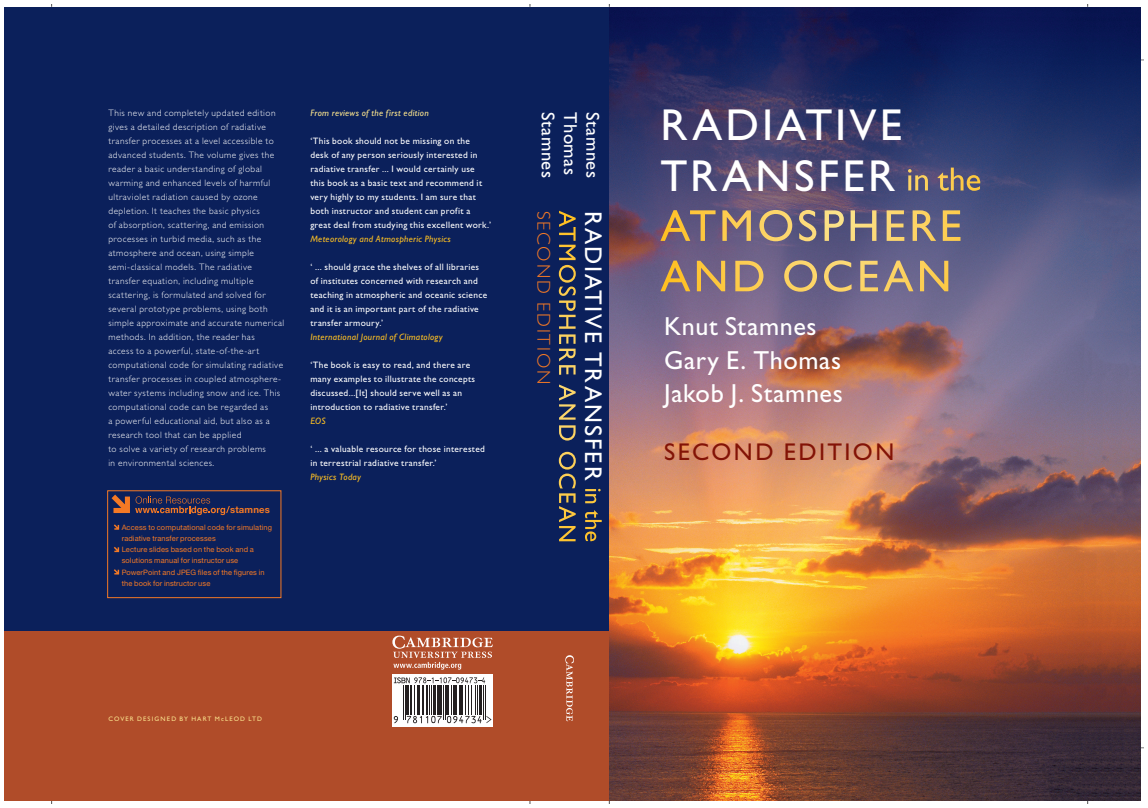
Lecture *Notes:*
Basic Scattering Processes



Based on Chapter 3 in K. Stamnes, G. E. Thomas, and J. J. Stamnes, Radiative Transfer in the Atmosphere and Ocean, Cambridge University Press, 2017.

Basic Scattering Processes (1)

In the next two chapters we will study the physical basis for the three types of light-matter interactions which are important in planetary media:

- scattering, absorption and emission.

In this chapter (Chapter 3) we concentrate on **scattering**, which may be thought of as:

- the 'first step' in both the emission and absorption processes.

We use the classical concept of the Lorentz atom to visualize the process of scattering, which encompasses both:

- **coherent** processes, such as refraction and reflection,

as well as the many

- **incoherent** processes, which are the main topic of this chapter.

Basic Scattering Processes (2)

We use the classical interaction of a plane wave with an isolated, damped, simple harmonic oscillator to introduce the **cross section** expressed in terms of:

- the **frequency of** the incident **light**, the **natural frequency** of the **oscillator**, and the **damping rate**.

A simple extension is then made to scattering involving excited quantum states to help understand three different scattering processes:

- Rayleigh, resonance, and Thomson scattering.

This approach also:

- gives the **Lorentz profile** for **absorption** in terms of the **classical damping rate**, which apart from a numerical constant agrees with the quantum mechanical (QM) result;
- allows for a **description of** the two principal mechanisms responsible for broadening of absorption lines in realistic molecular media: **pressure broadening** and **Doppler broadening**.

Basic Scattering Processes (3)

Radiation interacts with matter in three different ways through:

- **emission, absorption and scattering.**

We first contrast these three interactions in terms of their energy conversions between:

- **internal energy states** of matter, E_I (which includes kinetic energy), and
- **radiative energy**, E_R.

It is convenient to consider monochromatic radiation:

- **Emission** converts internal energy to radiative energy ($E_I \rightarrow E_R$).
- **Absorption** converts radiative energy to internal energy ($E_R \rightarrow E_I$).
- **Scattering** is a 'double-conversion' ($E_{R'} \rightarrow E_I \rightarrow E_R$) in which
- the radiative energy $E_{R'}$ is first absorbed by matter ($E_{R'} \rightarrow E_I$) and
- then radiated ($E_I \rightarrow E_R$).

Basic Scattering Processes (4)

Thus, the radiated (scattered) field, denoted by R, is generally:

- **modified in frequency, direction of propagation, and polarization relative to the absorbed (incident) field.**

Some general relationships between these interactions follow from the energy-conversion viewpoint:

- **emission and absorption appear to be inverse processes;**
- we may think of **scattering** as simply a combination of **absorption, followed by emission**;

In the continuum view:

- matter can be divided into finer and finer elements with no limits on the smallness of the values of the charge or matter within the elementary volumes, BUT
- the atomic theory is based on the notion of a fundamental **discreteness** of matter, thus placing a limit on the size of these basic volume elements.

Basic Scattering Processes (5)

Our microscopic description is based on:

- **the interactions of light with these 'building blocks', assumed to consist only of mass, and positive and negative electric charges bound together by elastic forces.**

If these basic volume elements are are assumed to have internal energy modes ("excitation"), coinciding with those derived from quantum theory (or determined from experiment), then:

- **Maxwell's theory provides all the tools we need to understand the interactions of these elements with electromagnetic radiation.**

Individual atoms are the agents of absorption, emission, and scattering, but:

- the mathematics of the classical theory often requires us to consider the matter to consist of an infinitely divisible **continuous** distribution of charge.
- Fortunately: the dimensions of atoms are so small that these two contradictory views never pose any practical problems.

Basic Scattering Processes (6)

We choose volume elements (in either real space, velocity space or energy space) sufficiently small that we can:

- consider the properties of matter to be uniform within each element, BUT
- these volumes will be large enough to contain a sufficiently large number of atoms so that the granularity (discreteness) of matter can be ignored.

With regard to the radiation field, we take two apparently contradictory views.

Classically:

- the EM field is a **continuous function of space and time**, AND the radiative energy within the small frequency range $[\nu, \nu + d\nu]$ is a **continuous function** of ν, and there is no limit to how small the energy differences can be.

Quantum mechanically:

- the radiation field consists of **discrete values of energy**, which are separated in increments of the minimum energy $h\nu$ at a given frequency. Here h is Planck's constant.

Basic Scattering Processes (7)

- The total energy density is determined by the total number of radiation quanta ("photons") times the energy $h\nu$ per quantum.
- As in the case of atoms, we can define the interval $d\nu$ to be sufficiently small that the energy may be considered to be constant over $d\nu$, but large enough to contain enough photons so that the discretization in energy is unobservable.
- We will sometimes refer to radiation in terms of a "field", and other times in terms of "photons".

This deliberate looseness allows us a flexibility:

- we may visualize light-matter interactions, **sometimes** in terms of **light particles**, **other times** in terms of a **continuous distribution** of an electromagnetic field.
- However: our actual mathematical description will usually be based on the classical theory. The classical approach can be extended to the description of discrete spectral line absorption (a distinct quantum process).

