

Lecture 9

The Beer-Bouguer-Lambert law. Rayleigh scattering.

Scattering and absorption by aerosols and clouds.

Objectives:

1. The Beer-Bouguer-Lambert law.
2. Principles of scattering.
3. Rayleigh scattering.
4. Scattering and absorption by aerosol and cloud particles.

Required Reading:

G: 5.1-5.4, 5.6, 5.7

Additional/advanced Reading:

G: 5.5,

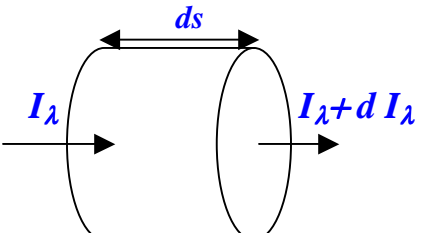
1. The Beer-Bouguer-Lambert law.

The fundamental law of extinction is the **Beer-Bouguer-Lambert law**, which states that the extinction process is linear in the intensity of radiation and amount of matter, provided that the physical state (i.e., T, P, composition) is held constant.

Consider a small volume ΔV of infinitesimal length ds and unit area ΔA containing optically active matter (gases, aerosols, and/or cloud drops). Thus, the change of intensity along a path ds is proportional to the amount of matter in the path.

For extinction $dI_\lambda = -k_{e,\lambda} I_\lambda ds$ [9.1]

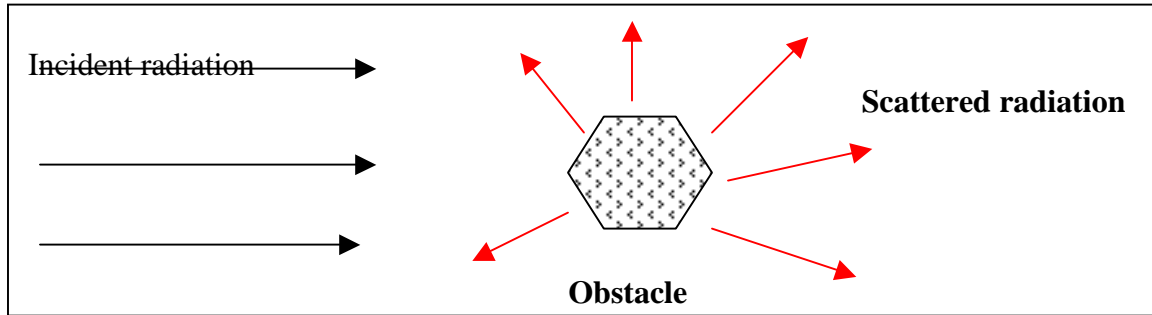
For emission: $dI_\lambda = k_{e,\lambda} J_\lambda ds$



where $k_{e,\lambda}$ is the **volume extinction coefficient** (L^{-1}) and J_λ is the **source function**.

Optical depth is $\tau_\lambda = \int_{s_1}^{s_2} k_{e,\lambda}(s) ds$; **Transmission function** is $T_\lambda = \exp(-\tau_\lambda)$

2. Principles of scattering.



Consider a single arbitrary particle consisted of many individual dipoles. The incident electromagnetic field induces dipole oscillations. The dipoles oscillate at the frequency of the incident field and therefore scatter radiation in all directions. In a given direction of observation, the total scattered field is a superposition of the scattered wavelets of these dipoles, accounting for their phase difference: scattering by the dipoles is coherent (i.e., there is a definite relation between phases). In general, these phase relations vary with the scattering direction.

NOTE: Scattering can be considered as two step process: (1) excitation and (2) reradiation. In addition to scattering, the excited charges may transform some part of incident radiative energy into other forms of energy. This process is called **absorption**. *Thus, scattering and absorption are not mutually independent.*

Scattering phase function $P(\cos\Theta)$ is defined as a non-dimensional parameter to describe the angular distribution of the scattered radiation as

$$\frac{1}{4\pi} \int_{\Omega} P(\cos \Theta) d\Omega = 1 \quad [9.2]$$

where Θ is called the **scattering angle** between the direction of incidence and observation.

