electric field,

\[ \tau^{-1}J = \frac{Ne^2}{m_e} E \]  \hspace{1cm} (1.129)

Thus, the static conductivity is \( \sigma = \frac{Ne^2}{m_e} \tau \).
For a plane harmonic wave, the differential Equation (1.126) becomes

\[-i\omega + \tau^{-1}]J = \frac{Ne^{2}}{m_{e}} E = \tau^{-1} \sigma E \tag{1.130}\]

After solving \( J \), we can get

\[ J = \frac{\sigma}{1 - i\omega \tau} E \tag{1.131}\]

Substitute Equation (1.131) to the general wave equation \( \nabla \times (\nabla \times E) + \frac{1}{c^{2}} \frac{\partial^{2} E}{\partial t^{2}} = -\mu_{0} \frac{\partial^{2} P}{\partial t^{2}} \)

we can get

\[ \nabla^{2} E = \frac{1}{c^{2}} \frac{\partial^{2} E}{\partial t^{2}} + \frac{\mu_{0} \sigma}{1 - i\omega \tau} \frac{\partial E}{\partial t} \tag{1.132}\]

For a homogenous plane-wave, \( E = E_{0} e^{i(kz - \omega t)} \), \( \mathbf{k} \) is a complex number, which can be written as \( \mathbf{k} = k_{r} + i k_{im} \), it must satisfy the following relation

\[ k^{2} = \frac{\omega^{2}}{c^{2}} + \frac{i\omega \mu_{0} \sigma}{1 - i\omega \tau} \tag{1.133}\]

When \( \omega \) is low, Equation (1.133) reduces to
\[ k^2 = i \omega \mu_0 \sigma = (1 + i)\sqrt{\omega \mu_0 \sigma / 2} \]  \hspace{1cm} (1.134)

In this case,

\[ k_r = k_{im} = \sqrt{\frac{\omega \sigma \mu_0}{2}} \]  \hspace{1cm} (1.135)

Similarly, the real and imaginary parts of refractive index \( n \) are equal

\[ n_r = n_{im} = \sqrt{\frac{\sigma}{2 \omega \varepsilon_0}} \]  \hspace{1cm} (1.136)

The skin depth, \( \delta \) indicating the distance at which the amplitude of the electromagnetic wave reduces to its 1/e, it can be given by

\[ \delta = \frac{1}{k_{im}} = \sqrt{\frac{2}{\omega \sigma \mu_0}} = \frac{\lambda_0}{c \pi \sigma \mu_0} \]  \hspace{1cm} (1.137)

Where \( \lambda_0 \) is the vacuum wavelength, Equation (1.137) indicates that good conductors are highly opaque. The relation between refractive index, \( n \) and plasma frequency, \( \omega_p \) can be given by
\[ n^2 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega \tau^{-1}} \tag{1.138} \]

The relation between the real and imaginary parts of \( n \) can be found

\[ n_r^2 - n_{im}^2 = 1 - \frac{\omega_p^2}{\omega^2 + \tau^{-2}} \tag{1.139} \]

\[ 2n_r n_{im} = \frac{\omega_p^2}{\omega^2 + \tau^{-2}} \left( \frac{1}{\omega \tau} \right) \tag{1.140} \]

The optical constant \( n_r \) and \( n_{im} \) can be solved numerically by Equations (1.139) and (1.140), we can see that the two constants are determined merely by \( \omega_p \), the relaxation time \( \tau \), and \( \omega \), the frequency of incident wave.

The typical relaxation times for metal are of the order of \( 10^{-13} \) s, and the plasma frequencies are around \( 10^{15} \) s\(^{-1} \). The relation between \( n_r \) and \( n_{im} \) with the frequency of light is plotted in Figure 13. The refractive index is less than 1 for a wide range of frequencies in \( \omega_p \) region. The imaginary part of refractive index (extinction coefficient) is large at low frequencies, its value decreases with increasing frequency, and it becomes pretty small at high frequencies.
1.3.5 Amplitude Scattering Matrix

In this section, we use electromagnetic theory to solve the scattering problem of a single particle. We start from the simplest problem of scattering: the scattering of an isolated particle with the arbitrary shape when it is illuminated by a plane harmonic wave. As we mentioned in Introduction part, the relative size between particle and incident wavelength matters. There are
two kinds of scattering depending on the relative size of the particle and the wavelength of incident light, named inelastic scattering and elastic scattering. When the scattering wavelength is different from incident wavelength, the scattering is named as inelastic scattering, such as Raman scattering. The scattering is elastic scattering if the scattering wavelength is same as the incident wavelength, one example is Rayleigh scattering by small, dielectric spherical particles. Rayleigh scattering can be used to explain the blue color of the sky and Mie scattering by any spherical particles. As shown in Figure 14, where the particle is placed in a Cartesian coordinate system and illuminated by a plane wave propagating along the Z-axis. Note that any point inside the particle can be chosen as the origin point of the coordinate. The basis vectors along the X-, Y- and Z-axes are defined as $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$, respectively. We also need to define the plane composed of scattering direction $\hat{e}_r$ and the forward scattering direction $\hat{e}_z$ as the scattering plane. The azimuthal angle between the X-axis and the scattering plane is marked as $\emptyset$. 
Figure 14 Scattering by an arbitrary isolated particle, the light propagates along the Z-axis, which is defined as the forward direction. The particle is placed at the origin of the coordinate.

The electric field of incident light can be divided into two component electric fields, the electric field that is parallel to the scattering plane, $E_{\parallel{\text{inc}}}$ and the electric field perpendicular to the plane, $E_{\perp{\text{inc}}}$, thus
\( E_{\parallel \text{inc}} = E_0 \parallel \exp(ikz - i\omega t) \)  \( (1.141) \)

\( E_{\perp \text{inc}} = E_0 \perp \exp(ikz - i\omega t) \)  \( (1.142) \)

\( E_{\text{inc}} = E_{\parallel \text{inc}} \hat{e}_{\parallel \text{inc}} + E_{\perp \text{inc}} \hat{e}_{\perp \text{inc}} \)  \( (1.143) \)

where the wave number, \( k = 2\pi n_2 / \lambda \), \( n_2 \) is the refractive index of the surrounding medium, \( \lambda \) is the incident wavelength. The basis vectors \( \hat{e}_{\parallel \text{inc}} \) and \( \hat{e}_{\perp \text{inc}} \) can be expressed by the combination of \( \hat{e}_x \) and \( \hat{e}_y \)

\( \hat{e}_{\parallel \text{inc}} = \sin \varnothing \hat{e}_x + \cos \varnothing \hat{e}_y \)  \( (1.144) \)

\( \hat{e}_{\perp \text{inc}} = \cos \varnothing \hat{e}_x - \sin \varnothing \hat{e}_y \)  \( (1.145) \)

We also notice that

\( \hat{e}_{\perp \text{inc}} \times \hat{e}_{\parallel \text{inc}} = \hat{e}_z \)  \( (1.146) \)

Besides that, the following relations can also be noticed

\( \hat{e}_{\perp \text{inc}} = -\hat{e}_\varnothing \)  \( (1.147) \)
\[ \hat{e}_{\text{inc}} = \sin \theta \hat{e}_r + \cos \theta \hat{e}_\theta \] (1.148)

where basis vectors \( \hat{e}_r, \hat{e}_\theta \) and \( \hat{e}_\phi \) are associated with the polar coordinate system \((r, \theta, \phi)\).

The component fields along X- and Y-axes of the incident filed can be expressed as \( E_{x\text{inc}} \) and \( E_{y\text{inc}} \), respectively. Thus, the other two component electric fields, \( E_{\parallel \text{inc}} \) and \( E_{\perp \text{inc}} \), can be written as

\[ E_{\parallel \text{inc}} = \cos \phi E_{x\text{inc}} + \sin \phi E_{y\text{inc}} \] (1.149)

\[ E_{\perp \text{inc}} = \sin \phi E_{x\text{inc}} - \cos \phi E_{y\text{inc}} \] (1.150)

In the far-field region, where the distance from the origin is large enough \((kr \gg 1)\), the scattered field \( E_{\text{sca}} \) is treated as transverse, where

\[ E_{\text{sca}} \sim \frac{e^{ikr}}{-ikr} A \quad kr \gg 1 \] (1.151)

Thus, \( E_{\text{sca}} \) can be written as

\[ E_{\text{sca}} = E_{\parallel \text{sca}} \hat{e}_{\parallel \text{sca}} + E_{\perp \text{sca}} \hat{e}_{\perp \text{sca}} \] (1.152)

We can also get the following relation from Figure 14.
\[
\hat{e}_{\parallel \text{sca}} = \hat{e}_\theta, \quad \hat{e}_{\perp \text{sca}} = -\hat{e}_\theta, \quad \hat{e}_{\perp \text{sca}} \times \hat{e}_{\parallel \text{sca}} = \hat{e}_r
\]  

(1.153)

The above equations can be summarized in a matrix form, which shows the relation between incident and scattered fields

\[
\begin{bmatrix}
E_{\parallel \text{sca}} \\
E_{\perp \text{sca}}
\end{bmatrix} = \begin{bmatrix}
S_2 & S_3 \\
S_4 & S_1
\end{bmatrix} \begin{bmatrix}
E_{\parallel \text{inc}} \\
E_{\perp \text{inc}}
\end{bmatrix}
\]  

(1.154)

where the term \( \begin{bmatrix} S_2 & S_3 \\ S_4 & S_1 \end{bmatrix} \) is called amplitude scattering matrix, in which the elements \( S_j (j = 1,2,3,4) \) are dependent on the scattering angle \( \theta \) and the azimuthal angle \( \phi \), and of course the particle size, composition as well as the orientation relative to the coordinate. The matrix shows the scattered as well as the total field at any given point, and also provides a complete description of scattering pattern.³

1.3.6 Scattering Matrix

In section 1.3.5, we have already learned that at any point inside and outside the particle, the electromagnetic fields can be obtained using Equation (1.154), and also the Poynting vector. Usually, what interest us is the Poynting vector of the points outside the particle. The time-averaged Poynting vector \( \mathbf{S} \) can be written as

\[
\mathbf{S} = \frac{1}{2} \text{Re}\{E_2 \times H_2^*\} = S_{\text{inc}} + S_{\text{sca}} + S_{\text{ext}}
\]  

(1.155)
\[ S_{inc} = \frac{1}{2} \text{Re}\{E_{inc} \times H_{inc}^*\} \quad (1.156) \]

\[ S_{sca} = \frac{1}{2} \text{Re}\{E_{sca} \times H_{sca}^*\} \quad (1.157) \]

\[ S_{ext} = \frac{1}{2} \text{Re}\{E_{inc} \times H_{sca}^* + E_{sca} \times H_{inc}^*\} \quad (1.158) \]

\( S_{inc} \) and \( S_{sca} \) are the Poynting vectors associated with the incident wave and the scattered field, respectively. \( S_{ext} \) can be treated as the interaction between the incident and scattered waves. Supposed we place a detector at a distance \( r \) from the particle in the far-field region, and the surface \( \Delta A \) is normal to \( \hat{e}_r \), we will have

\[ S_{sca} \cdot \hat{e}_r \Delta A = \frac{k}{2 \omega \mu} \frac{|A|^2}{k^2} \Delta \Omega \quad (1.159) \]

where \( \Delta \Omega = \Delta A / r^2 \) is the solid angle subtended by the detector. Then, we can calculate the Stokes parameter for the scattered light
\[ I_{sca} = \langle E_{\parallel sca}E_{\parallel sca}^* + E_{\perp sca}E_{\perp sca}^* \rangle \]
\[ Q_{sca} = \langle E_{\parallel sca}E_{\parallel sca}^* - E_{\perp sca}E_{\perp sca}^* \rangle \]
\[ U_{sca} = \langle E_{\parallel sca}E_{\perp sca}^* + E_{\perp sca}E_{\parallel sca}^* \rangle \]
\[ V_{sca} = i(E_{\parallel sca}E_{\parallel sca}^* - E_{\perp sca}E_{\perp sca}^*) \]

Thus, the relation between the incident and scattered Stokes parameters is as follows:

\[
\begin{bmatrix}
I_{sca} \\
Q_{sca} \\
U_{sca} \\
V_{sca}
\end{bmatrix}
= \frac{1}{k^2r^2}
\begin{bmatrix}
S_{11} & S_{12} & S_{13} & S_{14} \\
S_{21} & S_{22} & S_{23} & S_{24} \\
S_{31} & S_{32} & S_{33} & S_{34} \\
S_{41} & S_{42} & S_{43} & S_{44}
\end{bmatrix}
\begin{bmatrix}
I_{inc} \\
Q_{inc} \\
U_{inc} \\
V_{inc}
\end{bmatrix}
\]  

(1.160)

The matrix that is composed by \( S_{ij} \) is the scattering matrix. The 16 elements in the Muller matrix for a single particle can be calculated by the real and imaginary parts of the elements of the amplitude scattering matrix. The detailed information is summarized in Table 3.
Table 3. Scattering matrix elements.

