CHAPTER II

THEORY OF LIGHT SCATTERING AND DISCRETE DIPOLE APPROXIMATION

2.1 Introduction

One of the basic properties of particles consisting of charged bodies and exposed to electromagnetic radiation is that the induced electric and magnetic fields of these particles gets aligned due to external force fields. And is the key factor in computation of light scattering and other optical properties by particles under the influence of an incident electromagnetic field.

Randomly oriented nonspherical particles are important in light scattering and absorption studies as almost all natural particles systems are non-uniformly distributed nonspherical particle systems. In the macroscopic level random orientation signifies a uniform orientation distribution independent of the individual particle orientations. The light scattering properties for such particle systems are also independent of the incident and scattering directions. Theoretically dealing with randomly oriented particle systems require orientational averaging over all the independent scattering directions i.e. polar (θ) and azimuth (ϕ) directions respectively. The atmospheric particles and those forming terrestrial and cosmic dust, show light scattering and extinction characteristics which are typical to randomly oriented systems. Almost all the available numerical codes and algorithms for light scattering simulations of nonspherical particles (for e.g. T-Matrix and DDA) provides the option of selective averaging over particle properties including the scattering directions considered for a 3D scattering volume.

Considering independent orientation, simplifies the experimentations and computations for light scattering by aggregates or multiparticle systems [1, 2]. But for particle systems found in terrestrial and extra-terrestrial dust, the solution to the light scattering problem is not that simple, particularly attenuation of the incident energy in the narrow forward scattering band [3, 4]. In spite of all the simplifying approximations and assumptions, light scattering by particle clusters or aggregates requires considerable amount of intensive mathematical interpretations.

Basically averaging over orientation directions considers the range for θ and ϕ, as $\theta \in [0,\pi]$ is the polar (zenith) angle and $\phi \in [0,2\pi]$ is the azimuth angle [5, 6].

2.2 Light scattering and Maxwell's equations

The light scattering theory starts with the general Maxwell's electromagnetic equations. And a light scattering problems involves rigorous solutions of the four integral equations subjected to a set of physical boundary conditions. The most important components of light scattering theory are the Stokes parameters and the Poynting vectors of Maxwell's equation. Mathematical relations between these components are established using different formalisms in order to define the scattering problem associated with a particular scattering event and consequently to obtain the scattering parameters and 4×4 Mueller matrix elements that is,

$$F_{ij} = F_{11}, F_{12}, ... F_{44} \quad \textbf{2.1}$$

The Maxwell's equations for an arbitrary field can be written as can,

$$\nabla \cdot D = \rho \quad \textbf{2.2}$$

$$\nabla \cdot B = 0 \quad \textbf{2.3}$$

$$\nabla \times E = -\partial B / \partial t \quad \textbf{2.4}$$

$$\nabla \times H = J + \partial D / \partial t \quad \textbf{2.5}$$

where D is the electric displacement, ρ is the electric charge density, B is the magnetic induction, E is the electric field intensity, H is the magnetic field intensity, and J being the electric current density.

Considering a time harmonic field the wave equations can be written as,

$$E(r,t) = E_0 e^{-i(kr - wt)} \quad \textbf{2.6}$$

$$H(r,t) = H_0 e^{-i(kr - wt)} \quad \textbf{2.7}$$

where k is the wave vector and ω is the angular frequency.

Now the electromagnetic wave propagates in a homogeneous medium as [7],

$$E(r,t) = \text{Re}\{E(r) e^{-i\omega t}\} \quad \textbf{2.8}$$

$$H(r,t) = \text{Re}\{H(r) e^{-i\omega t}\} \quad \textbf{2.9}$$

Using these expressions the Maxwell's equation in the frequency domain can be written as,

$$\nabla \times E = i\omega B \qquad \mathbf{2.10}$$

$$\nabla \times H = -iwD_t \qquad \mathbf{2.11}$$

The second expression is obtained by using the continuity equation,

$$\nabla \cdot J = i\omega\rho \qquad \mathbf{2.12}$$

And $D_t = D + {}^{i}\!/_{\omega}\, J$ **2.13**

where D_t is the total electric displacement.

The principles that govern the light scattering properties of a scattering particle are [7],

1. The electric and magnetic fields have continuous tangential components across the boundary.
2. The solutions to the electromagnetic field equations must be divergence free.
3. The total field inside and outside the particle must be equal.
4. The tangential components of both electric and magnetic fields vanishes at infinite distance from the origin.

2.2.1 The Poynting vector and boundary conditions

Consider a small volume element of area ΔA and thickness Δt (Figure 2.1). The volume approaches zero when Δt and ΔA approaches zero. '$\mathbf{n}_1$' is the normal at the interface. D and B are assumed to be finite in the small element considered.

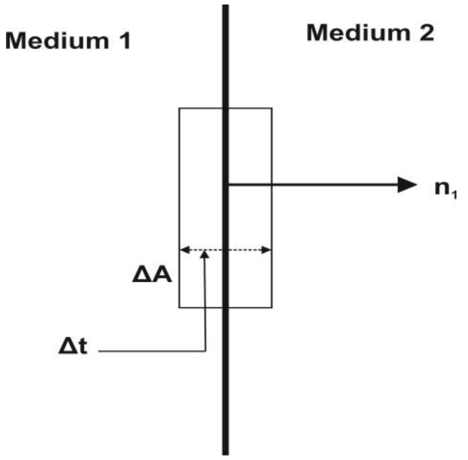

Figure 2.1 Discontinuity at the interface of two medium.

