Chapter 1

Introduction

In this chapter we discuss the light-matter interaction in the nano region. A focus is given towards the Mie scattering describing the interaction of light with plasmon-assisted nanoparticles which have size comparable to incident wavelength. Such interactions are considered and described for beams with structured patterns in the low and high convergence angles. Limitations of commercially available software and tools, particularly, on study of scattering of the tightly focused beams, are also highlighted. An algorithm has been developed considering the Mie theory and multipole expansion approach. Motivation behind attraction towards structured beams is elaborated by showing direct applications of such beams in practice.

1.1 Nanophotonics: Light-matter interaction at nanoscale

Light from natural and manmade sources, plays a crucial role in our daily lives. The interaction of the light wave with a material system generally includes a vast realm from classical and quantum electrodynamics, optical physics, imaging, from black holes to mesoscopic, nanophotonics, plasmonics etc. However, unless light comes in contact with matter, it will continue to travel undisturbed from the furthest outskirts of the universe. Our experiences with light are pivoted with its some of the fundamental features such as amplitude, wavelength, and polarization etc. when it interacts with a matter. Depending upon type of a matter such as crystalline, amorphous, molecular, and atomic, its interaction with light causes numerous phenomena like reflection, refraction, transmission, diffraction, dispersion, absorption, scattering, etc. [1, 2]. The process by which light-matter interacts, specifically absorption and scattering, are strongly influenced by the size and structure of the material.

The interaction between light and matter also varies with the change in length scales of the matter relative to the wavelength of the incident light. When light is incident on nanostructures, the properties observed are in contrast with those observed from their respective bulk material or in microscale. Such interactions are of great interest due to its uniqueness and numerous applications. Fig. 1.1 shows one such example of gold (Au) metal at different length scales varying from macroscale to nanoscale [3].

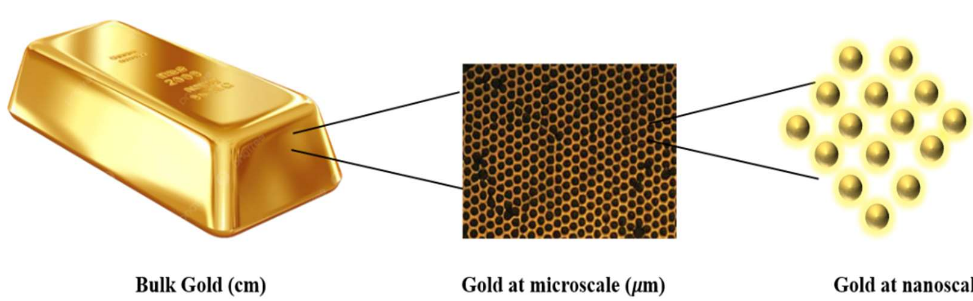

Fig. 1.1 Gold (Au) metal at different length scales [3].

The branch of optics where the behaviour of light-matter interaction at the nanometre scale is examined is referred as nanophotonics [4, 5]. With a shift from microscale towards nanoscale, light-matter interaction offers various opportunities in miniaturization of electronic devices, sensing technologies, optical tweezers, surface-enhanced Raman spectroscopy (SERS), bio-medical imaging, super lensing, microscopy, solar energy technology, super-resolution, and in many more areas [6-10]. Nanophotonics encompasses new ways of sculpting the flow of light with nanostructures and exhibits fascinating optical properties never seen in macro-world [4]. Fig. 1.2 presents different shapes of Au nanostructures available nowadays [11]. With these unique abilities to show plasmonic excitations, and to enhance local electromagnetic (EM) fields, nanophotonics has captured the attention of many researchers from past few decades. More specifically, plasmonics, i.e. the resonant interaction of light with metals, has drawn a significant attention lately due to its exceptional optical qualities and wide range of novel applications in sensing, microscopy, SERS, and many more [12-19].

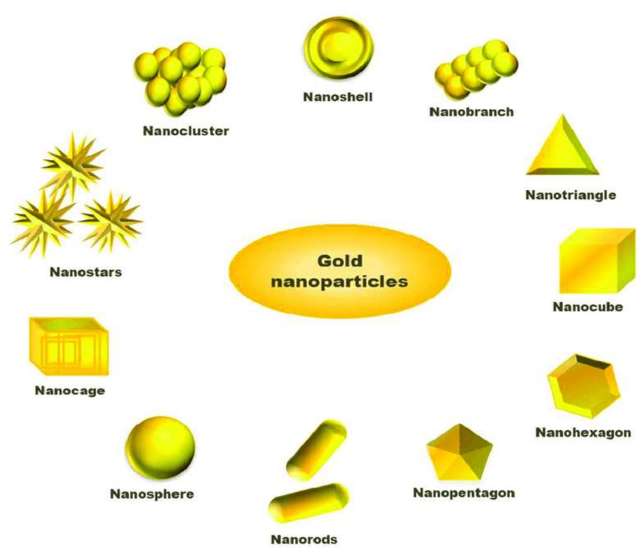

Fig. 1.2 Various nanostructures [11].

Moreover, plasmonics plays a key role in strengthening and enlarging the scope of nanophotonics due to the extraordinary features observed in sub-wavelength structures with spatial dimensions smaller than the wavelength of the incident beam [20-24]. The study of plasmonic response requires investigation in near-field, i.e. observations at a distance smaller than the wavelength of the incident light,

$$L < \frac{\lambda}{n}$$

where L is the subwavelength distance, λ is the wavelength of the incident beam in vacuum, and n is the refractive index of the surrounding medium [22-25]. To perform such investigations, techniques like nanoscopy, scanning near-field optical microscopy (SNOM), tip-enhanced Raman spectroscopy (TERS), atomic force microscopy (AFM) etc. are desired [26-31]. Near-field observations take advantage of the strong localized enhanced fields on the surface of plasmonic nanostructures.

1.2 Plasmonic Nanostructures

When it comes to studying optical phenomena involving nanostructured metal systems at the nanoscale, this branch of optical condensed matter science is also termed, as Nanoplasmonics. Such metal nanostructures have remarkable property of concentrating the optical energy on the nanoscale due to modes, a collective oscillations of electrons, whose quantum is known as surface plasmons [22-25]. Metal nanostructures supporting these plasmons are referred to as plasmonic nanostructures. Plasmonic nanostructures are promising candidates for future advancements in nanophotonics because of possessing unique ability to manipulate light at the nanoscale [31-33]. These nanostructures can be fabricated using metals such as gold (Au), silver (Ag), copper (Cu), aluminium (Al), and other noble metals since they have ability to support surface plasmon resonance. Due to incident EM waves of appropriate frequency and polarization, surface plasmons are generated on the metal-dielectric interface and/or on the surface of the nanostructures that have a bounded geometry such as metallic nanoparticles, nanoshells, and voids of various topologies.

1.2.1 Surface Plasmon Resonance

On illuminating the metal-dielectric interface by an external light electric field, the freely moving electrons at the metal surface got displaced from the lattice ion under the influence of the electric field of the light, and produced positive charges on the opposite surface of metal along the electric field as shown in Fig. 1.3. A restoring force also exists since there is an attraction between charges. This simultaneous displacement and attraction between charges, result in generation of surface plasmon polaritons (SPPs) [33]. A sustainable resonance of EM wave obtained is referred as surface plasmon resonance (SPR), whose frequency is determined by the restoring force and effective mass of the electron.