<table>
<thead>
<tr>
<th>$S_{11}$</th>
<th>$S_{31} = Re{S_2 S_4^* + S_1 S_3^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{12}$</td>
<td>$S_{32} = Re{S_2 S_4^* - S_1 S_3^*}$</td>
</tr>
<tr>
<td>$S_{13}$</td>
<td>$S_{33} = Re{S_1 S_2^* + S_3 S_4^*}$</td>
</tr>
<tr>
<td>$S_{14}$</td>
<td>$S_{34} = Im{S_1 S_2^* - S_3 S_4^*}$</td>
</tr>
<tr>
<td>$S_{21}$</td>
<td>$S_{41} = Im{S_2 S_4^* - S_3 S_1^*}$</td>
</tr>
<tr>
<td>$S_{22}$</td>
<td>$S_{42} = Im{S_2 S_4^* - S_3 S_1^*}$</td>
</tr>
<tr>
<td>$S_{23}$</td>
<td>$S_{43} = Im{S_1 S_2^* - S_3 S_4^*}$</td>
</tr>
<tr>
<td>$S_{24}$</td>
<td>$S_{44} = Re{S_1 S_2^* - S_3 S_4^*}$</td>
</tr>
</tbody>
</table>

In combination with the Stokes parameters shown in Table 2, we can calculate the corresponding scattering matrix. For example, the calculated scattering matrix will be

$$
\begin{bmatrix}
I_{sca} \\
Q_{sca} \\
U_{sca} \\
V_{sca}
\end{bmatrix} = \frac{1}{k^2 r^2} \begin{bmatrix}
S_{11} & S_{12} & S_{13} & S_{14} \\
S_{21} & S_{22} & S_{23} & S_{24} \\
S_{31} & S_{32} & S_{33} & S_{34} \\
S_{41} & S_{42} & S_{43} & S_{44}
\end{bmatrix} \begin{bmatrix} 1 \\
0 \\
0 \\
0 \end{bmatrix} = \frac{1}{k^2 r^2} \begin{bmatrix} S_{11} \\
S_{21} \\
S_{31} \\
S_{41} \end{bmatrix} \quad (1.162)
$$

if the incident light is unpolarized light. Omitting the factor $1/k^2 r^2$, we find $I_{sca}/I_{inc} = S_{11}$, $Q_{sca}/I_{inc} = S_{21}$, $U_{sca}/I_{inc} = S_{31}$ and $V_{sca}/I_{inc} = S_{41}$, which demonstrates that the effect of the particle in medium is polarization change of the incident light. Also, scattering is a reason for
polarizing light. The optical elements in the matrix $S_{ij}$ depend on the scattering direction. Any particle or particle cluster can be represented by the 4 x 4 Muller matrix. We give one more example to help readers understand the importance of the Muller matrix. Suppose the incident light is right circularly polarized, the scattering matrix will be

\[
\begin{bmatrix}
I_{sca} \\
Q_{sca} \\
U_{sca} \\
V_{sca}
\end{bmatrix} = \frac{1}{k^2 r^2}
\begin{bmatrix}
S_{11} & S_{12} & S_{13} & S_{14} \\
S_{21} & S_{22} & S_{23} & S_{24} \\
S_{31} & S_{32} & S_{33} & S_{34} \\
S_{41} & S_{42} & S_{43} & S_{44}
\end{bmatrix}
\begin{bmatrix}
1 \\
0 \\
0 \\
1
\end{bmatrix} = \frac{1}{k^2 r^2}
\begin{bmatrix}
S_{11} + S_{14} \\
S_{21} + S_{24} \\
S_{31} + S_{34} \\
S_{41} + S_{44}
\end{bmatrix}
\]

Equation (1.163) shows the irradiance $I_{sca}$ of the scattered wave is $S_{11} + S_{14}$. Similarly, for left circularly polarized incident light, the irradiance of the scattered wave will be $S_{11} - S_{14}$.

Therefore, $S_{14}$ can be treated as the difference of the irradiance of the scattered light for right and left circularly polarized light.

1.3.7 Extinction of an Arbitrary Nanoparticle

When one particle or a cluster of particles is placed in an electromagnetic field (Figure 9(a, b)), the intensity received by the detector will be smaller than that of the condition where there is no particle or particle cluster exist. The energy difference between the two conditions results from the extinction of the incident wave. For the nonabsorbing medium, the extinction is due to the absorption and scattering of the particle or particle cluster.
Figure 15 Extinction by a single particle.

Consider a particle is placed in a nonabsorbing medium and illuminated by an incident beam, as the schematic shown in Figure 15. The electromagnetic energy pass through the particle should equal to that through the surface $A$ of the imaginary sphere with a radius $r$, and $r$ is large enough to guarantee that it is in far-field region. The energy flow can be given by

$$ W_a = -\int_A S \cdot \hat{e}_r \, dA = -r^2 \int_{4\pi} \hat{r} \cdot \langle S(r) \rangle \cdot \hat{r}. $$  \hspace{1cm} (1.164)

$W_a > 0$ means the electromagnetic energy is absorbed by the particle, since the medium is nonabsorbing, it can be written as $W_a = W_{inc} - W_{sca} + W_{ext}$, where
\[ W_{\text{inc}} = - \int_A S_{\text{inc}} \cdot \mathbf{\hat{e}}_r dA \]
\[ W_{\text{sca}} = \int_A S_{\text{sca}} \cdot \mathbf{\hat{e}}_r dA \]  \hspace{1cm} (1.165)
\[ W_{\text{ext}} = - \int_A S_{\text{ext}} \cdot \mathbf{\hat{e}}_r dA \]

\[ W_{\text{ext}} \] is the sum of the energy absorption rate and the energy scattering rate. Since \( W_{\text{inc}} \) vanishes identically in a nonabsorbing medium, \( W_{\text{sca}} \) is the scattered energy passing through the surface \( A \) in an outward direction. \( W_{\text{ext}} \) can be given by

\[ W_{\text{ext}} = W_{\text{sca}} + W_{\text{inc}} \]  \hspace{1cm} (1.166)

We assume the incident electric field is X-polarized, it can be given by \( E_{\text{inc}} = E\mathbf{\hat{e}}_x \). At the imaginary surface,

\[ E_{\text{sca}} \sim \frac{e^{ik(r-x)}}{-ikr}XE, \]
\[ H_{\text{sca}} \sim \frac{k}{\omega\mu} \mathbf{\hat{e}}_r \times E_{\text{sca}} \]  \hspace{1cm} (1.167)
and \( \hat{e}_r \cdot X = 0 \). The symbol \( X \) is used to show the incident polarization is along the X-axis, and it is named as vector scattering amplitude. The relation between \( X \) and amplitude scattering matrix elements \( S_i \) can be given by

\[
X = (S_2 \cos \varnothing + S_3 \sin \varnothing) \hat{e}_{||sc} + (S_4 \cos \varnothing + S_1 \sin \varnothing) \hat{e}_{\perp sc} \tag{1.168}
\]

\[
W_{ext} = -\frac{k}{2\omega \mu} |E|^2 \text{Re} \left\{ \frac{e^{-ikr}}{ikr} \int_A e^{ikz} \hat{e}_x \cdot X^* dA \right\}
- \frac{e^{ikr}}{ikr} \int_A e^{-ikz} \cos \theta \hat{e}_x \cdot X dA \\
+ \frac{e^{ikr}}{ikr} \int_A e^{-ikz} \sin \theta \cos \varnothing \hat{e}_z \cdot X dA 
\tag{1.169}
\]

As \( kr \to \infty \), the limiting value of \( W_{ext} \) will be

\[
W_{ext} = I_t I e^{-k^2} \text{Re}\{(X \cdot \hat{e}_x)_{\vartheta=0}\} 
\tag{1.170}
\]

where \( I_t \) is the incident irradiance. The extinction cross section can be given by

\[
C_{ext} = \frac{W_{ext}}{I_t} = \frac{4\pi}{k^2} \text{Re}\{(X \cdot \hat{e}_x)_{\vartheta=0}\} 
\tag{1.171}
\]
1.4 The Interaction between Light and Noble Metals

The optical properties of single metal nanoparticle and nanoparticle aggregations including one-dimensional (1D), two-dimensional (2D) as well as three dimensional (3D) nanoparticles arrays have been investigated for several centuries. Noble metal nanoparticles distinguish themselves from other nanomaterials such as semiconductor quantum dots, magnetic nanoparticles, because of the collective electron oscillation that exists at the metal surface, which is named as plasmon. Some cheap metals, such as aluminum, copper, also show plasmonic properties under the illumination of incident light, whereas the effects are not so obvious. In this thesis, we only focus on particles or films composed of silver, since silver is cheaper and its plasmonic effect is stronger in the wavelengths from 300 to 1200 nm.

In ancient times, the artists have already known that the addition of gold or silver nanoparticle to the glass windows in the process of glass-forming could generate ruby red color, the most famous example might be the Lycurgus cup. The cup shows different colors depending on whether light source is inside or outside the cup. The scientific understanding of these properties has developed far more recently, though the features have been known and used for several centuries. Plasmonic materials see many applications in the fields of microscopy, biological and chemical sensing, subwavelength imaging and superlenses as well as optical computing. Although the advancement in modern technology has promoted the development of the surface plasmon physics and applications, the physics of plasmon oscillations in nanoparticles is less developed since it is much more complex.
1.4.1 Surface Plasmons

When silver or gold nanoparticles are illuminated by incident light, the conduction electrons will be coherently oscillated at the interface between the bulk metal and the dielectric medium, the phenomenon are named as surface plasmons (SPs). Depending on the dimensions of particles, there are two kinds of plasmons: Localized surface plasmons (LSPs) (a) and propagating surface plasmons or surface plasmon polaritons (SPPs) (b), as shown in Figure 16. When the size of a metallic particle is smaller than the incident wavelength, LSPs can be easily excited. If the size of the particle is larger enough, where its partial surface can be treated as a planar surface, SPPs can be excited at the interface between metals and dielectrics. Another kind of plasmons is volume plasmons, which can be excited in the bulk of the metal for larger 3D metal structures, it will not be discussed in the thesis. Plasma resonance has been introduced in Section 1.3.4, it is given by $\omega_p = \sqrt{ne^2/m_e\varepsilon_0}$, where $n$ is the electron density, $e$ is the charge of electron, $m_e$ is the electron mass and $\varepsilon_0$ is the electric permittivity of vacuum. It shows that the oscillation frequency is determined by four factors: the density of electrons, the mass of the electron, and the shape and size of electrons distribution. At the resonance frequency, the conduction electrons have largest oscillation amplitude, which results in the strong scattered field, as well as strong absorption. Depending on the size of the nanoparticle, dipole, quadrupole or even higher multipole plasmon modes will be excited.
Another important optical response is the enhanced electric field in the vicinity of the metallic nanoparticle at resonance wavelengths. The most promising application might be surface enhanced Raman scattering (SERS). The detailed introductions of SERS will be presented in Chapter 3. The near enhanced field is sensitive to the proximity of other plasmonic particles. When the particles are arranged into dimer, trimer or larger aggregates, the electron oscillations will constructively or destructively couple and generate more complicated optical

Figure 16 Schematic of (a) Localized surface plasmons (LSPs) and (b) Surface plasmon polaritons (SPPs).
response. The coupling might explain the reason why the Lycurgus cup shows different colors when the light is illuminated inside and outside the cup.

More interesting optical phenomena appear when the plasmonic nanoparticles are arranged into 1D or 2D arrays. When the particles are arranged into arrays, coherent or incoherent coupling among the particles in the arrays will happen, the resulting optical response can be totally different from that of a single particle. In the arrays, the particle will interact with the plasmons in neighboring particles, thus its LSPs resonance wavelength will be changed. Depending on the distance between the nanoparticles (smaller or larger than the wavelength of the incident wave), the interaction can be separated into two sorts: near field coupling and far field coupling. Different coupling modes will result in different spectral shift. Figure 17 shows two kinds of near field coupling modes in a 1D linear array where the interparticle distance is smaller than the incident wavelength: the longitudinal coupling mode (top) and the transverse
coupling mode (bottom). The particles shown in Figure 17 can be treated as simple point dipoles since the interparticle distance is much smaller than the incident wavelength. If the incident polarization is parallel to the array axis, the coupling between nanoparticles is named as longitudinal coupling mode coupling. In longitudinal coupling mode, the field line points in one direction (head to tail), which results in the enhanced electric field between the particles and redshifted resonance. In transverse coupling mode, the incident polarization is perpendicular to the array axis and the near fields of neighboring dipoles add destructively, which results in a blueshifted resonance. Far field coupling needs to be considered when the metallic nanoparticles are separated by a distance larger than the incident wavelength. When the interparticle distance is further increased, the plasmon resonance wavelength and its line width will display an oscillating behavior.

At the interface between metals and dielectrics (the two media with opposite sign of electric permittivity), SPPs can be supported. SPPs are confined to the vicinity of the interface and can propagate along the interface until its energy is totally dissipated by radiating into free space. The resonance is very sensitive to the environmental change that happens at the boundary, so it can be applied in surface plasmon resonance (SPR) spectroscopy, which is a technique to detect bimolecular binding interaction.
CHAPTER 2: METHODS

2.1 Introduction

Maxwell’s equations and the Lorentz force equation, as well as Newton’s second law constitute the foundations of classical electromagnetic theory. The development of electromagnetic theory relies essentially on Maxwell’s equations. Solving Maxwell’s equations for the interaction between incident light and nanostructured materials is the most fundamental way to study the optical properties of metal nanostructure, which partially relies on powerful computational methods.