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Basic Scattering Processes (8)

In this **'semi-classical'** theory:

- the **atom is described in quantum terms** but the **radiation is treated as a classical entity**.
- While this theory has been very successful, explanation of some phenomena (such as spontaneous emission) requires that both matter and radiation be quantized (called *quantum electrodynamics*).
- Fortunately, **quantum effects can fairly easily be incorporated in the classical approach**, and this artifice usually leads to results consistent with observation.
- For example, the Planck formula for the frequency distribution within a black-body cavity stems from quantum theory. Its adoption in the classical theory is straightforward.
- **We will mix classical and quantum concepts.**

Lorentz Theory for Radiation-Matter Interactions (1)

In 1910, Lorentz put forth a very successful microscopic theory of matter, in which he assumed that:

- the electrically neutral atoms of a substance consist of **negative charges** (electrons) and **equal positive charges** (the nucleus) **bound together by elastic forces**.
- These elastic forces are proportional to the distance of the charges from the center of charge (**Hooke's Law**).
- The **Lorentz theory combined with** the familiar **Coulomb forces** between electrical charges, and the **Maxwell theory** of the electromagnetic field:
- **provided the pre-quantum world with a satisfactory explanation of a vast number of phenomena**.

Lorentz Theory for Radiation-Matter Interactions (2)

- Some of the constants resulting from the Lorentz theory needed adjustment to agree with experiments; later on they were explained in a more basic way with quantum theory.
- In addition, **the field equations of Maxwell served to explain nearly all properties of radiation as an electromagnetic phenomenon**.
- A dramatic **failure** of the classical theory was its **inability to predict the blackbody frequency distribution law**. **This failure** eventually **led** M. Planck in 1900 **to** his paradigm-shattering notion of **quantized energy states of matter**.
- This advance, plus the failure of the classical theory to explain the photoelectric effect, led A. Einstein in 1914 to postulate that light itself is quantized*.
- The new quantum theory eventually replaced the old classical theory because of its successful application to a very broad range of phenomena.

*Only later in 1925 did these light particles become known as photons.

Lorentz Theory for Radiation-Matter Interactions (3)

- However, the **Lorentz theory has survived** to the present day, not because it in any way competes with the newer theory, but **because it has important advantages of concrete visualization** that the quantum theory often lacks.

- For this pedagogical reason (and because **it usually gives the correct answers when the unknown constants are provided by the accurate quantum theory**) we will use the Lorentz theory.
- Note, however, that the interpretation of many modern optical phenomena involving so-called 'coherent' radiation requires quantum theory.

However:

- to explain the propagation of natural (incoherent) radiation we seldom need to resort to these sophisticated descriptions.

Lorentz Theory for Radiation-Matter Interactions (4)

Of course:

- accurate numerical values of many of the interaction parameters required in the radiative transfer theory (for example molecular absorption cross sections) cannot be provided by the classical theory, BUT
- aerosol cross section calculations for spherical particles are accurately described by the classical **Mie-Debye** theory.
- Except in certain simple situations, we will consider the interaction parameters to be *given*, either
  - from **quantum-theoretical calculations**,
  - from **the Mie-Debye theory**, or
  - from **laboratory measurements**.

Scattering and Collective Effects in a Uniform Medium (1)

We will now use the Lorentz model and the classical radiation theory to visualize how light is affected in its passage through matter.

- We consider atoms and molecules to behave in basically similar ways.

Consider a **monochromatic plane wave incident upon a dielectric medium**[†] consisting of a uniform distribution **of non-absorbing Lorentz atoms**. The plane wave has:

- a fixed frequency, phase, and polarization (orientation of the electric field direction).

The imposed electric field creates:

- within each atom **an oscillating charge separation which varies in time with the same period as that of the incident field**.

[†]A dielectric material is an electrical insulator that can be polarized by an applied electric field.

Scattering and Collective Effects in a Uniform Medium (2)

The strength of the interaction is measured by:

- The **induced dipole moment** $\vec{p}$ which is proportional to two quantities:

1. the polarizability α_p, which depends upon the bonding forces between the constituent positive and negative charges; and
2. the imposed electric field $\vec{E}'$.

For simplicity we consider an isotropic medium, for which α_p is a scalar.

- The **induced dipole** (the product of the electronic charge and its displacement from the equilibrium arrangement within the atom) is mostly due to
- the oscillatory motion of the bound electrons which are much lighter than the nucleus.

What is the effect of the incident wave on an isolated atom?

Scattering and Collective Effects in a Uniform Medium (3)

Electromagnetic theory predicts that:

- **an oscillating charge will radiate an outgoing electromagnetic wave of the same frequency as the oscillation frequency.**

In general,

- **this radiated or scattered wave will have a definite phase shift with respect to the incoming plane wave.**

Thus,

- the scattered wave is **coherent** with the incoming wave. In this simplest of situations, **it propagates outward as a *spherical wave* with the typical dipole radiation pattern.**

The effect of a single nonabsorbing atom is thus to:

- **divert the flow of radiative energy, but not to destroy it.**

Scattering and Collective Effects in a Uniform Medium (4)

- However, the **collective** action of a **uniform**, optically dense medium is quite different. In fact, **no overall scattering will occur**!

This lack of scattering occurs despite the fact that each atom may interact quite strongly in the manner just described. To understand this paradox, consider the fact that:

- pure glass, water, or air transmit light freely with (at most) some bending of the rays at interfaces where there is a change in the refractive index.
- Moreover, away from interfaces, the basic radiance (I/m_{r}^2) is not attenuated along the ray (see **Theorem III**).

To understand how the induced dipole picture is compatible with the notion of an unattenuated refracted ray, we must

- **consider the interactions of the scattered waves with the incident field and with one another.**

Scattering and Collective Effects in a Uniform Medium (5)

The medium is assumed to be **perfectly uniform**. Each atom is forced to radiate spherically outgoing waves that are coherent with the incident wave:

- The net radiation field therefore is a **coherent superposition** of these scattered waves and the incident wave. Because of the coherence, the separate electric fields must be added with due regard to their relative phases.

Figure 1 illustrates light incident on a smooth plane boundary separating a vacuum (to the left) from a semi-infinite medium (to the right). We assume that the plane wave falls on this boundary at normal incidence.

- If the medium is **perfectly uniform**, then for every point P' on the boundary we can locate a second point P'' such that for a given direction of observation the path length difference is $\lambda/2$, where λ is the wavelength.
- The two scattered waves from P' and P'' cancel in this direction through **destructive interference**.