The surface current (J_A) and surface charge density (ρ_A) can be written as,

$$J_A = \lim_{\nabla t \to 0} \nabla_t J \qquad \textbf{2.14}$$

$$\rho_A = \lim_{\nabla t \to 0} \nabla_t \rho \qquad \textbf{2.15}$$

Now the boundary conditions could be written as [8],

The tangential component of E is continuous but H is discontinuous,

$$n_1 \times (E_2 - E_1) = 0 \qquad \textbf{2.16}$$

$$n_1 \times (H_2 - H_1) = J_A \qquad \textbf{2.17}$$

And normal component of B is continuous but D is discontinuous,

$$n \cdot (B_2 - B_1) = 0 \qquad \textbf{2.18.1}$$

$$n \cdot (D_2 - D_1) = \rho_A \qquad \textbf{2.18.2}$$

Applying the vector identity equation for the cross product of $E \times H$, we obtain,

$$\nabla \cdot (E \times H) = H \cdot (\nabla \times E) - E \cdot (\nabla \times H) \qquad \textbf{2.19}$$

We can write the Poynting theorem for time domain as [7],

$$\nabla \cdot (E \times H) + H \cdot \frac{\partial B}{\partial t} + E \cdot \frac{\partial D}{\partial t} + E \cdot J = 0 \qquad \textbf{2.20}$$

Where the term $E \times H$ is the Poynting vector S of the radiation field,

$$S = E \times H \qquad \textbf{2.21}$$

Now the total power provided by the source per unit volume of the medium is [8],

$$-\int_v E \cdot J dv = \int_S (E \times H) \cdot ds + \int_v \left(H \cdot \frac{\partial B}{\partial t} + E \cdot \frac{\partial D}{\partial t} \right) dv \qquad \textbf{2.22}$$

This is the energy conservation theorem which states that the decrease in energy of the electromagnetic field is equal to the energy of source electric and magnetic fields plus power density due to Poynting vector in the volume element.

Now in the frequency domain,

$$\nabla \cdot (E \times H^*) = i\omega (B \cdot H^* - E \cdot D^*) - E \cdot J^* \qquad \textbf{2.23}$$

Now the Poynting vector is a physically measurable quantity and it must be real. But the electric and magnetic field vectors E and H are complex quantities with real and imaginary values. But keeping in mind the ability of optical devices, measurements o of only the real or parts of E and H are taken. Considering only the real components of the Poynting vector,

$$S = \mathrm{Re}(E) \times \mathrm{Re}(H) \qquad \textbf{2.24}$$

The vector field equations for time harmonic waves are given by [7],

$$E(r,t) = \frac{1}{2}\left[E(r)e^{-i\omega t} + E^*(r)e^{i\omega t}\right] \qquad \textbf{2.25.1}$$

$$H(r,t) = \frac{1}{2}\left[H(r)e^{-i\omega t} + H^*(r)e^{i\omega t}\right] \qquad \textbf{2.25.2}$$

While measuring energy fields the measuring devices responds to time variations of the Poynting vector.

Therefore we can write,

$$\langle S \rangle = \lim_{t\to\infty} \frac{1}{T}\int_0^T S(t)dt \qquad \textbf{2.26}$$

Hence from equation 2.24 we have,

$$S = \mathrm{Re}(E) \times \mathrm{Re}(H) = \frac{1}{2}\left[E(r)e^{-i\omega t} + E^*(r)e^{i\omega t}\right] \times \frac{1}{2}\left[H(r)e^{-i\omega t} + H^*(r)e^{i\omega t}\right] \qquad \textbf{2.27}$$

$$= \frac{1}{4}\left[E(r)e^{-i\omega t} + E^*(r)e^{i\omega t}\right] \times \left[H(r)e^{-i\omega t} + H^*(r)e^{i\omega t}\right]$$

$$= \frac{1}{2}\left[E(r) \times H^*(r) + E(r) \times H(r)e^{-2i\omega t}\right]$$

$$\text{Or,} \langle S \rangle = \frac{1}{2}\mathrm{Re}\left\{E \times H^*\right\} \qquad \textbf{2.28}$$

Equation 2.28 is the expression for time averaged Poynting vector, defined as the real part of the vector product of electric field vector and the complex conjugate of magnetic field vectors.

To find out the characteristics of the far field electromagnetic wave, we need to find out the radiation field and Poynting vector inside and outside the scattering particle in the medium [7],

$$\langle S \rangle = \frac{1}{2}\mathrm{Re}\left\{E^{out} \times H^{out^*}\right\} = \frac{1}{2}\mathrm{Re}\left\{\left(E^{inc} + E^{sca}\right) \times \left(H^{*inc} + H^{*sca}\right)\right\}$$

$$= \langle S^{ext} \rangle + \langle S^{inc} \rangle + \langle S^{sca} \rangle \qquad \textbf{2.29}$$

where the Poynting vector for extinction phenomenon in the medium is given by,

$$\left\langle S^{ext} \right\rangle = \frac{1}{2}\mathrm{Re}\left\{E^{ext} \times H^{*ext}\right\} \qquad \textbf{2.29.1}$$

The Poynting vector for scattered wave is given by,

$$\left\langle S^{sca} \right\rangle = \frac{1}{2}\mathrm{Re}\left\{E^{sca} \times H^{*sca}\right\} \qquad \textbf{2.29.2}$$

And that for the incident electromagnetic wave is given by,

$$\left\langle S^{inc} \right\rangle = \frac{1}{2}\mathrm{Re}\left\{E^{inc} \times H^{*inc}\right\} \qquad \textbf{2.29.3}$$

2.2.2 Maxwell's equations for an isotropic dielectric media

Now for a scattering event the medium plays an important role. It is necessary to define all the properties of the medium in terms of physical parameters and incorporate them in the Maxwell's equations. The relations that govern the Maxwell's equations in an isotropic media is given by the constitutive relations [8],

$$B = \mu H \qquad \textbf{2.30.1}$$

$$D = \varepsilon E \qquad \textbf{2.30.2}$$

$$J = \sigma E \qquad \textbf{2.30.3}$$

where μ is the magnetic permeability, ε is electric permittivity and ρ is the electric conductivity.

Now for a material medium the electrical and magnetic properties of the medium must be taken into account. For a dielectric media the polarization must be taken into account. Equation 2.30.2 becomes,

$$D = \varepsilon_0 E + P \qquad \textbf{2.31}$$

Similarly Polarization P is the average electric dipole moment per unit volume,

$$P = \varepsilon_0 \chi_e E \qquad \textbf{2.32}$$

where ε_0 is the permittivity of free space and χ_e is the electric susceptibility.

Similarly a magnetic medium is characterized by the magnetic moment M.

So equation 2.30.1 becomes,

$$B = \mu_0 (H + M) \qquad \textbf{2.33}$$

where μ_0 is the permeability of free space.

M is the average magnetic dipole moment represented as,

$$M = \chi_m H \quad \textbf{2.34}$$

χ_m is the magnetic susceptibility.