In this chapter, we present several theoretical methods that utilized in the field of light matter interaction and the research. The methods include both analytical and numerical ones. Numerical methods are discrete dipole approximation (DDA) method, the multiple multipole (MMP) method, coupled dipole (CD) method and the finite difference time domain (FDTD) method. Analytical Methods include but not limited to Mie theory and T-matrix method. The different computational methods help us have a better understanding of the optical properties of metallic nanostructures. In the thesis, we limit our discussion to the methods that we have used, which includes Mie theory, DDA method, CD method.

2.2 Mie Theory

Mie theory, actually is not a theory, but rather an analytical method to solve Maxwell’s equations for scattering problem by a spherical particle. In 1908, Gustav Mie successfully explained the color effects connected with colloidal gold particles in his famous paper. For the
first time, he gave an outline of how to calculate light scattering by small spherical particles
using Maxwell’s electromagnetic theory. Electromagnetic scattering for a homogeneous isotropic
sphere usually is referred as Mie theory, although Mie is not the first one to formulate the
scattering problem.\textsuperscript{24,25} For the spherical particle that is smaller than the wavelength of incident
light, Mie theory could give a simple solution for the space inside and outside the spherical
boundary and calculate its scattering and absorption cross sections, $C_{\text{sca}}$ and $C_{\text{abs}}$, respectively.
Nowadays, the applications of Mie theory become much broader, since many scattering particles
or objects can be approximated as homogeneous isotropic spheres. When a spherical particle
with core-shell structure is illuminated by a plane wave, the electromagnetic fields both in the
core and shell, as well as the fields outside the particle and the incident light can be obtained by
using the vector spherical harmonics.

In Mie theory, the electric and magnetic fields of the incident plane wave can be expressed as $E_i$ and $H_i$

\begin{equation}
E_i = E_0 \sum_{n=1}^{\infty} i^n \frac{2n + 1}{n(n + 1)} \left( M_{\text{oln}}^{(1)} - i N_{\text{eln}}^{(1)} \right), \quad (2.1)
\end{equation}

\begin{equation}
H_i = \frac{-k}{\omega \mu} E_0 \sum_{n=1}^{\infty} i^n \frac{2n + 1}{n(n + 1)} \left( M_{\text{eln}}^{(1)} + i N_{\text{oln}}^{(1)} \right), \quad (2.2)
\end{equation}

where the electric field and magnetic field within the core, shell and outside of the particle are
obtained from
\[
E_1 = \sum_{n=1}^{\infty} E_n (c_n M_{o1n}^{(1)} - i d_n N_{eln}^{(1)}) \tag{2.3}
\]

\[
H_1 = \frac{-k_1}{\omega \mu_1} \sum_{n=1}^{\infty} E_n (d_n M_{eln}^{(1)} + i c_n N_{o1n}^{(1)}) \tag{2.4}
\]

\[
E_{sh, j} = \sum_{n=1}^{\infty} E_n (f_{nj} M_{o1n}^{(1)} - i g_{nj} N_{eln}^{(1)} + \nu_{nj} M_{eln}^{(2)} - i \omega_{nj} N_{o1n}^{(2)}) \tag{2.5}
\]

\[
H_{sh, j} = \frac{-k_j}{\omega \mu_j} \sum_{n=1}^{\infty} E_n (g_{nj} M_{eln}^{(1)} - i f_{nj} N_{o1n}^{(1)} + \omega_{nj} M_{eln}^{(2)} - i \nu_{nj} N_{o1n}^{(2)}), \tag{2.6}
\]

\[
E_s = \sum_{n=1}^{\infty} E_n (i a_n N_{eln}^{(3)} - b_n M_{o1n}^{(3)}) \tag{2.7}
\]

\[
H_s = \frac{k}{\omega \mu} \sum_{n=1}^{\infty} E_n (i b_n M_{eln}^{(3)} + a_n N_{o1n}^{(3)}) \tag{2.8}
\]

where the wavevectors in the surrounding environment and the \( j \)th shell are expressed as \( k \) and \( k_j \), respectively. \( \omega \) represents the angular frequency of the light. The permeabilities of the surrounding environment and \( j \)th shell, are given by \( \mu \) and \( \mu_j \), respectively. The degree of the
functions is \( n, a, b, c, d, g, f, w, v \) are expansion coefficients. The electric field and magnetic field in the core are \( E_1 \) and \( H_1 \), respectively. \( E_s, H_s \) are the scattered ones, respectively. \( E_{shj} \) and \( H_{shj} \) denote the fields with in the \( j \)th shell. \( E_0 \) represents the magnitude of incident electric field, and \( E_n \) is expressed as

\[
E_n = i_n \frac{E_0(2n + 1)}{n(n + 1)}
\]  

(2.9)

The vector functions \( M \) and \( N \) are expressed as:

\[
\begin{align*}
M_{oln} &= \cos \phi \pi_n(\cos \theta)z_n(\rho)\hat{e}_\theta - \sin \phi \tau_n(\cos \theta)z_n(\rho)\hat{e}_\phi \\
M_{eln} &= -\sin \phi \pi_n(\cos \theta)z_n(\rho)\hat{e}_\theta - \cos \phi \tau_n(\cos \theta)z_n(\rho)\hat{e}_\phi
\end{align*}
\]  

(2.10)

\[
\begin{align*}
N_{oln} &= \sin \phi n(n + 1) \sin \theta \pi_n(\cos \theta)\frac{z_n(\rho)}{\rho} \hat{e}_r \\
&\quad + \sin \phi \tau_n(\cos \theta)\frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\theta \\
&\quad + \cos \phi \pi_n(\cos \theta)\frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\phi
\end{align*}
\]  

(2.12)
\[ N_{eln} = \cos \phi n(n + 1) \sin \theta \pi_n(\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_r \]

\[ + \cos \phi \tau_n(\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\theta \]

\[ - \sin \phi \pi_n(\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\phi \]

(2.13)

Superscripts appended to the function \( M \) and \( N \) are the types of the spherical Bessel functions \( z_n \) where (1) denotes \( j_n(\rho) \) and (3) means the first kinds of \( h_n(\rho) \). And (2) refers the \( j_n(\rho) \) for \( N \) functions and \( y_n(\rho) \) for \( M \) functions, the dimensionless \( \rho = kr \) (\( r \) is the radius of the shell, and \( k \) is the wavevector). \( \phi \) and \( \theta \) are the spherical polar angles. For the functions, \( \tau_n \) and \( \pi_n \), the equations are as follows:

\[ \pi_n = \frac{P_n^1}{\sin \theta} \]  

(2.14)

\[ \tau_n = \frac{dP_n^1}{d\theta} \]  

(2.15)

where \( P_n^1 \) refers to the associated Legendre functions of the first kind with an order of 1 and a degree of \( n \).

At each interface, the expansion coefficients can be expressed as the following equations if the boundary conditions are applied:
\[ E_{\theta}^{in} = E_{\theta}^{out}, \quad (2.16) \]

\[ E_{\theta0}^{in} = E_{\theta0}^{out}, \quad (2.17) \]

\[ H_{\theta}^{in} = H_{\theta}^{out}, \quad (2.18) \]

\[ H_{\theta0}^{in} = H_{\theta0}^{out} \quad (2.19) \]

where the superscripts \textit{in} and \textit{out} in the Equations (2.16) – (2.19) symbolize the electromagnetic fields inside and outside the interface, respectively.

The extinction and scattering cross section can be calculated by the following equations

\[ C_{\text{ext}} = \frac{2\pi k^2}{2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n) \quad (2.20) \]

\[ C_{\text{sca}} = \frac{2\pi k^2}{2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2) \quad (2.21) \]

Since \( C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} \), \( C_{\text{abs}} \) can also be calculated. The extinction, scattering and absorption efficiencies can be obtained by dividing the optical cross sections with the physical cross sections of the particles.
2.3 Discrete Dipole Approximation Method

As we mentioned in section 2.2, Mie theory is a powerful method to calculate the scattering and absorption cross sections of spherical nanoparticles. However, the Mie theory can only be used in solving the scattering of light by spherical nanoparticles, exact solutions can hardly be generated for particles with complicated shape, such as stars, bars or prisms. Therefore, we need to turn our attention to numerical methods, like DDA method. The DDA method is an accurate and powerful technique to calculate the scattering and absorption of particles with arbitrary geometry. In 1964, DeVoe first introduced the basic idea of DDA method, when he was trying to study the optical properties of molecular aggregates. However, the idea can only be applied to the aggregates that are smaller than the wavelength since the retardation effects were avoided. In 1973, Purcell and Pennypacker proposed the DDA method including retardation effects, with which they studied the optical properties of interstellar dust grains. Draine and Flatau et al. further improved and developed the method in the following years. The DDA method has been proved to be a powerful tool in studies of light scattering from both nonmetallic dust particles and metallic particles.

There are many available computational codes for DDA methods, for example DDSCAT, ZDD, and ADDA. A comparison of these independent DDA codes is reported by Antti Penttila et al. In this section, we will review the modified DDSCAT computational code developed by Draine et al. A detailed information about the computational codes can be found from Draine’s papers.

In the method, a target particle with an arbitrary shape is divided into $N$ polarizable cubes whose positions are denoted with $\mathbf{r}_i$, with polarizabilities $\alpha_i$. There is no restriction to what
occupies the cubic lattice sites, which means DDA can represent an object or several objects of arbitrary shape and composition. When the incident polarization is applied to the target particle, the polarization of each cube position and the localized electric field are calculated by solving the electrodynamics properties, thus the optical properties can be obtained.

The polarization induced in each dipole as a result of the interaction with a local electric field $E_{\text{loc},i}$ will be (omitting the frequency factors $e^{i\omega t}$):

$$P_i = a_i E_{\text{loc},i}, \quad i = 1, 2, \ldots, N$$

(2.22)

where $E_{\text{loc},i}$, for isolated particles, is the sum of an incident field and a contribution from all other ($N - 1$) dipoles in the same particle, which equals to the retarded plus incident electric fields where the retarded part comes from all the other dipoles. For a given wavelength of incident light, $\lambda$, the local electric field $E_{\text{loc},i}$ can be expressed as:

$$E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{retard},i} = E_0 \exp(ik \cdot r_i) - \sum_{j=1}^{N} A_{ij} \cdot P_j, \quad i = 1, 2, \ldots, N,$$

(2.23)

$E_0$ is the amplitude of the incident light, $k = 2\pi/\lambda$ is the wave vector of the incident light with the wavelength of $\lambda$. $A$ is the interaction matrix and has the following form:
\[ A_{ij} \cdot P_j = k^2 \exp(ikr_{ij}) \frac{r_{ij} \times (r_{ij} \times P_j)}{r_{ij}^3} \]
\[ + \exp(ikr_{ij}) (1 - ikr_{ij}) \frac{r_{ij}^2 P_j - 3r_{ij}(r_{ij} \cdot P_j)}{r_{ij}^5} \quad i = 1, 2, \ldots, N \]  

(2.24)

where \( r_{ij} = r_i - r_j \) represents the vector distance between the two dipoles \( i \) and \( j \). Combining Equations (2.22), (2.23) and (2.24), we can obtain

\[ (\alpha_i^{-1})P_j + \sum_{\substack{i=1 \atop j \neq i}}^{N} A_{ij} \cdot P_j = E_{inc,i}, \quad i = 1, 2, \ldots, N \]  

(2.25)

It can also be expressed as a \( 3N \) linear equation as

\[ A'P = E \]  

(2.26)

where the diagonal elements of the matrix, \( \alpha_i^{-1} \), comes from the polarizability and the off-diagonal elements are symmetric. \( E \) and \( P \) in Equation (2.26) are both \( 3N \)-dimensional vectors, and \( A' \) is a \( 3N \times 3N \) matrix. By solving Equation (2.26), the \( 3N \) complex linear equations, we can obtain the polarization and local electric field of each cube, thus the extinction cross section and other related optical properties.

The extinction and scattering cross sections can be obtained from the dipole polarization and local electric field, the forms are as follows:
where \( \hat{n} \) is the unit vector along each direction of scattering, and \( \Omega \) is the integration angle in the space. The absorption cross section can also be calculated. The obtained extinction, scattering and absorption cross sections have units of area, where the corresponding efficiencies of structures can be calculated by dividing the cross sections with the physical area of the particles or films.