NOTE: Another form of [9.2]

$$\frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} P(\cos\Theta) d(\cos\Theta) d\phi = 1$$

NOTE: The phase function is often expressed as

$$P(\cos \Theta) = P(\theta', \phi', \theta, \phi)$$

where (θ', ϕ') and (θ, ϕ) are the spherical coordinates of incident beam and direction of observation. Using the spherical geometry it can be shown (see G: Appendix 1) that

$$\cos(\Theta) = \cos(\theta')\cos(\theta) + \sin(\theta')\sin(\theta) \cos(\phi' - \phi),$$

The **asymmetry factor g** is defined as

$$g = \frac{1}{2} \int_{-1}^1 P(\cos \Theta) \cos \Theta d(\cos \Theta) \quad [9.3]$$

$g=0$ for isotropic scattering

Forward scattering refers to the observations directions for which $\Theta < \pi/2$:

$g > 0$ scattering in the forward direction

Backward scattering refers to the observations directions for which $\Theta > \pi/2$:

$g < 0$ scattering in the backward direction

NOTE: $\Theta = 0^\circ$ is often called forward scattering and $\Theta = 180^\circ$ is called backscattering.

Scattering domains

Rayleigh scattering: $2\pi r/\lambda \ll 1$, and the refractive index m is arbitrary (applies to scattering by molecules and small aerosol particles)

Rayleigh-Gans scattering: $(m - 1) \ll 1$ (not useful for atmospheric application)

Mie-Debye scattering: $2\pi r/\lambda$ and m are both arbitrary but for spheres only (applies to scattering by aerosol and cloud particles)

Geometrical optics: $2\pi r/\lambda$ is very large and m is real (applies to scattering by large cloud droplets).

3. Rayleigh scattering

- Because the sizes of atmospheric molecules are much smaller than the wavelengths of solar and IR radiation, the scattering by atmospheric gases is the Rayleigh scattering.
- In the Rayleigh scattering approximation, a molecule (or a small particles) is considered as an individual dipole.

Consider a small homogeneous spherical particle (e.g., a molecule) with size smaller than the wavelength of incident radiation \vec{E}_0 . Let \vec{p}_0 be the induced dipole moment, then from the classical electromagnetic theory we have

$$\vec{p}_0 = \alpha \vec{E}_0$$

where α is the polarizability of the particle.

According to the classical electromagnetic theory, the scattered electric field at the large distance r (called far field scattering) from the dipole is given (in cgs units) by

$$\vec{E} = \frac{1}{c^2} \frac{1}{r} \frac{\partial^2 \vec{p}}{\partial t^2} \sin(\gamma)$$

where γ is the angle between the scattered dipole moment \vec{p} and the direction of observation.

In oscillating periodic field, the dipole moment is given in terms of induced dipole moment by

$$\vec{p} = \vec{p}_0 \exp(-ik(r - ct))$$

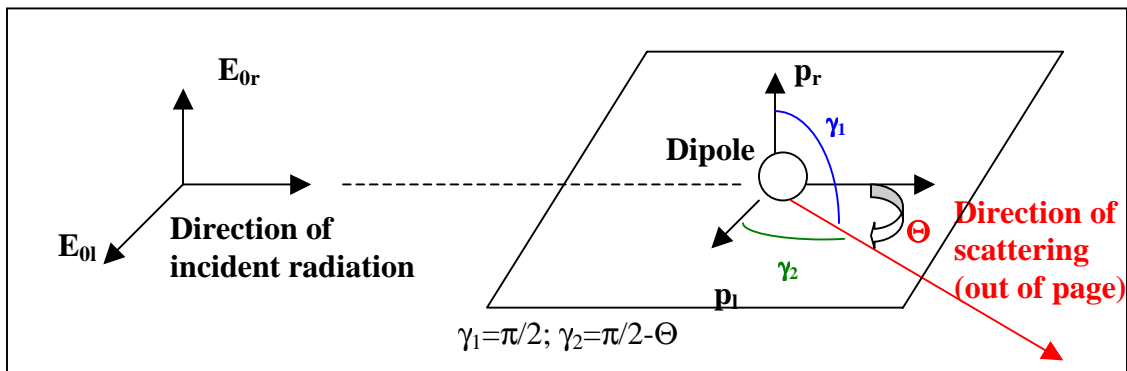
and thus the electrical field is

$$\vec{E} = -\vec{E}_0 \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma)$$