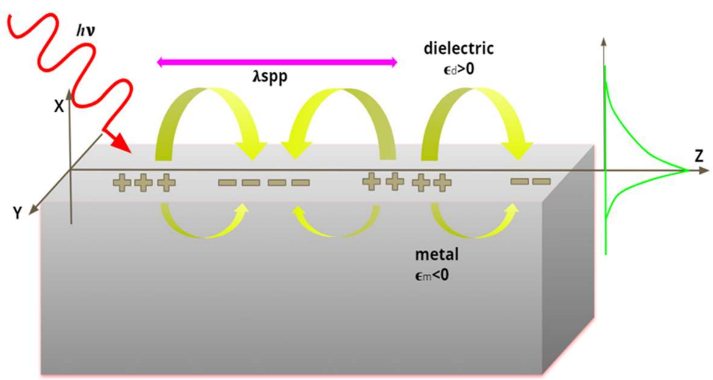

Fig. 1.3 Surface plasmon polariton.

In Fig. 1.3, the geometry consists of two semi-infinte media with dielectric constants ϵ_m, and ϵ_d of a metal and a dielectric material respectively. There are certain conditions for SPR excitation [21-25]:

1) The SPR get excited by transverse magnetic (TM) polarized light incident on the metal-dielectric interface, where as no surface modes exist for transverse electric (TE) polarized incident beam [21-24]. For TM modes, the EM fields in the metal and dielectric material is [25]

$$E_j(r,t) = \left(E_{xj}, 0, E_{zj}\right)e^{-k_{zj}|z|}e^{i(k_{xj}x-\omega t)}, \quad (1.1a)$$

$$H_j(r,t) = \left(0, H_{yj}, 0\right)e^{-k_{zj}|z|}e^{i(k_{xj}x-\omega t)} \quad (1.1b)$$

Where (j= metal (m), dielectric (d)), k_{zj} is the z component of the wave vector (k-vector) in the medium j, and k_{xj} is the x component of the wave vector. ω is the radial frequency of the radiation. Substituting Eq. (1.1a, 1.1b) into Maxwell's equation and applying the continuity conditions $E_{xm} = E_{xd}$; and $H_{ym} = H_{yd}$ and using the relation $k_{zj}^2 + k_{xj}^2 = \left(\epsilon_j \frac{\omega}{c}\right)^2$ lead to:

$$\frac{k_{zm}}{\epsilon_m} + \frac{k_{zd}}{\epsilon_d} = 0 \quad (1.2)$$

where ϵ_j is the relative permittivity of the medium j and c is the speed of light in the vacuum [25].

2) Surface plasmons generated on the metal-dielectric interface depend on the fact that the dielectric function of the metal must have negative real part i.e., $Re(\epsilon_m) < 0$. This condition highlights the requirement that the real part of the dielectric constants of two interfaces have opposite sign and satisfy: $Re(\epsilon_m) < -\epsilon_d$. At frequencies below the plasma frequency, the collective oscillations of free electrons dominate, and the real part of the metal's permittivity become negative.

3) Using this relation and the phase matching condition $k_{xm} = k_{xd} = k_x$, the SPP wavevector (k_{SP}) is given as,

$$k_x = k_{SP} = \frac{2\pi}{\lambda}\left(\frac{\epsilon_m\epsilon_d}{\epsilon_m+\epsilon_d}\right)^{1/2} \quad (1.3)$$

This is also known as the dispersion relation of the propagating surface plasmons, and is valid even if ϵ_m is complex. Wave vector of the incident beam is large enough to satisfy the momentum matching i.e. $k_x = k_{SP}$. The matching of the momentum of the incident light with that of the surface plasmon wave is achieved by using techniques like prism coupling (via Kretschmann or Otto configurations) or grating coupling[21-25].

A plasmonic metal is considered to be good enough when it satisfies these two properties simultaneously,

$$Re(\epsilon_m) < 0, \text{ and } Im(\epsilon_m) \ll Re(\epsilon_m).$$

The ratio of real and imaginary parts of metal's permittivity, termed as Quality factor ($Q = -Re(\epsilon_m)/Im(\epsilon_m)$. It provides an estimate to the number of oscillations a surface plasmon may undergoes before it decays and subsequent increase in the local optical-field intensity when an external optical field excites SPs resonantly [21-24]. The resonant amplification in the near-field intensity is proportional to Q^2, and for noble metals, ranges between 10^2 and 10^4.

1.2.2 Localized Surface Plasmon Resonance

Nanostructures composed of subwavelength structural units such as nanoparticles, nanoshells, voids of various topologies, etc., the surface plasmons cannot propagate more than the size of this structural unit, and becomes localized [25]. The plasmons generated on the surface of nanostructures that have a bounded geometry are termed as localized surface plasmon polaritons (LSPs) [21-25]. The resonance arising due to conduction electrons of metallic nanostructures coupled to the incident EM field is referred to as localized surface plasmon resonance (LSPR) as represented in Fig. 1.4.

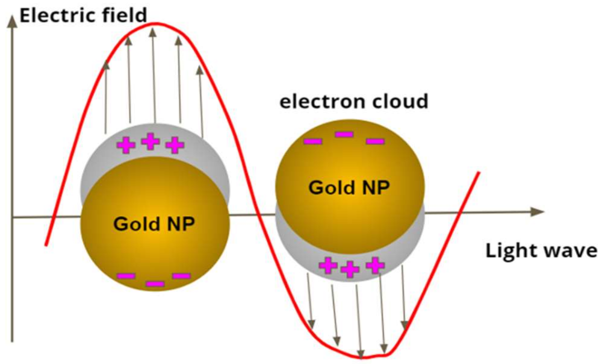

Fig. 1.4 Localized surface plasmon polaritons.

The SPR discussed in the preceding section is a different type of excitation than LSPR. The SPPs are propagating surface waves, generated on the planar interface whereas LSPs are bounded on the nanoparticle's surface, making them non-propagating surface waves. LSPs can be excited by direct light illumination, in contrast to propagating SPPs which can be excited only by employing the phase-matching techniques such as prism coupling, grating coupling etc. [22-24].

Nanoparticles composed of subwavelength structural units exhibit LSPR, and are termed as plasmonic nanoparticles. Plasmonic nanoparticles have emerged as an exciting platform for manipulating light-matter interactions at the nanoscale. They are capable to show strong scattering efficiency, and large optical field enhancement in comparison to their bulk counterpart. The ability of metallic nanoparticles to sustain an EM resonance while being much smaller than the incident wavelength has become the point of attraction. Since an LSP is confined to a bounded surface, it results in a significant EM field enhancement at small metallic particles due to the small volume of the LSP mode. Spherical nanoparticles have sparked a flurry of research in the field of nanophotonics and nanoplasmonics, and it has innovative applications in optical trapping and binding, surface-enhanced Raman scattering, photonic imaging, biosensors, solar energy technology, and many others [34-37].

1.3 Different plasmon-assisted nanoparticles

Plasmon-assisted nanoparticles utilize LSPR to enhance the light-matter interactions at the nanoscale. The excitations of plasmonic metal nanoparticles absorb and scatter light at optical frequencies, making their resonant characteristics easily observable to the unaided eye. One of the most ancient examples is the famous fourth-century Lycurgus cup from the British Museum, whose glass looks green in reflected light but ruby red in the transmitted light [38]. Those colour changes are the plasmonic effects due to the interaction of light with tiny metal nanoparticles embedded in the glass.