### 2.4 Coupled Dipole Method

A simplified form of DDA methods that can be applied to spherical nanoparticles or spherical nanoparticles arrays is called the Coupled Dipole method.\(^{38}\) In the method, the quadrupole or higher plasmonic modes of nanoparticle are omitted, only dipole plasmonic modes are considered. The wavevector of the incident light in the method is vertical to the long axis of a nanoparticles array. A simple analytical solution to Equation (2.24) can be obtained if we assume that the induced polarization of each particle has same values. The polarization, \( P \), of each particle can be expressed from the polarizability as:

\[
C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{inc,j}^* \cdot P_j) \tag{2.27}
\]

\[
C_{sca} = \frac{k^4}{|E_0|^2} \int d\Omega \left| \sum_{j=1}^{N} [P_j - \hat{n}(\hat{n} \cdot P_j)] \exp(-ik\hat{n} \cdot r_j) \right|^2 \tag{2.28}
\]
\[ P = \frac{a_s E_0}{1 - a_s S} = \frac{E_0}{1/a_s - S} \quad (2.29) \]

and the extinction cross section of each particle can be calculated as:

\[ C_{ext} = 4\pi k Im \left( \frac{P}{E_0} \right) = 4\pi k Im \left( \frac{1}{1/a_s - S} \right) \quad (2.30) \]

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

\[ S = \sum_{n \neq 1} \left[ \frac{(1 - ik r_{ij})(3\cos^2 \theta_{ij} - 1)e^{ik r_{ij}}}{r_{ij}^3} + \frac{k^2 \sin^2 \theta_{ij} e^{ik r_{ij}}}{r_{ij}} \right] \quad (2.31) \]

The polarizability, \( a_s \), can be expressed by:

\[ a_s = \frac{3a_1}{2k^3} \quad (2.32) \]

where \( k \) is the wavevector of the incident light and \( a_1 \) is the expansion coefficient that is derived from the Mie theory

\[ a_1 = \frac{\mu m^2 j_1(m\rho)[\rho j_1(\rho)]' - \mu_1 j_1(\rho)[m\rho j_1(m\rho)]'}{\mu m^2 j_1(m\rho)[\rho h_1(\rho)]' - \mu_1 h_1(\rho)[m\rho j_1(m\rho)]'} \quad (2.33) \]
where $\mu_1$ represents the magnetic permeability of the particle, while $\mu_0$ denotes the magnetic permeability outside the particle. $m$ is the ratio of the refractive index in and out of the particle. $\rho = kr$, where $r$ is the radius of the particle, $j_1$ and $h_1$ are the usual spherical Bessel functions.
CHAPTER 3: RELATION BETWEEN THE INTENSITY OF THE ENHANCED ELECTRIC FIELD NEAR A SINGLE ROD AND THE ENHANCED RAMAN SCATTERING FACTOR


3.1 General Introduction

Nobel metal nanoparticles (especially coinage metals), different from semiconductor quantum dots, will generate many interesting features when exposed to electromagnetic radiation. The most attractive and useful property might be SPs supported by the plasmonic nanostructures, which result in remarkably enhanced electromagnetic field in the vicinity of the nanostructures. The property will benefit the surface enhanced Raman spectroscopy (SERS), where the Raman scattering spectrum is used as the fingerprint of a molecule for detection. It has found applications in surface and interface analyses and material, biological as well as medically related trace analysis. However, the detection sensitivity (because of its extremely small cross section) and reproducibility of SERS measurements are the two critical issues that restrain the applications. First, the background information of Raman scattering will be briefly reviewed. Different from Rayleigh scattering, Raman scattering is an inelastic scattering. The scattering photons of inelastic scattering have different frequency with that of incident photons. The molecule at virtual energy states will relax back to ground energy state by light scattering, while the radiated energy could be different from the incident one since the molecule might relax to different vibration state. The scattering frequency can be smaller than the incident frequency,
which is called Stokes scattering, or larger than the incident frequency, named Anti-Stokes scattering. The two kinds of Raman scattering are shown in Figure 18.

Figure 18 Schematic of two kinds of Raman scatterings: Stokes scattering and Anti-stokes scattering.

The researchers always wanted to enhance the Raman scattering intensity of a molecule. In 1977, P. Van Duyne first reported the enhanced Raman scattering of a molecule when it is placed in the vicinity of a metal substrate.47 The Raman scattering enhancement was attributed to the excitation of LSPs. At almost the same time, J. Alan Creighton reported a similar phenomenon,48 while they believed the enhancement is due to the formation of charge-transfer complexes. The exact mechanisms are still under debate; we prefer electromagnetic theory proposed by P. Van Duyne in this work. In the following decades, the Raman scattering enhancement factors as high
as $10^{13-14}$ have been reported.\textsuperscript{49,50} Basically, the nanoparticles with sharp tips or curvatures will generate higher enhanced electric fields than sphere because of the presence of so-called “hot spots” or “lightning rod effect”. G. C. Schatz demonstrated that peak value of the electric filed of the coupling dimer or dimers array can be significantly larger than that of the isolated nanoparticle.\textsuperscript{39,51} For the detailed information about the coupling metal nanostructures, we refer the readers to the review article.\textsuperscript{11} The two main mechanisms proposed by P. Van Duyne and J Alan Creighton were named as electromagnetic and chemical enhancement, respectively.\textsuperscript{52-59} The enhancement factor was believed to be proportional to the enhanced local electric field $|E|^2$ of the metal nanoparticle at both excitation and scattering (radiation) wavelengths in the most-accepted electromagnetic enhancement theory.\textsuperscript{60} The original prediction was acquired by Kerker and co-workers based on a spherical particle,\textsuperscript{61,62} while researchers found that other factors may also affect the proportional relation between enhancement factor and electric field intensity in the following studies. For example, Chen et al. demonstrated that the Raman scattering response also relies on the polarization and intensity of the scattered light.\textsuperscript{63}

Metal nanostructures with different shapes were also used to obtain high Raman scattering signals, including but not limited to cubes, rods, stars and nanowires. Applying the theory generated based on spherical particle to other systems with different particle shapes may be unappropriated since many other factors will affect the Raman scattering enhancement factor. To accurately determine the Raman scattering enhancement factor, a proper method or model comparing the factor with calculated electric field intensity becomes necessary. In this work,\textsuperscript{64} we used an electrodynamics model to examine the relation between the enhancement factor and electric field intensity at the position of the molecule at scattering wavelengths.
We found that the deviation between these two factors can be largely different depending on the polarization states of the incident wave for a silver rod system. The finding will promote the understanding of the mechanism of SERS and improve the future theoretical prediction of SERS enhancement factors.

3.2 Results and Discussion

3.2.1 Raman Scattering Enhancement Factor

The new experimental and theoretical studies are challenging the mature classical electromagnetic theory, for example the calculation of Raman scattering enhancement factor in this study. Raman enhancement factor is an important value for the characterization of SERS effect.\textsuperscript{65} The increase of the enhancement factor is due to the increase of cross-section of the molecule.\textsuperscript{47,66} For more details about Raman enhancement factor, we refer the readers to this wonderful review.\textsuperscript{65} In the study, the available DDA method is modified to allow us to calculate the cross section of molecule when a metallic nanoparticle is placed in its vicinity. In this model, we only consider the Stokes shifted Raman scattering wavelength and the molecule is represented by an oscillating molecular dipole. The Raman enhancement factor is defined as the ratio between scattering cross section of molecule with a metal nanoparticle and that of the isolated molecule, as given by Equation (3.1).

\[
\text{Raman enhancement factor} (f) = \frac{\text{scattering cross section of molecule with a near nanoparticle}}{\text{scattering cross section of isolated molecule}} \quad (3.1)
\]

87
3.2.2 System with a Spherical Particle

Figure 19 Schematic of spherical nanoparticle with a molecule in its vicinity where the incident light is along the X-axis. $d$ represents the distance between the molecule and the spherical nanoparticle. $r = 50$ nm. (b) The relation between the Raman enhancement factor and the enhanced electric field intensity when $d$ is varied from 2 to 16 nm.

To testify the reliability of our model, we first compare the enhancement factor of the Raman scattering of a molecule when it is placed in the vicinity of a spherical silver nanoparticle with the calculated enhanced local electric field intensity of the particle at the position of the molecule. The diameter of sphere that we use is 100 nm. Note that the calculation results are also applicable to the spherical particles with different size. The diagram is shown in Figure 19(a). In the study, we gradually vary the distance between the spherical particle and the molecular dipole from 2 to 16 nm. The calculated data are summarized in Figure 19(b), which shows the relation between the Raman enhancement factor and the electric field intensity at the position of the molecule. Figure 19(b) shows the two factors agree with each other very well, which follows the theory proposed by Kerker et al. It demonstrates the dependability of the modified DDA method.
3.2.3 Scattering Spectra of Rods along Different Axes

Figure 20 Scattering spectra for a rod with a diameter of 40 nm and a length of 100 nm when its long axis is along the (black) X-, (red) Y- and (green) Z-axes, respectively. The incident light is along the X-axis; the polarization is along the Y-axis. The inset is the zoom in scattering spectra in the wavelengths from 300 to 500 nm.

In the study, a silver rod with a length of 100 nm and diameter of 40 nm is used to examine the relation between the Raman enhancement factor and the enhanced local electric field. The scattering spectra for the rods with different orientations are shown in Figure 20. The incident light is along the X-axis and its polarization is along the Y-axis. The long axis of silver rod is parallel to (black) X-, (red) Y- and (green) Z-axes, respectively. The rod shows the longitudinal
resonance mode at the wavelength of 580 nm (red curve) where the rod axis is parallel to the incident polarization direction, while its transverse resonance mode shows at the wavelength of 400 nm (black curve) where the rod axis is perpendicular to the incident polarization direction.

3.2.4 Electric Field Vector Plots of Rods

![Electric field vector plots](image)

Figure 21 Electric field vector plots in the XY plane when the rod is oriented along the (a) Y-axis and (b) X-axis at the wavelength of 580 nm and illuminated by an incident light of a plane wave. The electric field vector plots are through the rod center.

We also calculate the electric field vector of the rod when it is illuminated by the plane wavelength to have a better understanding of plasmon resonance modes. We choose the incident wavelength as 580 nm since the scattering intensity is the largest at all the conditions. The incident polarization is parallel to the rod axis in Figure 21(a), while the polarization is perpendicular to the rod axis in Figure 21(b). Both Figure 21(a) and (b) show that the electric field vectors are neatly oriented whether the rod is along the Y- or X-axis. The electric field vector plots of the rod will be used to compare with these of rods when they are illuminated by
molecular dipoles. To get clear figures, the E-field vectors are amplified by a factor of 0.2 and 5, respectively.
3.2.5 Rod along the Y-axis with a Molecule

We start our discussion from the conditions when the silver rod is oriented along the Y-axis, as the schematic shown in Figure 22(a) where a molecule is placed on top of it. The distance between the molecule and rod surface, $d_1$, is kept at constant 4 nm. Note that the distance is
randomly chosen. The position of the molecule relative to the end of the rod is expressed as \( p_l \).

The scattering spectra for the system when \( p_l \) is varied from position \( p_l = 0 \) nm to position \( p_l = 50 \) nm are shown in Figure 22(b). The scattering spectrum of a single molecular dipole is also included in Figure 22(b). The induced polarization of the molecular dipole is parallel to the rod axis since the incident polarization is also along the Y-axis. The spectrum of the isolated molecular dipole shows a smooth curve with decreasing intensity with increasing wavelength, different from conventional believing, no resonance peak appears. However, both the longitudinal and transverse mode resonance peaks can be excited when the rod is illuminated by the molecular dipole, as the spectra shown in Figure 22(b). The peak intensity at the wavelength of 580 nm is the largest when \( p_l = 0 \) nm, and it drops to the lowest when \( p_l \) is increased to 10 nm. The intensity gradually increases when \( p_l \) is increased from 10 to 50 nm. Using the equations above, we can calculate the enhancement factor of the Raman scattering. We can also calculate the enhanced local electric field at the corresponding position of the molecule when the rod is illuminated by the plane wave. The results at the wavelengths of 400 nm and 580 nm are shown in Figure 22(c) and (d), respectively.

Overall, the Raman enhancement factor (and local electric field intensity) of the system at the wavelength of 400 nm is much smaller than that of the system at the wavelength of 580 nm. The deviations between these two factors are not huge except for the condition when \( p_l = 0 \) nm. The value difference at the wavelength of 400 nm has no significant meaning since both factors are very small. Meanwhile, these two factors give a huge difference in Figure 22(d). For example, the Raman enhancement factor is about 2 when \( p_l = 10 \) nm, while the local enhanced electric field can be as high as 200. It is surprised that these two factors become pretty close when the
molecular dipole is placed in the center position ($p1 = 50$ nm). We attribute the minimal
difference to the symmetrical system when the molecule is placed at the center position.

3.2.6 Electric Field Vector Plots of Rods along the Y-axis

Figure 23 Electric field vector plots of the rods at the wavelength of 580 nm when the rods are illuminated by the molecular dipole at (a) $p1 = 10$ nm and (b) $p1 = 50$ nm and oriented along the Y axis. All the electric field vector plots are through the rod center.

To account for the large difference between the Raman enhancement factor and local electric field, the electric field vector plots of the rod at the wavelength of 580 nm when it is illuminated by the molecular dipole are drawn in Figure 23. Figure 23(a) and (b) show the vector plots for the molecular dipole at $p1 = 10$ nm and 50 nm, respectively. The vectors in Figure 23(a) and (b) are amplified by a factor of 10000 and 4000, respectively. The amplification factors are much larger than that in Figure 21, since the intensity of the scattered light from the molecular dipole is much smaller than the intensity of a plane wave. Compare with the electric field vectors in Figure 21(a), we noticed that the induced dipole patterns inside the rod are different from these when rod is illuminated by the molecular dipole at $p1 = 10$ and 50 nm. The dipoles in Figure
23(a) are pretty weak, and the dipoles completely cancel out since the vectors are opposite from each other. These two reasons lead to the weak Raman enhancement factors in Figure 22(d), as shown by the red curve.