Again for an isotropic media,

$$\varepsilon = \varepsilon_0 \varepsilon_r = \varepsilon_0 (1 + \chi_e) \quad \textbf{2.35.1}$$

$$\mu = \mu_0 \mu_r = \mu_0 (1 + \chi_m) \quad \textbf{2.35.2}$$

where ε_r and μ_r are the relative permittivity and permeability of the medium.

2.3 Theory and mathematical formalism of Discrete Dipole Approximation (DDA)

DDA basically approximates a target by a finite array of polarizable points or dipoles. The points acquire dipole moments in response to the incident electric field and produce secondary sets of radiation or the scattered fields. The dipoles within a scattering volume also interacts with one another via their electric fields resulting in the total scattered radiation [9, 10].

2.3.1 Short theoretical background of DDA

The preliminary idea of DDA (also called dipole method or CDM) was introduced by DeVoe in 1964 [11, 12]. But in its current widely used form, DDA was first proposed by Purcell and Pennypacker [9]. DDA replaces the particle scatterer by point dipoles. These dipoles interact with each other and also with the incident field, giving rise to a system of linear equations. These equations can be solved in order to obtain dipole polarizations for the scattering system. After going through rigorous mathematical treatment all the scattering parameters can be obtained as functions of the dipole polarizations. The theoretical framework of DDA was first reviewed extensively and modified by Draine and Goodman [13] and later by Draine and Flatau [14]. Since the discrete dipole approximation can also be obtained from the volume integral equation, the mathematical analysis put forwarded by Lakhtakia and Mulholland is most widely used for the solution [8, 15].

The mathematical expressions of DDA can be derived from the Clausius-Mossotti (or Lorentz-Lorenz) relation which relates the dielectric properties of a material to the polarizability of the primary elements or atoms. It is based on the theoretical assumption that the atoms are located on a cubic lattice [16].

It is possible to obtain exact solutions to all the sets of mathematical equations relating to the scattering problem associated with point dipoles. The approximation part of the DDA theory is the N-point dipoles which gives a set of N linear equations. It is important to properly specify the positions (location $\mathbf{r}_j$ of the dipoles, j = 1, ... ,*N)* and the dipole polarizabilities $\boldsymbol{\alpha}_j$ of the associated dipoles.

2.3.2. Mathematical formalism of DDA

The basic assumption for obtaining solutions to DDA scattering equations is that all the point dipoles must represent dipole polarizabilities of a small volume element within the continuum target particle. In the final version of the approximation, the whole volume of the target must be taken into account in terms of shape and size.
A specific target geometry can be treated as follows [14],

For simplification the target orientations are assumed to be fixed with respect to a specific coordinate system $\hat{x}, \hat{y}, \hat{z}$.

1. A primary lattice is generated with lattice spacing *d.* And initial space coordinates of an arbitrary point situated near origin is taken as (x_0, y_0, z_0).

2. As for the approximation, dipole arrays are used to represent the entire volume V of the target particle.

3. The lattice spacing *d* and the position of primary lattice (x_0, y_0, z_0) are changed to achieve a relatively accurate approximation of the target volume and dipole positions.

Each of the dipoles are assigned lattice sites as j = 1, ... ,N, with each occupied sites having a cubic subvolume d^3. The entire dipole array is rescaled in a way that the lattice spacing $d = \left(V/N\right)^{1/3}$ and total volume of all the occupied sites Nd^3 is equal to the volume V of the target material.

4. A dipole polarizability α_j is assigned to all the occupied lattice sites specified by j**.**

For measuring the dipole polarizabilities, Clausius-Mossotti relation are used [5],

$$\alpha_j^{CM} = \frac{3d^3}{4\pi}\frac{\varepsilon_j - 1}{\varepsilon_j + 2} \qquad \textbf{2.36}$$

where ε_j is the dielectric function of the scatterer at a particular location $\mathbf{r}_j$ with respect to the origin.

Draine and Goodman derived the lattice dispersion relations (LDR) using Clausius-Mossotti relations, as in equation 2.36 and introduced two correction terms $O[(kd)^3]$ and $O[(kd)^2]$ [13, 17]. A new concept has been introduced, that an infinite lattice of polarizable points with dipole polarizability $\alpha(\omega)$ can be defined by the dispersion relations of a material with a continuous refractive index $m(\omega)$.

In the long-wavelength limit i.e. $kd << 1$, it is possible to obtain a solution to dispersion relations.

The dipole polarizabilities for each of the lattice points $\alpha(\omega)$ is expanded in series in powers of kd and $m^2 = \varepsilon$ as [10],

$$\alpha^{LDR} \approx \frac{\alpha^{CM}}{1 + \left(\alpha^{CM}/d^3\right)\left[\left(b_1 + m^2 b_2 + m^2 b_3 S\right)(kd)^2 - (2/3)\, i (kd)^3\right]} \qquad \textbf{2.37}$$

where the values of constants b_1, b_2 and b_3 are determined as follows,

$b_1 = -1.891531$, $b_2 = 0.1648469$ and $b_3 = -1.7700004$

Also the term S can be defined as,

$$S = \sum_{j=1}^{3}\left(\hat{a}_j \hat{e}_j\right)^2 \qquad \textbf{2.38}$$

where $\hat{a}_j$ and $\hat{e}_j$ are unit vectors for direction and polarization of incident wave.

For validity of DDA two conditions must strictly be fulfilled [14],

1. The first one is the $|m|kd$ condition i.e.

$$|m|kd \le 1 \qquad \textbf{2.39}$$

which states that lattice spacing d must be small compared to incident wavelength within the target.

2. 'd' must be small compared to any structural lengths within the target geometry for e.g. atomic spacing.

The total volume of solid material excluding vacant spaces within the target material is considered as V.

The total volume for an array of N dipoles with lattice spacing d can be written as,

$$V = Nd^3 \qquad \textbf{2.40}$$

which is also the volume of the whole target material.

Now a term is introduced to specify the geometrical size of the target as “effective radius (a_{eff})”,

$$a_{eff} \equiv (3V/4\pi)^{1/3} \qquad \textbf{2.41}$$

The effective radius of a material target can be defined as the radius of a sphere with equal volume as that of the target. Also any specific scattering problem could be defined by quantity named “size parameter”,

$$x \equiv ka_{eff} = 2\pi a_{eff}/\lambda \quad x \equiv ka_{eff} \qquad \textbf{2.42}$$

This important expressions takes into account all physical parameters that influence a scattering event including incident wavelength.

