Kingdom of Saudi Arabia
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Light-scattering simulations from nanoparticles based on Mie theory

A graduation project submitted to the Department of Physics in partial fulfillment of the requirements for the degree of Bachelor of Science in physics

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Riyadh- KSA- 2024

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بسم الله الرحمن الرحيم

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الشكر

أولاً وقبل كل شيء، أود أن أحمد الله العلي العظيم، الرحمن الرحيم، على بركاته التي منّ بها عليّ أثناء دراستي وإتمام هذه الأطروحة. وصلى الله على خاتم أنبيائه محمد (صلى الله عليه وسلم) وعلى آله وصحبه أجمعين.

كما أتوجه بالشكر العميق إلى مشرفي الدكتور عاشور محمد أحمد على توجيهاته الاستثنائية خلال مشروع البحث هذا. لقد أثرت خبرته وبصيرته بشكل كبير على اتجاه عملي.

بالإضافة إلى ذلك، أود أن أعرب عن خالص امتناني لعائلتي، التي قدمت لي التشجيع والإلهام باستمرار. لقد كان حبهم ودعمهم وإيمانهم الراسخ بي أمرًا حيويًا في رحلتي الأكاديمية.

Acknowledgment

First and foremost, I would like to praise Allah the Almighty, the Most Gracious, and the Most Merciful for His blessing given to me during my study and in completing this thesis. May Allah's blessing goes to His final Prophet Muhammad (peace be up on him), his family and his companions.

I am also profoundly grateful to my supervisor, Dr. Ashour Mohamed Ahmed, for his exceptional guidance during this research project. His expertise and insights have significantly influenced the direction of my work.

Additionally, I wish to convey my heartfelt gratitude to my family, who have consistently provided encouragement and inspiration. Their love, support, and steadfast belief in me have been vital to my academic journey.

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الملخص العربي

عنوان المشروع: محاكاة تشتت الضوء من الجسيمات النانوية استنادًا إلى نظرية مي

ذات شكل (Ag) في هذه الدراسة، تم استكشاف تشتت الضوء بواسطة جزيئات نانوية فضية النانوية على كفاءات Ag كروي باستخدام نظرية مي. تم تحليل تأثير نصف قطر جزيئات النانوية يشهد انزياحًا نحو وذلك مع Ag التشتت. وُجد أن الرنين البلازمي السطحي لجزيئات زيادة نصف قطر الجزيئات النانوية. يُعزى هذا الانزياح نحو الأحمر إلى تقليل القوة الكولومبية المستعادة. علاوة على ذلك، تصبح أوضاع البلازما من الدرجة الأعلى أكثر بروزًا في الجزيئات النانوية الأكبر. ايضا مع زيادة حجم الجزيئات النانوية، يتسع كل من شدة التشتت وعرض قمة الرنين بشكل تدريجي

Abstract

In this study, the scattering of light by spherical silver (Ag) nanoparticles was investigated using Mie theory. The effects of the Ag nanoparticle radius on scattering efficiencies were examined. It was found that the surface plasmon resonances of Ag nanoparticles experience a red shift as the radius of the nanoparticles increases. This red shift is attributed to a reduction in the restoring Coulomb force. Additionally, higher-order plasmon modes become prominent in larger nanoparticles. As the size of the nanoparticles increases, both the scattering intensity and the width of the resonance peak gradually broaden.

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Chapter1

General Introduction

1.1**Light**

Light is a form of electromagnetic radiation that occupies a specific part of the electromagnetic spectrum visible to the human eye. It is classified as a transverse electromagnetic wave, and its wave nature was first demonstrated through diffraction and interference experiments. Like all electromagnetic waves, light can travel through a vacuum.

Electromagnetic radiation spans a vast range of wavelengths, from gamma rays to radio waves. Within this broad spectrum, the wavelengths that humans can see form a narrow band, ranging from approximately 700 nanometers (nm) for red light to around 400 nm for violet light [1]. The regions adjacent to this visible spectrum are also referred to as light, with infrared on one end and ultraviolet on the other. The speed of light in a vacuum is a fundamental physical constant.

Electromagnetic radiation acts as a form of energy that propagates as both electric and magnetic waves, traveling in packets called photons. A photon is an elementary particle that represents a quantum of the electromagnetic field, encompassing various forms of electromagnetic radiation, including light and radio waves. Photons travel at the speed of light in a vacuum, carry no electric charge, are generally considered to have zero rest mass, and are stable particles. The concept of the photon was introduced by Albert Einstein in 1905 in his explanation of the photoelectric effect.

Light exhibits dual nature: it behaves as both a particle (photon) and a wave. This duality explains why light travels in straight lines and also how it can bend or diffract around objects.