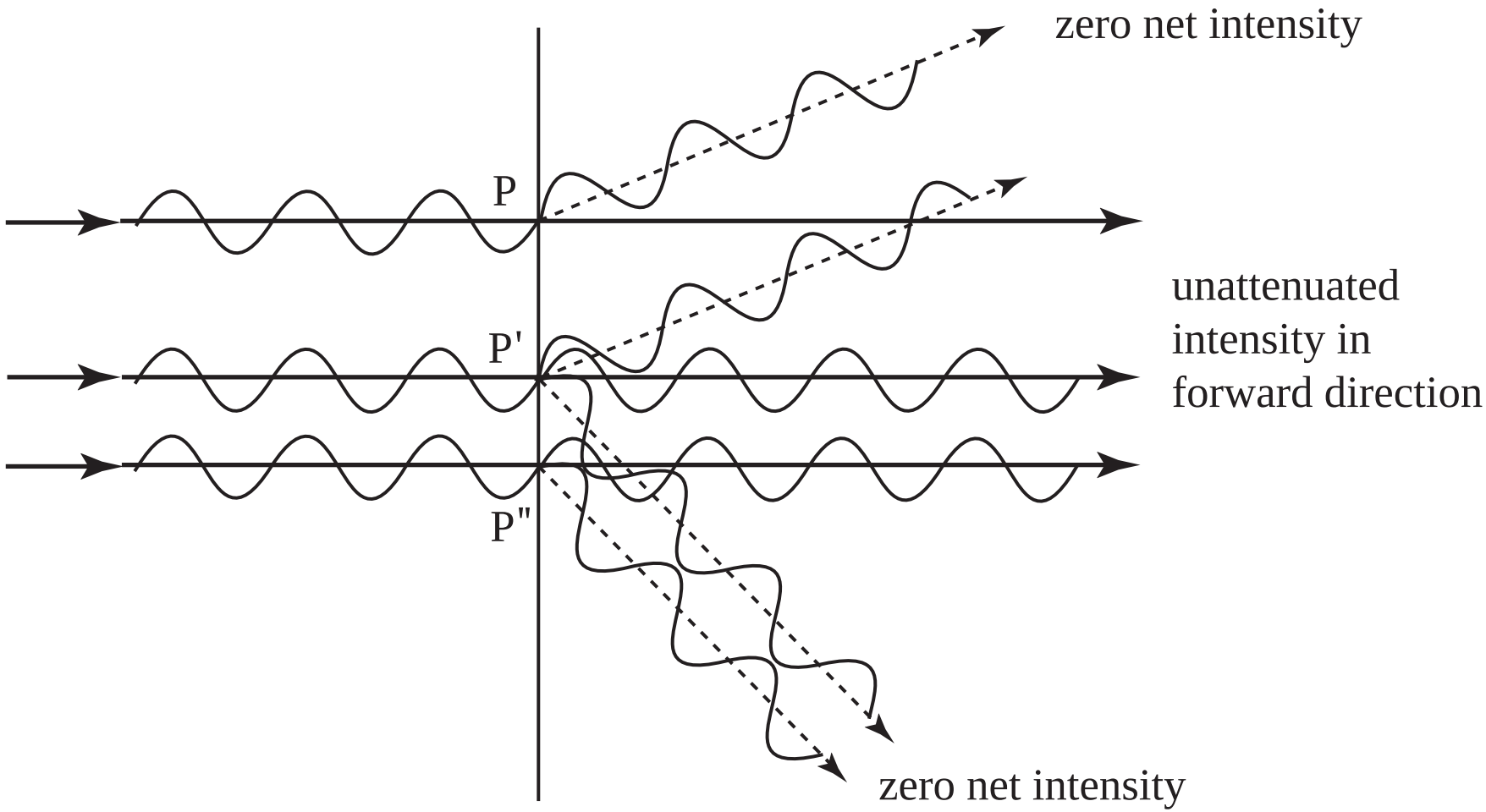

Figure 1: **The radiation fields scattered from the point P'' and P' are 90° out of phase and therefore interfere destructively.**

Scattering and Collective Effects in a Uniform Medium (6)

For all other directions of observation (other than the forward direction):

- we can always find other pairs of points for which perfect cancellation occurs. As a result of destructive interference the **incident wave is completely extinguished inside the medium** (the **Ewald-Oseen Extinction Theorem**).

If the medium to the right is a slab of finite extension, then:

- all that remains of the incident light is the transmitted and reflected rays, in the forward and backward directions, respectively.

We might expect the net result for the transmitted ray to be the same as if there were no medium at all, but:

- as a result of the repeated scatterings and re-emissions along the ray, **its forward progress is slowed down by a factor** $1/m_{\mathrm{r}}$, where m_{r} is the real part of the refractive index of the medium ($m_{\mathrm{r}} = c/v_{\mathrm{p}}$, c is the speed of light in vacuum, and v_{p} is the phase velocity in the medium).

Scattering and Collective Effects in a Uniform Medium (7)

If the incident light falls obliquely on the smooth planar interface of Fig. 1 and the medium is assumed to be a finite slab, then:

- the scattered waves will survive in **two directions <u>outside</u> the medium corresponding to** those of the familiar **specularly reflected and transmitted rays** in geometric optics.

The direction of propagation of the refracted ray within the medium is given by **Snell's law**. Thus:

- both refraction and reflection are manifestations of a coherent superposition of waves, each caused by a single, more fundamental scattering process.

In fact, any type of "reflection" when analyzed in detail will be found to be:

- the result of the same basic type of coherent scattering described above, although the myriad of collective processes occurring in optical media "hides" the basic underlying scattering pattern of each individual atom or molecule.

Scattering from Density Irregularities (1)

Since **no real substance is perfectly uniform**, we ask:

- what is the effect of irregularities, or inhomogenieties, distributed throughout the medium?

These irregularities can take various forms:

- even in pure solids, **crystal defects** may be present, or there may be **irregularities in the orientation of the atoms, or in the density** (and thus in the refractive index) from place to place.
- Fluctuations occur in the number density n (or in other thermodynamic properties depending upon density) because no actual substance is perfectly uniform.

- **The atomic nature of the substance causes it to have *statistical variations in density* that are present in all phases (gas, liquid, solid), but are most apparent in gases and liquids.**

Scattering from Density Irregularities (2)

These density inhomogeneities, Δn (whose spatial scales are small compared to λ) give rise to:

- corresponding changes in the number of induced dipoles per unit volume,

$$\vec{\mathcal{P}} = n\alpha_p \vec{E}',$$

where

- $\vec{\mathcal{P}}$ is the **bulk polarization** of the medium, α_p is the **polarizability**, and $\vec{E}'$ is the imposed electric field.

The electric and magnetic fields at some distance away from two source points P and P':

- will interfere as in a uniform medium (see Fig. 1), but in this case the result is ***an incomplete cancellation***.

Scattering from Density Irregularities (2)

- The "excess" (surviving) electric field $\vec{E}$ in the scattered wave is proportional to the **change** in the bulk polarization, $\Delta\vec{\mathcal{P}}$, so that:

$$\vec{E} \propto \Delta\vec{\mathcal{P}} = \alpha_p \Delta n.$$

- Since the radiance of an electromagnetic wave is proportional to the **square** of the electric field amplitude (averaged over a wave period), the change in the radiance becomes:

$$\overline{\Delta I} \propto \overline{(\Delta E)^2} \propto \overline{(\Delta \mathcal{P})^2} \propto \overline{(\Delta n)^2}.$$

- **The statistical theory for fluctuations in an ideal gas predicts that:**

$$\overline{(\Delta n)^2} \propto n.$$

Scattering from Density Irregularities (2)

Thus, we are led to the conclusion that for an ideal gas the scattered radiance is proportional to the number of atoms per unit volume:

- ***the scattering behaves as if the atoms scatter independently of one another***.
- This remarkable result was understood and used by Lord Rayleigh in his classic explanation of the blue sky in a series of papers between 1899 and 1903.
- Mathematical proofs were provided by R. Smoluchowski in 1908 and by A. Einstein in 1910.
- A consequence of this result is that light can be simultaneously refracted and scattered by air molecules.
- This foremost example of scattering is called **Rayleigh scattering**.

Scattering in Random Media (1)

We have seen that, although a uniform medium transmits light in a collective transparent manner:

- the **randomly distributed inhomogeneities** or imperfections (in an otherwise uniform medium) **scatter light** as if the individual atoms were **unaffected** by the radiation from their neighbors.

With the exception of the forward direction, it can be shown that:

- **for most planetary media, the individual scattered spherical wavelets have no permanent phase relationships.**

This randomness of the phases of the superposed scattered wavelets implies that:

- **the net radiance due to all the scattering centers is simply the sum of the individual radiences.**
- This **incoherent scattering** property is typical for planetary materials, consisting of mixtures of substances and of several types of inhomogeneities.

Scattering in Random Media (2)

For example:

- the presence of small bubbles of air trapped in water or ice will give rise to a milky appearance due to the spatial inhomogeneities in the index of refraction.
- We shall generally refer to the scattering centers in such substances (so called **random** media) as **particles**.
- They are generally different in composition from the atoms of the ambient media, and are distributed randomly within the ambient media.
- The assumption of **independent scatterers** is violated if the particles are too closely packed.
- The **average spacing between particles should be several times their diameters** to prevent intermolecular forces from causing correlations between neighboring scattering centers.

