

Lecture 8.

Molecular (Rayleigh) scattering.

1. Beer-Bouguer-Lambert law (Extinction law).
2. Basics of scattering.
3. Molecular (Rayleigh) scattering.

Required reading:

S: 1.6; 4.1, 4.3; 5.1, Appendix 1;

Suggested reading

Liou: 3.3; Stephens: 4.2, 5.5; Petty: 4, 7, 12

Advanced reading

Bohren, C. F., and D. R. Huffman, *Absorption and scattering of light by small particles*. John Wiley&Sons, New York, pp. 531, 1983.

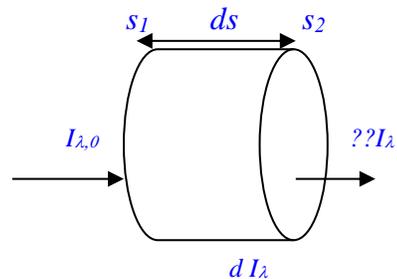
1. Beer-Bouguer-Lambert law (Extinction law).

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 $dI_\lambda = -k_{e,\lambda} I_\lambda ds$ [8.1a]

For emission: $dI_\lambda = k_{a,\lambda} B_\lambda ds$ [8.1b]



where $\kappa_{e,\lambda}$ is the **volume extinction coefficient** (LENGTH⁻¹), where $\kappa_{a,\lambda}$ is the **volume absorption coefficient** (LENGTH⁻¹), and B_λ is the **Planck function**. Here the amount is the particle number concentration.

Recall that extinction is due to scattering and absorption:

$$k_{e,\lambda} = k_{s,\lambda} + k_{a,\lambda} \quad [8.2]$$

Integrating Eq.[8.1a], we have

$$I_{\lambda} = I_{0,\lambda} \exp\left(-\int_{s_1}^{s_2} k_{e,\lambda}(s) ds\right) = I_{0,\lambda} \exp(-\tau_{\lambda}) \quad [8.3]$$

where $I_{0,\lambda}$ and I_{λ} are the incident and transmitted intensities, respectively.

NOTE: optical depth τ is unitless.

NOTE: “same name”: **optical depth = optical thickness = optical path**

Transmission function is defined as

$$T_{\lambda} = I_{\lambda} / I_{0,\lambda} = \exp(-\tau_{\lambda}) \quad [8.4]$$

UNITS: transmission function is unitless (between 0 and 1)

2. Basics of scattering.

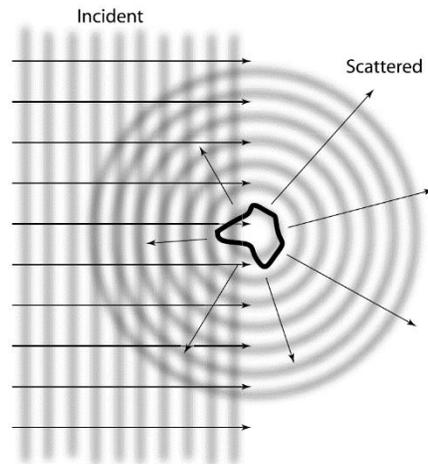


Figure 8.1 Simplified visualization of scattering of an incident EM wave by a particle.

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 certain 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).

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

$$\boxed{\frac{1}{4\pi} \int_{\Omega} P(\cos \Theta) d\Omega = 1} \quad [8.5]$$

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

Another form of Eq.[8.5]

$$\frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} P(\cos \Theta) \sin \Theta d\Theta d\varphi = 1 \quad [8.6]$$

NOTE: The phase function is often written with the notations $(\theta', \varphi', \theta, \varphi)$ or $(\mu', \varphi', \mu, \varphi)$

$$P(\cos \Theta) = P(\theta', \varphi', \theta, \varphi) \quad [8.7]$$

$$P(\cos \Theta) = P(\mu', \varphi', \mu, \varphi)$$

where (θ', φ') and (θ, φ) are the spherical coordinates of incident beam and direction of observation: θ' and θ are the zenith angles, and φ' and φ are the azimuth angles; and $\mu = \cos(\theta)$ and $\mu' = \cos(\theta')$.