The frequency of the surface plasmons generated on the surface of metallic nanoparticles, and the local field enhancement depends on their shape, size, composition, and symmetry. The topology of a particle plays a significant role in determining the sensitivity of various optical sensors. Though localized surface plasmon resonance (LSPR) is also realized in some conducting metal oxides and semiconductor quantum dots, metallic nanoparticles are considered to be the most favourable in plasmonic applications [39, 40]. Generally, Au, Ag, and Cu metallic nanoparticles are studied due to their LSPR peaks in the visible-near infrared (vis-NIR) region of wavelength [41-44]. In this thesis, we have investigated different metallic nanoparticles exhibiting plasmonic response.

1.3.1 Monometallic/Uncoated nanoparticles

Among the available noble metals Au, and Ag shown in Fig. 1.5, are the well-known examples and garnered the most attention in terms of synthetic refinement and clarification of the resulting nanoscale properties. The Au nanoparticle has high chemical and physical stability, and also shows an ease in functionalization with organic and biological molecules [45, 46]. On the other hand, Ag nanoparticles have also received significant attention because they possess the highest molar extinction coefficient of any metal. The Ag nanoparticles show higher sensitivity to the surrounding medium refractive index and offer appreciable near-field intensity enhancement due to high scattering efficiency and low absorption cross-section. However, the synthesis of uniform and symmetric shapes of Ag nanoparticles is a challenging task apart from its possibility of oxidation which degrades the performance in different media. Unlike Ag nanoparticle, Au nanoparticle does not get oxidized due to its high chemical stability, and least reactive nature which adds to the possibility of higher levels of size homogeneity in Au nanoparticles [45, 46]. Unfortunately, the scattering efficiency of Au nanoparticle is lower in comparison to the Ag nanoparticles.

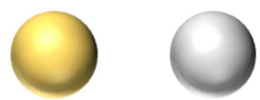

Fig. 1.5 Monometallic (a) Au, (b) Ag nanoparticles.

1.3.2 Core-shell/coated nanoparticles

However, monometallic Au and Ag nanoparticles have been the center of attraction for many years to researchers but they have limited practical use because of a severe susceptibility to oxidation of Ag nanoparticles and restricted scattering efficiency of Au nanoparticles. Yet, important outcomes and results are possible by manipulating the nanoparticle structure or composition in multicomponent type nanoparticles that provide insight into how to truly control novel plasmonic properties. Such initiatives can be applied to a broad range of nanoparticle systems. The Ag and Au based alloys or core-shell nanoparticles have turned out to be the better options such as Ag@Au nanoparticles, and Au@Ag nanoparticles [45-49]. Since the functionality of core-shell NP can be controlled by varying the core and shell thickness, and coated nanoparticles show promising applications in molecular sensing, bio-diagnostics, and many more.

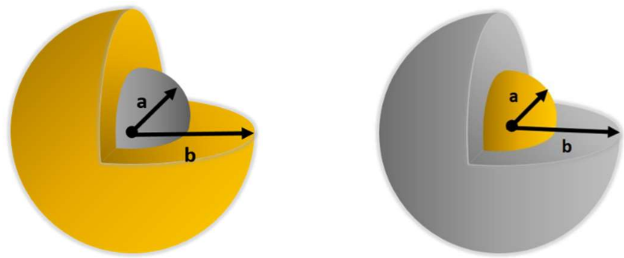

Fig. 1.6 Core -shell nanoparticles **(a)** Ag@Au nanoparticle, **(b)** Au@Ag nanoparticle.

We can opt for core-shell configurations such as Au@Ag nanoparticles and Ag@Au nanoparticles as represented in Fig. 1.6. Au@Ag core-shell nanoparticles are observed to maintain their spherical morphology in different media [50-52]. In practical terms, the Ag@Au structure carries many drawbacks, including high suppression of the optical properties of Ag by the Au shell, as well as significant challenges in synthesizing a probe with a uniform structure. On the contrary, it has been observed that coating Au core with Ag (Au@Ag) prevents surface oxidation and gives a high level of intensity enhancement in comparison with monometallic Ag nanoparticle and Au nanoparticle, and Au coated over Ag core (Ag@Au) nanoparticle. A significant enhancement factor has been reported when a two-dimensional (2D) assembly of Ag coated Au nanoparticle is used in SERS [53]. A study on the near-field intensity enhancement due to the coating of Ag on Au core is an emerging topic of investigation as it allows tailoring the scattering efficiency required for various applications.

1.4 Scattering of Light

Light scattering refers to the redistribution of light energy and its profile after interaction with scatterer, particles or some colloids present in the medium. Scattering of light is a natural phenomenon and its optical effects are observed commonly in our surroundings such as the blue colour of sky, red sunsets, the white color of clouds, etc. Depending upon material size and the amount of energy transferred in the process, spatial and temporal fluctuations in the medium's properties, scattering processes are classified in different categories such as Raman scattering, Rayleigh scattering, and Mie scattering, etc. as mentioned in Fig. 1.7 [25, 54-56]. Spatial fluctuations such as variation in material structure, density, refractive index, result in elastic scattering, where the scattered light retains the same wavelength as the incident light. On the other hand, time-dependent changes, such as molecular motion, acoustic waves, result in inelastic scattering, where the scattered light undergoes a wavelength shift due to energy exchange with the medium [25]. The Rayleigh and Mie scatterings are the elastic ones, whereas Raman scattering, Brillouin Scattering involves inelastic scattering. The nature of the scattering is highly influenced by the size of the particle and the Rayleigh and Mie scattering approaches are commonly used to explain such scatterings. Rayleigh scattering is used when the particle size is much less than the wavelength of light. For spherical particles having a size comparable to the wavelength of the incident light, Mie scattering is useful.

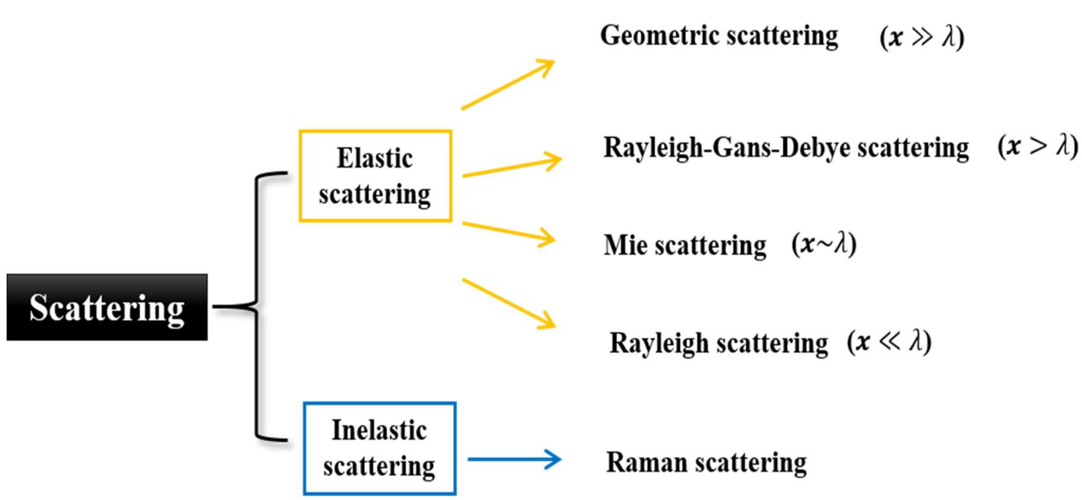

Fig. 1.7 Scattering of light in nature.