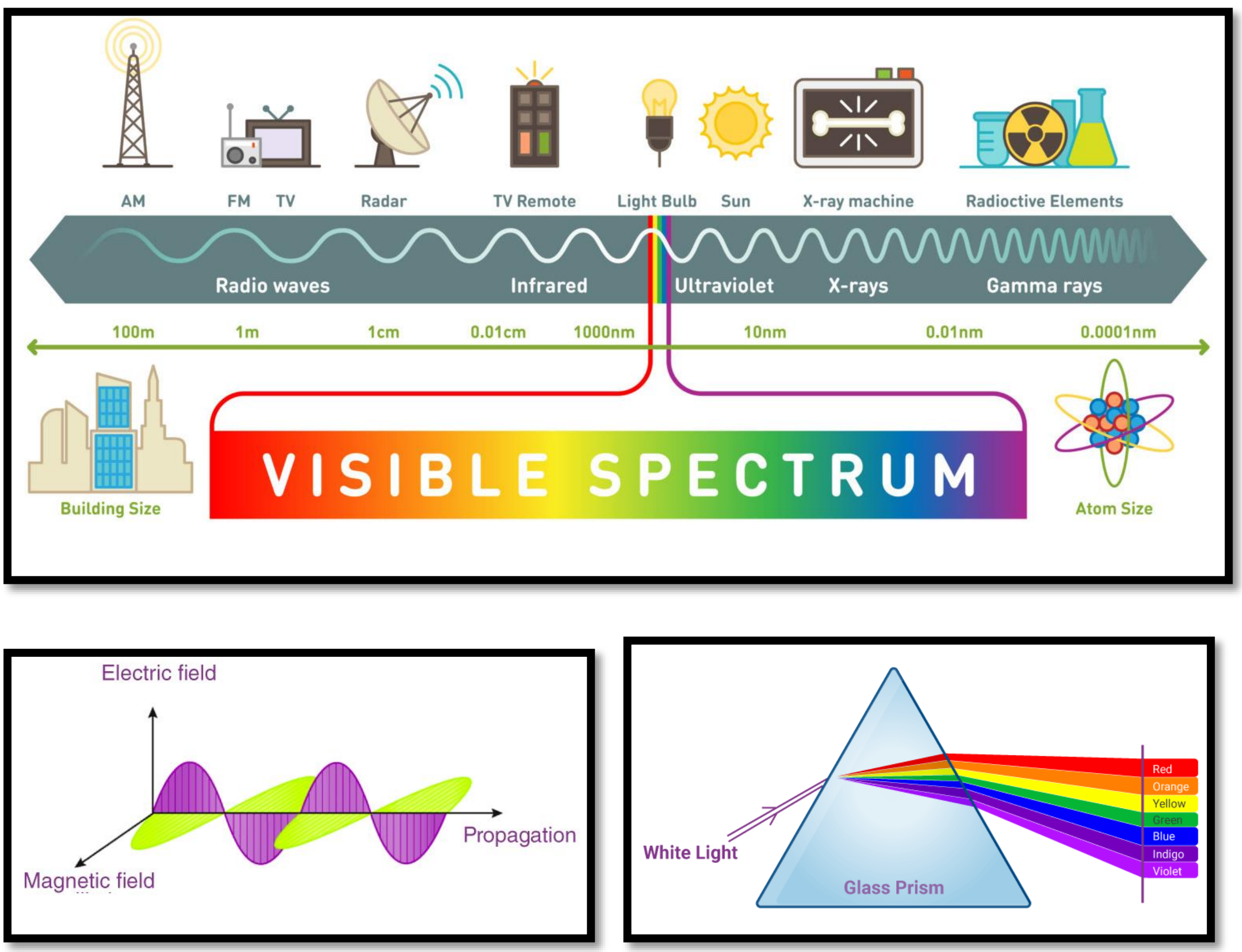

Figure 1.1 (a) Electromagnetic spectrum, (b) Electromagnetic wave, and (c) Visible light

1.2Light-Matter Interaction

When light interacts with matter, it can undergo several processes depending on its wavelength and the type of matter it encounters [2]. These processes include transmission, reflection, refraction, diffraction, absorption, and scattering.

Transmission is the simplest interaction, occurring when light passes through an object without interacting significantly with it. A common example is light passing through a window.

Reflection occurs when incoming light strikes a very smooth surface, such as a mirror, and bounces off. This is typical in scenarios where the surface is polished and smooth.

Refraction happens when light travels from one medium to another, such as from air to glass. As the light enters the new medium, it slows down and changes direction. This change in direction depends on the light’s wavelength, causing the spectrum of wavelengths to separate and spread out into a rainbow.

Diffraction occurs when light encounters an object that is similar in size to its wavelength. When light passes through a sufficiently thin slit, it diffracts and spreads out. If the light is visible, this process can also create a rainbow effect.

Absorption takes place when incoming light interacts with an object, causing its atoms to vibrate and convert the light energy into heat, which is then radiated. For instance, anyone with a dark-colored car on a hot day will experience the effects of absorption as the surface heats up.

Scattering occurs when incoming light bounces off an object in many different directions. A well-known example of this is Rayleigh scattering, where sunlight is scattered by the gases in our atmosphere, resulting in the blue color of the sky.