3.2.7 Rod along the X-axis with a Molecule

![Diagram of silver rod with molecule](image)

Figure 24 (a) Schematic of the silver rod that oriented along the X-axis with a molecule in its vicinity (b) Scattering spectra for the system when the position of the molecule relative to the end of the rod is varied from $p_2 = 0$ nm to 50 nm and for the isolated molecular dipole. (c, d) The relations between Raman enhancement factor (red curve) and the enhanced electric field intensity (blue curve) at the wavelengths of 400 and 580 nm, respectively. The diameter of the rod is 40 nm, the length is 100 nm. $d_2 = 4$ nm.

In this section, we compare the two factors when the rod is oriented along the X-axis to see whether the originally believed relation still holds true or not in this condition. The schematic is shown in Figure 24(a), where the rod with a molecular dipole in its vicinity is oriented along the
X-axis. The induced polarization in the molecular dipole will be perpendicular to the rod axis in the condition since the incident polarization is along the Y-axis. Same as previous set up, the distance between the molecular dipole and the rod surface, \(d_2\), is kept at 4 nm. The position of the molecular dipole relative to the rod end is varied from \(p_2 = 0\) nm to \(p_2 = 50\) nm. The scattering spectra for the systems when the position of the molecular dipole is varied are shown in Figure 24(b), and the scattering spectrum of an isolated dipole is also included. The peak intensity at the wavelength of 580 nm almost does not change when \(p_2\) is increased from 0 to 10 nm, then the intensity gradually drops when \(p_2\) is further increased. No peaks can be noticed at the wavelength of around 580 nm when \(p_2 = 50\) nm. The resonance peak change is related to the symmetry of the rod system, which had been discussed at full length in our previous paper.67

The relations between the Raman enhancement factors and the local enhanced electric field at the wavelength of 400 nm and 580 nm are shown in Figure 24(c) and (d), respectively. Same as the comparisons in Section 3.2.5, the Raman enhancement factors (local electric field) when the rod is illuminated by a plane wave at the wavelength of 400 nm are much smaller than that of the conditions at the wavelength of 580 nm. Also, Figure 24 shows the two values are pretty close at the wavelength of 400 nm, which is transverse mode resonance of the rod. It might be because of the smaller values of these two factors. A significant difference between the two factors also happens at the wavelength of 580 nm, as the curves shown in Figure 24(d). The enhanced local electric field is only 4, while the largest Raman enhancement factor can be as high as 190. The results demonstrated that the relation between the two factors does not follow the prediction, and we cannot simply predict the Raman enhancement factor of a molecule when
it is placed near a nanoparticle by calculating the enhanced local electric field of the nanoparticle illuminated by a plane wave at a scattering wavelength.

3.2.8 Electric field Vector Plots of Rod along the X-axis

![Electric field vector plots](image)

**Figure 25** Electric field vector plots of the rods at the wavelength of 580 nm when the rods are illuminated by the molecular dipole at (a) $p_2 = 10$ nm and (b) $p_2 = 50$ nm and orient along the X-axis. All the electric field vector plots are through the rod center.

To assist the understanding of the mechanisms leading the large deviation between the two factors, we draw the electric field vector plots of the rod when it is illuminated solely by the molecular dipole at the wavelength of 580 nm when the molecular dipole is at different position. To be consistent with the discussion in **Section 3.2.6**, we choose the conditions when $p_2 = 10$ nm and 50 nm, the results are shown in Figure 25(a) and (b), respectively. The vectors in Figure 25(a) and (b) are amplified by 3000 and 6000, respectively. Figure 25(a) shows almost all the vectors are along the rod axis, which results in the large Raman enhancement factor. The result is also consistent with the large longitudinal resonance peak at the wavelength of 580 nm. While,
the induced dipoles are totally disordered and cancel out, which brings about the low Raman enhancement factor and the weak resonance peak as indicated by the green curve in Figure 24(b).

3.3 Conclusions

Using a system composed of a molecular dipole and a silver nanorod, we demonstrated that the correlation between the Raman enhancement factor and the local electric field deviates from that derived from systems based on spherical nanoparticles. From the study, we learned that the correlation between the two factors cannot be simply generalized to the systems with nanoparticles of different shapes. We also demonstrated that the difference is because of the different resonance modes of the rod at various illumination conditions when the molecule is placed at different positions near the rod. For the system with arbitrary shapes, direct calculations should be applied using the model we discussed in the thesis.
CHAPTER 4: TOTAL TRANSMISSION AND REFLECTION IN A TWO-DIMENSIONAL RECTANGULAR PRISMS ARRAY


4.1 General Introduction

Isolated noble metal nanoparticle, as the simplest type of plasmonic structure, can support LSPs. The LSPs resonance wavelengths can be affected by the type of metal, the dielectric environment as well as the size and shape of nanoparticles. The excitation of LSPs can significantly enhance the electric field intensity in the vicinity of the nanoparticle. The LSPs also results in the maximal optical absorption of the particle at the resonance frequency. The control of LSPs resonance has drawn attention for the applications in dynamic switching and for tuning the functionality of plasmonic devices including plasmonic nanolasers, surface enhanced Raman spectroscopy and white-light generation. The main obstacle that limits the application of LSPs that excited on the surface of single nanoparticle is the rapid dissipation of plasmon energy. We had already learned that the optical response are different from that of isolated nanoparticles when the nanoparticles are patterned into one- or two- dimensional arrays. Zou et al. demonstrated the existence of narrow plasmonic/photonic extinction and scattering line shapes in one- and two- dimensional silver nanoparticles array, while single nanoparticle usually generates broad linewdths. The regular plasmonic arrays enable controllable collective mechanisms of interaction between the nanoparticles yielding a local concentration of the
electric field since the optical energy scattered by one particle will be collected by the neighboring particle as plasmons. The interaction between the nanoparticles in the array, or the coherent coupling, will also generate other features, such as Fano-shaped resonance peak. Fano resonance, named after Italian physicist Ugo Fano, is an asymmetric line shape of the scattering spectra and generated by the inference between two modes of broad and narrow widths. Fano resonance has an inherent sensitivity to the changes of the geometry and local environment, which renders it to be promising in the development of chemical or biological sensors. The two typical Fano spectral lines are shown in Figure 26 and a symmetric resonance with Lorentzian shape is also included. Many plasmonic nanostructures and metamaterials will produce Fano resonance, we refer the readers to a recent review for more interesting perspectives.

In addition to the appearance of Fano-shaped resonance peaks, the scattering (mainly the reflection) will also be enhanced due to the coherent coupling between the nanoparticles. The dipole coupling shows a transverse electric (TE) mode character where the resonance wavelength is dependent on the neighboring distance perpendicular to the direction of the incident polarization. Nikitin et al. examined the plasmonic resonances in a 2D gold nanoparticles array, they noticed that the Fano-shaped spectral features in both the transmission and reflection spectra. Meanwhile, they also identified two distinct lattice response: Rayleigh anomaly and lattice plasmon modes. In their work, they mainly focused on the optical properties when the array is illuminated by TM-polarized light.
In this work, a film with switchable total transmission and total reflection is achieved. By slightly changing the wavelength, the transition from total transmission (reflection) to total reflection (transmission) can occur in several wavelengths. Both Fano-shaped resonance peak and broad resonance peak are noticed in the study, the electric field behavior for different spectral positions are also investigated. The study shows that the Fano-shaped resonance peak is associated with quadrupole coupling among nanoparticles and the broad resonance peak is because of dipole coupling among the nanoparticles in the array. The theoretical work is of importance for the plasmonic bio- and chemical sensing.
4.2 Results and Discussions

The schematic of a free-standing 2D prisms array is shown in Figure 27(a). The array is placed in the YZ plane in the air, the incident light propagates along the X-axis and the polarization is either along the Y- or Z-axis. The parameters of the prism are as follows: height is expressed as $h$, the width is expressed as $w$. The neighboring distance between prisms along the Y- and Z-axes are expressed as $d_y$ and $d_z$, respectively.

4.2.1 TE and TM mode

Technically, a transverse electric (TE) wave has $E_z = 0$ and $H_z \neq 0$, in which all the electric field components are transverse to the direction of propagation. Conversely to TE mode,
transverse magnetic (TM) wave has $H_z = 0$ and $E_z \neq 0$. In this work, we define the XZ plane as the plane of incidence. The coupling between the excited metal nanoparticles will show different mode characters. It shows a TE mode character if the resonance wavelength depends on the interparticle distance perpendicular to the incident polarization direction. While, it shows a TM mode character if the resonance wavelength depends on the interparticle distance parallel to the incident polarization direction. Previous studies have demonstrated that the coherent dipolar coupling between the nanoparticles in the array displays a TE mode character. The study shows TE mode is associated with the excited dipole mode of the prism and the TM mode is associated with the excited quadrupole mode of the prism.

4.2.2 The Effect of Prism Width

We start our discussion from a rectangular prisms array with relatively smaller nanoparticles. The height of prisms, $h = 150$ nm, and the widths are either 100 nm or 300 nm. The calculated transmission spectra are shown in Figure 28. The incident polarization is along the Y-axis in Figure 28(a,b), it is along the Z-axis in Figure 28(c,d). The widths of the prims are 100 nm in Figure 28(a,c), while they are 300 nm in Figure 28(b,d). The interparticle distance along the Y-axis, $d_y$, are kept at constant 500 nm, and the distance along the Z-axis is varied from 500 to 900 nm at all the conditions. Figure 28(a,c) show that the reflection is pretty low when the widths of the prisms are 100 nm. However, we can still notice the difference between the spectra when the incident polarization direction is different. In Figure 28(a) where the incident polarization is along the Y-axis, the resonance dip shifts to red with increasing $d_z$, which is in agreement with previous theoretical and experimental works. However, the wavelengths of the resonance dips almost show no change with increasing $d_z$ in Figure 28(c) where the incident polarization is
along the Z-axis. The transmission (reflection) keeps increasing (decreasing) when $d_z$ is increased from 500 to 900 nm, which is explained as the coherent dipolar coupling between the silver prisms. The dip resonance wavelength happens at the wavelength of 500 nm, which is close to the neighboring particle distance along the Y-axis, 500 nm. The coherent coupling shows a TE mode character. This kind of coherent coupling between the nanoparticles has been discussed in full length in this reference. The arrays show very weak reflection when the widths of prisms are 100 nm since the interparticle distances are relatively large and also the size of prisms is too small to have effective coupling.
The transmission properties and features become totally different when the width of the prism is increased to 300 nm. As expected, the transmission intensities are significantly reduced because of stronger coupling between the nanoparticles with relatively smaller distance and larger particle size. The transmission spectra shapes are distinguishably different if we compare Figure 28(b,d) with Figure 28(a,c). Close to total transmission (reflection) appears when $d_z$ is larger than 600 nm, and the intensity of the transmission peak (dip) is almost invariant when $d_z$ is...
further increased. The appearance of the total transmission (reflection) is also due to the coherent coupling between the excited dipoles. We also noticed that the resonance peak wavelength is close to the neighboring particle distance along the Z-axis. Even though we can get both total transmission and reflection when the incident polarization is along the Y-axis, the difference between the resonance wavelengths can be over 100 nm. This difference is significantly smaller when the incident polarization is along the Z-axis, it is only several wavelengths, as the spectra shown in Figure 28(d). However, the transmission intensity also becomes smaller. Sharp Fano resonance peaks at the wavelength close to $d_z$ appear. We also notice that total reflection appears at shorter wavelengths or the left side of total transmission (if we can call it total transmission) in Figure 28(d), while it appears at longer wavelengths or the right side of total transmission. Figure 28(d) also shows that the transmission efficiency change happens sharply over only several wavelengths. The appearance of the Fano resonance peaks will be discussed in the following sections. One arising question is whether it is possible to get sharper transition between total transmission and reflection.

4.2.3 Effect of Prism Height

In this section, we discuss the effects of prism height and try to get some clues to achieve switchable total transmission and reflection within few wavelengths. The transmission spectra for the arrays are shown in Figure 29. The incident polarization is along the Y-axis in Figure 29(a,b), it is long the Z-axis in Figure 29(c,d).
The heights of the prims are 150 nm in Figure 29(a,c)) and 200 nm in Figure 29(b,d). The other parameters are as follows: \( w = 200 \text{ nm}, \ dy = 500 \text{ nm} \) and \( dz \) is varied from 500 to 900 nm. Compare Figure 29(a, c) with Figure 29(b, d), we find that the general trends of the transmission spectra do not have large difference, which demonstrates that the heights of prisms have a weak effect on the transmission properties of the arrays. Both Figure 29(a, b) show switchable total transmission and reflection. However, the Fano resonance features in Figure 29(d) are much more obvious than those shown in Figure 29(c), and the magnitude difference between the highest and the lowest transmission efficiencies in the Fano resonance shape becomes larger. When \( dz = 700 \text{ nm} \), the transmission efficiency increases from 0 to 70%, which is the largest
efficiency change when \( h = 150 \text{ nm} \). From the comparisons between Figure 29(c) and (d), we can conclude that higher prims height is preferred to get sharp efficiency change from total transmission to total reflection. The conditions when \( h = 200 \text{ nm} \) will be considered in the later study.