Scattering in Random Media (3)

- This requirement would appear to rule out independent scattering in aqueous media where such short-range correlations are the very essence of the liquid state.
- In particular, pure water is composed of transitory water clusters of random size held together by hydrogen bond forces.
- Sea water contains a diversity of ion clusters, depending upon the various types of dissolved salts. **Scattering therefore occurs from the clusters rather than from individual water molecules.**

An important point is that:

- **these clusters are much smaller than the wavelength of visible light**.

The dependence of scattering in pure water is $\lambda^{-4.3}$ (it is λ^{-4} in air), suggesting that there is indeed incoherency between the scattered wavelets:

- **From the optical point of view** the clusters are **uncorrelated.**

Scattering in Random Media (4)

- Aerosols (solid or liquid particles suspended in the atmosphere) may have important radiative effects.

Even though the concentrations of scattering 'particles' may be present only in 'trace' amounts:

- they usually have much larger scattering cross sections than the molecules. Thus they often have an important influence on the transfer of radiation.
- The distribution of sky brightness may be severely altered by atmospheric aerosols (dust, soot, smoke particles, cloud water droplets, raindrops, ice crystals, etc.), which may be present only in the parts per million by volume.

Similarly:

- 'trace' amounts of suspended organic and inorganic particles in seawater may be of dominant importance to the radiation field in ocean water.
- Most natural surface materials (soil, snow, vegetation canopies) are classified as random media.

Scattering in Random Media (5)

These materials are composed of:

- **randomly-distributed collections of diverse scattering elements, which scatter light incoherently.**

A counter-example is the surface of calm water, for which:

- cooperative effects account for the specularly-reflected and transmitted light. Then radiative transfer theory cannot be used; we must use Maxwell's equations, as for example, in the Fresnel theory of reflection.

In most media of interest to us:

- the dimensions of scattering particles are comparable to, or exceed the wavelength of light. In such cases, their 'radiation patterns' are often very complicated.

Scattering in Random Media (6)

- As in the case of small density irregularities, the radiance of the direct beam is largely a result of collective, coherent effects, but it is also weakened by the fact that the **secondary radiation** diverts energy into other directions.
- We will refer to this secondary scattered radiation as **diffuse radiation**, because in contrast to direct (collimated or uni-directional) radiation it is distributed over many directions, in general through 4π sterradians.
- Scattering in random media occurs over the small spatial scales of the particles themselves, in contrast with light interactions with irregularities having larger spatial scale. For example:
- convection or overturning of air parcels causes a mixing of irregular warm and cool air masses over scales of the order of centimeters to meters.
- Variations of air density and temperature lead to variations over the same scale in the refractive index of the air, which in turn alters the direction of light rays in a chaotic manner, and explains the twinkling of stars (scintillation).

Scattering in Random Media (7)

On a still larger scale:

- the air density of a planetary atmosphere declines exponentially with height over characteristic scales of the order of 5 to 8 km. The distortion of the image of the setting sun is a result of the vertical gradient of the refractive index of air.
- Refraction must be dealt with by considering the coherent wave nature of the radiation.

First-order and Multiple Scattering (1)

- In **uniform media**: mutual interactions between the various scattered waves and between each scattered wave and the incident wave are of utmost importance.
- In **random media**: the particles scatter independently of one another, and their individual contributions add together as if there were no mutual interactions.

Consider the illumination of the atmosphere by the Sun. Assume that the particles are well separated, so that each is subjected to direct solar radiation. Then:

- A small portion of the direct radiation incident on the particle will be scattered, giving rise to scattered or diffuse radiation.
- If the *diffuse radiation* arriving from all parts of the medium *is negligible* compared with the direct radiation, the medium is said to be **optically thin**.
- If we were to double the number of scatterers in an optically-thin medium, the scattered or diffuse radiation would also be doubled.

First-order and Multiple Scattering (2)

However it often happens that:

- the diffuse radiation itself is an important additional source of radiation, becoming a source for still more scattering, etc. The diffuse radiation arising from scattering of the direct solar beam is called **first-order** or **primary** scattering.

If additional scattering events need to be included:

- the radiation is said to be **multiply scattered**, and the medium in which this is important is said to be **optically thick**.

Thus, in many situations of interest in planetary media:

- the radiation field is determined not only by the transmitted incident radiation field, but also by the "self-illumination" from the medium itself.

This incoherent multiple scattering could be regarded as a collective effect,

- but it should not be confused with the coherent, collective effects already discussed.

Interaction Cross Sections of Matter with Radiation (1)

We derive some basic equations for the interaction cross sections of matter with radiation, and present a simple example of how the interaction works in a very specific, simplified situation.

For an isolated molecule and including only the natural damping interaction, the analysis yields:

- (1) a strong resonant interaction which occurs when the light frequency is very near one of the natural oscillation frequencies of the molecule; and
- (2) a much weaker interaction which affects all light frequencies, and which provides a very good model for **Rayleigh scattering**.
- In either case, the interaction is that of elastic scattering.
- Our treatment does not explicitly consider the coherence of the incoming and outgoing waves, although such consideration is necessary in order to derive the corresponding extinction of the incoming beam.

Interaction Cross Sections of Matter with Radiation (2)

- The combination of both the direct and scattered fields is important in dense media, where the oscillators themselves affect the local electric field. However we ignore this effect.
- A simple generalization of the meaning of the damping constant to include collisional effects provides a first-order description of pressure broadening.
- The Lorentz line profile predicted by this simple model is in very good agreement with measurements of high spectral resolution.
- We also include the Doppler-broadening effects of thermal motions on the line profile. We then describe the net result of pressure and Doppler broadening, the so-called Voigt broadening.
- The Rayleigh angular scattering pattern is then derived from the same simple model.

Scattering from a Damped, Simple Harmonic Oscillator (1)

In certain applications, we may **treat a molecule as a simple harmonic oscillator with a single natural oscillation frequency** ω_0:

- The molecule is assumed to consist of an electron bound to a positively-charged nucleus with a certain 'spring-constant', related to the natural oscillator frequency.

When this simple system is irradiated by a linearly-polarized monochromatic plane electromagnetic wave of angular frequency ω:

- the electron undergoes a harmonic ***acceleration*** in response to the oscillating electric field.
- The **motion of the nucleus**, being much more massive than an electron, is considered to be a rigid support, and **may be neglected**.
- The relative displacement of positive and negative electrical charges causes the formation of an induced electric dipole.

Scattering from a Damped, Simple Harmonic Oscillator (2)

According to classical theory:

- acceleration of an electric charge gives rise to the emission of electromagnetic radiation.
- A large-scale example is a dipole antenna which emits radio waves. Without energy loss, absorption of light by the oscillator increases its motion indefinitely.

- Loss of energy in a mechanical oscillator, such as a spring, occurs as the result of a frictional **damping force**, which is approximated as being proportional to the velocity.
- To account for the energy loss due to the emitted wave, a damping force must exist. For an isolated molecule, this damping force may be thought of as a **radiation resistance**.

Scattering from a Damped, Simple Harmonic Oscillator (3)

The classical radiative damping force (assumed to be suitably small) is given by

$$\vec{F} = -m_e \gamma \vec{v},$$

where

$$\gamma = e^2 \omega_0^2 / 6\pi\epsilon_0 m_e c^3. \tag{1}$$

Here

- m_e is the electron mass, $\vec{v}$ is its velocity,
- e is its charge, ω_0 is the natural angular frequency,
- ϵ_0 is the vacuum permittivity, and c is the speed of light in a vacuum.

In an insulating solid, or in a gas where the electron is subjected to an additional force from collisions with the lattice, or with other molecules:

- the damping rate γ takes the form of a collisional frequency, given by the inverse of the mean time between collisions.

Scattering from a Damped, Simple Harmonic Oscillator (4)

The power emitted by an accelerated charge, may be found by considering:

- the equation of motion of a damped, simple harmonic oscillator, subject to a forcing electric field of amplitude $\vec{E}'$ and angular frequency ω.