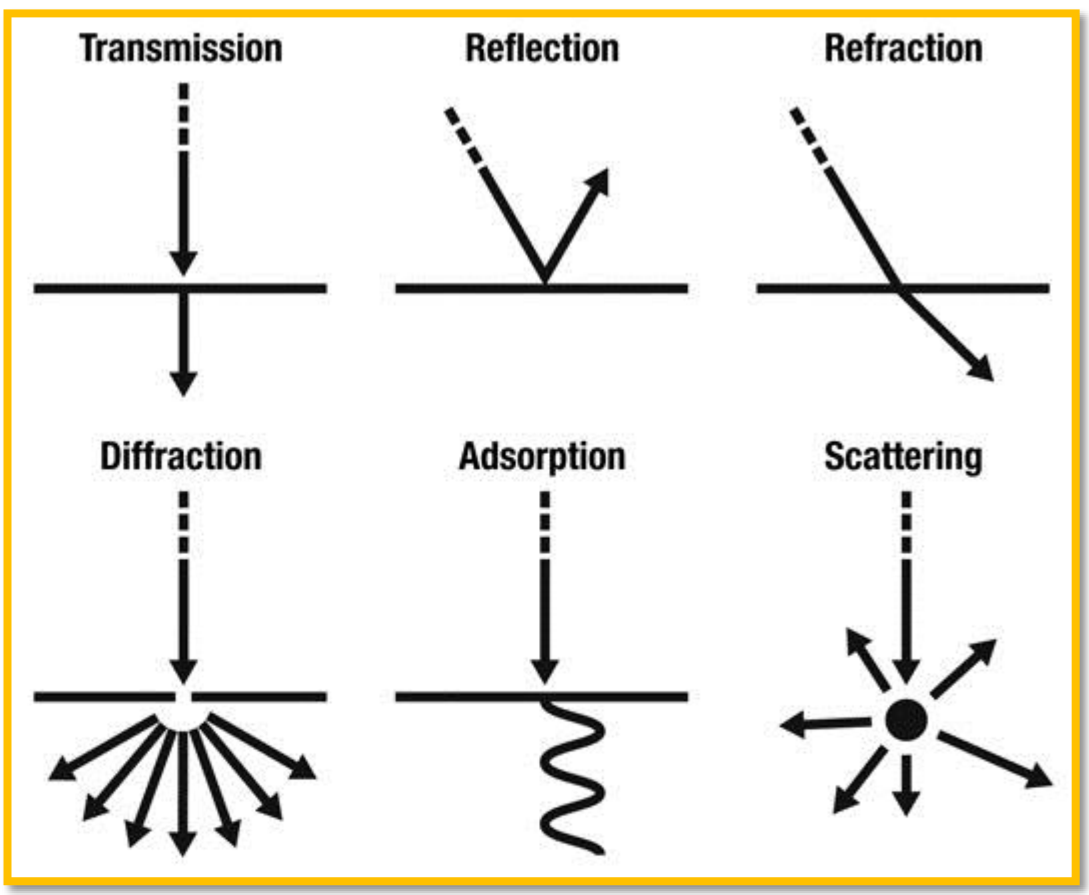

Figure 1.2. Methods of light interacts with matter

1.3Scattering of Light

In physics, scattering refers to the change in the direction of motion of a particle due to a collision with another particle. Such collisions can occur without direct physical contact, as seen when two like-charged ions repel each other due to electric Coulombic forces.

Light scattering is the phenomenon where light rays deviate from their straight path when they encounter obstacles such as gas molecules, dust, or water vapor. The particles cause the light to be redirected in different angles, enabling us to see objects when light scatters off their surfaces. As a result, the light rays are scattered in various directions. The extent of light scattering depends on several factors, including the size of the particles causing the scattering, the wavelength of the light being scattered, and the density of the medium containing the particles. The intensity of the scattered light is influenced by both the size of the particles and the wavelength of the light.

This scattering phenomenon leads to various optical effects, such as the Tyndall effect and the blue color of the sky, both of which are observable in everyday life. The Tyndall effect, also known as the Tyndall phenomenon, occurs when a light ray is scattered in a medium containing tiny suspended particles, like smoke or dust. This makes the light beam visible as it enters a room through a window. The effect is named after the

British scientist John Tyndall, who extensively studied it in the 19th century.

Shorter wavelengths and higher frequencies scatter more effectively due to the wavy nature of the light and its likelihood of intersecting with particles. The wavier the light, the more it will scatter after colliding with particles. Conversely, longer wavelengths, which have lower frequencies and are straighter, are less likely to collide with particles.

Scattering of light is responsible for optical phenomena such as the blue color of the sky. Particles and gases in the Earth's atmosphere scatter sunlight in all directions, with blue light being scattered more than other colors because it propagates as shorter waves. This is why the sky appears blue most of the time.

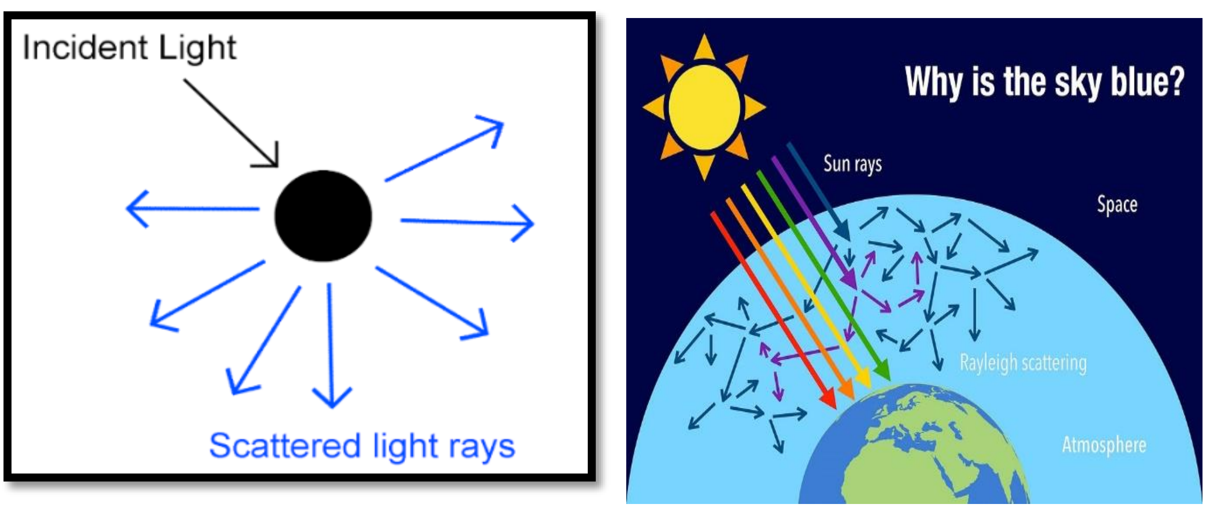

Figure 1.3. (a) Scattering light from nanoparticle (b) Scattering in the sky

1.4Types of Light Scattering

Light scattering is a diverse field with various types of scattering phenomena, each characterized by specific mechanisms, wavelengths, and applications. Understanding these different types of scattering is crucial for fields ranging from materials science to astronomy. Here are some of the key types of light scattering:

Rayleigh scattering is an elastic scattering process that occurs when light interacts with small particles, such as atoms or molecules. This type of scattering results in radiation being scattered uniformly in all directions. Importantly, Rayleigh scattering is wavelength-dependent, with shorter wavelengths being scattered more effectively than longer ones. This phenomenon is responsible for the blue sky we observe on clear days; the blue light from the sun is scattered about ten times more than red light as it interacts with molecules in the atmosphere. Consequently, while blue light is scattered into the eyes of observers, red light largely escapes back into space.