Mie scattering, is named after German physicist Gustav Mie, and is considered to be the reason behind the white color of clouds in the sky, and the origin of solar corona was answered using Mie solutions [56-59]. In 1908, he performed simulations to explain the color effects connected with colloidal Au particles, and provided an approach for calculating the light scattering by small spherical particles by utilizing Maxwell's EM theory [59]. With the help of these computations, he explained the reason behind changing the color of Au colloids with changing the size of the Au spheres, which was later interpreted in terms of surface plasmon resonances.

1.4.1 Mie Theory and Multipole Expansion

EM scattering by a homogeneous, spherical particle composed of isotropic material can be analyzed readily using the Mie theory, which is also referred to as Lorenz-Mie theory, or even Lorenz-Mie-Debye theory. Mie theory provides a general rigorous solution based on Maxwell's EM theory, which explains the optical scattering by a homogeneous sphere of arbitrary size in a homogeneous medium, regardless of the composition of the sphere and the surrounding medium [58-60].

Scattering of light wave from a single nanoparticle is considered which implies that the particle scattering the incident beam is unaffected by the neighbouring particles, and a multiple scattering is also neglected. This theory provides exact solutions to the problem and give information about the contribution of each mode [59]. This theory has been extended to the interaction of light in absorbing medium, coated spheres, magnetic spheres, distorted spheres, a chiral and anisotropic spheres, to name a few. Mie theory not only validates various advanced theories but also it is a basis to the radiative transfer, Lidar, and optical particle characterization [61-64].

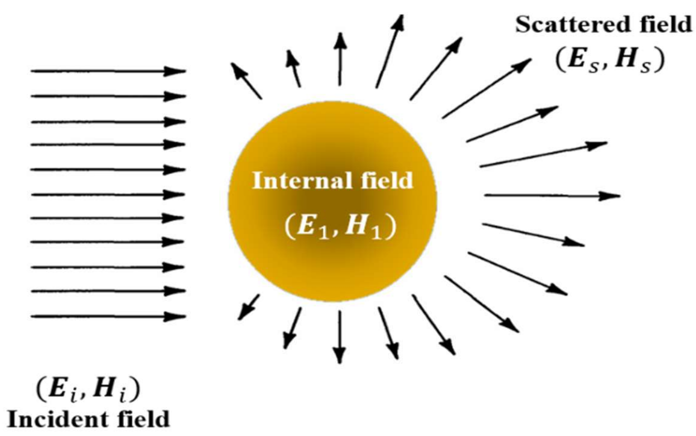

Fig. 1.8 Mie Scattering.

Fig. 1.8 shows the interaction between a spherical nanoparticle and an incident EM field (E_i, H_i). (E_1, H_1) represents the internal field i.e. absorbed by the metallic nanoparticle, and (E_s, H_s) is the EM field scattered by the nanoparticle [65]. For a theoretical calculation, the scattering of a linearly polarized plane wave with a spherical nanoparticle of radius size $'r'$ embedded in a surrounding medium (refractive index, n_m) is considered. Mie solutions include spherical polar coordinates (r, θ, ϕ), and dimensionless size parameters $(x = 2\pi n_m r/\lambda)$ on the surface of the nanoparticle.

The analytical solution of the incident, internal, and scattered EM field is given by Mie theory using a multipole expansion (ME) approach and incorporating vector spherical harmonics, and spherical Bessel and Hankel functions [65-68]. Decomposing the field to its constructing modes is another advantage of using ME formalism, and each of these modes has certain properties such as directivity, confinement, etc. The electric field has a general form

$$\boldsymbol{E}(\boldsymbol{r}) = \sum_{m=0}^{\infty} \sum_{n=m}^{\infty} (B_{emn}^{(p)} \boldsymbol{M}_{emn}^{(p)} + B_{emn}^{(p)} \boldsymbol{M}_{emn}^{(p)} + A_{emn}^{(p)} \boldsymbol{N}_{emn}^{(p)} + A_{omn}^{(p)} \boldsymbol{N}_{omn}^{(p)}) \quad (1.4)$$

where $\boldsymbol{M}_{emn}$, $\boldsymbol{N}_{emn}$, $\boldsymbol{M}_{omn}$, & $\boldsymbol{N}_{omn}$ are the vector spherical harmonics. The scalar fields satisfy the Helmholtz equation and Maxwell's equation, and are constructed using generating functions which

$$\Psi_{emn}^{(p)} = cos\ (m\phi)\ P_m^n(cos\ \theta)\ z_n^{(p)}(kr) \tag{1.5}$$

$$\Psi_{omn}^{(p)} = sin\ (m\phi)\ P_m^n(cos\ \theta)\ z_n^{(p)}(kr) \tag{1.6}$$

A_{emn}, A_{omn}, B_{emn}, and B_{omn} are the expansion coefficients, derived using orthogonality relations. The subscripts 'e' and $'o'$ represent the even and odd parity of the scalar potential, $'m'$ is the order of an associated Legendre polynomial $P_n^m(cos\theta)$, and degree $'n'$ is referred as the order of multipoles [65, 69].

$z_n^{(p=1,2,3,4)}$ is any of the four spherical Bessel functions j_n, y_n, $h_n^{(1)}$, and $h_n^{(2)}$ in order of $'p'$ respectively. Since, the incident field is finite at the origin, and the spherical Bessel function of the first kind (j_n) appropriately represents the incident field at the origin instead of the spherical Bessel function of the second kind (y_n). $h_n^{(1)}$ has the physical meaning of an outgoing wave, and is referred as the spherical Hankel function of the first kind (or spherical Bessel function of the third kind). The spherical Hankel function of the second kind, $h_n^{(2)}$ (or spherical Bessel function of the fourth kind) signifies an incoming wave. Thus, for an incident field and internal field, Bessel function of first kind (j_n) is appropriate, and $p = 1$ in eq. (1.4), whereas spherical Hankel function of the first kind $h_n^{(1)}$ is considered for a scattered EM field, i.e. $p = 3$ [65, 70].

Eq. (1.4) can be derived for different incident beams using orthogonality relations for $\boldsymbol{M}_{emn}$, $\boldsymbol{N}_{emn}$, $\boldsymbol{M}_{omn}$, & $\boldsymbol{N}_{omn}$. The scattered ($\boldsymbol{E}_s$) and internal ($\boldsymbol{E}_{int}$) fields can be evaluated by satisfying the boundary conditions for the electric and magnetic fields over the surface of nanoparticle. Based on the orthogonality relations between multipoles, it is deduced that scattered field ($\boldsymbol{E_s}$) can only have those orders, which are present in the incident field ($\boldsymbol{E_i}$).

The scattered field (E_s, H_s) depends on certain parameters and functions namely:

- Refractive index (real/complex)
  - Nanoparticle
  - Surrounding medium
- Size parameters (dimensionless)
- Spherical Bessel and Hankel functions

The mathematical expressions of incident, and scattered EM fields are presented in detail in Chapter 2.