4.2.4 Optimal Conditions

![Graphs showing transmission spectra](image)

Figure 30 Transmission spectra for the silver rectangular prisms array when the incident polarization is along (a) the Y-axis and (b) the Z-axis. \( h = 200 \text{ nm}, w = 300 \text{ nm}, d_y = 500 \text{ nm}, d_z \) is varied from 500 to 900 nm.

In Section 4.2.3, we have demonstrated that a higher prism height is desirable to achieve sharper efficiency transition for the 2D array. The largest transmission efficiency change is only 70%, which is not large enough to fulfill the goal of achieving switchable total transmission and reflection within a few nanometers. The prism height is 200 nm in this section, the calculated transmission spectra when the incident polarization is along the Y- or Z-axis are shown in Figure 30(a) and (b), respectively. The resonance dips become significantly wider when the \( h \) is
increased from 150 nm to 200 nm, this can be noticed from the comparisons between Figure 30(a) and Figure 29(a,b) where all the prism widths are 300 nm. Figure 30(a) further verifies that the transition from total transmission to total reflection is possible when the incident polarization is along the Y-axis, though the transition is more moderate. The Fano resonance feature becomes less sharp if we compare spectra in Figure 30(b) with that in Figure 28(d), in which \( w \) is 100 nm.

As we expected, the magnitude difference between the highest and the lowest transmission intensity becomes larger. With the increasing \( dz \), the intensity difference between the dip transmission and peak transmission increases first and then drops and the Fano resonance feature becomes narrower, as the spectra shown in Figure 30(b). The calculations show that the maximal magnitude difference between the lowest and the highest transmission when the incident polarization is parallel to Z-axis could be obtained when \( dz = 800 \) nm.
4.2.5 Comparisons between the Spectra Calculated by Different Methods

![Graphs showing transmission spectra](image)

Figure 31 Transmission spectra calculated using the DDA (solid lines) method and CD (dashed lines) method where the incident polarization is along (a) the Y-axis and (b) the Z-axis. The parameters of the prism is as follows: \( h = 150 \text{ nm} \), \( w = 300 \text{ nm} \), \( d_y = 500 \text{ nm} \), \( d_z = 800 \text{ nm} \).

Till now, we have considered the effects of prism width, prims height and neighboring distance between nanoparticles as well as the orientation of the incident polarization on the transmission spectra for the arrays. We also demonstrate the conditions where the sharpest Fano resonance feature happens. The calculations show that the prism height has minimal effect on the transmission properties for the arrays, while a higher height is desirable to obtain sharp transition from total reflection to total transmission. The results also show that increasing neighboring particles distance will lead to sharp Fano resonance feature. A larger prism width will broaden the magnitude difference between the lowest and highest transmission intensity and the Fano resonance features. Prisms with \( w = 300 \text{ nm} \) and \( h = 200 \text{ nm} \) are the optimal structure to achieve
the sharpest transition between the total transmission and total reflection as indicated by Figure 30(b). The resonance peaks will shift to wavelengths over 1000 nm if we further increase the prism size.

One question that still needs to be solved is the mechanism leading to the Fano resonance features as well as the switch between total transmission and reflection. In this section, we focus on investigating the mechanisms that result in all these features. The resonance features are generated by the coherent coupling among the excited dipoles when the incident polarization is along the Y-axis, which has been proved in several previous papers. A better way to prove the hypothesis is just considering the dipolar coupling among all the nanoparticles and then comparing the transmission features with those we calculate in the work. The comparisons can be achieved by using CD method, in which only the dipolar coupling between the nanoparticles is considered. Rectangular silver prisms array with \( h = 150 \text{ nm} \), \( w = 300 \text{ nm} \), \( d_y = 500 \text{ nm} \) and \( d_z = 800 \text{ nm} \) is used as an example for the comparisons between the transmission spectra generated using DDA and CD methods. The calculations (not included in this work) indicate that a spherical particle with a radius of 180 nm has a similar resonance feature with that of the rectangular prism. The neighboring nanoparticle distance are kept the same as those in the prisms array, \( d_y = 500 \text{ nm} \) and \( d_z = 800 \text{ nm} \). The comparisons between the transmission spectra calculated using the two methods are shown in Figure 31(a) and (b), where the incident polarization is along the Y- and Z-axis, respectively. Figure 31(a) shows that the main feature of the spectrum at the wavelength of around 800 nm that created by using DDA method can be qualitatively reproduced by the spectrum calculated using CD method. The consistency between these two spectra proved that the total transmission/reflection is mainly because of the dipolar
coupling between the nanoparticles. However, the thing becomes different when we turn our attention to the condition where the incident polarization is along the Z-axis. Figure 31(b) shows that the Fano resonance feature that produced by using DDA method cannot be reproduced using CD method, which indicates that the appearance of the sharp transmission change is not due to the dipolar coupling between the prisms.

4.2.6 Absorption Spectra for the Array

To further study the mechanism leading to the Fano resonance feature that occurs when the incident polarization is along the Y- or Z- axis, we also calculate the absorption contributions of the excited dipoles when their orientations are only along the X-, Y- or Z-axis, individually. Using the modified DDA method, we can separate the contributions to the total absorption of the excited dipoles along different orientations. The isolated contributions of excited dipoles along different axes are shown in Figure 32(a) and (b), where the incident polarization is along the Y- and Z-axis, respectively. To have a clear understanding of each contribution, the total absorption spectrum is also included.
Figure 32 Absorption spectra for the silver rectangular prisms array from contributions of excited dipoles along the (black) X-, (red) Y- and (green) Z-axis only and also the (blue) total absorption when the incident polarization is along the (a) Y-axis and (b) Z-axis. $h = 150$ nm, $w = 300$ nm, $d_y = 500$ nm, $d_z = 800$ nm.

When the incident polarization is along the Y-axis, the total absorption is dominated by the contribution along the Y-axis. No resonance peak appears at the wavelengths of around 950 nm, even dipoles along the X-axis also contribute to the total absorption. The results support the hypothesis that the transmission features generated when the incident polarization is along the Y-axis are due to the coherent dipolar coupling among the nanoparticles. Figure 32(b) shows that the coupling between the nanoparticles show a quadrupole characteristic since both the dipoles along the X- and Z-axes contribute to the total absorption.

4.3 Conclusions

We numerically examine the transmission spectra for a 2D array composed of rectangular silver prisms under TE- and TM-polarized incident light. The dependence of resonance feature of the transmission spectra on prism heights, widths, and neighboring prism distances is investigated. The calculations show the switch between total transmission and total reflection can
be achieved under TE mode condition. Using the CD method, we find that the coupling among excited dipoles can be attributed to the resonance feature where the resonance wavelength is determined by the neighboring prism distance perpendicular to the incident polarization direction. Under TM mode, the resonance wavelength is determined by the neighboring prism distance parallel to the incident polarization direction and the generated Fano resonance shape is due to the interference between the narrow resonance peak from excited quadrupoles and the broad transmission peak from the excited dipoles. The transition from the total transmission to the total reflection is sharper, while the magnitude of the change is smaller compared to that in the TE mode. We also demonstrate that the prisms with a 200 nm height and a 300 nm width generated desired sharp transition from total transmission to total reflection in the visible wavelengths.
CHAPTER 5: DIFFERENT TRANSMISSION ENHANCEMENT MECHANISMS IN A SANDWICHED NANOFILM


5.1 General Introduction

The finding of extraordinary optical transmission (EOT) phenomenon through a perforated thin film conducted by Ebbesen and coworkers in 1998 revitalizes the interest of researchers to study the optical properties of metal film with/without holes from both theoretical and experimental approaches. EOT is a phenomenon that the transmission through a subwavelength aperture in an otherwise opaque metallic film is significantly enhanced. Although the EOT has been demonstrated, no well-accepted theory had been proposed to explain the phenomenon. Most researchers believe that the enhanced transmission is due to the coupling between the propagating SPPs excited at the top and bottom surfaces of the metallic film. However, the theory cannot explain the resonance peak shift with the film thickness change. Lezec and Thio et al. came up with the composite diffracted evanescent wave model in which the generation of EOT phenomenon is due to the interference of diffracted evanescent waves produced at the subwavelength surface structures such as holes, grooves and slits. Takakuru et al. used Fabry–Pérot-like modes to interpret the phenomenon when studied the interaction of transverse magnetic-polarized light with a single slits and slits array.

Bonod et al. predicted that the presence of holes is not necessary for the generation of EOT phenomenon. The EOT can also be produced in a continuous metal film as long as it is
appropriately manipulated. Compared with perforated metal film, the continuous film shows more promising applications in optics and plamonics because of its relatively higher electronic conductance. The disadvantage of the continuous metal film, its natural-opacity property, largely limits its applications, which makes the generation of EOT in continuous meal film become important. Several groups have tried to enhance the transmission of a continuous metal film by coating the film with nanoparticles or nanoparticles arrays. Zayats et al.\textsuperscript{96} proposed a nanostructure to enhance the transmission properties of the continuous film by coating the film with periodically metal or dielectric ridges on one or both interfaces, and they believed that the enhanced transmission is due to the resonant tunneling via SPPs. The work of Xiao et al.\textsuperscript{97} demonstrated that the nanowire periods affect the Fano-shaped resonance spectra when the incident polarization is perpendicular to the nanowire grating in the nanostructured film. In these works, the periodically arranged nanostructures or nanoparticles are usually deposited on the surface of metal film or the substrate. Although most researchers agree that the presence of nanostructures or nanoparticles can enhance the transmission properties of a continuous metal film, few achieved total transmission.

Recently, Liu et al.\textsuperscript{98} and Papanikolaou et al.\textsuperscript{99} designed new nano-film systems where the metal film is sandwiched by nanoparticles arrays, respectively. The studies provided us with a new approach to enhance the transmission of metal film irrespective of the relatively low transmission efficiency. The distance-related optical properties of the system that is composed of an individual nanoparticle and a metal film offers us a clue to resolve the long-standing dilemma. Through checking all the studies that using sandwiched film systems to achieve EOT, we noticed that no one has considered the effect of the distance between the nanoparticles or nanostructures
lying on top and bottom surface of the metal film. However, the coupling between the LSPs of
the nanoparticles in the array as well as the coupling between LSPs of the nanoparticles and
SPPs of the metal film should play an important role in enhancing the transmission properties of
the metal film.

Based on the hypothesis that the distance between the nanoparticles lying below and above
the metal film should be a key factor in affecting the transmission properties of the metal film,
we proposed a sandwiched silver film system. The sandwiched silver film is composed of five
layers: a continuous silver film with a thickness of 50 nm in the middle, two glass substrates
touching the film and two prims arrays on the top of the glass substrates. Through varying the
parameters of the nano-film system, two different mechanisms leading to the enhanced
transmission were investigated. One mechanism generates a kind of Fano-shaped resonance
peaks depending on the neighboring nanoparticle distance between the prisms, which is believed
to be due to the coupling of the propagating SPPs. The other mechanism produces broad
resonance peak, which depends on the distance between the prisms lying below and above the
flat film, or in other words, on the thickness of the glass substrates. We demonstrate that the
enhancement results from the excited LSPs. We also further demonstrate that the two
mechanisms can work cooperatively to enhance the transmission of the silver film when the
thickness of the glass substrate is delicately engineered.
5.2 Results and Discussions

Figure 33 Schematic of sandwiched nano-film. The thickness of silver film is $t$, the thickness of glass layers is $d$. The neighboring prism distances are expressed as $D_y$ and $D_z$ along the Y- and Z-axes, respectively. The parameters of the rectangular prism: height is $h$, width is $w$. The incident light is along the X-axis, the polarization is either along the Y- or Z-axis.

The schematic of the sandwiched nano-film is shown in Figure 33, which contains five layers. The yellow layer in the middle represents the continuous silver film with a thickness, $t$, of 50 nm. The blue layers touching the thin film are the glass substrates, and the thickness is denoted as $d$. Through varying the thickness of the glass substrate, we can change the distance between the nanoparticle and the silver film. The outer top and bottom layers are the 2D nanoprism array layers, where the prism height is $h$, the prism width is $w$. The system is arranged in the YZ plane, and the incident light is along the X-axis, the polarization is either along the Y- or Z-axis. The interparticle distances along the Y and Z-axes are represented by $D_y$ and $D_z$. 
respectively. In the calculations, the effects of the interparticle distance are studied by changing the $D_z$, and keeping $D_y$ as a constant value. The refractive index of the glass substrate is taken as 1.5.

5.2.1 Comparisons of the Transmission of Different Film Systems

![Graph comparing transmission spectra for different film systems](image)

Figure 34 Comparisons of the transmission spectra for several different nano-film systems. Black solid curve: The isolated continuous silver film with a thickness of 50 nm. Green curves: The silver film sandwiched by glass substrates and one nanoprisms array lying above and below it. Solid and dashed lines represent the conditions when the incident polarization is along the Y- and Z-axes, respectively. $D_y = 300$ nm, $D_z = 600$ nm. The transmission spectra are overlapped whether the incident polarization is along the Y- or the Z-axis.