Mie scattering is an elastic scattering mechanism that occurs with relatively large particles or molecules whose dimensions are comparable to or larger than the wavelength of the incident light. Unlike Rayleigh scattering, Mie scattering produces non-uniform scattered radiation and is not significantly wavelength-dependent. This type of scattering contributes to the white light we see in clouds and fog, as the larger particles scatter all wavelengths of light more uniformly, resulting in a whitish appearance.

Brillouin scattering is an inelastic scattering mechanism primarily observed in the light scattering from solid materials. In this process, the wavelength of the incident radiation is modified due to interactions with sound waves or phonons within the material, resulting in very small shifts in energy. This scattering provides insights into the acoustic properties of materials and is valuable in fields such as condensed matter physics and materials science.

Raman scattering is another inelastic scattering process in which the frequency of the scattered light changes due to the gain or loss of energy corresponding to the energy levels in atoms or molecules. This technique is widely used for diagnostic analysis across various fields, including chemistry and biology. However, Raman scattering is typically very weak and much less intense than Rayleigh scattering, making it challenging to extract the Raman signal from the dominant Rayleigh signal. Careful techniques are required to isolate and analyze the Raman signal, especially for small frequency shifts.

Thomson scattering is an elastic scattering process involving the interaction of light with charged particles. This mechanism is closely related to Compton scattering, which is an inelastic form of Thomson scattering that occurs when the energy of the incident radiation approaches the rest energy of the charged particle. Thomson scattering is significant in plasma physics and astrophysics, while Compton scattering plays a crucial role in medical imaging, particularly in the attenuation of X-rays, which contributes to the contrast seen in X-ray photographs.

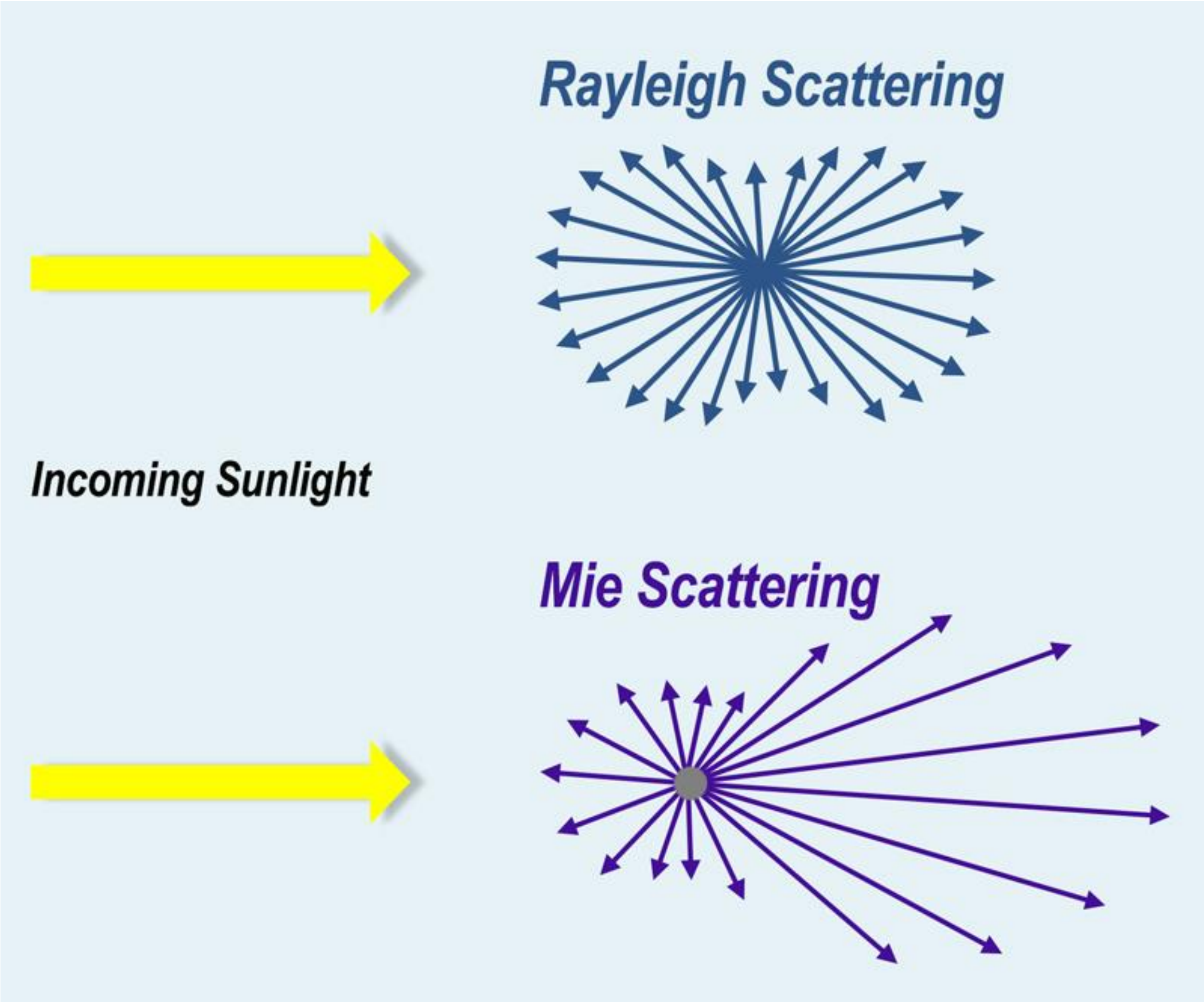

Figure 1.4. Rayleigh and Mie scattering

1.5Nanoparticle:

Nanoparticles are particles of matter with diameters typically ranging from 1 to 100 nanometers (nm) [3]. However, the term can also encompass larger particles up to 500 nm. They are of significant scientific interest as they bridge the gap between bulk materials and atomic or molecular structures. At the nanoscale, materials can exhibit size-dependent properties that differ markedly from their bulk counterparts. These nanoparticles possess a variety of unique properties relative to bulk materials. Their large surface-to-volume ratio means that a higher percentage of atoms or molecules are located on their surface, enhancing reactivity, adsorption, and catalytic properties. At the nanoscale, physical, chemical, electronic, magnetic, mechanical, thermal, and optical properties can diverge significantly from those of bulk materials due to quantum effects, allowing for tunable properties based on size.

The high surface area-to-volume ratio provides a substantial driving force for diffusion, especially at elevated temperatures, and can reduce the incipient melting temperature. For instance, 2.5 nm gold nanoparticles melt at around 300°C, compared to the bulk melting point of 1064°C. Additionally, copper nanoparticles smaller than 50 nm exhibit super hard characteristics and lack the malleability and ductility seen in bulk copper. Silver nanoparticles of varying sizes can display different colors due to surface plasmon resonance effects.

The use of engineered nanoparticles in consumer products has surged in recent years. They find applications in drug delivery systems, cancer targeting, dentistry, and various other industries. However, concerns remain regarding the unknown environmental and health impacts of nanoparticles, highlighting the need for further study and regulation.

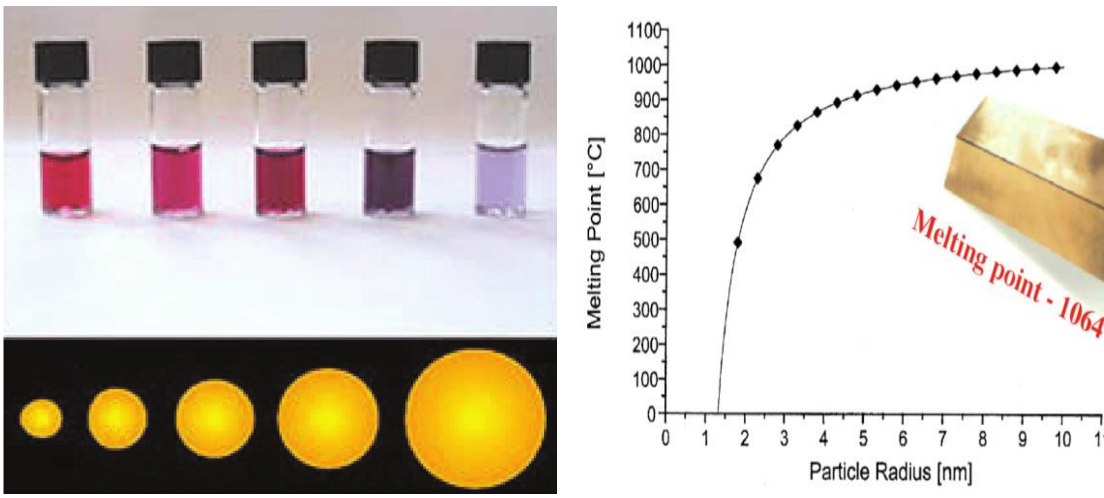

Figure 2.1. (a) Color of nanoparticle with change size (b) Melting point of Au with nanoparticle radius

1.6Surface plasmon resonance

In recent decades, the optical properties of plasmonic nanostructures have garnered significant interest, both theoretically and experimentally. A key feature attracting this attention is the presence of surface plasmon resonances (SPRs) at discrete frequencies (or wavelengths). SPRs occur when the free electrons within plasmonic nanoparticles (NPs) oscillate coherently in response to the alternating electric field of incident light. This oscillation induces surface polarization, resulting from the separation of negative charges (free electrons) and positive charges (ionic metal core) within each NP [4].

The Coulombic restoring force causes the electrons to oscillate back and forth on the NP surface, producing a dipole oscillation. This surface polarization generates a strong localized electric field around the NP, which is many orders of magnitude greater than the incident electric field. Plasmonic nanostructures have revolutionized nanophotonics by enhancing the interaction between light and nanostructures. The SPR of these nanostructures is highly sensitive to various factors, including size, geometry, gap distance, the refractive index of the surrounding environment, and the material composition of the NPs.

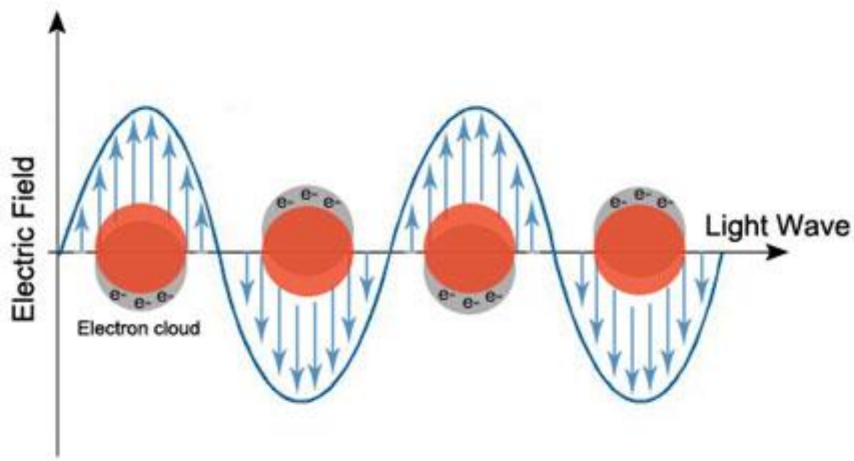

Figure 1.6. Surface plasmon resonances of metal nanoparticles

1.7Mie theory applications

Mie theory plays a crucial role in various fields, particularly in meteorological optics and particle characterization. Here are some key applications:

Atmospheric Science

Mie scattering occurs when the diameters of atmospheric particulates are comparable to or larger than the wavelengths of light. Common sources of Mie scattering include dust, pollen, smoke, and microscopic water droplets that form clouds. This type of scattering predominantly takes place in the lower atmosphere, where larger particles are more abundant, and is especially significant under cloudy conditions.