Decomposing the electrical vector on two orthogonal components perpendicular and parallel to the plane of scattering (a plane containing the incident and scattering beams), We have

$$E_r = -E_{0r} \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma_1)$$

$$E_t = -E_{0t} \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma_2)$$



Using that

$$I = \frac{1}{\Delta\Omega} \frac{c}{4\pi} |E|^2,$$

the perpendicular and parallel intensities (or linear polarized intensities) are

$$\begin{aligned} I_r &= I_{0r} k^4 \alpha^2 / r^2 \\ I_l &= I_{0l} k^4 \alpha^2 \cos^2(\Theta) / r^2 \end{aligned}$$

Using that the natural light (incident beam) is not polarized ($I_{0r} = I_{0l} = I_0/2$) and that $k = 2\pi/\lambda$, we have

$$I = I_r + I_l = \frac{I_0}{r^2} \alpha^2 \left(\frac{2\pi}{\lambda} \right)^4 \frac{1 + \cos^2(\Theta)}{2} \quad [9.4]$$

Eq.[9.4] gives the intensity scattered by molecules (Rayleigh scattering) for unpolarized incident light,

Rayleigh scattering phase function for incident unpolarized radiation is

$$P(\cos(\Theta)) = \frac{3}{4} (1 + \cos^2(\Theta)) \quad [9.5]$$

Eq.[9.4] may be rewritten in the form

$$I(\cos(\Theta)) = \frac{I_0}{r^2} \alpha^2 \frac{128\pi^5}{3\lambda^4} \frac{P(\Theta)}{4\pi} \quad [9.6]$$

- Rayleigh scattering results in the sky polarization. The degree of linear polarization is

$$LP(\Theta) = -\frac{Q}{I} = -\frac{I_l - I_r}{I_l + I_r} = \frac{\cos^2 \Theta - 1}{\cos^2 \Theta + 1} = \frac{\sin^2 \Theta}{\cos^2 \Theta + 1}$$

Eq. [9.6] may be rewritten in the terms of **the scattering cross section**

$$I(\cos(\Theta)) = \frac{I_0}{r^2} \sigma_s \frac{P(\Theta)}{4\pi} \quad [9.7]$$

Here the scattering cross section (in units of area) by a single molecule is

$$\sigma_s = \alpha^2 \frac{128\pi^5}{3\lambda^4}$$

The polarizability α is given by the Lorentz-Lorenz formula

$$\alpha = \frac{3}{4\pi N} \left(\frac{m^2 - 1}{m^2 + 2} \right)$$

where N is the number of molecules per unit volume and $m = n - ik$ is the refractive index.

For air molecules in solar spectrum: n is about 1 but strongly depends on λ , and $k = 0$.

Thus the polarizability can be approximated as

$$\alpha \approx \frac{1}{4\pi N} (n^2 - 1)$$

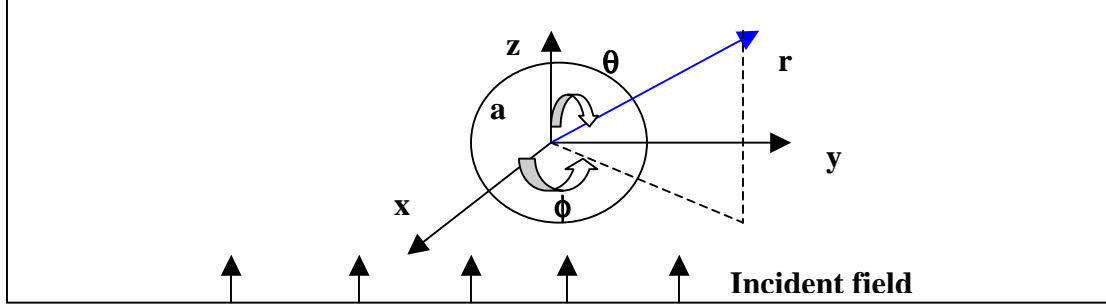
Therefore, the scattering cross section of air molecules becomes

$$\sigma_s = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4 N^2} f(\delta) \quad [9.8]$$

where $f(\delta)$ is the correction factor for the anisotropic properties of air molecules, defined as $f(\delta) = (6+3\delta)/(6-7\delta)$ and $\delta=0.035$