According to classical theory:

- a charge set into accelerated motion radiates an electromagnetic wave with the time-averaged power given by:

$$P(\omega) = \frac{e^4\omega^4}{12\pi m_e^2\epsilon_0 c^3}\frac{E'^2}{[(\omega_0^2-\omega^2)^2+\gamma^2\omega^2]} \qquad [\mathrm{W}]. \tag{2}$$

The ratio of this scattered power to the power per unit area carried in the incident field, $\epsilon_0 c E'^2/2$, is just

- the total **scattering cross section:**

$$\sigma_n(\omega) = \frac{P(\omega)}{\epsilon_0 c E'^2/2} = \frac{e^4}{6\pi m_e^2\epsilon_0^2 c^4}\left[\frac{\omega^4}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}\right] \qquad [\mathrm{m}^2]. \tag{3}$$

Case I: Resonance Scattering; Lorentz Profile (1)

Here we allow the frequency of the incident light to be "tuned" to a discrete energy level of a molecule (**resonance scattering**):

- In this case the strength of the interaction is typically many orders of magnitude greater than the non-resonant interaction.

Let the driving frequency ω be very close to resonance with the natural oscillation frequency ω_0: $\delta\omega \equiv \omega_0 - \omega << \omega$.

Then:

- $\omega_0^2 - \omega^2 = (\omega + \delta\omega)^2 - \omega^2 = 2\omega\delta\omega + (\delta\omega)^2 \approx 2\omega(\omega_0 - \omega)$.

Substituting into Eq. 3, using the definition of γ from Eq. 1, we find:

$$\sigma_n^{\text{res}}(\omega) = \frac{e^2}{m_e \epsilon_0 c}\left[\frac{(\gamma/4)}{(\omega_0 - \omega)^2 + (\gamma/2)^2}\right].$$

Case I: Resonance Scattering; Lorentz Profile (2)

Returning to ordinary frequency $\omega = 2\pi\nu$, $\omega_0 = 2\pi\nu_0$, we have:

$$\sigma_n^{\rm res}(\nu) = \frac{e^2}{4m_e\epsilon_0 c}\,\frac{1}{\pi}\left[\frac{(\gamma/4\pi)}{(\nu_0-\nu)^2+(\gamma/4\pi)^2}\right]. \tag{4}$$

The frequency-dependent part of this result is called:

The Lorentz profile:

$$\Phi_{\rm L}(\nu) = \frac{\gamma/4\pi}{\pi\left[(\nu_0-\nu)^2+(\gamma/4\pi)^2\right]}. \tag{5}$$

$\Phi_{max} = \Phi_{\rm L}(\nu_0) = 4/\gamma$. Requiring:
$(1/2)\Phi_{\rm L}(\nu_0) = (2/\gamma) = \Phi_{\rm L}(\nu) \quad \Longrightarrow \quad \Delta\nu = \nu - \nu_0 = \gamma/4\pi$.
Thus:
the frequency **line width** (full width at half maximum): $2\Delta\nu = \gamma/2\pi$ [s^{-1}] of the Lorentz profile is proportional to the damping parameter γ.

Case I: Resonance Scattering; Lorentz Profile (3)

$\Phi_{\rm L}(\nu)$ is normalized. This can be seen by changing variables to $x = 4\pi(\nu - \nu_0)/\gamma$. Integrating over x, and noting that $4\pi\nu_0/\gamma >> 1$, one finds:

$$\int_0^\infty d\nu \Phi_{\rm L}(\nu) = \frac{1}{\pi}\int_{-4\pi\nu_0/\gamma}^{\infty} \frac{dx}{1+x^2} \rightarrow \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dx}{1+x^2} = 1. \tag{6}$$

Since the Lorentz profile (Fig. 2) is normalized:

$$\int_0^\infty d\nu \sigma_n^{\rm res}(\nu) = \frac{e^2}{4m_e\epsilon_0 c} \qquad \Longrightarrow \tag{7}$$

- the integrated, or total classical cross section is constant, depending only upon fundamental atomic constants.

Note that increasing the value of γ:

- **decreases** the strength of the spectral line in the **line core**, the region $|\nu - \nu_0| \leq \gamma/4\pi$, BUT
- **strengthens** the **line wings**, the region where $|\nu - \nu_0| > \gamma/4\pi$. In the distant parts of the line, $\Phi_{\rm L}(\nu)$ varies as ν^{-2}.

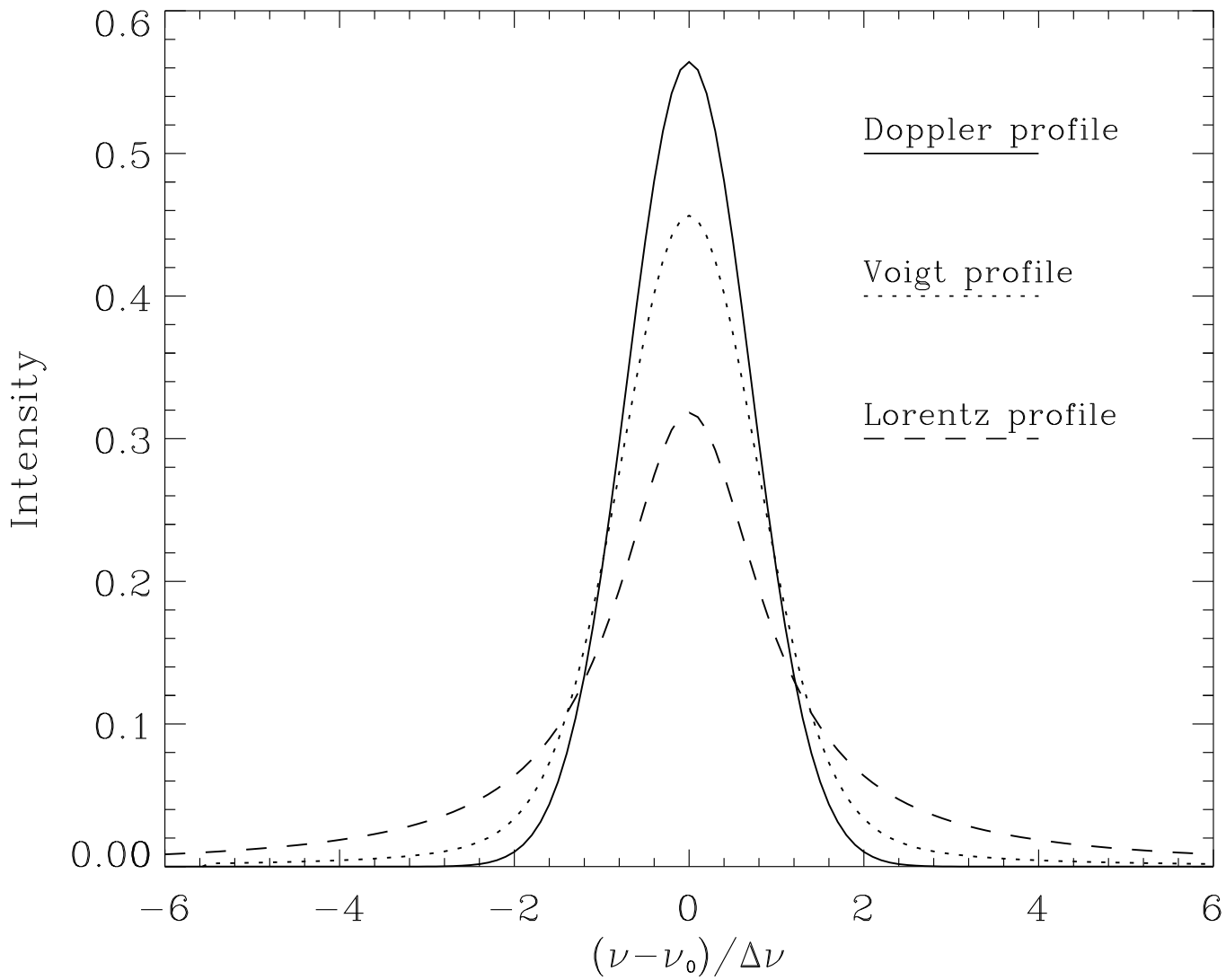

Figure 2: **Comparison of normalized Lorentz, Voigt, and Doppler profiles versus $x = (\nu - \nu_0)/\Delta\nu$. $\Delta\nu$ is the Doppler width α_D for both Doppler broadening and Voigt broadening and is the Lorentz with $\alpha_{\rm L}$ for Lorentz boradening. $a = \alpha_{\rm L}/\alpha_{\rm D} = 1$ was used for the Voigt profile.**