Cancer Detection and Screening

Mie theory is utilized in determining whether the scattered light from tissue samples corresponds to healthy or cancerous cell nuclei. This is achieved through angle-resolved low-coherence interferometry, a technique that enhances detection accuracy.

Clinical Laboratory Analysis

Mie theory is a foundational principle in nephelometric assays, which are widely used in medicine to measure various plasma proteins. This approach allows for the detection and quantification of a wide array of plasma proteins through optical scattering measurements.

Particle Sizing

Mie theory is frequently applied in laser diffraction analysis to assess particle sizing effects. This method provides valuable insights into the size distribution of particles in different materials.

1.8 Objective

The objective of this work is to conduct light-scattering simulations of nanoparticles using Mie theory. Specifically, it aims to investigate how the diameter of silver (Ag) nanoparticles influences the light scattering cross-sectional area. By understanding this relationship, we seek to provide insights into the optical properties of these nanoparticles. The findings are expected to enhance our understanding of how nanoparticle size affects light interaction, which can have significant implications for their applications in fields such as biosensing, imaging, and photonics.

Chapter 2: Theoretical analysis

2.1Maxwell's equations

Maxwell's equations consist of four fundamental equations that collectively describe the production and interrelation of electric and magnetic fields. Formulated by physicist James Clerk Maxwell in the 19th century, these equations encapsulate experimental laws governing electromagnetism.

The statements of these four equations are:

(1) electric field diverges from electric charge, an expression of the Coulomb force

(2) there are no isolated magnetic poles, but the Coulomb force acts between the poles of a magnet

(3) electric fields are produced by changing magnetic fields, an expression of Faraday's law of induction

(4) circulating magnetic fields are produced by changing electric fields and by electric currents

$$\nabla \cdot E = \frac{\rho}{\epsilon_0} \qquad (2.1)$$

$$\nabla \cdot B = 0 \qquad (2.2)$$

$$\nabla \times E = -\frac{\partial B}{\partial t} \qquad (2.3)$$

$$\nabla \times H = J + \frac{\partial D}{\partial t} \qquad (2.4)$$

Figure 2.3 Maxwell's equations

Where

$\boldsymbol{E}$ = electric field strength; $1\ \mathrm{V/m} = 1\ \mathrm{m\,kg\,s^{-3}\,A^{-1}}$
$\boldsymbol{D}$ = electric displacement; $1\ \mathrm{A\,s/m^2} = 1\ \mathrm{C/m^2}$
$\boldsymbol{H}$ = magnetic field strength; $1\ \mathrm{A/m}$
$\boldsymbol{B}$ = magnetic induction or magnetic flux density ;
$1\ \mathrm{V\,s/m^2} = 1\ \mathrm{T} = 1\ \mathrm{Wb/m^2}$
ρ = charge density; $1\ \mathrm{A\,s/m^3} = 1\ \mathrm{C/m^3}$
$\boldsymbol{j}$ = electrical current density; $1\ \mathrm{A/m^2}$
$\boldsymbol{P}$ = polarization density of a medium, $1\ \mathrm{A\,s/m^2}$
$\boldsymbol{M}$ = magnetization density of the medium, $1\ \mathrm{V\,s/m^2}$
$\varepsilon_0 \simeq 8.859 \times 10^{-12}\ \mathrm{A\,s/V\,m}$ is the permittivity of vacuum
$\mu_0 = 4\pi \times 10^{-7}\ \mathrm{V\,s/A\,m}$ is the permeability of vacuum
$\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ Nabla-operator
$\partial/\partial t$ = differentiation with respect to time.

2.2Mie theory

The interaction of light with metallic nanoparticles leads to the scattering and absorption of incident waves. The scattering as a function of wavelength can be calculated using Mie theory. This formulation involves solving Maxwell's equations for the interaction of light with a metallic nanoparticle in spherical polar coordinates. The solutions are expressed as an infinite series, with the constant coefficients determined by the appropriate boundary conditions at the surface of the sphere.

The scattering efficiency ($Qsca$) of a spherical nanoparticle with area πr^2, are given by the following equations [5] [6]

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2), \qquad (5)$$

Where, a_n and b_n are the Mie coefficients for the coated core and can be given in the forms,

$$a_n = \frac{\psi_n(y)[\,\psi_n'(n_2y) - A_n\varphi_n'(n_2y)] - \,n_2\psi_n'(n_2y)[\psi_n(n_2y) - A_n\varphi_n(n_2y)]}{\varphi_n(y)[\,\psi_n'(n_2y) - A_n\varphi_n'(n_2y)] - \,n_2\varphi_n'(n_2y)[\psi_n(n_2y) - A_n\varphi_n(n_2y)]}, (6)$$

$$b_n = \frac{n_2\psi_n(y)[\,\psi_n'(n_2y) - B_n\varphi_n'(n_2y)] - \,\psi_n'(n_2y)[\psi_n(n_2y) - B_n\varphi_n(n_2y)]}{n_2\varphi_n(y)[\,\psi_n'(n_2y) - A_n\varphi_n'(n_2y)] - \,\varphi_n'(n_2y)[\psi_n(n_2y) - B_n\varphi_n(n_2y)]}, (7)$$

