Appendix: Light scattering

General

Light scattering by particles is often best described using spherical coordinates. The particle center is located at the origin (0,0,0), and in case of rotationally symmetric particles, the symmetry axis is chosen to coincide with the *z*-axis. The angles in the spherical coordinate system are given by θ and ϕ, in which $\theta \in [0, \pi]$ is the polar angle measured from the positive *z*-axis and $\phi \in [0, 2\pi\rangle$ the azimuthal angle measured from the *x*-axis in the *xy*-plane (see Fig. 10.4).

The transverse electromagnetic plane-wave incident along the direction of $\hat{n} = \hat{\theta} \times \hat{\phi}$ on a scatterer can then be described by two components $E_{\|}$ and $E_{\perp}$ in the $\hat{\theta}$ and $\hat{\phi}$ directions, respectively. The scattered wave is an outgoing spherical wave. The scattering matrix $\mathbf{S}$ linearly transforms the components of the incoming electric field into the components of the scattered wave: [154]

$$\begin{pmatrix} E_{\|} \\ E_{\perp} \end{pmatrix} = \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \frac{e^{ikr}}{r} \begin{pmatrix} E_{\|}^{in} \\ E_{\perp}^{in} \end{pmatrix} \tag{10.1}$$

The four elements of the scattering matrix, the amplitude functions S_1, S_2, S_3 and S_4, are all complex functions that depend on the directions of incidence and scattering and on the particle size and morphology. For spherical particles, the off-diagonal elements S_3 and S_4 are zero, and the extinction cross section efficiency is given:

$$Q_{ext} = \frac{\lambda}{\pi R^2} \,\mathrm{Im}[S_1 + S_2] \tag{10.2}$$

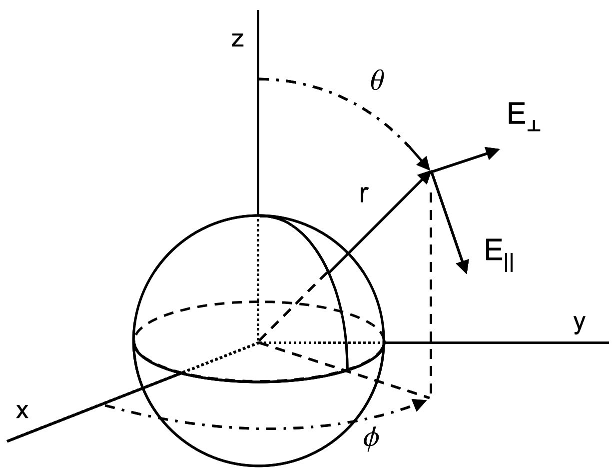

Figure 10.4: Spherical coordinate system.

Mie theory

The solution of Maxwell's equations to the problem of scattering and absorption of light by a sphere illuminated by a plane-wave was given by Gustav Mie in the beginning of the 20th century. [1] It is based on the method of separation of variables and described in many text books, see e.g., Refs. [34, 175, 176]. The differential equations can be solved separately for the parameters r, θ, and ϕ. The electric fields of the incoming and scattered waves are then expressed in a series of spherical harmonic functions. The geometry excludes some of the spherical harmonics in these series, since amplitude of the fields must be finite at the origin, and the (outgoing) scattered wave must vanish at large distances from the particle. By applying the boundary conditions that the tangential components of the fields must be continuous at the surface of the particle, the coefficients of the scattered and the internal fields can be solved as a function of the known coefficients of the incoming fields.

The exact analytical results via the method of separation of variables can only be applied to a limited number of particle geometries. [154] Besides the solution for an isotropic sphere, solutions of concentric core/shell spheres, [44] concentric multilayered spheres, infinite cylinders, homogeneous and core/shell spheroids, [177, 178] and a sphere on a surface [179] have been presented in literature.

T-matrix formalism

The T-matrix or transition matrix method was first introduced by Waterman for homogeneous particles in the late 1950s and later improved by several people. Nowadays, it is a widely used technique to calculate the optical properties of nonspherical particles. Like in the frame-work of Mie-theory, the incoming and scattered fields are expanded in vector spherical harmonics. The T-matrix is the matrix that relates the expansion coefficients of the scattered field p_{mn} and q_{mn} to the coefficients of the incoming field a_{mn} and b_{mn}:

$$\begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix} = \begin{pmatrix} \mathbf{T}^{11} & \mathbf{T}^{12} \\ \mathbf{T}^{21} & \mathbf{T}^{22} \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} \tag{10.3}$$

From the T-matrix, the elements of the scattering matrix **S** and other quantities can be calculated. A fundamental and convenient feature of the T-matrix is that it only depends on the size, composition and shape of the scatterer.