Now for the first criterion (equation 2.39) to be adequately satisfied for number of dipoles N, we require that,

$$N > (4\pi/3)|m|^3 x^3 \qquad \textbf{2.43}$$

It is evident that materials with large values of $|m|$ and ka_{eff}, require extremely large number of dipoles to satisfy the criterion. But a practical limit constraints the dipoles that can be employed in a system based on the memory requirements and Random Access Memory (RAM) capabilities of a scientific workstation. This limit is $N < 10^6$. So, DDA is not very effective for larger size parameters and refractive index (m) values [18].

2.3.3 Calculation of scattering parameters, efficiencies and cross sections

The calculation of scattering parameters, scattering, absorption and extinction efficiencies and cross-sections requires extensive solutions of the electromagnetic scattering equations involving the incident and scattered radiation fields associated with the target particles. The DDA formalism considers each point dipole as an independent source of secondary radiation or scattered wave.

Now considering the total number of dipoles j = 1, ... ,N at specific positions $\mathbf{r}_j$ and with polarizabilities α_j, the polarization $\mathbf{P}_j$ for each of the individual dipoles can be written as,

$$\mathbf{P}_j = \alpha_j \mathbf{E}_j \qquad \textbf{2.44.1}$$

where $\mathbf{E}_j$ is the electric field at $\mathbf{r}_j$ due to the incident electromagnetic radiation.

The incident electric field can be written as,

$$\mathbf{E}_{inc,j} = \mathbf{E}_0 \exp\left(i\,\mathbf{k}\cdot\mathbf{r}_j - i\omega\, t\right) \qquad \textbf{2.44.2}$$

where E_0 is the amplitude of the incident beam and contribution of each of the mutually interacting $N-1$ dipoles to the incident field on a specific dipole is given by,

$$\mathbf{E}_j = \mathbf{E}_{inc,j} - \sum_{k\neq j} \mathbf{A}_{jk}\mathbf{P}_k \qquad \textbf{2.45}$$

where $-\mathbf{A}_{jk}\mathbf{P}_k$ is the electric field at the position $\mathbf{r}_j$ due to the contribution of the adjacent dipole at $\mathbf{r}_k$ with polarization $\mathbf{P}_k$ (including retardation effects).

Each element of $\mathbf{A}_{jk}$ is in the form of a 3×3 matrix with 9 elements, which is called the Mueller Matrix. Also the expression for $\mathbf{A}_{jk}$ is given by [14],

$$\mathbf{A}_{jk} = \frac{\exp\left(ikr_{jk}\right)}{r_{jk}} \times \left[k^2\left(\hat{r}_{jk}\hat{r}_{jk} - \mathbf{I}_3\right) + \frac{ikr_{jk} - 1}{r_{jk}^{\;2}}\left(3\hat{r}_{jk}\hat{r}_{jk} - \mathbf{I}_3\right)\right],\ j \neq k, \qquad \textbf{2.46}$$

where $k \equiv \frac{2\pi}{\lambda}$, $r_{jk} \equiv \left|\mathbf{r}_j - \mathbf{r}_k\right|$ $\hat{r}_{jk} \equiv \left(\mathbf{r}_j - \mathbf{r}_k\right)/r_{jk}$ and $\mathbf{I}_3$ is a 3×3 identity matrix.

To simplify the complex scattering problem $\mathbf{A}_{jj}$ is defined as $\mathbf{A}_{jj} \equiv \alpha_j^{-1}$.

With this modification, the only problem now is to find the polarization $\mathbf{P}_j$ satisfying a system of 3N complex linear equations. For a monochromatic incident wave the self-consistent solution for all the oscillating dipole moments $\mathbf{P}_j$ can be calculated from these polarization equations. The extinction, absorption and scattering cross sections can also be calculated from these equations as complex functions of polarization [9, 10]. The solutions to these equations gives the amplitude scattering matrix which can be used to calculate the Mueller Matrix elements.

The solution to the set of linear equations is given by,

$$\sum_{k=1}^{N} \mathbf{A}_{jk}\mathbf{P}_k = \mathbf{E}_{inc,j} \qquad \textbf{2.47}$$

After solving these equations for all the $\mathbf{P}_j$ values the cross section values can be calculated. Now we require the expressions of optical theorem to derive the extinction cross section (C_{ext}) values,

$$C_{ext} = \frac{4\pi\, k}{|E_{inc}|^2}\,\mathrm{Im}\left(E_{inc}^{*} \cdot \alpha E_{inc}\right) \qquad \textbf{2.48.1}$$

Now the rate of energy attenuation of the incident beam is,

$$\left(\frac{dE}{dt}\right)_{ext} = \frac{\omega}{2}\,\mathrm{Im}(E_{inc}^{*} \cdot \mathbf{P}) = \frac{\omega}{2}\,\mathrm{Im}[\mathbf{P} \cdot (\alpha^{-1})^{*}\mathbf{P}^{*}] \qquad \textbf{2.48.2}$$

Hence we can write equation 2.48.1 as,

$$C_{ext} = \frac{4\pi\, k}{|\mathbf{E}_0|^2}\sum_{j=1}^{N}\mathrm{Im}\left(\mathbf{E}_{inc,j}{}^{*} \cdot \mathbf{P}_j\right) \qquad \textbf{2.48.3}$$

Taking ‘ω’ as the angular frequency of the incident light and the expression for energy absorbed as:

$$\left(\frac{dE}{dt}\right)_{abs} = \frac{\omega}{2}\{\mathrm{Im}[\mathbf{P} \cdot (\alpha^{-1})^{*}\mathbf{P}^{*}] - \frac{2}{3}k^{3}\mathbf{P} \cdot \mathbf{P}^{*} \qquad \textbf{2.48.4}$$

Here the additional term k^3 is a contribution of the radiative reactions.