Where A_n and B_n are derived from the relations

$$A_n = \frac{n_2\psi_n(n_2x)\psi_n'(n_1x) - n_1\psi_n'(n_2x)\psi_n(n_1x)}{n_2\varphi_n(n_2x)\psi_n'(n_1x) - m_1\varphi_n'(n_2x)\psi_n(n_1x)}, \qquad (8)$$

$$B_n = \frac{n_2\psi_n(n_1x)\psi_n'(n_2x) - n_1\psi_n(n_2x)\psi_n'(n_1x)}{n_2\varphi_n'(n_2x)\psi_n(n_1x) - n_1\varphi_n(n_2x)\psi_n'(n_1x)}. \qquad (9)$$

Where (n_1, n_2), (x, y), and (r_1, r_2) represent the refractive indices, size parameters, and radii of the core and the shell, respectively. Ψ refers to Riccati function and φ represents Bessel function.

Chapter3: Results and Discussions

3.1 Effect of Ag nanoparticle diameter on the light scattering cross-sectional area

The scattering cross-sectional area of the pure Ag nanoparticle calculated based on Mie theory. The radius of nanoparticles are ranging from 5 to 100 nm in air as seen in Figure 7. There is Mie resonance wavelength peak for each Au thickness. The resonance peak has the highest amplitude on all curves. After the peak, the scattering rapidly decreases. These peaks were increased and shifted to the longer wavelength with increasing the diameter of the nanoparticle. Such increment backs to the plasmon resonance of the Ag nanoparticles, which greatly affect the electromagnetic wave and induce more scattering towards longer wavelengths.

The coherent oscillations of free electrons within the plasmonic nanoparticles in response to the alternating electric field of the incident light produce surface polarization around the nanoparticles. As the size increased, the charge separation between negative charges (free electrons) and positive charges (ionic metalcore) is increased. Hence, the Coulomb attraction force between the oscillating electrons and ions core will be decreasing. This is resulting in lowering the plasmon resonance energy, which is red-shifted in the plasmon resonance peak.

The relation between the Ag radius and the Mie resonance wavelength peak is shown in Figure 8. The peak position rapidly increases with Au diameter. The peak shifted from 355 to 580 nm as the Ag radius increase from 5 to 200 nm.

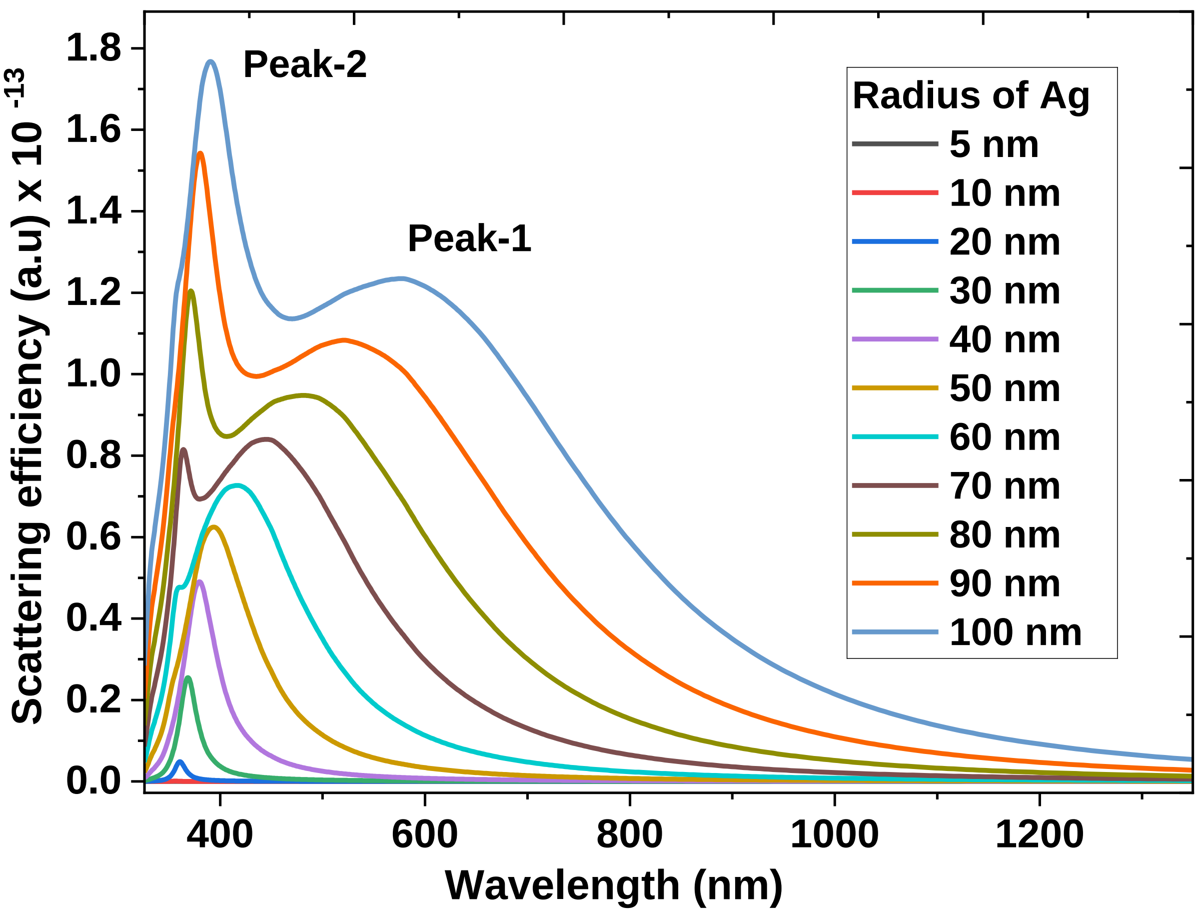

Figure 3.1 The calculated scattering cross-sectional area of Ag nanoparticle with different diameters ranged from 5 to 100 nm in air.