1.4.2 Observations based on the plasmonic response of the nanoparticles

At nanoscale, variation in behaviour of optical phenomena is observed during light-matter interaction, due to rise in unique phenomena such as plasmonic resonances, enhancement in near-field intensity, etc. Thus investigation of such interactions becomes important, and to determine the changes in optical behaviour such as absorption and scattering of light, certain investigations needs to be done. One can determine the electric field absorbed and scattered by the nanoparticle, and increased intensity in the local field due to unique plasmonic features of nanoparticles by the Mie theory. Described below are the various near-field and far-field measurements that can be performed to understand the influence of plasmonic excitations during interaction of light with nanoparticles:

1. **Far-field cross-section**: Majority of light-matter investigations are usually done by considering far-field cross sections. The incident beam becomes extinct in the presence of the particles. This extinction depends on the chemical composition of the particles, their size,

shape, orientation, the surrounding medium, the number of particles, the polarization state and the frequency of the incident beam [65, 71]. The extinction of the beam can be described as absorption of the beam either by the particles or in the surrounding medium (for absorptive medium with complex refractive index), and scattering of the beam by the particles. For a given incident intensity, the measure of how strongly a particle scatters or absorbs light is given by the scattering (C_{sca}) and absorption (C_{abs}) cross sections, respectively [65, 70-72]. The extinction cross-section (C_{ext}) is determined as $C_{ext} = C_{sca} + C_{abs}$. For a linearly polarized incident beam, C_{scat} is defined as the ratio of the scattered power (W_{sca}) and incident intensity (I_{inc}), where

$$W_{sca} = \frac{1}{2} \, Re \int_0^{2\pi} \int_0^{\pi} \left(E_{s\theta} H_{s\phi}^* - E_{s\phi} H_{s\theta}^* \right) r^2 sin\theta d\theta d\phi \qquad (1.7)$$

Similarly, C_{abs}, and C_{ext} can be determined.

2. **Near-field Enhancement**: Near-field optical behaviour refers to the distance smaller or comparable to the wavelength of light during light-matter interaction, where the conventional far-field approximation no longer holds [73]. The enhancement in the near-field region is observed due to evanescent waves, and generation of plasmons that do not propagate to the far-field. The investigation for such strongly confined field in near-field is done at a distance which is very close to the nanoparticle by using some sharp, subwavelength probe as in SNOM, AFM, TERS etc. [26, 29, 30] The enhancement in local field and intensity are significant in near-field and is discussed in detail in **Section 1.5**.
3. **Tailoring of Coherence and Polarization of light**: This analysis can be extended to determine the tailored properties of the incident beam after scattering through such plasmonic nanoparticles [74, 75]. Few recent studies indicate that plasmonic structures play significant role in modifying the coherence and polarization properties of light in both near and far-fields. The spatial coherence of a light beam can be enhanced or reduced by the excitation of SPPs

and this has been demonstrated using a metallic double-slit configuration [76]. Plasmonic response of nanoparticles and their modes influence the coherence and polarization of light. Nanoparticles accompanied by plasmonic effects and large local field enhancement modulate the scattered light and the coherence and polarization aspects of the scattering elements [77]. The coherence and polarization properties can be measured in near and far-fields using a coherency matrix (using a two-dimensional field approach) [78, 79].

$$\hat{J}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) = \begin{bmatrix} J_{xx}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) & J_{xy}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) \\ J_{yx}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) & J_{yy}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) \end{bmatrix} \tag{1.8}$$

where, $\hat{J}(\boldsymbol{r_1}, \boldsymbol{r_2}, z) = \langle E^{\dagger}(\boldsymbol{r_1}, z; t) E(\boldsymbol{r_2}, z; t) \rangle$

Here, $E_x(\boldsymbol{r}, z; t)$, and $E_y(\boldsymbol{r}, z; t)$, are the components of complex electric field vector in the x- and y-directions, and $\langle\, \rangle$ denotes the ensemble average of the fields. $E^{\dagger}(\boldsymbol{r}, z; t)$ is the corresponding complex conjugate of the fields $E(\boldsymbol{r}, z; t)$.

1.5 Plasmonic response and near-field intensity enhancement

The scattering of light and other EM radiation by extremely small particles in the near-field is of great interest to a range of science and engineering disciplines. Scattering of light by nanoparticles due to their plasmonic properties shows useful results in intensity enhancement in the near-field. The amount and angular distribution of light scattered by a particle and the amount absorbed when it is exposed to a beam of light with specific characteristics depend on the particle's nature such as size, shape, and composition [73].

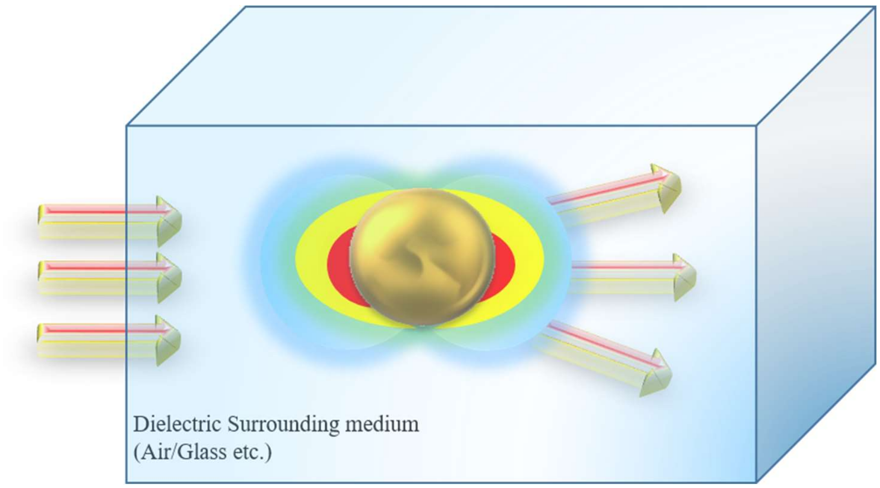

Fig. 1.9 Plasmonic response of a nanoparticle leading to enhancement in the near-field.

Along with particle morphology, the surrounding medium also impacts the intensity enhancement. A real refractive index of the medium represents that the medium is non-absorbing, whereas a complex refractive index suggests the medium is absorbing [65]. Fig. 1.9 shows the enhancement in the near-field due to the excitation of plasmons when a nanoparticle is illuminated by an EM wave. The NPs in the near-field ($r = a$) provide the information about the evanescent waves or plasmons which are usually lost in the far-field ($r >> a$), where *r* is the distance from the centre of the NP and *a* is the radius of the NP [80]. To access the information in the near-field, an enhancement factor *K* is defined which is evaluated as the total field intensity ($E_{total} = E_{incident} + E_{scattered}$) averaged over the NP surface normalized by the intensity at the centre of the NP [72, 80]. The average intensity enhancement is given as

$$K = \frac{1}{4\pi|E_i(0,0,0)|^2} \int_0^{2\pi} \int_0^{\alpha} |E_{tot}(a,\theta,\phi)|^2 sin\theta \, d\theta \, d\phi, \qquad (1.9)$$

In a far-field, the tangential components of the electric field (E_θ and E_ϕ) are significant and the radial component (E_r) nearly vanishes, whereas the near-field intensity is mainly due to contributions from the radial component of the electric field. To study the near-field intensity enhancement accurately, the average radial and tangential intensity enhancements (K_r and K_t) are considered separately using orthogonality of the multipoles. Our main focus is to investigate the average radial enhancement (K_r) due to excitation of localized surface plasmons which is discussed in detail for different cases in **Chapter 2**.