Using this scattering cross section, one can calculate the optical depth of the entire atmosphere due to molecular scattering as

$$\tau(\lambda) = \sigma_s(\lambda) \int_0^{top} N(z) dz \quad [9.9]$$



In the far-field zone (i.e., at the large distances from a sphere), the solution of the vector wave equation can be obtained as

$$E_r^s = H_r^s \approx 0$$

$$E_\theta^s = H_\varphi^s \approx \frac{-i}{kr} e^{-ikr} \cos(\varphi) \sum_1^\infty \frac{2n+1}{n(n+1)} \left[a_n \frac{dP_n^1(\cos \theta)}{d\theta} + b_n \frac{P_n^1(\cos \theta)}{\sin \theta} \right]$$

$$-E_\varphi^s = H_\theta^s \approx \frac{-i}{kr} e^{-ikr} \sin(\varphi) \sum_1^\infty \frac{2n+1}{n(n+1)} \left[a_n \frac{dP_n^1(\cos \theta)}{\sin \theta} + b_n \frac{P_n^1(\cos \theta)}{d\theta} \right]$$

where P_n^1 are the associated Legendre polynomials, and a_n and b_n are **Mie coefficients** which don't depend on the angles but depend on size parameter $\mathbf{x} = 2\pi a/\lambda$ (a is the radius of the particle) and variable $\mathbf{y} = \mathbf{x} \mathbf{m}$ (\mathbf{m} is relative refractive index of the particle).

Let's define two **Mie scattering functions**:

$$S_1(\theta) = \sum_{n=1}^\infty \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos \theta) + b_n \tau_n(\cos \theta)]$$

$$S_2(\theta) = \sum_{n=1}^\infty \frac{2n+1}{n(n+1)} [b_n \pi_n(\cos \theta) + a_n \tau_n(\cos \theta)]$$

where π_n and τ_n are so-called **angular functions**

$$\pi_n(\cos \theta) = \frac{1}{\sin(\theta)} P_n^1(\cos \theta); \quad \tau_n(\cos \theta) = \frac{d}{d\theta} P_n^1(\cos \theta)$$

Thus we may re-write equation for the solution of the vector wave equation as

$$E_{\theta}^s = \frac{-i}{kr} e^{-ikr} \cos(\varphi) S_2(\theta)$$

$$-E_{\varphi}^s = \frac{-i}{kr} e^{-ikr} \sin(\varphi) S_1(\theta)$$

Let's define the perpendicular and parallel components of the electric field as

$$E_r^s = -E_{\varphi}^s \quad \text{and} \quad E_l^s = E_{\theta}^s$$

and decompose the incident electric vector into the perpendicular and parallel components as

$$E_r^i = \exp(-ikz) \sin \varphi \quad \text{and} \quad E_l^i = \exp(-ikz) \cos \varphi$$

Then, can have

$$\begin{bmatrix} E_l^s \\ E_r^s \end{bmatrix} = \frac{\exp(-ikr + ikz)}{ikr} \begin{bmatrix} S_2(\theta) & 0 \\ 0 & S_1(\theta) \end{bmatrix} \begin{bmatrix} E_l^i \\ E_r^i \end{bmatrix} \quad [9.10]$$

Eq.[9.10] is a fundamental equation of scattered radiation by a sphere including polarization.

The scattered intensity components in the far field are

$$I_l^s = I_l^i \frac{i_2}{k^2 r^2}$$

$$I_r^s = I_r^i \frac{i_1}{k^2 r^2}$$

where i_1 and i_2 are so-called the **intensity function** for the perpendicular and parallel components, respectively, $i_1(\theta) = |S_1(\theta)|^2$ and $i_2(\theta) = |S_2(\theta)|^2$

From Mie theory it follows that the **extinction cross-section** of a particle is

$$\sigma_e = \frac{4\pi}{k^2} \text{Re}[S(0^0)] \quad [9.11]$$

But for the forward direction (i.e. $\theta = 0^0$), we have

$$S_1(0^0) = S_2(0^0) = \frac{1}{2} \sum_{n=1}^{\infty} (2n+1)(a_n + b_n)$$

Let's introduce the **efficiencies (or efficiency factors)** for extinction, scattering and absorption as

$$\boxed{Q_e = \frac{\sigma_e}{\pi a^2} \quad Q_s = \frac{\sigma_s}{\pi a^2} \quad Q_a = \frac{\sigma_a}{\pi a^2}} \quad [9.12]$$

where πa^2 is the particle area projected onto the plane perpendicular to the incident beam.