The scattering angle Θ is expressed in terms of $(\theta', \varphi', \theta, \varphi)$ as (see S: Appendix 1)

$$\cos(\Theta) = \cos(\theta')\cos(\theta) + \sin(\theta')\sin(\theta) \cos(\varphi' - \varphi) \text{ or}$$

$$\cos(\Theta) = \mu' \mu + (1 - \mu'^2)^{1/2} (1 - \mu^2)^{1/2} \cos(\varphi' - \varphi)$$

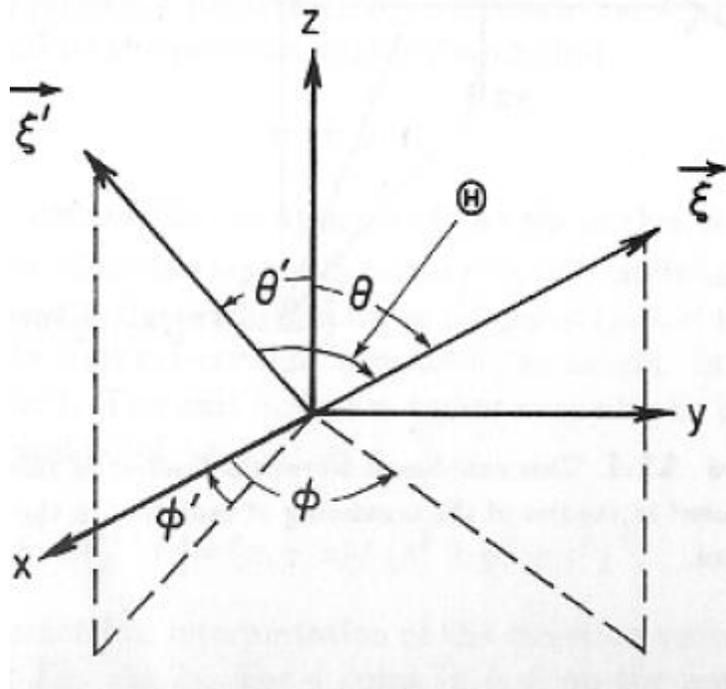


Figure A1.2 from Stephens, Appendix 1, p.468

The **asymmetry factor** g is defined as

$$g = \frac{1}{2} \int_{-1}^1 P(\cos \Theta) \cos \Theta d(\cos \Theta) \quad [8.8]$$

$g=0$ 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

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 applications)

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: $2\pi r/\lambda \gg 1$ and m is real (applies to scattering by large cloud droplets, rain, drops and ice crystals).

3. Molecular (Rayleigh) scattering.

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

$$\vec{p}_0 = \alpha \vec{E}_0 \quad [8.9]$$

where α is the **polarizability** of the particle.

NOTE: Do not confuse the polarization of the medium with polarization associated with the EM wave.

The scattered electric field at the large distance r (called far field scattering) from the dipole is given (in cgs units) by

$$\vec{E} = \frac{1}{c^2} \frac{1}{r} \frac{\partial \vec{p}}{\partial t} \sin(\gamma) \quad [8.10]$$

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

$$\vec{p} = \vec{p}_0 \exp(-ik(r - ct)) \quad [8.11]$$

and thus the electrical field is

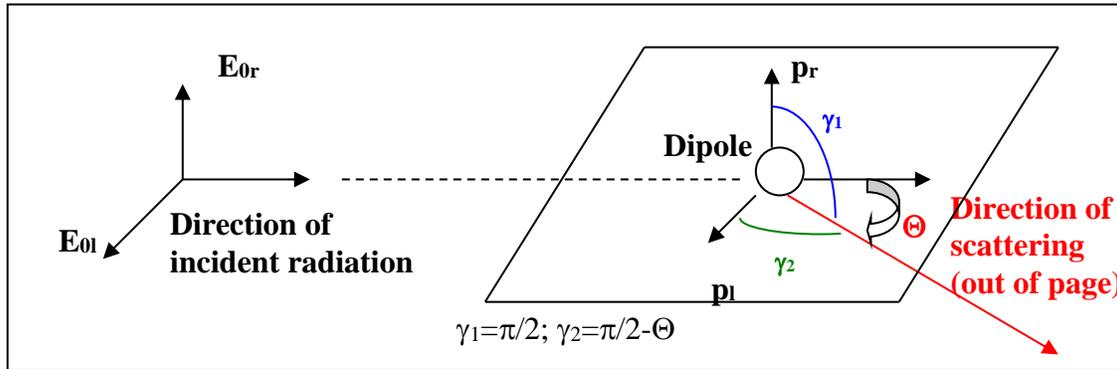
$$\vec{E} = -\vec{E}_0 \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma) \quad [8.12]$$