Many researchers have studied the optical transmission of a metal film with nanostructures or nanoparticles on one or both film interfaces. First, we examine the system with only one
2D array on the surface of the silver film and compare its transmission with that of the proposed sandwiched nano-system. The transmission spectrum for an isolated continuous silver film with a thickness of 50 nm is also calculated. The height of the silver prism is taken as 50 nm, and the width is 150 nm. The thickness of the glass substrate that we used is 20 nm. The transmission spectra for the films with different structures are shown in Figure 34. The black curve is the transmission spectrum for the isolated silver film. Figure 34 shows that the transmission of an isolated metallic film is pretty week, the efficiency is below 5% at long wavelengths. The efficiency can be slightly enhanced when the film is coated with one 2D nanoprisms array where the interparticle distance is 300 nm and 500 nm along the Y- and Z-axes, respectively. However, the significantly enhanced transmission can be obtained when the film is coated with two 2D nanoprisms arrays on its both sides with glass layers in between, which is the structure we proposed. The transmission peaks can be observed at both short and long wavelengths. Two kinds of resonance peaks can be observed when the incident polarization is along the Z axis, a sharp Fano-shaped resonance peak with larger intensity at around wavelengths of 600 nm and a much broader peak at the wavelength of around 1100 nm. Figure 34 demonstrates that the transmission for the film can be enhanced in comparison with that of both the isolated film and the film coated with one 2D nanoprisms array. For example, the transmission efficiency for the sandwiched nanofilm at around 1030 nm is 40%, while it is only about 1% for the single continuous film. The increasing transmission efficiency proves that the sandwiched nanofilm is an effective way to enhance the transmission of the silver film.
5.2.2 Effect of Neighboring Prism Distance

In section 5.2.1, we learned that the direction of polarization state has a large effect on the transmission efficiency for the film. When the incident polarization is along the Y-axis, only one broad resonance peak appears at the studied wavelengths, while two kinds of peaks appear when the incident polarization is along the Z-axis. To examine the two different mechanisms leading to the enhanced transmission, the interparticle distances along the Z-axis is varied.

Figure 35 Transmission spectra for the sandwiched nanofilm when the incident polarization is parallel to (a) the Y-axis and (b) the Z-axis. $w = 150$ nm, $h = 50$ nm, $D_y = 300$ nm, $D_z$ is varied from 400 to 800 nm.

Figure 35 shows the transmission spectra for the sandwiched film when the incident polarization is along the (a) Y- and (b) Z-axis. The parameters for the system are taken as follows: $h = 50$ nm, $w = 150$ nm, and $d = 20$ nm. $D_y$ is kept as constant 300 nm, $D_z$ is varied from 400 to 800 nm. Similar to the spectra shown in Figure 34, broad peaks always appear in the wavelengths ranging from 900 to 1200 nm whether the incident polarization is along the Y- or Z-axis. It indicates that the appearance of the broad peak is irrelevant to the polarization direction.
of the incident light. Figure 35(a) shows the broad peak initially evolves narrower and slightly shifts to blue with increasing $D_z$. The peak intensity and the wavelength almost keep unchanged with increasing $D_z$ when $D_z$ is larger than 500 nm. Overall, the effect of the neighboring particle distance of the 2D array on the transmission efficiency at around 1000 nm is pretty weak. This can also be noticed in Figure 35(b). The weak interparticle distance dependence of the resonance peak indicates that the appearance of this broad peak is due the coupling between the LSPs of the individual prism and LSPs of the silver film rather than the coupling of the propagating SPPs. In addition to the broad resonance peak at long wavelengths, Fano-shaped resonance could also be obtained at short wavelengths and its resonance wavelength changes proportionally to the neighboring distance along the Z-axis. The sharp peak wavelength gradually redshifts with increasing $D_z$. 

122
5.2.3 Effect of Glass Layer Thickness

To verify the prediction that the appearance of the broad peaks is due to the coupling between the LSPs of the particles and the silver film, we changed $d$ from 20 to 60 nm. The spectra are shown in Figure 36, where $h = 50$ nm, $w = 150$ nm, $D_y = 300$ nm, $D_z = 600$ nm, and the incident polarization is along the Y- and Z-axes, respectively. Figure 36(a) shows the broad peak resonances at long wavelengths are sensitive to the thickness change of the glass substrate when $d$ is small. The peak wavelength evolves from 1010 nm to 950 nm when $d$ is increased from 20 nm to 30 nm. The peak wavelength slightly changes when $d \geq 30$ nm. In both Figure 36(a) and (b), the broad peak shifts to blue with increasing $d$, and the peak intensity continuously drops, which implies that the coupling between the central flat film and the prisms in the arrays becomes weaker with increasing separation between them. Although the general trends of the peak wavelength change in Figure 36(a) and (b) are the same, the efficiency change in Figure
36(a) is much more significant than that in Figure 36(b). The calculations suggest that the transmission efficiency change is more sensitive to the variation of $d$ when the incident polarization is parallel to the Y-axis. Quite interestingly, Figure 36(b) shows that sharp peak profile and intensity at shorter wavelengths can also be affected by the thickness of the glass substrate. As the black curve shown in Figure 36(b), the sharp peak wavelength shifts from 630 nm to 690 nm when $d$ is increased from 20 to 60 nm. The peak intensity gradually drops when $d$ is increased from 30 to 60 nm, and the peak becomes much broader. The broadened narrow peak and the blueshifted broad peak are going to merge into one when $d$ is increased to 60 nm, which offers us a new approach to enhance the transmission of the metal film by combining the effects of both LSPs and propagating SPPs.

5.2.4 Electric Field Contours

The electric field contours for the nano-film system at both the sharp peak wavelength and broad peak wavelength are calculated to identify the mechanisms leading to these two kinds of peaks when the incident polarization is along the Z-axis. The sharp Fano-shaped resonance peak appears at the wavelength of 640 nm, and the broad peak appears at 1030 nm. Figure 37(a,b) show the field distributions at the wavelength of 640 nm, and Figure 37(c,d) show the field distributions at the wavelength of 1030 nm. Figure 37(a,c) are in the XY plane, Figure 37(b,d) are in the XZ plane. Figure 37(a) shows a continuous and enhanced electric field at the bottom of the metal film without any gaps. In comparison with Figure 37(c), the fields in Figure 37(a) are much stronger. Figure 37(b) shows a strong coupling between the neighboring prisms as well as the weak coupling between the prisms located at the top and bottom of the film.
Figure 37 Electric field distribution contours in the (a, c) XY-plane and (b, d) XZ-plane when the incident polarization is along the Z axis at the wavelengths of (a, b) 640 nm and (c, d) 1030 nm. The monitor is placed in the center of nano-film system at all the conditions. $h = 50$ nm, $w = 150$ nm, $D_y = 300$ nm, $D_z = 600$ nm, $d = 20$ nm.

Figure 37(a,b) demonstrate that the appearance of the sharp resonance peak is mainly due to the coupling of the propagating SPPs, which is associated with the interparticle distance. By contrast, the electric field concentrates at the corners of the prisms located at the bottom of the metal film in Figure 37(d). The neighboring prisms do not show strong coupling effects, which are consistent with the fact that the transmission properties of the film do not depend on the interparticle distance. Figure 37(c) also shows disrupted feature in comparison the flat feature in Figure 37(a). Both Figure 37(c) and (d) indicate the LSPs feature and their effect on the enhanced transmission of the metallic film.
5.2.5 Other Parameters Affecting Transmission

We also examine other parameters that might be affecting the transmission efficiency of the nano-film. First, we break the symmetry of the sandwiched film by laterally shifting the relative positions of the prisms lying below and above the central silver layer. The shift is expressed as $s$, which is varied from 10 nm to 150 nm along the Y-axis and from 10 to 300 nm along the Z-axis. In Figure 38(a, c), the incident polarization is along the Y-axis, it is along the Z-axis in Figure 38(b, d).

Figure 38 Transmission spectra of the sandwiched films when the incident polarization is along (a, c) the Y-axis and (b, d) the Z-axis. The prisms lying below the above the film are shifted with respect to each other along (a, b) the Y-axis and (c, d) the Z-axis.
38(b, d). The shift happens at the Y axis in Figure 5.5(a, b), it at the Z axis in Figure 5.5(c, d). The other parameters are as follows: \( h = 50 \text{ nm} \), \( w = 150 \text{ nm} \), \( D_y = 300 \text{ nm} \), and \( D_z = 600 \text{ nm} \). Note that the transmission spectra when \( s = 0 \text{ nm} \) are not included in the figures, since they overlap with the spectra happens when \( s = 10 \text{ nm} \). The spectra show that the transmission peak are quite robust for relatively small shift \((s \leq 50 \text{ nm})\). The calculations show that the symmetry of sandwiched film system is not critical for the generation of the broad peaks.

5.3 Conclusions

In this work, two different mechanisms leading to enhanced transmission of a continuous film are studied. One mechanism shows that the sharp resonance peak position is proportional to the neighboring nanoparticle distance in the 2D nanoparticle array and can be explained by the coupling of propagating SPPs. The other mechanism shows that the broad resonance peak at longer wavelength is dependent on the distance between the prisms array and the central metallic film or the thickness of the glass substrate that we applied. The enhanced transmission is due to the LSPs rather than the propagating SPPs. When the distance between the central film and the prism array is changed, the two mechanisms can work cooperatively and get further enhanced transmission for the film. Moreover, other parameters that might affect the transmission property of the metallic film are also studied.
6.1 General Introduction

In this section, the work that we presented in Chapter 5 is further extended. We demonstrate that the transmission efficiency of the nano-film can be further improved by increasing the thickness of glass substrates. The transmission properties of a continuous metal with or without holes have sparked considerable interest due to the novel physical properties involved, especially after the discovery of EOT phenomenon for a metal film perforated with subwavelength hole arrays. Most researchers paid their attention to the optical properties of metal film with single holes or holes arrays since the system have been thoroughly studied. Several different, even contradictory mechanisms have been proposed to explain the EOT phenomenon for metal film with holes. However, the continuous metal film without holes shows much more potential applications in optoelectronics devices because of its perfect electronic conductance when compared with that of metal film with holes. The disadvantage of continuous metal film is also obvious, its naturally opaque property highly limits its potential applications. According to our previous work, we find that the transmission efficiency of a single metal film with a thickness of 50 nm is below 5% in the wavelengths from 500 to 1300 nm. Continuous metal nanostructures with near-perfect transmission/reflection are desirable in optoelectronic applications and deserve much more attention.

Everyone agrees that the optical properties of the metal nanostructures are related to the plasmonic modes that they can support, although a well-accepted theory of the enhanced
transmission has not been reported. Metal film perforated with holes or holes arrays can support both localized and propagating (hole) surface plasmons,\textsuperscript{113} which will become much more complicated when different plasmonic modes interact with each other. Researchers have demonstrated that continuous metal film can also display similar optical properties with that of metal film with holes as long as it is properly modulated.\textsuperscript{95} The modulation includes narrow-grooved gratings,\textsuperscript{114} ridges,\textsuperscript{101} nanoparticle arrays\textsuperscript{98,115} and other consciously arranged structures.\textsuperscript{116,117} Among them, metal films with nanoparticle arrays are intensively studied, where the enhanced transmission is due to the interactions between LSPs of the metal nanoparticles (arrays) and SPPs excited on the metal film. To achieve better transmission property of a continuous film, many theoretical and experimental studies have been carried out. Shi \textit{et al.} constructed an asymmetric nanostructured gold film with a 2D array of gold nanoblocks placed on top of the film.\textsuperscript{118} They attributed the enhanced transmission to the surface plasmon mode at the air-gold interface leaking to the substrate. Zayats \textit{et al.} studied the optical transmission of a metal film with a thickness of 40 nm with ridge gratings on one or both film interfaces using a numerical method.\textsuperscript{101} The transmission at some wavelengths can be enhanced by more than 100 times compared to that of a single film with same thickness. Liu \textit{et al.} investigated the optical transmission of a metal film sandwiched by deep subwavelength metal cylinder arrays, the results show the transmission can be largely enhanced.\textsuperscript{115} In their works, the highest transmission efficiency was around 80\% for a film with a thickness of 40 nm. In addition, electromagnetically induced transparency or enhanced transmission has also been widely studied based on metal-insulator-metal waveguide system.\textsuperscript{119,120} Liu \textit{et al.} proposed a structure that is composed of a continuous metal film sandwiched by 2D hexagonal metal-dielectric multilayer core-shell
nanoparticle arrays to get enhanced transmission. Recently, a new-type of continuous metal film with two composite layers consisting of metallic and dielectric stripes was proposed by Zhou et al., where the light scattered from the metal film by the scattering from two composite layers. Even though many researchers claimed they could get “transparent” continuous metal film using deliberately arranged nanoparticle arrays, the transmission efficiency is very hard to get 100%, even 90% unless a very thin metal film was applied. However, the thickness of the metal film is the factor we must take into account, since the transmission efficiency will be impaired with increasing film thickness.

Another question that we noticed is that few researchers paid attention to the effects of the distance change between the nanoparticle arrays and metal film on the transmission property of the film. The excitation of the propagating and localized SPs in metal film can dramatically modify its optical response. The excitation of the LSPs in the nanoparticles that in the vicinity of the metal film can also modify the optical response of the metal film. SPPs excited in the interface of the metal film have both transversal and longitudinal electric fields, LSPs of the nanoparticles are also confined in a certain distance near the particles. Naturally, we believe the optical transmission of the sandwiched metal film should be affected by the distance between them.