Thus we have

$$Q_e = \frac{\sigma_e}{\pi a^2} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \operatorname{Re}[a_n + b_n]$$

NOTE: Q_e approaches 2 for large size particles

From Mie theory it follows that the **scattering cross-section** of a particle is

$$Q_s = \frac{\sigma_s}{\pi a^2} = \frac{2}{x^2} \int_0^{\pi} [i_1(\theta) + i_2(\theta)] \sin(\theta) d\theta$$

Using the recurrence properties of the associated Legendre polynomials we can re-write the above equation as

$$Q_s = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) [|a_n|^2 + |b_n|^2]$$

Finally, the absorption efficiency can be calculated as

$$\boxed{Q_a = Q_e - Q_s}$$

Recall definition of Stokes parameters (see Lecture 2), which uniquely characterize the electromagnetic waves. Let I_o, Q_o, U_o and V_o be the Stokes parameters of incident field and I, Q, U and V be the Stokes parameters of scattered radiation

$$\begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix} = M \begin{bmatrix} I_o \\ Q_o \\ U_o \\ V_o \end{bmatrix}$$

where M is the **transformation matrix**

$$M = \begin{bmatrix} M_{11} & M_{12} & 0 & 0 \\ M_{12} & M_{11} & 0 & 0 \\ 0 & 0 & M_{33} & -M_{34} \\ & & M_{34} & M_{33} \end{bmatrix}$$

and

$$M_{11} = \frac{1}{2k^2 r^2} [S_1(\theta)S_1^*(\theta) + S_2(\theta)S_2^*(\theta)]$$

$$M_{12} = \frac{1}{2k^2 r^2} [S_2(\theta)S_2^*(\theta) - S_1(\theta)S_1^*(\theta)]$$

$$M_{33} = \frac{1}{2k^2 r^2} [S_2(\theta)S_1^*(\theta) + S_1(\theta)S_2^*(\theta)]$$

$$-M_{34} = \frac{1}{2k^2 r^2} [S_1(\theta)S_2^*(\theta) - S_2(\theta)S_1^*(\theta)]$$

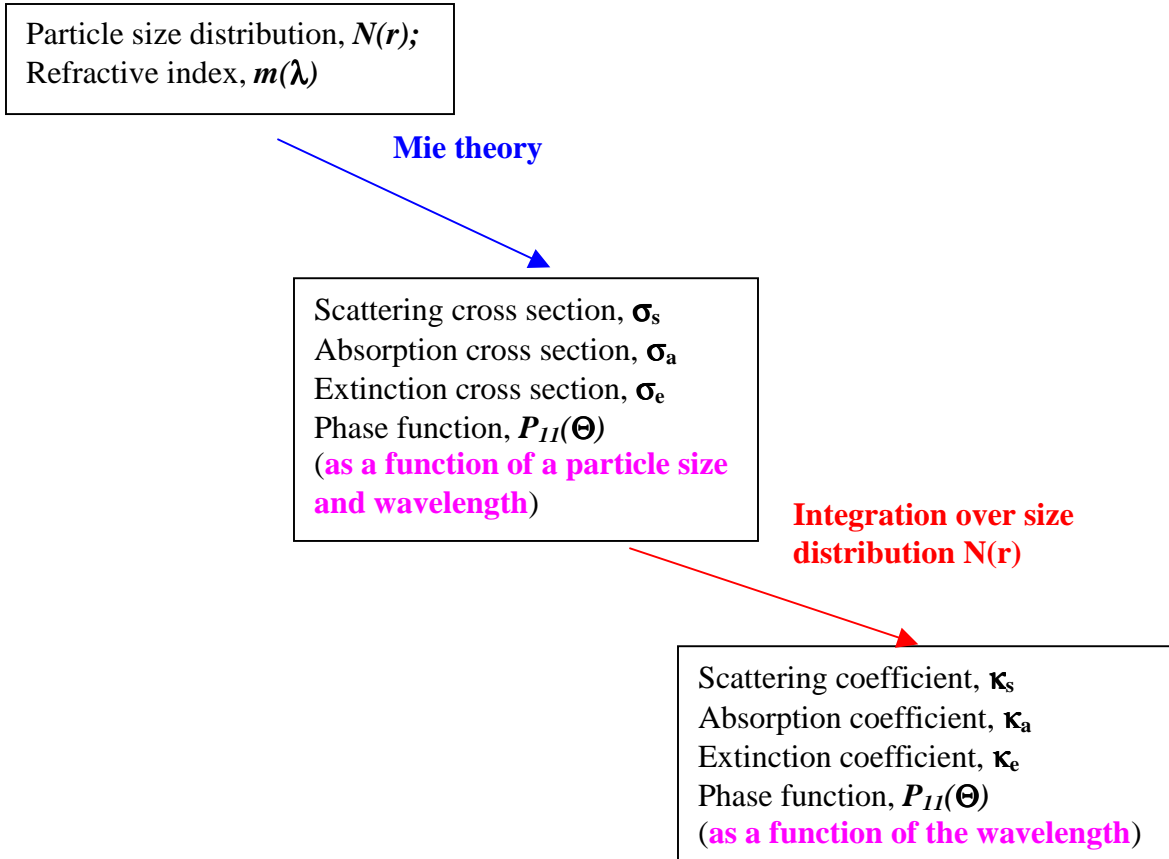
Let's define the **scattering phase matrix** $P(\theta)$ as