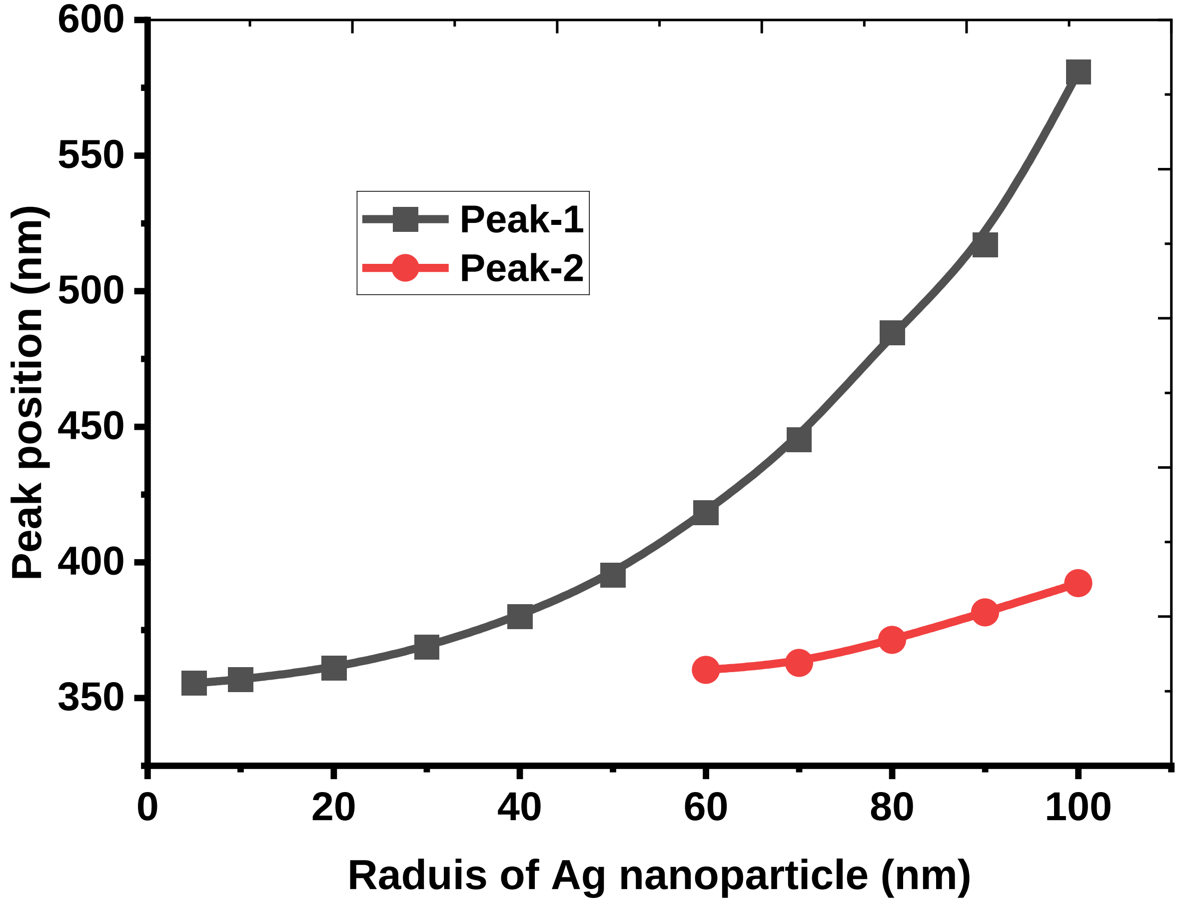

Figure 3.2 The resonance wavelength peaks position as a function of the radius of Ag nanoparticle

Conclusion

Mie theory was employed to calculate the optical response of silver (Ag) nanoparticles while varying their radius. It was observed that the plasmonic peaks of Ag nanoparticles are red-shifted with an increasing radius. Additionally, the introduction of higher-order plasmon modes complicates the spectra as the radius changes. Consequently, Ag nanoparticles have potential applications in various fields, including photothermal therapy, sensors, optical imaging, surface-enhanced Raman spectroscopy, photovoltaics, catalysis, and cancer therapy.

References

[1] E. Austin et al., Visible Light Part I. Properties and Cutaneous Effects of Visible Light. J Am Acad Dermatol. 2021 Feb 25;84(5):1219–1231. doi: 10.1016/j.jaad.2021.02.048

[2] J. Weiner and P.T. HO, Light-Matter Interaction: Fundamentals and Applications, John Wiley 2003. DOI:10.1002/9783527617883

[3] S. Shrestha et al., Nanoparticle processing: Understanding and controlling aggregation. Advances in Colloid and Interface Science, Volume 279, May 2020, 102162. https://doi.org/10.1016/j.cis.2020.102162

[4] M. A. Basyooni et al., Plasmonic hybridization between two metallic nanorods. Optik 172 (2018) 1069–1078. https://doi.org/10.1016/j.ijleo.2018.07.135

[5] A. M. Ahmed et al., Scattering spectra of magneto-plasmonic core/shell nanoparticle based on Mie theory. Mater. Res. Express 6 (2019) 085073. https://doi.org/10.1088/2053-1591/ab2145

[6] F.-X. Chen et al., Design and optimization of Ag-dielectric core-shell nanostructures for silicon solar cells. AIP ADVANCES 5, 097129 (2015) http://dx.doi.org/10.1063/1.4930957