In previous work, we found that the highest transmission efficiency for a continuous silver film with a thickness of 50 nm is around 40%, however, it hardly fulfils the requirement of optoelectronics applications. In this work, we show that the transmission efficiency can be further enhanced because of the constructive inference between the LSPs and propagating SPPs when the thickness of the glass substrates reaches over 100 nm. In the study, the interparticle
distance does not have a large influence on the highest transmission efficiency, while the transmission peak will split into two narrow peaks with increasing interparticle distance when the incident polarization is along the Z-axis. We also find that the height and width of the nanoparticle have minimal effect on the transmission properties of the metal film, however, the size of the nanoparticle do have an effect on the FWHM of the transmission spectrum.

6.2 Results and Discussion

6.2.1 Effect of Glass Substrate Thickness

Figure 39 (a) Transmission spectra for the sandwiched nano-film when the incident polarization is along the Z-axis where the thickness of the glass substrate, $d$, is increased from 50 to 150 nm. (b) The evolvement of the transmission spectra with the thickness of glass substrate. Black lines: the relation between peak wavelength and $d$. Blue lines: the relation between peak transmission efficiency and $d$. The parameters of the sandwiched nano-film are as follows: $h = 50$ nm, $w = 150$ nm, $D_y = 300$ nm, $D_z = 600$ nm.

In previous study, we noticed that the resonance peak locating at short wavelengths which depends on the neighboring interparticle distance redshifts with increasing $d$, while the resonance peak at long wavelengths which depends on distance between the nanoparticles array and the
metal film blueshifts with increasing $d$. So very naturally, we envisage that the transmission efficiency might be further enhanced when we combine these two kinds of peaks. To verify our hypothesis, we further increase the thickness of glass substrate from 50 to 150 nm. The calculation results are shown in Figure 39(a), where the incident polarization is along the Z-axis. The structural parameters are as follows: $h = 50$ nm, $w = 150$ nm, $D_y = 300$ nm, $D_z = 600$ nm. The thickness of the silver film is 50 nm. When $d = 50$ nm, we can clearly notice two broad peaks in the wavelengths between 600 and 1000 nm. The two peaks gradually merge into one with increasing $d$, and the peak intensity also gradually increases just as we expected. When $d$ is increased to 110 nm, the transmission efficiency is boosted to more than 70%, which demonstrates the feasibility of further improving the transmission property of the continuous metal film by increasing the thickness of glass substrates. The broad peak becomes narrower when the thickness of the glass substrate is further increased and the transmission efficiency can also be slightly improved. The peak intensity decreases and a shoulder peak appears when $d$ is larger than 110 nm. The broad peak completely splits into two narrow peaks when $d = 150$ nm, as the magenta curve shown in Figure 39(a). The detailed relation between the highest transmission efficiency and the thickness of the glass substrate is shown in Figure 39(b), where $d$ is varied from 50 to 200 nm. The relation between the highest peak wavelength and the thickness of glass substrate is also included. The blue curve shows that the transmission efficiency increases first then decreases with increasing $d$, it reaches to the highest point, 75%, when $d$ is 120 nm. The transmission efficiency becomes pretty low when the glass thickness is further increased. From Figure 39(a), we know that the two broad peaks merge into one when $d$ is larger
than 70 nm. After that, the peak wavelength only slightly redshifts when $d$ is varied from 80 to 200 nm, as the black curve shown.

6.2.2 Thickness of Silver Film

![Transmission spectra for the continuous nano-film with varying thickness](image)

Figure 40 Transmission spectra for the continuous nano-film with varying thickness where $d = 110$ nm, $D_y = 300$ nm, $D_z = 600$ nm, $h = 50$ nm, $w = 150$ nm. The incident polarization is along the Z axis.

We successfully demonstrate that the transmission efficiency of the continuous metal film can be largely enhanced by combing both the localized and propagating plasmon polaritons, the efficiency increases to near 80%. Another factor that we need to consider is the thickness of the glass substrate. We vary the thickness of the metal film from 10 to 70 nm under other fixed parameters, the results are shown in Figure 40, where $d = 110$ nm, $D_y = 300$ nm, $D_z = 600$ nm, $h =$
50 nm, \( w = 150 \text{ nm} \). The thickness of the metal film is changed for the following reasons: (a) to testify whether the largely enhanced transmission of our proposed structure can be held for thicker or thinner metal film (b) to precisely compare our results with other researchers’ studies of different film thickness (c) to study the trend of transmission efficiency change with varying film thickness. In the study, we noticed that few have considered changing the thickness of the metal film. No one can deny the importance of the thickness of metal film in real applications. As the spectra shown in Figure 40, the general trend is that the transmission efficiency decreases with increasing film thickness, this is within our expectation (efficiency: 96%, \( t = 10 \text{ nm} \); efficiency: 26%, \( t = 70 \text{ nm} \)). For a metal film with a thickness of 20 nm, the highest transmission efficiency happens at the wavelength of 760 nm, which is 91%. For a film with a thickness of 40 nm, it is near 80% at the wavelength of 820 nm. Another advantage of the proposed structure is its easy-manipulation, many structural parameters can be varied, such as the size of nanoparticle, the interparticle distance, the height of glass substrates. In the following study, the thickness of the silver film is kept as constant 50 nm.
6.2.3 Effect of Neighboring Prisms Distance

Figure 41 Transmission spectra for the continuous nano-film when the incident polarization is along (a) the Y-axis and (b) the Z-axis. $D_y = 300$ nm, $D_z$ is varied from 300 to 900 nm, $h = 50$ nm, $w = 150$ nm.

To investigate the influence of the structural parameters on the transmission properties of the nano-film or to find the conditions to show the best transmission performance, we vary some parameters of the proposed structure, the first one is the interparticle distance. In the study, the interparticle distance along the Y-axis is kept as constant 300 nm, the distance along the Z axis is varied from 300 to 900 nm. The transmission spectra are shown in Figure 41(a) and (b), where the incident polarization is along the Y- and Z-axes, respectively. Figure 41(a) shows that the transmission efficiency is pretty low when the incident polarization is along the Y-axis. The resonance peak intensity decreases and redshifts with increasing $D_z$, which does not give us much useful information in getting better transmission property. In the following study, we only focus on the transmission spectra for the nano-film system when the incident polarization is along the
Z-axis. Compared with the spectra in Figure 41(a), the overall transmission efficiencies in Figure 41(b) are much higher where the incident polarization is along the Z-axis. The highest transmission efficiency occurs when $D_z = 600$ nm, while the difference among the peak intensities are not obvious. The transmission peak becomes broader first with increasing $D_z$ then splits into two narrow peaks, just as the spectra shown in Figure 40(a) where the broad peak also splits into two with increasing glass thickness. The narrow peaks also show pretty high transmission efficiencies. It demonstrates that the change of interparticle distance will vary the HWFM of the spectrum as well as the resonance wavelength.

6.2.4 Effect of Prism Height and Width

![Figure 42 Transmission spectra for the nano-film when the incident polarization is along (a) the X-axis and (b) the Z-axis. $D_x = 300$ nm, $D_z$ is varied from 300 to 900 nm. $h = 50$ nm, $w = 150$ nm.](image)

The last structural parameter that we considered is the size of the nanoparticle. In Figure 42(a) and (b), we study the effects of the height and width of the prism on the transmission
properties of the nano-film system, respectively. The thickness of glass substrate is 110nm. The interparticle distance along Y and Z-axes are 300 and 600 nm, respectively. In Figure 43(a), the height of the nanoprism is varied from 30 to 110 nm while the width of the nanoparticle is kept constant 150 nm. Figure 42(a) shows the transmission peak intensity increases when $h$ is increased from 30 to 50 nm. However, it almost has no effects on the transmission peak system when $h \geq 50$ nm, which is different from the study of Liu et al.\textsuperscript{115} In the work of Liu et al., the transmission efficiency has an evident change with increasing nanoparticle height even the nanoparticles are touching the film. In Figure 42(b), the width of the nanoprism is varied from 100 to 250 nm while the height of the nanoparticle is held constant 50 nm. When the width of the nanoprism is 100 nm, the spectrum shows two sharp peaks with low intensities. A broad peak with the highest intensity occurs when $w$ is increased to 150 nm. However, the broad peak intensity decreases first then shows no change when $w$ is further increased. The peak becomes slightly broader with increasing $w$, the phenomenon is similar to the transmission spectra in Figure 42(a). Both figure 42(a) and (b) show the influence of the prism width and height on the transmission of the nano-film is limited, but the size of the nanoparticle does affect the transmission property of the metal film.

In our study, we notice that when the size of nanoparticle is small ($w \leq 150$ nm, $h \leq 90$ nm), the transmission spectra show narrow peaks, especially at large interparticle distances. In some cases, the transmission spectrum shows two narrow peaks when the interparticle distance is large. The transmission spectra show much broader peaks when the size of nanoparticle increases and the peak intensity was affected by the interparticle distance more greatly. We believe that the
shape of nanoparticle may also have an effect on the transmission property of the metal film, which needs to be further studied.

6.3 Conclusions

In conclusion, largely enhanced transmission for the continuous metal film was achieved by the constructively interference between the localized and propagating surface plasmons excited in the nanoparticles and the film using the proposed nano-film system as long as the thickness of glass substrates is large enough. The transmission spectrum can be tuned by changing the interparticle distances as well as the size of the nanoparticles. The proposed structure showed much higher transmission efficiency for both thin and thick metal films.
CHAPTER 7: SUMMARY

Light interactions with single nanoparticles and two-dimensional arrays of plasmonic nanostructures were studied using theoretical methods. For single silver nanoparticle, when it is illuminated by the incident light, the enhanced near field that associated with localized surface plasmon can be used to enhance the Raman scattering of molecule. The phenomenon is known as surface enhanced Raman scattering (SERS). In Chapter 3, we reexamined the relation between Raman enhancement factor and the near field intensity of a silver rod at scattering (radiation) wavelength. Different from the prediction that Raman enhancement factor is proportional to the near field intensity of the metallic nanoparticle, we found that the two factors can be largely different. For silver rod, the relation cannot be hold true whether the incident polarization was parallel to the rod long axis or perpendicular to it. The difference was the largest when the molecule was placed near the rod edge at both conditions, and the two factors agreed with each other well when the molecule was placed at central part of rod. Using silver rod as an example, we demonstrated that the relation between Raman enhanced factor and enhanced near field intensity that is based on spherical particle cannot be simply applied other nanoparticles with different shape. The correct Raman scattering enhancement factor should be calculated using the introduced electrodynamic model.

The optical response can be totally different when single nanoparticles are arranged into 1D or 2D arrays. More optical phenomena can be generated because of the coupling between nanoparticles in the arrays. Take 1D nanoparticle array as an example, the resonance wavelength
will redshift when the incident polarization is parallel the chain, which is named as longitudinal coupling mode, however, the resonance wavelength will blueshift when the incident polarization is perpendicular to the chain, which is named as transverse coupling mode. Note that the incident light direction is perpendicular to the chain at both conditions. In Chapter 4, different coupling modes leading to total transmission/reflection for a free standing 2D rectangular prisms array were studied. The optical response of 2D nanoparticles array is more complicated than that of 1D array since the coupling between nanoparticles can be affected by more parameters, such as interparticle distance along both directions and the incident polarizations states, etc. We demonstrated that total transmission and reflection can be easily switched by slightly changing the incident wavelength, which shows as a broad Fano-shaped resonance peak. The appearance of the broad Fano resonance peak was due to the coherent dipolar coupling among the prisms, which showed a transverse electric (TE) mode where the resonance wavelength depends on the interparticle distance perpendicular to the incident polarization. A sharp Fano spectral profile was noticed when the quadrupole coupling among the prisms happens, which showed a transverse magnetic (TM) mode. The transition from 100% reflection to transmission can be achieved within 10 nm, while achieving 100% transmission is challenging, the largest transmission is around 80%.

In Chapter 5, we demonstrated that the transmission of a continuous film can be largely enhanced when the film is sandwiched with two 2D prisms arrays. Two different kinds of transmission peaks were observed at both short and long wavelengths. The sharp peak showing at short wavelengths followed the conventional believing that the resonance wavelength depends
on the interparticle distance in the arrays, which was attributed to the coupling of propagating SPPs. The broad peak showing at long wavelengths strongly depended on the distance between the nanoparticles array and the continuous film, which is the thickness of the glass substrates. We believed that the appearance of the broad peak is due to the coupling of the LSPs of the film and the prisms. We showed that these two kinds of peaks would merge into one peak with larger intensity when the thickness of glass substrates is further increased, the detailed study was shown in Chapter 6. In Chapter 5, we demonstrated that sandwiched nano-film structure can enhance the transmission of a continuous silver film, while the largest transmission efficiency is only around 40% for a film with a thickness of 50 nm. We extended the work finished in Chapter 5 and found that the transmission can be further enhanced when the thickness of glass substrates is increased. The transmission efficiency is around 80% when the glass thickness is increased to 110 nm.

From single nanoparticles to 2D nanoparticles arrays, our work promotes the understanding of the interaction between light and plamsonic nanomaterials. Theoretical study will ultimately boost the applications of plasmonic materials in biosensor, optical devices, spectroscopic technique, solar energy materials, etc.


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