$$M(\theta) = C P(\theta)$$

and that

$$\frac{1}{4\pi} \int_{\Omega} P_{11}(\theta) d\Omega = \int_0^{2\pi} \int_0^{\pi} \frac{P_{11}(\theta)}{4\pi} \sin(\theta) d\theta d\varphi = 1$$

Strategy to compute optics of spherical particles:



Integration over the size distribution:

For a given type of particles characterized by the size distribution $N(r)$, the extinction, scattering and absorption coefficients (in units LENGTH^{-1}) are determined as

$$k_e = \int_{r_1}^{r_2} \sigma_e(r) N(r) dr ; \quad k_s = \int_{r_1}^{r_2} \sigma_s(r) N(r) dr ; \quad k_a = \int_{r_1}^{r_2} \sigma_a(r) N(r) dr \quad [9.13]$$

The **single scattering albedo** gives the percentage of light which will be scattered in a single scattered event and it is defined as

$$\omega_0 = \frac{k_s}{k_e} \quad [9.14]$$

NOTE: $\omega_0 = 1$ for no absorption

Scattering phase function

$$P(\Theta) = \frac{\int_{r_1}^{r_2} P(\Theta) \sigma_s N(r) dr}{\int_{r_1}^{r_2} \sigma_s N(r) dr} \quad [9.15]$$