Case I: Resonance Scattering; Lorentz Profile (4)

The above expression was derived from strictly classical considerations of a single electron forced by the oscillating electric field of the incident wave. In actuality:

- there is more than one resonant frequency, so that we refer to the ith frequency, or quantum transition: $\sigma_n^{\rm res}(\nu) \rightarrow \sigma_{ni}^{\rm res}(\nu)$

In addition:

- we have ignored the QM character of the process, which involves the notion of a transition from a ground state to a quantized excited state.
- The correct QM derivation yields a nearly-identical expression, containing an extra multiplicative factor, called the **oscillator strength**, f_i.

Thus:

- we may write the cross section in the following form showing the relationship between the line profile, the oscillator strength, and the **line strength** $\mathcal{S}_i$:

$$\sigma_{ni}^{\rm res}(\nu) = \frac{e^2 f_i}{4 m_e \epsilon_o c} \Phi_{\rm L}(\nu) \equiv \mathcal{S}_i \Phi_{\rm L}(\nu).$$

Case I: Resonance Scattering; Lorentz Profile (5)

Conservative versus Non-conservative Scattering

It is convenient to classify scattering processes, depending upon:

- whether or not the photon changes frequency upon scattering.

In analogy with elastic and inelastic collisions between two material particles:

- the issue is whether or not there is a net change of energy and momentum following the 'collision'.
- Light carries momentum (of order $h\nu/c$), and one might expect that the absorption and subsequent re-emission of light would impart both a momentum impulse and a change of energy (frequency) of the photon.
- For the UV/visible/IR radiation fields of interest to us, this process is negligible compared with the damping (or more correctly, broadening) effects resulting from the uncertainty of the upper state lifetime.

Case I: Resonance Scattering; Lorentz Profile (6)

- For resonance scattering, Rayleigh scattering, and Mie-Debye scattering the change in emitted frequency is very small, compared with the incident frequency.

- The term **coherent scattering** is sometimes used to describe this case, since the process involves interference between the incident and scattered waves.

However:

- this term could lead to confusion, since it might lead one to believe that it does not apply to scattering from random media.

Inelastic scattering involves:

- an exchange of internal energy of the medium with that of the radiation field.
- Typically, the exchange results in a net **loss of radiative energy** and a **gain of internal energy** of the medium in the form of heat or chemical energy.

Case I: Resonance Scattering; Lorentz Profile (7)

Such processes are possible when the matter contains a number of accessible energy states. For example:

- **rotational Raman scattering** occurs when the excited 'virtual' state of a molecule radiatively decays, not to the original state (Rayleigh scattering), but to a state higher in rotational energy (the **Stokes component**) or lower in rotational energy (the **anti-Stokes component**).
- For illumination by monochromatic light, the scattered spectrum will be a series of closely spaced lines on either side of the central **Cabannes line**.

The basic aspects of rotational Raman scattering can be understood classically. We replace our notion of an induced dipole fixed in space by one that is also rotating:

- The dipole will then emit not only its fundamental ('carrier') frequency, but 'sideband' frequencies consisting of sums and differences of the basic frequency and the frequencies corresponding to the energies of rotation.
- Since rotational energy states are quantized, this combination results in a number of discrete "beat frequencies" (see Exercise 3.4).

Case I: Resonance Scattering; Lorentz Profile (8)

A closely-related process is **fluorescence**, which applies to two bound states:

- Here the molecule is originally in its ground (lowest energy) state, and returns after scattering to a higher energy state.

Raman scattering and fluorescence are 'cross-wavelength' processes, in that:

- scattered photons of more than one discrete frequency are involved. Raman scattering is important for some ocean and lidar applications.

Another classification is whether the scattering process results in partial absorption of the light energy:

- If there is negligible absorption: the scattering process is said to be **conservative** or **elastic**, referring to the conservation of radiative energy.
- If there is some absorption, it is **non-conservative** or **inelastic**.

To avoid confusion of the terms 'elastic' and 'inelastic' with processes involving collisions of molecules, we may use the terms 'conservative' and 'non-conservative' when referring to light scattering.

Case I: Resonance Scattering; Lorentz Profile (9)

Natural Broadening

As seen from Eq. 5:

$$\Phi_{\mathrm{L}}(\nu) = \frac{\gamma/4\pi}{\pi\left[(\nu_0 - \nu)^2 + (\gamma/4\pi)^2\right]} \tag{8}$$

the shorter the upper-state lifetime, the broader the frequency line width of the profile, $\Delta\nu = \gamma/4\pi$. (Recall: $\gamma \propto$ the inverse of the mean time duration of the upper state, normally controlled by collisions.) This inverse relationship is consistent with:

- **Heisenberg's Uncertainty Principle**, relating the "uncertainty" in knowledge of the energy of a quantum system $\Delta E = h\Delta\nu$ to the "uncertainty" in knowledge of the lifetime Δt of the energy state. In this context:
- Heisenberg's relationship is written $\Delta E \Delta t \approx (h/2\pi)$. Thus, in the absence of collisions $\Delta t \equiv t_r \approx (2\pi\Delta\nu)^{-1}$, where t_r is the radiative lifetime. This situation is called **natural broadening**.

Case I: Resonance Scattering; Lorentz Profile (10)

Pressure Broadening

Natural broadening applies to an isolated molecule, unperturbed by collisions with its neighboring molecules within a radiative lifetime, t_r. For a strong (**allowed**) transition in the shortwave spectrum, a typical value is $t_r \sim 10^{-8}$ s. Thus:

- the natural line width α_N is $\sim 1/2\pi t_r \sim 1 \times 10^7$ s^{-1}. In wave number units $\alpha_{\mathrm{N}} = 1/2\pi t_r c = 5 \times 10^{-4}$ cm^{-1} which is very much smaller than observed in atmospheric spectra.

For vibrational and rotational transitions in the IR, t_r is much longer, of the order of $t_r \sim 10^{-1}$ to 10^1 s, with even smaller values of α_{N}. Thus:

- **natural broadening is completely negligible in atmospheric applications.**

Collisions between molecules result in collisionally-induced transitions, which occur temporarily in the **joint** system of two molecules in close vicinity:

Case I: Resonance Scattering; Lorentz Profile (11)

- The net effect of these nearly resonant transitions on the emitted energy is very small, since roughly half of the transitions are excitations, and the other half de-excitations of energy states. **These processes effectively reduce the lifetime of the upper state, and thus broaden the line.**

- The reduced lifetime is called the optical lifetime t_{opt}. It may be shown that under rather general conditions (see Exercise 3.6) the collision process leads to a Lorentz profile with a line width $\alpha_{\rm L} \approx 1/2\pi t_{opt}$:

$$\Phi_{\rm L}(\nu) = \frac{\alpha_{\rm L}}{\pi\left[(\nu-\nu_0)^2+\alpha_{\rm L}^2\right]}. \tag{9}$$

The theory of collisional line broadening is quite complicated. However, according to theoretical predictions:

- $\alpha_{\rm L}$ depends linearly on the number density of the perturbing molecules, and upon the relative speed of the collision partners, $v_{\rm rel}$.