1.6 Motivation

Nanoparticles play a significant role in near-field enhancement of around $10^4 - 10^8$ and significant investigations have been carried out on the role of shape, size, material of the nanoparticle, and medium around the particle on the near-field enhancement and plasmonic response [22-25]. Based on the material's morphology and wavefront of the incident beam, the interaction between light and matter may show different optical behaviour. The way electric field absorbed or scattered not only relies on nanoparticle's composition but also has appreciable dependence upon incident beam properties such as polarization, wavelength. However, this issue has not been investigated in the context of tailored light sources and their interaction with nanoparticles except for some limited studies in recent years. The significance of such initiatives can be understood with emerging tools and techniques on light shaping using commercially available advanced devices such as spatial light modulators, and other diffractive optical elements for shaping fundamental features of the light such as beam profile, polarization, and spectrum. A few studies highlight near-field enhancement due to changes in beam profile instead of morphological aspects, such as different polarization of beams. By altering the structure of a metal's surface, and shaping the incident beam, the properties of surface plasmons in particular their interaction with light-can be tailored. Furthermore, the field enhancement near a nanoparticle not only depends on the plasmonic structure but also on the illumination [33]. This is because the origin of field enhancement is the collective accumulation of the freely oscillating charges near the metal surface, giving rise to intense Coulombic fields in that region. Therefore, a combination of beam shaping with materials may offer a new potential for developing new types of photonic devices and this area needs a deep dive. My works presented in the thesis cover these aspects with a detailed study on beam shaping and algorithms development to investigate the interaction of structured beams with the nanoparticles using the Mie scattering.

1.6.1 Structured Laser Beams

Recently, it has become possible to control the various degrees of freedom of the light, which affects its fundamental features such as diffraction and interference [81, 82]. By manipulating the spatial profile, phase or polarization, a beam can be structured to have a precise control over the diffraction. This shaping of the beam profile helps in achieving the specific desired intensity distribution, and polarization, and the way the beam illuminates the target. Beams providing the ability to have customized optical fields are termed as “Structured laser beams”. Beams having different profiles interact with materials differently. A sharper and tighter focus can be attained by structuring the polarization of the beam in the tight focusing condition which will be described in detail in the coming chapters of the thesis [83-86]. In optical tweezers structured laser beams are utilized to capture and control microscopic particles, which is crucial in biological and chemical research. Structured laser beams have fuelled many applications from imaging, microscopy, metrology, communication, quantum information processing to light-matter interaction [87-91]. A beam can be structured by using various optical elements such as lenses, mirrors, spatial light modulator (SLM), waveplates etc. [92]. In this section, we are mainly discussing about controlling the spatial wavefront of a beam using polarization of the beam.

A polarization, one of the fundamental features of light, characterizes the vibration of the electric field [93-95]. Polarized light is pervasive in our world, which we need to quantify, comprehend, and be able to employ to our benefit. Polarization can have any arbitrary feature such as linear, circular, elliptical, or more complex patterns like radial or azimuthal polarization as represented in Fig. 1.10.

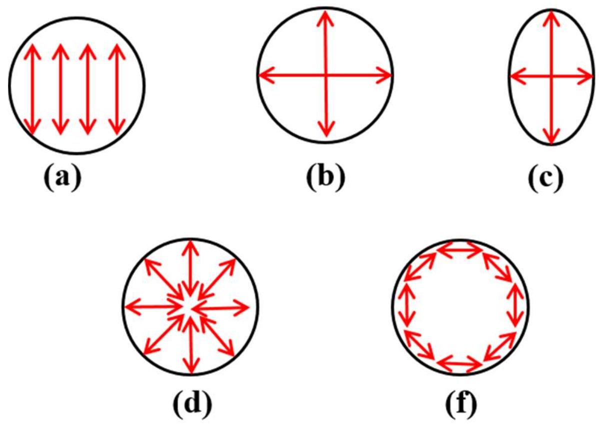

Fig. 1.10 Beam profile for a **(a)** Linear, **(b)** Circular, **(c)** Elliptical, **(d)** radial, and **(e)** Azimuthal Polarization.

Optical elements such as polarizers, quarter waveplate, S-waveplate, SLM etc. are commonly used to generate different polarization states, and the representative change in polarization in the space is shown in Fig. 1.11. A randomly polarized light when passed through a linear polarizer, a uniform linearly polarized light is generated. A linearly polarized light passing through a quarter waveplate kept at 45° angle to its polarization axis produces a uniform circularly polarized light. On the other hand, an elliptically polarized is produced when the quarter waveplate is kept at any angle other than 45° to its polarization axis. S-waveplate comprises of space-variant retarder, which converts linear polarization to radial and azimuthal polarization.

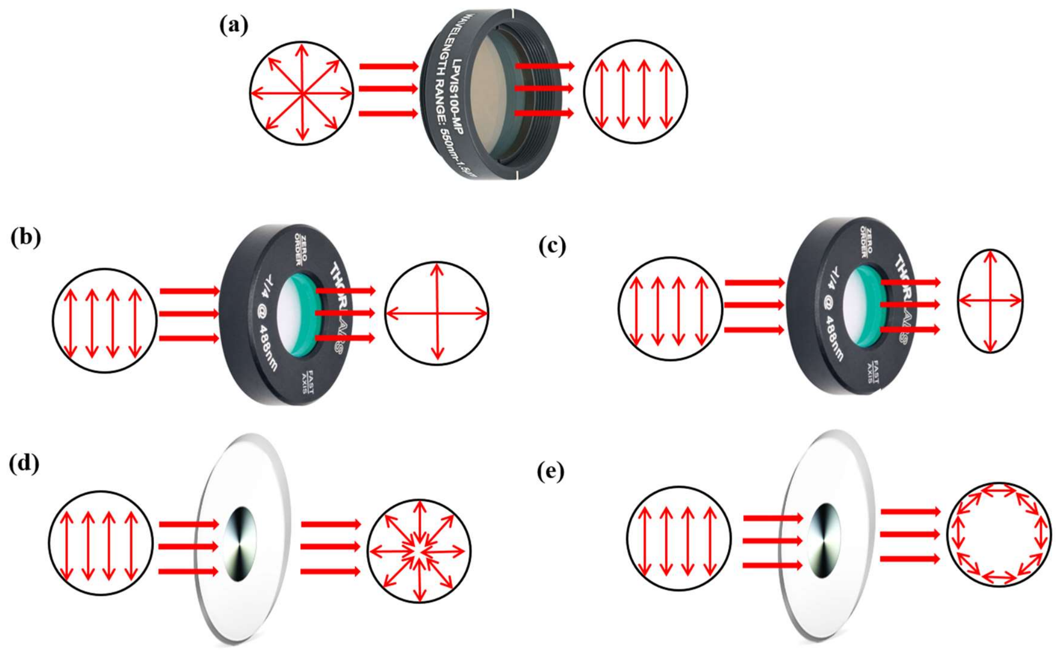

Fig. 1.11 (a) A Polarizer converting randomly polarized light into linearly polarized light [96], **(b)** a circularly polarized, and **(c)** an elliptically polarized light produced using a Quarter wave-plate [97], and **(e), (f)** a S-waveplate used to produce radially polarized and azimuthally polarized light respectively [98].