The expression for absorption cross section (C_{abs}) becomes,

$$C_{abs} = \frac{4\pi\, k}{|E_0|^2}\sum_{j=1}^{N}\left\{\mathrm{Im}\left[\mathbf{P}_j \cdot \left(\alpha_j{}^{-1}\right)^{*}\mathbf{P}_j{}^{*}\right] - \frac{2}{3}k^{3}|\mathbf{P}_j|^{2}\right\} \qquad \textbf{2.49}$$

Once these cross sections are known it is possible to obtain the scattering cross section (C_{sca}) by using the expression,

$$C_{sca} = C_{ext} - C_{abs} \qquad \textbf{2.50.1}$$

The scattering cross section can be computed using the power radiated by the oscillating dipoles. Now since the power radiated by the oscillating dipole is,

$$\left(\frac{dE}{dt}\right)_{sca} = \frac{\omega^4}{3c^3}\mathbf{P}\cdot\mathbf{P}^* \qquad \textbf{2.50.2}$$

Therefore,

$$C_{sca} = \frac{k^4}{|E_{inc}|^2}\int d\Omega\left|\sum_{j=1}^{N}[\mathbf{P}_j - \hat{\mathbf{n}}(\hat{\mathbf{n}}\cdot\mathbf{P}_j)]\exp(-ik\hat{\mathbf{n}}\cdot r_j)\right| \qquad \textbf{2.50.3}$$

Also the expression for asymmetry parameter 'g' can be written as,

$$g \equiv \langle\cos\theta\rangle = \frac{k^3}{C_{sca}|E_{inc}|^2}\int d\Omega\hat{\mathbf{n}}\cdot\mathbf{k}\sum_{j=1}^{N}[P_j - \hat{\mathbf{n}}(\hat{\mathbf{n}}\cdot\mathbf{P}_j)]\exp(-ik\hat{\mathbf{n}}\cdot r_j) \qquad \textbf{2.51}$$

Again, in the far field the scattered electric field can be written as,

$$\mathbf{E}_{sca} = \frac{k^2\exp(ikr)}{r}\sum_{j=1}^{N}\exp\left(-ik\hat{r}\cdot\mathbf{r}_j\right)\left(\hat{r}\hat{r} - \mathbf{I}_3\right)\mathbf{P}_j \qquad \textbf{2.52}$$

A complex scattering matrix was introduced by Draine to compute the light scattering properties of targets approximated by dipole arrays [10] as,

$$f_{ml}(\theta_s,\varphi_s) \qquad \textbf{2.53}$$

where index l = 1,2 represents orthogonal incident polarization states $\hat{e}_{01}$ and $\hat{e}_{02}$ with $\hat{e}_{02} = \hat{k}_0 \times \hat{e}_{01}$ while m = 1,2 denotes the scattered polarization states $\hat{e}_1 = \hat{e}_{\parallel s} = \hat{\theta}_s$ and $\hat{e}_2 = \hat{e}_{\perp S} = \hat{\phi}_s$, also θ_s and ϕ_s denotes the polar and azimuthal directions of scattering plane respectively.

The scattering matrix f_{ml} can be related to the polarization states as follows,

The scattering field equations need to be solved for the two orthogonal polarization states $\hat{e}_{01}$ and $\hat{e}_{02}$.

Therefore, an incident electric field takes the form,

$$\mathbf{E}_{inc,j} = \mathbf{E}_0\hat{e}_l\exp\left(i\,\mathbf{k}\,\hat{k}_0\cdot\mathbf{r}_j - i\omega t\right) \qquad \textbf{2.54}$$

' $\hat{e}_l$ ' being the incident wave polarization state, and where **k** is the wave vector.

Assuming $\mathbf{P}_j^l$ to be the polarization for jth dipole, a new term can be defined as,

$$\mathbf{p}_j^l \equiv \mathbf{E}_0^{-1} \exp\left(i\omega t\right) \mathbf{P}_j^l \qquad \textbf{2.55}$$

The scattering properties of any arbitrary target can be fully characterized by a 2×2 complex matrix $f_{ml}\left(\hat{k}_0, \hat{k}\right)$ where $\hat{k}_0$ and $\hat{k}$ represents the incident and scattered directions [10]. The expression for this matrix can be written in terms of polarization as,

$$f_{ml}\left(\hat{k}_0,\hat{k}\right) \equiv k^3 \sum_{j=1}^{N} \mathbf{p}_j^l \cdot e_m^* \exp\left(i\mathbf{k}\hat{k}_0 \cdot \mathbf{r}_j\right) \qquad \textbf{2.56}$$

where $\hat{e}_m$ is the polarization state of the scattered wave.

For an arbitrary incident wave the field equation is:

$$\mathbf{E}_{inc} = \mathbf{E}_0 \exp\left(i\mathbf{k}\hat{k}_0 \cdot \mathbf{r} - i\omega t\right)$$

$$= \mathbf{E}_0 \exp\left(i\mathbf{k}\hat{k}_0 \cdot \mathbf{r} - i\omega t\right) \sum_{l=1}^{2} a_l \hat{e}_{0l} \qquad \textbf{2.57}$$

where $\mathbf{E} \equiv \left(\mathbf{E}_0 \cdot \mathbf{E}_0^*\right)^{1/2}$ and $a_l = \mathbf{E}_0^{-1}\mathbf{E}_0 \cdot \hat{e}_{0l}^*$

Similarly the scattered wave can now be written as,

$$\mathbf{E}_{sca} = \frac{\mathbf{E}_0}{\mathbf{k}r} \exp\left(i\mathbf{k}\hat{k}_0 \cdot \mathbf{r} - i\omega t\right) \sum_{m=1}^{2} \hat{e}_m \sum_{l=1}^{2} f_{ml} a_l \qquad \textbf{2.58}$$

The scattered and the incident wave at the origin ($\mathbf{E}_{inc}(0)$) can now be related as,

$$\begin{pmatrix} \mathbf{E}_{sca} \cdot \hat{\theta}_s \\ \mathbf{E}_{sca} \cdot \hat{\varphi}_s \end{pmatrix} = \frac{\exp\left(i\mathbf{k}_{sca} \cdot r\right)}{\mathbf{k}r} \begin{pmatrix} f_{11} & f_{12} \\ f_{21} & f_{22} \end{pmatrix} \begin{pmatrix} \mathbf{E}_{inc}(0) \cdot \hat{e}_{01}^* \\ \mathbf{E}_{inc}(0) \cdot \hat{e}_{02}^* \end{pmatrix} \qquad \textbf{2.59.1}$$

However since the most general form of the amplitude scattering matrix [3] is given as,

$\begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix}$ in literature, equation 2.59.1 may also be expressed as,

$$\begin{pmatrix} \mathbf{E}_{sca} \cdot \hat{\theta}_s \\ -\mathbf{E}_{sca} \cdot \hat{\varphi}_s \end{pmatrix} = \frac{\exp\left(i\mathbf{k}_{sca} \cdot r\right)}{-i\mathbf{k}r} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} \mathbf{E}_{inc}(0) \cdot \hat{e}_{i\|} \\ \mathbf{E}_{inc}(0) \cdot \hat{e}_{i\perp} \end{pmatrix} \qquad \textbf{2.59.2}$$

where $\hat{e}_{i\|}$ and $\hat{e}_{i\perp}$ represents the parallel and perpendicular polarization directions.