Case I: Resonance Scattering; Lorentz Profile (12)

Thus, we may scale the pressure-broadened Lorentz width for an arbitrary number density, n and temperature T, since $v_{\rm rel} \sim \sqrt{T}$:

$$\alpha_{\rm L} \approx \alpha_{\rm L}({\rm STP}) \frac{n v_{\rm rel}}{n_{\rm L} v_{\rm rel}({\rm STP})} = \alpha_{\rm L}({\rm STP}) \frac{n\sqrt{T}}{n_{\rm L}\sqrt{T_o}} \tag{10}$$

where

- $n_{\rm L} = 2.687 \times 10^{19}$ cm^{-3} is Loschmidt's number (the number density of air at STP), and $T_o = 273.16$ K is the standard temperature.

A typical value for t_{opt} is 10^{-10} s at STP, yielding a line width of 2×10^9 s^{-1}, or in wave number units $\alpha_{\rm L} = 0.05$ cm^{-1}:

- **This value greatly exceeds both the natural line width ($\alpha_{\rm N} = 1/2\pi t_r c = 5 \times 10^{-4}$ cm^{-1}) and the Doppler line width (see below), so that pressure broadening is dominant at STP for all wavelengths.**

Case I: Resonance Scattering; Lorentz Profile (13)

Doppler Broadening

The second major source of line broadening is that due to small **Doppler shifting** of the emitted and absorbed frequencies. As shown later:

- the shift is of order $v_{\rm rel}\nu/c = v_{\rm rel}\tilde{\nu}$, where c is the light speed. For CO_2 at STP, in the strong 15 μm band, the Doppler shift is $\sim 8 \times 10^{-4}$ cm^{-1}.

Thus:

- Doppler broadening is negligible near the surface, but grows in importance with height, since it varies as $\sqrt{T}$ and $\alpha_{\rm L}(z)$ falls off exponentially with z.
- Doppler and pressure broadening are equal in importance where $n/n_o \approx 0.016$, which occurs at a height of about 30 km (see Appendix C, Standard Atmospheres). Below we examine the Doppler broadening in greater detail.

Case I: Resonance Scattering; Lorentz Profile (14)

- Doppler broadening stems from the simple fact that molecules are in motion when they absorb, and when they emit.

When a photon undergoes resonance scattering:

- there is a relative Doppler shift between the incident and the scattered photon.

Given that one always observes the net effect of an ensemble of scattering molecules:

- the result will be a spreading of the frequency of an initially monochromatic photon.

The velocity distribution of absorbing molecules will satisfy the **Maxwell-Boltzmann law**. Therefore:

- they will absorb in proportion to the number having a certain velocity component along the line-of-sight.

Case I: Resonance Scattering; Lorentz Profile (15)

Finally, suppose the molecules are excited by collisions, and undergo many elastic collisions so that the 'memory' of the direction of the colliding molecule is lost. Then:

- the excited molecules will emit according to their velocity distribution, which is Maxwellian by assumption.

In all three cases (scattering, absorption, and emission), we find that:

- the line profile is dominated by thermal Doppler shifts, if the spread in frequency is larger than that caused by natural or pressure broadening.

To describe the effects of thermal broadening on absorption, consider the frequency of the photon in two reference frames (ν and ν'):

- ν is the frequency in the **laboratory frame**, which is the normal frame of an observer. ν' is the frequency in the **atom's (rest) frame**.

Case I: Resonance Scattering; Lorentz Profile (16)

The relationship between these two frequencies is obtained by considering:

- an atom with speed v moving toward the observer with a line-of-sight velocity $v \cos\theta$, where θ is the angle between the direction of motion and the line-of-sight.

Suppose the molecule receives a photon of frequency ν in the lab frame. Then, if the molecule were at rest with respect to the lab frame:

- in one second it would 'see' exactly c/λ oscillations, where λ is the irradiating monochromatic wavelength.

However, because the molecule is moving toward the emitter:

- it 'sees' an additional number of oscillations equal to the distance it travels in one second, divided by the wavelength.

Thus:

- the number of oscillations the atom encounters is: $(c/\lambda + v \cos\theta/\lambda)$.

Case I: Resonance Scattering; Lorentz Profile (17)

This quantity is just:

- the frequency seen in the atom's frame, $\nu' = c/\lambda'$. Hence:

$$\nu' = \nu + \frac{v\cos\theta}{\lambda} = \nu + \nu(v/c)\cos\theta = \nu[1 + (v/c)\cos\theta].$$

- **The molecule will therefore absorb according to its absorption cross section at the shifted frequency ν'.**

Suppose we align the rectangular coordinate system so that the x-direction coincides with the line-of-sight. Then:

- **the absorption cross section appropriate to the molecule moving with the velocity component v_x is $\sigma_n[\nu(1 + (v_x/c)]$.**

Case I: Resonance Scattering; Lorentz Profile (18)

The number of molecules moving with this velocity component is given by the Maxwell-Boltzmann distribution:

$$f(v_x)dv_x = \left(\frac{m}{2\pi k_{\rm B}T}\right)^{1/2} e^{-v_x^2/v_o^2} dv_x \tag{11}$$

where

- $v_o = \sqrt{2k_{\rm B}T/m}$ is the most probable speed of the molecules.

The cross section at the frequency ν due to all line-of-sight components is given by:

$$\begin{aligned} \sigma_n(\nu) &= \int_{-\infty}^{+\infty} dv_x f(v_x)\sigma_n[\nu(1+(v_x/c)] \\ &= \left(\frac{m}{2\pi k_{\rm B}T}\right)^{1/2} \int_{-\infty}^{+\infty} dv_x e^{-v_x^2/v_o^2}\sigma_n[\nu(1+(v_x/c)]. \end{aligned} \tag{12}$$

We now need to assume the functional form for the cross section in the molecule's frame.

Case I: Resonance Scattering; Lorentz Profile (19)

For simplicity we first assume that the broadening in the molecule's frame is much less than the thermal (Doppler) broadening. In effect, we are assuming that:

- the molecule absorbs according to an infinitely narrow peak, that is $\sigma_n(\nu) = \mathcal{S}\Phi(\nu') \approx \mathcal{S}\delta(\nu' - \nu_0) = \mathcal{S}\delta[\nu - \nu_0 + \nu(v_x/c)]$.

Substituting in the above integral and integrating, we obtain:

$$\sigma_n(\nu) = \mathcal{S}\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} \exp\left[-c^2(\nu - \nu_0)^2/\nu_0^2 v_o^2\right]. \tag{13}$$

Letting $\alpha_{\mathrm{D}} \equiv \nu_0 v_o/c$, which is called the *Doppler width*, we find:

$$\sigma_n(\nu) = \mathcal{S}\Phi_{\mathrm{D}}(\nu) = \frac{\mathcal{S}}{\sqrt{\pi}\alpha_{\mathrm{D}}} \exp\left[-(\nu - \nu_0)^2/\alpha_{\mathrm{D}}^2)\right]. \tag{14}$$

It can be verified that the Doppler line profile $\Phi_{\mathrm{D}}(\nu)$ is properly normalized. The mathematical form of Eq. 14 is recognized as a **Gaussian** distribution, of $(1/e)$-width α_{D}, and line width $\alpha_{\mathrm{D}}\sqrt{\ln 2}$.

Case I: Resonance Scattering; Lorentz Profile (20)

Consider now the more general case: **the broadening in the rest frame cannot be ignored compared with the thermal (Doppler) broadening.** Suppose this is given by Lorentz broadening (Eq. 9), with a total line width $\alpha_{\rm L}$. Substitution of Eq. 9 ($\Phi_{\rm L}(\nu) = \frac{\alpha_{\rm L}}{\pi\left[(\nu-\nu_0)^2+\alpha_{\rm L}^2\right]}$) into Eq. 12, yields:

$$\sigma_n(\nu) = \mathcal{S}\frac{a}{\pi^{3/2}\alpha_{\rm D}}\int_{-\infty}^{+\infty}\frac{dye^{-y^2}}{(v-y)^2+a^2} \equiv \mathcal{S}\Phi_{\rm V}(\nu) \tag{15}$$

where the **damping ratio** is $a \equiv \alpha_{\rm L}/\alpha_{\rm D}$ and $v \equiv (\nu-\nu_0)/\alpha_{\rm D}$.