The main idea of this thesis is to study interaction of structured beam with plasmon-assisted nanoparticles, and analyze the effects on near-field intensity enhancement, and the nanoparticles are of extremely small size. To maximize the probability of interaction of a nanoparticle with the incident beam, and to avoid the abrupt focusing into a subwavelength focal spot, the beam illuminating a nanoparticle need to be strongly focused. The strength of focusing depends on the convergence angle, and with increasing value of convergence angle a tighter focal spot is obtained. To make a beam strongly focus, a high numerical aperture (NA) lens system is required by increasing the convergence angle. The focusing of an incident beam with smaller convergence angle is considered to be low NA focusing [2]. In the conventional low NA focusing, the intensity distribution in the focal plane exhibits well known Airy-pattern. Moreover, the polarization distribution of the incident beam, in contrast to the low NA focusing, plays an important role in shaping the focal structure of a high NA system. With decreasing convergence angle, polarization distribution does not play a significant role in shaping the focal spot.

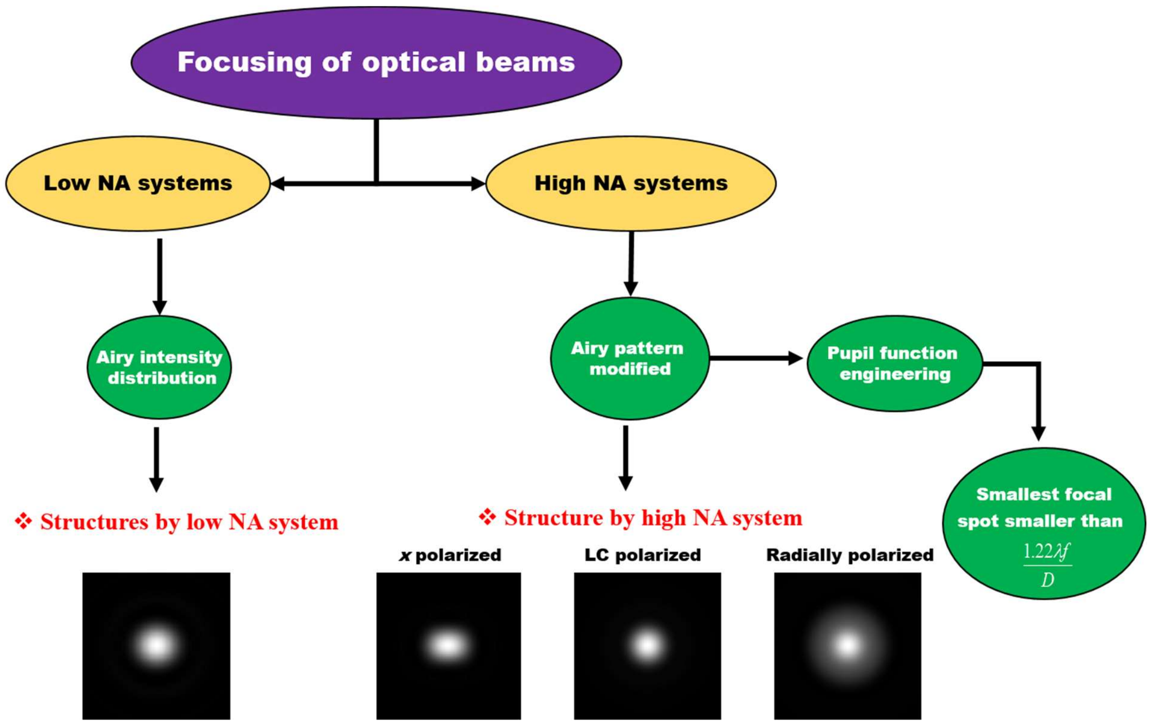

Fig. 1.12 Structure of a focal spot in low NA, and high NA focusing system. Variation in focal spot based on polarization of incident beam in high NA focusing system.

Fig. 1.13 illustrates the distribution of focal spot for low NA and high NA focusing system [99, 100]. The focusing spot for a low NA system is an Airy pattern, which is circular symmetric for any polarization say linear, radial, or azimuthal. On the contrary, this circular symmetry is removed for a linearly polarized beam in a high NA system, and the focal spot at the focus appears to be of ellipsoidal shape due to emerging contribution of the longitudinal polarization component [99-101]. On the other hand, a circularly polarized beam brings back the symmetry in the focal spot for high NA focusing. A symmetric shape focal spot is also obtained for a radially polarized beam in high NA focusing but the focal spot is larger in size as compared to circularly polarized light.

Beams corresponding to these high NA focusing system are called as **“Tightly focused beams”**. Tightly focused beams are the beams having high angle of convergence, which have emerging interests and find uses in various areas such as SERS, optical tweezers, data storage, plasmonics, near-field optics and many more [72, 102-105]. Detailed introduction of tightly focused beams and mathematical expressions are discussed in **Chapter 3, 4**.

1.7 Algorithms and commercially available tools

Light scattered during light-matter interaction provide information on the physical properties of the sample or scatterer. Scattering by spherical particles are at the heart of current research in Optics and Electromagnetics. Light scattering and absorption by a single small sphere, a central topic for EM scattering theory, in the fields of material and optical physics, chemistry, nanotechnology, radio/antenna engineering, and applied mathematics, among others [106]. A lot of literature on the light scattering by Stratton, van de Hulst, Kerker, and Bohren and Huffman is available [65, 107-109].

1.7.1 Available software and coding tools

Various scattering theories are present such as Mie theory, Finite difference time domain method (FDTD), Finite Element Method (FEM), Discrete Dipole Approximation (DDA) etc. [110]. Some commercial software such as COMSOL Multiphysics, Ansys-Lumerical, DDSCAT (Discrete Dipole Scattering Code), CST Studio Suite are also accessible for simulating light scattering by nanoparticles, which are designed to handle a wide range of particle sizes, shapes, and materials [110-114]. These software offers

- Simulations for light scattering by complex nanostructures, metamaterials, plasmonic structures, arbitrarily shaped nanoparticles
- Computation of scattering, absorption and extinction efficiencies
- Analysis of near-field and far-field optical behaviour

- Supports multiple wavelength simulations and parameter sweeps

These tools have high-accuracy simulation capabilities even for extremely small structures, and are largely used in research and industries which includes nanophotonics, plasmonic applications. Unfortunately, most of the focus of these software is towards dealing with the complexity of the structure and analysis of a plane wave scattering. The main aim of this thesis is to study interaction of nanoparticles with structured beam specifically tightly focused beam (**Section 1.6.1**, and **Chapter 3, 4, 5**). Though some of software offer some tools for beam shaping, but it requires a lot of addition of so many functions and variables which makes system simulation more complex, in addition to complex nanostructures. A direct tool is not available for giving a source like a tightly focused beam which also require defining of the polarization structure for the incident beam. Even after designing such a complex system, one needs to rely on some coding software such as MATLAB, Python, Mathematica, etc. for post-processing analysis of the near-field optical behaviour (**Section 1.5**, and **Chapter 2**). Currently, structuring a tightly focused beam, and investigating complex numerical problems in a commercial software is still a challenging task. COMSOL Multiphysics, Lumerical, and CST Studio use MATLAB as an interface to perform complex simulations or EM analysis, and as a post-processing tool.