In a typical T-matrix calculation, the field inside the scatterer is also expanded in vector spherical harmonics, with coefficients c_{mn} and d_{mn}. These coefficients are related to the coefficients a_{mn} and b_{mn} of the incident field by the matrix **Q**. The elements of the matrix **Q** are 2-dimensional integrals over the surface of the particle. [180] The T-matrix method is therefore also referred to as the extended boundary condition method. The T-matrix is calculated from the matrix **Q** by

$$\mathbf{T} = -\mathbf{Q}_2 \, [\mathbf{Q}]^{-1} \tag{10.4}$$

in which the matrix **Q** is equal to $\mathbf{Q}_2$, except that in the evaluation of the matrix elements the Bessel functions of the first kind have to be replaced by Hankel functions.

The formulas for T-matrix calculations become much simpler for axially symmetric particles with the rotational axis along the z-axis, because the surface integrals then reduce to single integrals over the polar angle θ and the T matrix becomes diagonal with respect to the indices m and m'.

The T-matrix of a coated particle can be written in terms of the T-matrix $\mathbf{T}_1$ of a homogeneous particle with a radius equal to that of the core and a refractive index of m_1/m_2, and the matrices $\mathbf{A}_2$ and $\mathbf{B}_2$ that form the T-matrix of a homogeneous particle of the same (total) size and refractive index m_2 by $-\mathbf{B}_2 \cdot \mathbf{A}_2^{-1}$: [155]

$$\mathbf{T} = -[\mathbf{B}_2 + \mathbf{B} \cdot \mathbf{T}_1] \cdot [\mathbf{A}_2 + \mathbf{A} \cdot \mathbf{T}_1]^{-1} \tag{10.5}$$

The matrices **B** and **A** are equal to the matrices $\mathbf{B}_2$ and $\mathbf{A}_2$, except that in the evaluation of the matrix elements the Bessel functions of the first kind have to be replaced by Hankel functions.

T-matrix program

The calculations in Chapter 8 and 9 were done using a Fortran code written by Moroz, [41] based on the T-matrix codes by Mishchenko and Quirantes. The codes are available on the World Wide Web and described in several papers in the literature. [153, 155, 156, 180, 180, 181] The outcomes for spherical particles were benchmarked to results from Mie-theory calculations. Results for anisotropic particles were compared to analytical results for oblate spheroids from Asano [34, 178] (using the method of separation of variables) and results published by Kelly *et al.*. [33]

Convergence

For computations, the expansion of the electromagnetic fields is cut-off after a finite number N_{max}. The convergence of the extinction and scattering cross sections is checked by a subroutine. [156] When convergence is not obtained within a certain accuracy, N_{max} is increased. An increase in N_{max} results in larger computer usage (it also determines the size of the submatrices T^{ij}), and can result in computational instability. For a coated particle, the convergence of the T-matrices in equation 10.5 require different N_{max} to converge. In the calculations, the largest of the value of N_{max} required to obtain convergence is used. The routine also checks for the convergence of the surface integrals, which is determined by the number of Gaussian integration points. In literature, a rule of thumb for coated particles is that this number should be about 4 N_{max}. [155] In our calculations, the number of Gaussian integration points was set to 6 N_{max}.

For larger particles and/or larger anisotropy, it is well known that computation of the T-matrix can be an ill-conditioned process. Due to the large numbers in the **Q**-matrix,

Table 10.1: Convergence parameter N_{max} as a function of size anisotropy for an oblate ellipsoidal silica-core/Au-shell particle in silica with sphere-equivalent-dimensions of R_{core} = 156 nm and R_{total} = 181 nm (system A) and R_{core} = 228 nm and R_{total} = 266 nm (system B).

System	Aspect ratio	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
1	N_{max}	8	10	12	14	16	18	20	20
2	N_{max}	12	14	14	18	20	26	28	-

the matrix inversion involved in the computation of the T-matrix (see Equations 10.3 and 10.5) can become numerically unstable. Therefore, especially for a-spherical particles, special attention has to be paid to the convergence of the calculation.

For spherical Au-shell particles of about the size in the experiments reported here, convergence is obtained at typical values of $7-13$ for N_{max} in the wavelength ranging from 1900 nm to 300 nm. Table 10.1 shows the increase in the convergence parameter N_{max} for the calculations for oblate ellipsoidal Au-shells as the particle anisotropy is increased for the systems studied in Chapters 8 (system A) and 9 (system B).