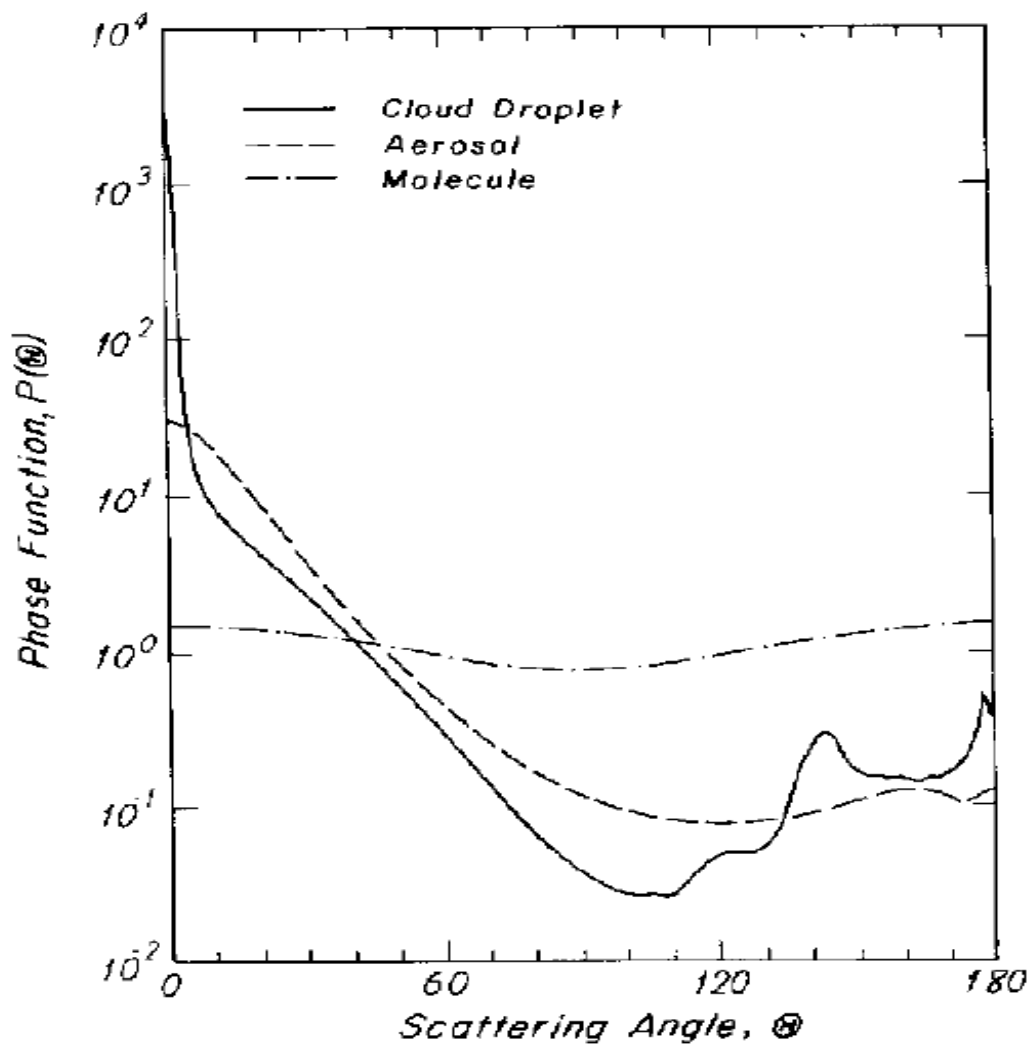


Figure 9. 1 Examples of scattering phase functions at a wavelength of 0.5 μm .

- **Optical properties of the external mixture** (i.e., the mixture of several types of particles)

$$k_e = \sum_i k_e^i \quad k_s = \sum_i k_s^i \quad k_a = \sum_i k_a^i \quad [9.16]$$

where k_e^i , k_s^i and k_a^i are calculated for each particle type characterized by its particle size distribution $N_i(r)$ and a refractive index (or effective refractive index) m_i .

NOTE: Do not sum the single scattering albedo and scattering phase functions !!!

NOTE: If an atmospheric layer has molecules, aerosols and/or cloud particles, one calculates the **effective optical properties** of this layer as an external mixture of the optical properties of these constituents.

➤ **Optics of cloud particles.**

- In contrast to atmospheric aerosols, the cloud droplets consist of a single species – water. Thus, to calculate the absorption and scattering cross sections of cloud droplets, one needs to know the size of droplets and the refractive index of water versus wavelength.

NOTE: Cloud droplet sizes vary from a few micrometers to 100 micrometers with average diameter in 10 to 20 μm range.

Differences in optics of water drops and ice particles are due to

- Particle shapes;
- Differences between the refractive indices of water and ice.

Using the **effective radius** (see lecture 8)

$$r_e = \frac{\int \pi r^3 N(r) dr}{\int \pi r^2 N(r) dr}$$

and the **liquid water content** (LWC) (see Lecture 8):

$$LWC = \rho_w V = \frac{4}{3} \rho_w \int \pi r^3 N(r) dr$$

the extinction coefficient of cloud droplets is

$$k_e = \int \sigma_e(r) N(r) dr = \int Q_e \pi r^2 N(r) dr$$

and that $Q_e \approx 2$ for water droplets at solar wavelengths, we have

$$k_e \approx \frac{3}{2} \frac{LWC}{r_e} \quad [9.17]$$

The parameterizations of the optical properties of clouds vs. LWC and r_e :

$$\begin{aligned} k_e &= LWC(a_1 r_e^{a_2} + a_3) \\ 1 - \bar{\omega}_0 &= a_4 r_e^{a_5} + a_6 \\ g &= a_7 r_e^{a_8} + a_9 \end{aligned} \quad [9.18]$$

where a_i are the coefficients determined by fitting these expressions to exact computations using Mie theory; $\bar{\omega}_0$ is the single scattering albedo and g is the **asymmetry factor**.