1.7.2 Modeling

Here, in this thesis, MATLAB platform is selected to build my own algorithms to examine the near-field enhancement based on the interaction of the structured beam with nanoparticles [115]. My algorithms offer several advantages for performing custom numerical analysis:

- Freedom of scripting and easy to handle, and understanding
- MATLAB scripts are easy to document, version control and share
- Various built-in functions, and toolboxes help to perform complex numerical tasks required for simulations.
- Post-processing tool in other software because of ease in data handling, import and export.

Considering several applications of MATLAB, we present algorithm for scattering of the structured laser beam through nanoparticles based on Mie theory which will be discussed in detail in coming chapters for different incident beams.

1.8 Applications

Structured light is the capacity to regulate optical fields in two dimensions: spatially and temporally. In terms of spatial control, this means amplitude (intensity), phase (wavefront), and polarization; in terms of temporal control, it means controlling the frequency spectrum and time [81, 82, 87]. Structured beams have a wide range of applications across many fields, from industrial processes to medical technologies and scientific research. Various surgical laser tissue interactions can be precisely controlled with beam shaping [116]. OAM beams are claimed to have applications in optical tweezers, optical wrenches, etc. and are widely used in the field of biomedicine [117]. Structured beams like HG beams, LG beams said to have improved signal clarity, and reduce interference while free-space communication [118]. Here, are some applications discussed below:

1.8.1 Surface enhanced Raman Spectroscopy

Most of the conventionally available spectroscopies uses a linearly polarized incident beam as a light source. Nevertheless, structured beams are advantageous in sensing applications, and various spectroscopies such as surface enhanced Raman spectroscopy (SERS), tip-enhanced

Raman spectroscopy (TERS), etc. SERS is widely used in chemical analysis and biological sensing applications, whereas TERS having capability of high spatial resolution in nanometre scale and high detection sensitivity has garnered significant interest. Tightly focused perfect radially polarized beam (PRPB) has been used as an illumination source to achieve dynamic manipulation and enhancement of the nanofocusing field, and gradient Raman mode in TERS and enhancement in SERS sensitivity [102, 119]. PRPB presents a sharp ring size that coincides with sharp resonance of SPP, and hence improve the excitation efficiency of SPP on the metal surface. This method eventually improves the sensitivity of SERS, and gradient Raman mode in TERS. Such systems with structured excitation source have great potential in single molecule detection. In Fig. 1.14, we have proposed to use structured laser beam for illuminating plasmonic structure which will lead to enhanced SERS signals.

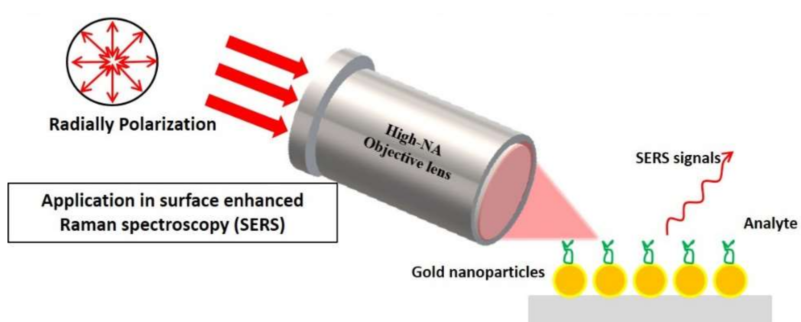

Fig. 1.13 Structured laser illumination in Surface Enhanced Raman Spectroscopy.

1.8.2 Mie Scattering Algorithm

During the past decade Mie scattering theory and related computational methods for computing scattered light intensity for spherical scatterers have evolved significantly. Mie scattering holds application in characterization of optical properties of aerosols and clouds, in analysis of size and structure of biological cells by interpreting the scattering of light, in food industry to check the quality of food, and many more fields [120-124]. A few of them are discussed here briefly.

1.8.2.1 Optimal measurement of water droplet size

Undesirable emerging of fire in forest or onboard a ship causes significant damage. Water-mist spray offering cooling, oxygen displacement, and radiation attenuation mechanisms conducive to fire extinguishment, has emerged as a promising alternative for fighting such high-risk fires [125, 126]. Optimal water droplet size in the mist barrier is determined using radiative transfer analysis which can help in managing minimum thermal transmission from fires through radiation. Using Mie Scattering theory and a radiative transfer analysis of the mist layer one can analyze the radiative properties of water droplets.

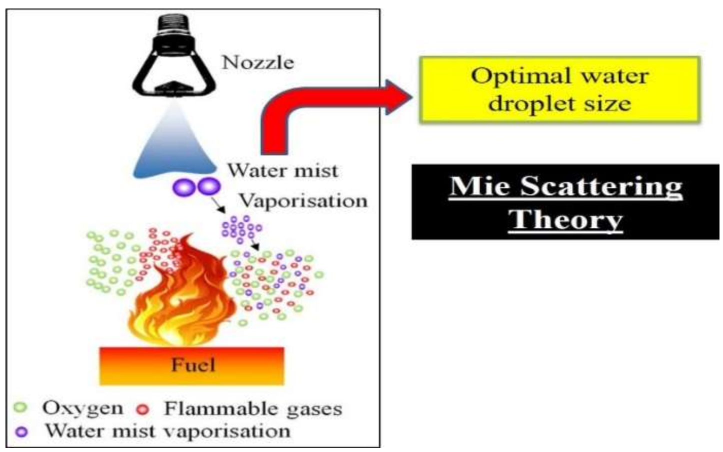

Fig. 1.14 Optical measurement of water droplet size using Mie Scattering theory [125, 126].

1.8.2.2 Coal mine dust concentration measurement

Accurate and effective measurement of dust concentration in coal mine is an essential thing to increase the visibility in the mine environments and protect workers from getting affected by occupational diseases such as occupational pneumoconiosis. Mie scattering theory is widely used to examine the effects of dust particle size, refractive index and scattering angle on the distribution of intensity of scattered light.

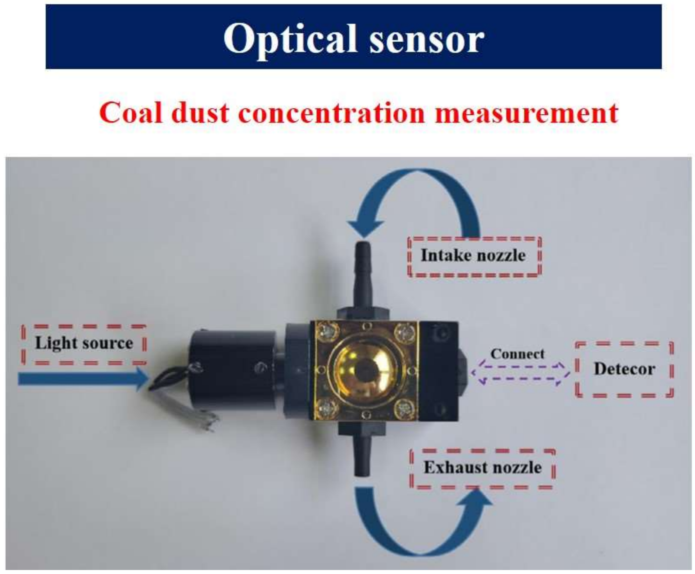

Fig. 1.15 Coal mine dust concentration optical sensor designed using Mie Scattering theory [127].

An optical sensor is designed by analysing the scattering structure which can precisely measure the dust concentration in coal mine with better stability [127]. Fig. 1.16 shows optical part of the designed sensor to measure dust concentration.