$\hat{e}_{i\perp} = \hat{k}_0 \times \hat{e}_{i\|}$.

So, we may also write,

$$\begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix}\begin{pmatrix} \mathbf{E}_{inc}(0)\cdot \hat{e}_{i\|} \\ \mathbf{E}_{inc}(0)\cdot \hat{e}_{i\perp} \end{pmatrix} = -i\begin{pmatrix} f_{11} & f_{12} \\ -f_{21} & -f_{22} \end{pmatrix}\begin{pmatrix} \mathbf{E}_{inc}(0)\cdot \hat{e}^*_{01} \\ \mathbf{E}_{inc}(0)\cdot \hat{e}^*_{02} \end{pmatrix} \quad \textbf{2.59.3}$$

Now the scattering matrix elements can be calculated from f_{ml},

$$f_{11} = iS_2 \quad \textbf{2.59.4}$$

$$f_{12} = -iS_3 \quad \textbf{2.59.5}$$

$$f_{21} = -iS_4 \quad \textbf{2.59.6}$$

$$f_{22} = iS_1 \quad \textbf{2.59.7}$$

2.3.4 Mueller Matrix or Scattering Matrix

The scattering properties of a finite target is fully described by the Stokes parameters (I_i, Q_i, U_i, V_i) of an incident wave and (I_S, Q_S, U_S, V_S) of the scattered wave. Stokes vector 'I' is the total light intensity, 'Q' is the difference of light intensities polarized at 0^o and 90^o respectively, 'U' is the difference between intensities polarized at angles $+45^0$ and -45^0 respectively and finally 'V' is the difference in intensities polarized at right and left circular polarization directions.

The scattered and incident waves can be related as [19],

$$\begin{pmatrix} I_S \\ Q_S \\ U_S \\ V_S \end{pmatrix} = \frac{1}{k^2R^2} F \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix} \quad \textbf{2.60}$$

where F is the 16 element matrix or 4×4 Mueller matrix or scattering matrix of the target particle, k is the wave vector and R is the distance between the scatterer and the detector. These stokes parameters are related to the Mueller Matrix in the form of a matrix equation given as,

$$\begin{pmatrix} I_S \\ Q_S \\ U_S \\ V_S \end{pmatrix} = \frac{1}{k^2R^2} \begin{pmatrix} F_{11} & F_{12} & F_{13} & F_{14} \\ F_{21} & F_{22} & F_{23} & F_{24} \\ F_{31} & F_{32} & F_{33} & F_{34} \\ F_{41} & F_{42} & F_{43} & F_{44} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix} \quad \textbf{2.61}$$

For randomly oriented spherical or nonspherical particle systems the Mueller matrix 'F' reduces to a matrix with 8 non – zero and independent elements.

And can be written in a simple form considering matrix elements and their mirror components due to symmetry [4, 5, 20-22],

$$F = \begin{pmatrix} F_{11} & F_{12} & 0 & 0 \\ F_{21} & F_{22} & 0 & 0 \\ 0 & 0 & F_{33} & F_{34} \\ 0 & 0 & F_{-43} & F_{44} \end{pmatrix} \qquad \textbf{2.62}$$

Finally the Mueller Matrix elements can be theoretically computed from the amplitude scattering matrix elements as follows [3],

$$F_{11} = \left(|S_1|^2 + |S_2|^2 + |S_3|^2 + |S_4|^2\right)/2$$

$$F_{12} = \left(|S_2|^2 - |S_1|^2 + |S_4|^2 - |S_3|^2\right)/2$$

$$F_{13} = \mathrm{Re}\left(S_2 S_3^* + S_1 S_4^*\right)$$

$$F_{14} = \mathrm{Re}\left(S_2 S_3^* - S_1 S_4^*\right)$$

$$F_{21} = \left(|S_2|^2 - |S_1|^2 + |S_3|^2 - |S_4|^2\right)/2$$

$$F_{22} = \left(|S_1|^2 + |S_2|^2 - |S_3|^2 - |S_4|^2\right)/2$$

$$F_{23} = \mathrm{Re}\left(S_2 S_3^* - S_1 S_4^*\right)$$

$$F_{24} = \mathrm{Im}\left(S_2 S_3^* + S_1 S_4^*\right)$$

$$F_{31} = \mathrm{Re}\left(S_2 S_4^* + S_1 S_3^*\right)$$

$$F_{32} = \mathrm{Re}\left(S_2 S_3^* - S_1 S_4^*\right)$$

$$F_{33} = \mathrm{Re}\left(S_1 S_2^* + S_3 S_4^*\right)$$

$$F_{34} = \mathrm{Im}\left(S_2 S_1^* + S_4 S_3^*\right)$$

$$F_{41} = \mathrm{Im}\left(S_4 S_2^* + S_1 S_3^*\right)$$

$$F_{42} = \mathrm{Im}\left(S_4 S_2^* - S_1 S_3^*\right)$$

$$F_{43} = \mathrm{Im}\left(S_1 S_2^* - S_3 S_4^*\right)$$

$$F_{44} = \mathrm{Re}\left(S_1 S_2^* - S_3 S_4^*\right)$$

Now the differential scattering cross sections are measured from the Mueller matrix elements as [18] follows,

Since the scattered intensity is given by,

$$I_{sca} = \frac{1}{r^2}\left(\frac{d_{sca}}{d\Omega}\right)_{sca,inc} I_{inc} \qquad \textbf{2.63.1}$$