(Note here k denotes $2\pi/\lambda$).

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

$$E_r = -E_{0r} \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma_1) \quad [8.13]$$

$$E_l = -E_{0l} \frac{\exp(-ik(r - ct))}{r} k^2 \alpha \sin(\gamma_2) \quad [8.14]$$



Using that

$$I = \frac{1}{\Delta\Omega} \frac{c}{4\pi} |E|^2 \quad [8.15]$$

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

$$I_r = I_{0r} k^4 \alpha^2 / r^2 \quad [8.16]$$

$$I_l = I_{0l} k^4 \alpha^2 \cos^2(\Theta) / r^2 \quad [8.17]$$

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

$$I = I_r + I_l = \frac{I_0}{r^2} \alpha^2 \left(\frac{2\pi}{\lambda} \right)^4 \frac{1 + \cos^2(\Theta)}{2} \quad [8.18]$$

Eq. [8.18] gives the intensity scattered by molecules (Rayleigh scattering) for unpolarized incident light.

Rayleigh scattering phase function for incident unpolarized radiation is

$$P(\cos(\Theta)) = \frac{3}{4} (1 + \cos^2(\Theta)) \quad [8.19]$$

Eq.[8.18] may be rewritten in the form

$$I(\cos(\Theta)) = \frac{I_0}{r^2} \alpha^2 \frac{128\pi^5}{3\lambda^4} \frac{P(\Theta)}{4\pi} \quad [8.20]$$

Eq. [8.20] may be rewritten in the terms of the scattering cross section

$$I(\cos(\Theta)) = \frac{I_0}{r^2} \sigma_s \frac{P(\Theta)}{4\pi} \quad [8.21]$$

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

$$\sigma_s = \alpha^2 \frac{128\pi^5}{3\lambda^4} \quad [8.22]$$

The **polarizability** of a point dipole is given by the Lorentz-Lorenz formula

$$\alpha = \frac{3}{4\pi N_s} \left(\frac{m^2 - 1}{m^2 + 2} \right) \quad [8.23]$$

where N_s is the number of molecules per unit volume and $m=n - ix$ in the refractive index.

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

Thus the polarizability can be approximated as

$$\alpha \approx \frac{1}{4\pi N_s} (n^2 - 1) \quad [8.24]$$

Therefore, the scattering cross section of an air molecule becomes

$$\sigma_s = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4 N_s^2} f(\delta) \quad [8.25]$$

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 estimate the **optical depth** of the entire atmosphere **due to molecular scattering** as

$$\tau(\lambda) = \sigma_s(\lambda) \int_0^{top} N(z) dz \quad [8.26]$$

NOTE: The Rayleigh scattering cross section (Eq.[8.22]) and hence optical depth are inversely proportional to the fourth power of the wavelength (\Rightarrow blue color of the sky)

Approximation of molecular Rayleigh optical depth (i.e., optical depth due to molecular scattering) down to pressure level p in the Earth's atmosphere:

$$\tau(\lambda) \approx 0.0088 \left(\frac{P}{1013mb} \right) \lambda^{-4.15+0.2\lambda} \quad [8.27]$$

where the wavelength λ is in μm .

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

$$LP(\Theta) = -\frac{Q}{I} = -\frac{I_l - I_r}{I_l + I_r} = -\frac{\cos^2 \Theta - 1}{\cos^2 \Theta + 1} = \frac{\sin^2 \Theta}{\cos^2 \Theta + 1} \quad [8.28]$$