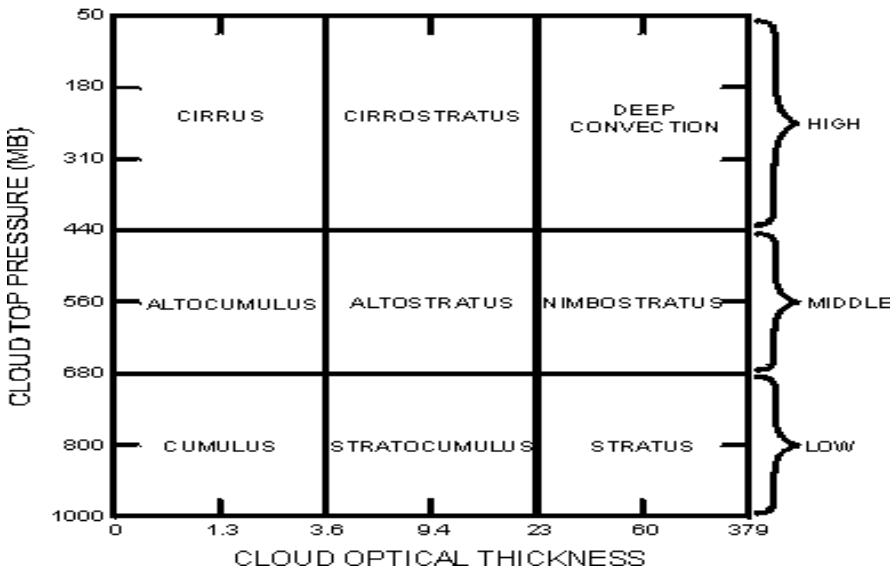


Figure 9.2 ISSCP classification of cloudy pixel used in remote sensing of clouds

NOTE: ISSCP stands for the International satellite Cloud Climatology Program.

➤ **Scattering and absorption by ice particles.**

Optical properties of ice crystals depend on

- i) Sizes and shapes;
- ii) Orientations
- iii) Ice refractive index

Approaches to predict ice crystal optics:

- i) Ray-optics approach (also called ray tracing approach) based on geometrical optics for the size parameters ($2\pi r/\lambda$) of 15-20 and larger;
- ii) Finite differences time domain (FDTD) method for the size parameters smaller than about 20;
- iii) Laboratory measurements of optical properties (e.g., phase function) of the ice crystals of known shapes and sizes.

NOTE: Improved ray tracing techniques use the Monte Carlo method to trace photons in complex ice crystals, accounting for absorption and polarization. For the recent review of various techniques, see Liou K.N., Y. Takano and P. Yang, Light scattering and radiative transfer in ice crystal clouds: applications to climate research in *Light Scattering by Nonspherical Particles*, Academic Press, 2000.

➤ **Optics of inhomogeneous and/or non-spherical particles.**

- In climate and remote sensing applications, it is often assumed that aerosol particles are spherical and homogeneous. However, aerosol particles often consist of several chemical species (called the internal mixture) and can have various shapes.

Strategy to characterize aerosol optics:

Consider a collection of aerosol particles as the external mixture of particles made of a single species and/or internally mixed particles.

There are several approaches (called **mixing rules**) to calculate the **effective refractive index** m_e of the internally mixed (or aggregated) particles using the refractive indices of the individual components:

a) **Volume (or mass) weighted mixing:**

$$m_e = \sum_j m_j f_j$$

where m_j is the refractive index of j-species and f_j is its volume fraction.

b) **Bruggeman approximation** for two randomly mixed species:

$$f_1 \frac{\epsilon_1 - \epsilon_e}{\epsilon_1 + 2\epsilon_e} + f_2 \frac{\epsilon_2 - \epsilon_e}{\epsilon_2 + 2\epsilon_e} = 0$$

where ϵ_i are the dielectric constants of two materials and f_i are their volume fractions.

Recall that the refractive index is $m = \sqrt{\epsilon}$

c) **Maxwell-Garnett approximation** for two species when one is a matrix (host material) with the dielectric constant ϵ_2 and another is an inclusion with ϵ_1 :

$$f_1 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} = \frac{\epsilon_e - \epsilon_2}{\epsilon_e + 2\epsilon_2}$$

$$f_2 \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} = \frac{\epsilon_e - \epsilon_1}{\epsilon_e + 2\epsilon_1}$$

NOTE: b) and c) approaches can be extended for the n-component mixtures.

Approaches to calculate optical properties of non-spherical particles:

- i) Extension of Mie theory: calculates the optical properties of two concentric spheres; cylinders, disks
- ii) Geometrical optics approximation (for sizes much larger than the wavelength);
- iii) T-matrix technique: calculates the optical properties of axisymmetric particles (i.e., bodies-of-revolution, for instance, spheroids);
- iv) Discrete dipole approximation (DDA) (also called the coupled dipole approximation): calculates the optical properties of the particles of any shapes with sizes smaller than about 5λ .