And since for unpolarised incident light the Stokes vector can be written in the form,

$$S_i = I(1,0,0,0) \qquad \textbf{2.63.2}$$

Therefore when the scattered light E_S is polarized parallel to the scattering plane (XY), that is when $E_S \parallel XY$, then,

$$\frac{dC_{sca}}{d\Omega} = \frac{1}{2k^2}\left(|S_2|^2 + |S_3|^2\right) = \frac{1}{2k^2}\left(F_{11} + F_{21}\right) \qquad \textbf{2.64}$$

and when $E_S \perp XY$,

$$\frac{dC_{sca}}{d\Omega} = \frac{1}{2k^2}\left(|S_1|^2 + |S_4|^2\right) = \frac{1}{2k^2}\left(F_{11} - F_{21}\right) \qquad \textbf{2.65}$$

So the total intensity of scattered light (using equation 2.64 and 2.65) is given as,

$$\frac{dC_{sca}}{d\Omega} = \frac{1}{2k^2}\left(|S_1|^2 + |S_2|^2 + |S_3|^2|S_4|^2\right) = \frac{1}{k^2}F_{11} \qquad \textbf{2.66}$$

where F_{11} is the first Mueller matrix element and for unpolarized incident light it is often termed as the phase function or scattering function.

Another important expression from the Mueller matrix is that for the polarization ‘P’ defined as,

$$P = \frac{(F_{21}^2 + F_{31}^2)^{1/2}}{F_{11}} \qquad \textbf{2.67}$$

For incident unpolarised light it is often termed as degree of linear polarization and given as,

$$P = -\frac{F_{12}}{F_{11}} \qquad \textbf{2.68}$$

2.4 Size and shape averaging of the scattering parameters

The Mueller matrix has 16 elements or scattering parameters F_{ij} where i, j = 1 to 4. These matrix elements depends on the scattering angle (θ), wavelength (λ) and effective size (a_{eff}) of the unknown scatterer. The most important element for any scattering event is the first element F_{11} phase function [4, 23-25].

Following the properties of Stokes vector where the scattering fields are additive or total field is a simple vector sum of the individual fields, we can conclude that for the scattering matrix elements the detected scattered field can be calculated by combining the intensities scattered by all the particles in the system [23, 24]. For a complex system of nonspherical particles distributed over wide ranges of shapes and size distribution, averaging over both constituting shapes and sizes is necessary to arrive at any meaningful conclusion. Averaging over the light scattering properties of individual particles gives the scattering matrix elements in the final form $F_{ij}(\lambda,\theta)$. The size averaged scattering matrix elements for an incident wavelength of λ, at any scattering angle θ for a particular shape is of the form [26, 27],

$$F_{N,ij}^{shape} = F_{ij}^{size}(\lambda,\theta) = \int_{r_{\min}}^{r_{\max}} F_{ij}(r,\lambda,\theta)\, n(r)\, dr \qquad \textbf{2.69}$$

Now suppose N is any arbitrary number such that N = 1,2,3…… and the total value of N signifies the number of random shapes present in the scattering volume for a particular scattering system. Again $F_{ij}(r,\lambda,\theta)$ is any arbitrary light scattering matrix element for a single scattering particle of volume equivalent sphere radius r at any scattering angle θ, and $n(r)dr$ is the number of particles having radii between r and $r + dr$, also $r_{\max}$ and $r_{\min}$ are the volume equivalent sphere radii of the largest and smallest member of the particle size distribution.

Hence the total scattering matrix element considering both shape and size dispersed systems can be obtained by averaging their values over the total number of shapes (which are already size averaged for each shape) as,

$$F_{ij,size}^{shape} = \sum_{1}^{N} F_{N,ij}^{shape} \quad \textbf{2.70}$$

Letting,

$$\left\langle F_{N,ij}^{shape} \right\rangle = \left\langle F_{ij}(\theta) \right\rangle_{size} = \int_{r_{\min}}^{r_{\max}} F_{ij}(\theta, r)\, n(r)\, dr \quad \textbf{2.71.1}$$

where $\left\langle F_{ij}(\theta) \right\rangle_{size}^{shape} = \sum_{1}^{N} F_{N,ij}^{shape}$

$$\left\langle C_{N,sca}^{shape} \right\rangle = \left\langle C_{sca} \right\rangle_{size} = \int_{r_{\min}}^{r_{\max}} C_{sca}(r)\, n(r)\, dr \quad \textbf{2.71.2}$$

where $\left\langle C_{sca} \right\rangle_{size}^{shape} = \sum_{1}^{N} C_{N,sca}^{shape}$

$$\left\langle C_{N,ext}^{shape} \right\rangle = \left\langle C_{ext} \right\rangle_{size} = \int_{r_{\min}}^{r_{\max}} C_{ext}(r)\, n(r)\, dr \quad \textbf{2.71.3}$$

where $\left\langle C_{ext} \right\rangle_{size}^{shape} = \sum_{1}^{N} C_{N,ext}^{shape}$

$$\left\langle C_{N,abs}^{shape} \right\rangle = \left\langle C_{abs} \right\rangle_{size} = \int_{r_{\min}}^{r_{\max}} C_{abs}(r)\, n(r)\, dr \quad \textbf{2.71.4}$$

where $\left\langle C_{abs} \right\rangle_{size}^{shape} = \sum_{1}^{N} C_{N,abs}^{shape}$

and where i, j = 1 to 4. All the size and shape averaged values of scattering parameters are of the form given by equations 2.71.1 to 2.71.4 [26, 27],

The distribution function $n(r)$ can be normalized as,

$$\int_{r_{\min}}^{r_{\max}} n(r)\, dr = 1 \quad \textbf{2.72}$$

In case of averaging, it is necessary to find out the volume scattering function (VSF) denoted by $\beta(\theta)$. This quantity gives the combined scattered fields due to the contributions of all the shape and size averaged intensities.

For a randomly oriented axially symmetric system $\beta(\theta)$ is represented as [24 - 28],

$$\beta_{size}(\theta) = \frac{1}{k^2} \int_{r_{\min}}^{r_{\max}} F_{ij}(\theta, r) n(r) dr \quad \textbf{2.73}$$

or, $\beta(\theta) = \langle \beta_{size}(\theta) \rangle^{shapes}$ **2.74**

where the units of $\beta(\theta)$ is per steradians per centimetre (sr^{-1} cm^{-1}).

Now degree of linear polarization is written as [5],

$$P(\theta) = -\frac{\langle S_{12}(\theta) \rangle_{size}^{shape}}{\langle S_{11}(\theta) \rangle_{size}^{shaoe}} \text{ such that } |P(\theta)| \leq 1$$ **2.75**

These two components $\beta(\theta)$ and $P(\theta)$ are the most important components in case of light scattering studies with unpolarized incident light which is evident in case of studies of terrestrial and extra-terrestrial dust particles and atmospheric aerosols as applicable in this thesis work.

References

1. Ishimaru, Akira. *Wave propagation and scattering in random media.* New York: Academic press, volume 2, 1978.
2. Tsang, L., Kong, J.A., and Shin, R.T. Radiative transfer theory for active remote sensing of a layer of nonspherical particles. *Radio Science*, 19(2):629-642, 1984.
3. Bohren, C.F., and Huffman, D.R. *Absorption and scattering by a sphere.* Wiley-VCH Verlag GmbH, 1983.
4. Van de Hulst, H.C. *Light Scattering by Small Particles, Dover Publications,* New York, 1981.
5. Mishchenko, M.I., Hovenier, J.W. and Travis, L.D. *Light Scattering by Nonspherical Particles: Theory, Measurements, and Applications, Academic Press,* San Diego, California, 2000.
6. Draine, B.T. and Flatau, P.J., Discrete-dipole approximation for scattering calculations. *JOSA A*, 11(4):1491-1499, 1994.
7. Kocifaj, M. *Lecture Notes: Light scattering by Small Particles Atmospheric Optics and Astrophysical Application Part I–Theory, Institute of Experimental Physics,* University of Vienna and Astronomical Institute, Slovak Academy of Sciences, 2007.
8. Doicu, A., Wriedt, Th. and Eremin, Y.A. *Light Scattering by Systems of Particles Null-Field Method with Discrete Sources: Theory and Programs, Springer Series in Optical Sciences,* 124, Springer-Verlag Berlin Heidelberg, 2006.
9. Purcell, E.M. Pennypacker, C.R. Scattering and absorption of light by nonspherical dielectric grains, *Astrophysical J.,* 186:705, 1973.
10. Draine, B.T. The discrete-dipole approximation and its application to interstellar graphite grains, *Astrophys. J.,* 333:848-872, 1988.
11. DeVoe, H. Optical properties of molecular aggregates. I. Classical model of electronic absorption and refraction. *The Journal of chemical physics,* 41(2):393-400, 1964.

12. DeVoe, H. Optical properties of molecular aggregates. II. Classical theory of the refraction, absorption, and optical activity of solutions and crystals. *The Journal of chemical physics*, 43(9):3199-3208, 1965
13. Draine, B.T., Goodman, J.J. Beyond Clausius-Mossotti: Wave propagation on a polarizable point lattice and the discrete dipole approximation. *Astrophys.J.* 405:685, 1993.
14. Draine, B.T. and Flatau, P.J. Discrete-dipole approximation for scattering calculations. *J. Opt. Soc. Am. A*, **11**:1491, 1994.
15. Lakhtakia, A and Mulholland, G.W. On two numerical techniques for light scattering by dielectric agglomerated structures. *J. Res. Natl. Inst. Stand. Technol.*, 98:699, 1993.
16. Lorentz, H.A. *The theory of electrons and its applications to the phenomena of light and radiant heat*, Teubner, Leipzig, 1916.
17. Goedecke G.H. and O'Brien, S.G. Scattering by irregular inhomogeneous particles via the digitized Green's function algorithm, *Appl. Opt.* 27:2431-2438, 1988.
18. Draine, B.T. and Flatau, P.J. User Guide to the Discrete Dipole Approximation Code DDSCAT7.3.0, arxiv.org/pdf/1305.6497, 2013. (Last accessed 11-04-2018).
19. Volten, H., De Haan, J.F. Hovenier, J.W. Schreurs, R. Vassen, W., Dekker, A.G, Hoogenboom, H.J., Charlton, F. and Wouts, R. Laboratory measurements of angular distributions of light scattered by phytoplankton and silt. *Limnology and oceanography*, 43(6):1180-1197, 1998.
20. Perry, R.J., Hunt, A.J. and Huffman, D.R., Experimental determinations of Mueller scattering matrices for nonspherical particles. *Applied Optics*, 17(17):2700-2710, 1978.
21. Asano, S. and Sato, M. Light scattering by randomly oriented spheroidal particles. *Appl. Opt.*, 19(6):962-974, 1980.
22. Braak, C.J., De Haan, J.F., Van der Mee, C.V.M., Hovenier, J.W. and Travis, L.D., Parameterized scattering matrices for small particles in planetary atmospheres. *J. Quant. Spec. Rad. Trans.*, 69(5):585-604, 2001.

23. Gogoi, A., Choudhury, A. and Ahmed, G.A., Mie scattering computation of spherical particles with very large size parameters using an improved program with variable speed and accuracy. *J. Modern Optics*, 57(21):2192-2202, 2010.
24. Ahmed, G. A., *Design considerations of a laser based air quality monitoring system coupled to a microprocessor linked data recording and processing unit,* PhD thesis, Gauhati University, Guwahati, 2001.
25. Jonasz, M., and Fournier G. R. *Light Scattering by Particles in Water Theoretical and Experimental Foundations*, Elsevier, Amsterdam, 2007.
26. Mishchenko, M. I., Travis, L. D., Lacis, A. A. *Scattering absorption and emission of light by small particles,* Electronic Edition, Goddard Institute for Space Studies, New York, 2004 url: http://www.giss.nasa.gov/~crmim/books.html.
27. Hansen, J. E. and Travis, L. D. Light scattering in planetary atmospheres. *Space Sci. Rev.*, 16(4):527-610, 1974.
28. Gogoi, A., Borthakur, L.J., Choudhury, A., Stanciu, G.A. and Ahmed, G.A., Detector array incorporated optical scattering instrument for nephelometric measurements on small particles. *Meas. Sci. Technol.*, 20(9):095901, 2009.