- $\Phi_V(\nu)$ is called the **Voigt profile**, which can be shown to be properly normalized. It represents the combined effects of both Lorentz and Doppler broadening.

- The Voigt profile shows a Doppler-like behavior in the line core, and Lorentz-like ($1/\nu^2$) behavior in the line wings.

- For small damping ratios ($a \to 0$), we retrieve the Doppler result; for $a > 1$, the Voigt profile resembles the Lorentz profile for all frequencies.

Case I: Resonance Scattering; Lorentz Profile (21)

Realistic line-broadening processes

The collisional processes considered up to now are so-called **adiabatic interactions**, implying only very gentle interactions with other molecules. Unfortunately:

- the quantum-mechanical line-broadening theory describing more realistic collisional perturbations of the upper state is extremely difficult.
- The far wings of lines are most affected by **non-adiabatic interactions.**

Empirical corrections are sometimes applied:

- the power of the exponent b in the ν^{-b} formula is altered from its canonical value of $b = 2$ to obtain so-called **super-Lorentzian** ($b < 2$) and **sub-Lorentzian** ($b > 2$) wing behavior.

Fortunately, the line core and near-wings remain Lorentzian even under severe collisional interactions. Thus, with increasing gas pressure:

- line overlapping usually is more important than far-wing effects. The net effect is greater line broadening, in agreement with Eq. 10: $\alpha_{\mathrm{L}} = \alpha_{\mathrm{L}}(\mathrm{STP})\frac{n\sqrt{T}}{n_{\mathrm{L}}\sqrt{T_o}}$.

Case I: Resonance Scattering; Lorentz Profile (22)

In liquids and solids, the effects of nearby molecules are of course even more important than in the densest gases:

- Their absorption spectra may be extremely complex resulting from the myriad of energy states created by the mutual interactions. In most situations, first-principles analysis is impossible. Fortunately:
- the spectra frequently overlap to the point where the absorption spectra appear to be nearly continuous and slowly-varying with frequency.

Then the situation is simplified from the point of view of the radiative transfer:

- It is *sufficient to use low spectral resolution measurements and tabulation of the optical properties*, provided one can collect samples of the material for transmission experiments in the laboratory.

If materials are so opaque that standard transmission experiments are impossible:

- Reflection and absorption experiments are required, combined with the use of *Fresnel's equations* and various theoretical relationships.

Case II: Rayleigh Scattering (1)

Suppose $\omega << \omega_0$. Then Eq. 3: $\sigma_n(\omega) = \frac{e^4}{6\pi m_e^2 \epsilon_0^2 c^4}\left[\frac{\omega^4}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}\right]$ $[\mathrm{m}^2]$ becomes:

$$\sigma_n^{\mathrm{RAY}}(\omega) = \frac{e^4\omega^4}{6\pi m_e^2\epsilon_0^2 c^4\omega_0^4} = \frac{1}{6\pi}(\frac{\omega}{c})^4(\frac{e^2}{m_e\epsilon_0\omega_0^2})^2. \tag{16}$$

- Note the well-known ω^4 (or $1/\lambda^4$) dependence of Rayleigh scattering.
- $\sigma_n^{\mathrm{RAY}}(\omega)$ may be related to the molecular polarizability, α_p, defined in terms of the induced dipole moment and the imposed electric field.
- For $\omega << \omega_0$ we have $\alpha_p = e^2/4\pi m_e\epsilon_0\omega_0^2$ (see Exercise 3.1).

Using this result in Eq. 16, and the relation $\lambda = c/\nu = 2\pi c/\omega$, we find:

$$\sigma_n^{\mathrm{RAY}}(\lambda) = \frac{8\pi}{3}(\frac{2\pi}{\lambda})^4\alpha_p^2. \tag{17}$$

- Finally: we can add together the separate molecular contributions for a gaseous medium consisting of scatterers with random orientations and positions.

Case II: Rayleigh Scattering (2)

A dilute mixture of gases, such as air, can be described in terms of:

- a weighted average of the real refractive indices, denoted by m_{r}, which may be related to the mean polarizability through:

The Lorentz-Lorenz equation:

$$\alpha_p = (m_{\mathrm{r}} - 1)/2\pi n.$$

Our final form for the macroscopic Rayleigh scattering coefficient is thus:

$$\sigma^{\mathrm{RAY}}(\lambda) \equiv \sigma_n^{\mathrm{RAY}} n = \frac{32\pi^3 (m_{\mathrm{r}} - 1)^2}{3\lambda^4 n} \qquad [\mathrm{m}^{-1}]. \tag{18}$$

Case II: Rayleigh Scattering (3)

For purely-scattering dielectric **spheres** of radius $a << \lambda$, Lorentz showed that:

$$\alpha_p = \frac{m_{\rm r}^2 - 1}{m_{\rm r}^2 + 2} a^3. \tag{19}$$

The cross section then follows immediately from Eq. 17.

Other forms for the Rayleigh scattering cross section are obtained if the particles:

- are anisotropic, non-spherical, partially absorbing, inhomogeneous, *etc.*

Since $m_{\rm r}$ varies with wavelength:

- the actual cross section departs somewhat from the λ^{-4} behavior. A convenient formula (accurate to 0.3%) for the Rayleigh scattering cross section for air is:

$$\sigma_n^{\rm RAY} = \lambda^{-4} \sum_{i=0}^{3} a_i \lambda^{-2i} \times 10^{-28} \quad [{\rm cm}^2] \quad (0.205 < \lambda < 1.05\ \mu{\rm m})$$

where the coefficients are $a_0 = 3.9729066$, $a_1 = 4.6547659 \times 10^{-2}$, $a_2 = 4.5055995 \times 10^{-4}$, and $a_3 = 2.3229848 \times 10^{-5}$.

Case II: Rayleigh Scattering (4)

Although the classical Lorentz dispersion theory is still quite useful in understanding some phenomena in liquids and solids:

- it has been more profitable to treat them as continuous media.

The scattering is considered to occur as a result of:

- optical inhomogeneity arising from impurities and imperfections, as well as statistical fluctuations of density and concentration. These fluctuations:
- are due to various types of collective oscillations, set up by thermal motions.

This approach, pioneered by Smoluchowski and Einstein, is required even for scattering from gases, because:

- the coherent interference of the scattered waves would predict zero scattering in a homogeneous medium. However, gases in planetary atmospheres generally

scatter **as if** there were no mutual interactions (except in the forward direction).

The Scattering Phase Function (1)

We wish to describe the amount of radiation emanating from a small volume element as a result of:

- scattering due to radiation coming from the Sun or from other parts of the medium.

The angle Θ between the directions of incidence $\hat{\Omega}'$ and observation $\hat{\Omega}$ is given by:

$$\cos\Theta = \hat{\Omega}' \cdot \hat{\Omega}.$$

This angle is called the **scattering angle:**

- **Forward scattering** refers to observation directions for which $\Theta < \pi/2$, and **backward scattering** for $\Theta > \pi/2$.

The **total** scattering cross section was defined in Eq. 3 $\sigma_n(\omega) = \frac{e^4}{6\pi m_e^2 \epsilon_0^2 c^4}\left[\frac{\omega^4}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}\right]$ $[\mathrm{m}^2]$ as:

- the total power per unit area scattered **in all directions** divided by the incident power per unit area of the incident plane wave.

The Scattering Phase Function (2)

Similarly:

- the scattered power per unit area per sterradian **in a particular direction of observation** divided by the power per unit area of the incident plane wave

is called:

- the **angular** scattering cross section:

$$\sigma_n(\Theta) \qquad [\mathrm{m}^2 \cdot \mathrm{sr}^{-1}].$$

Azimuthal asymmetry (ϕ-dependence) of the scattering phase function:

- will usually disappear when averaging over all orientations of scatterers.

Thus, it is almost always permissible to assume that:

- the scattering cross section is the same everywhere along a cone of half-angle Θ.

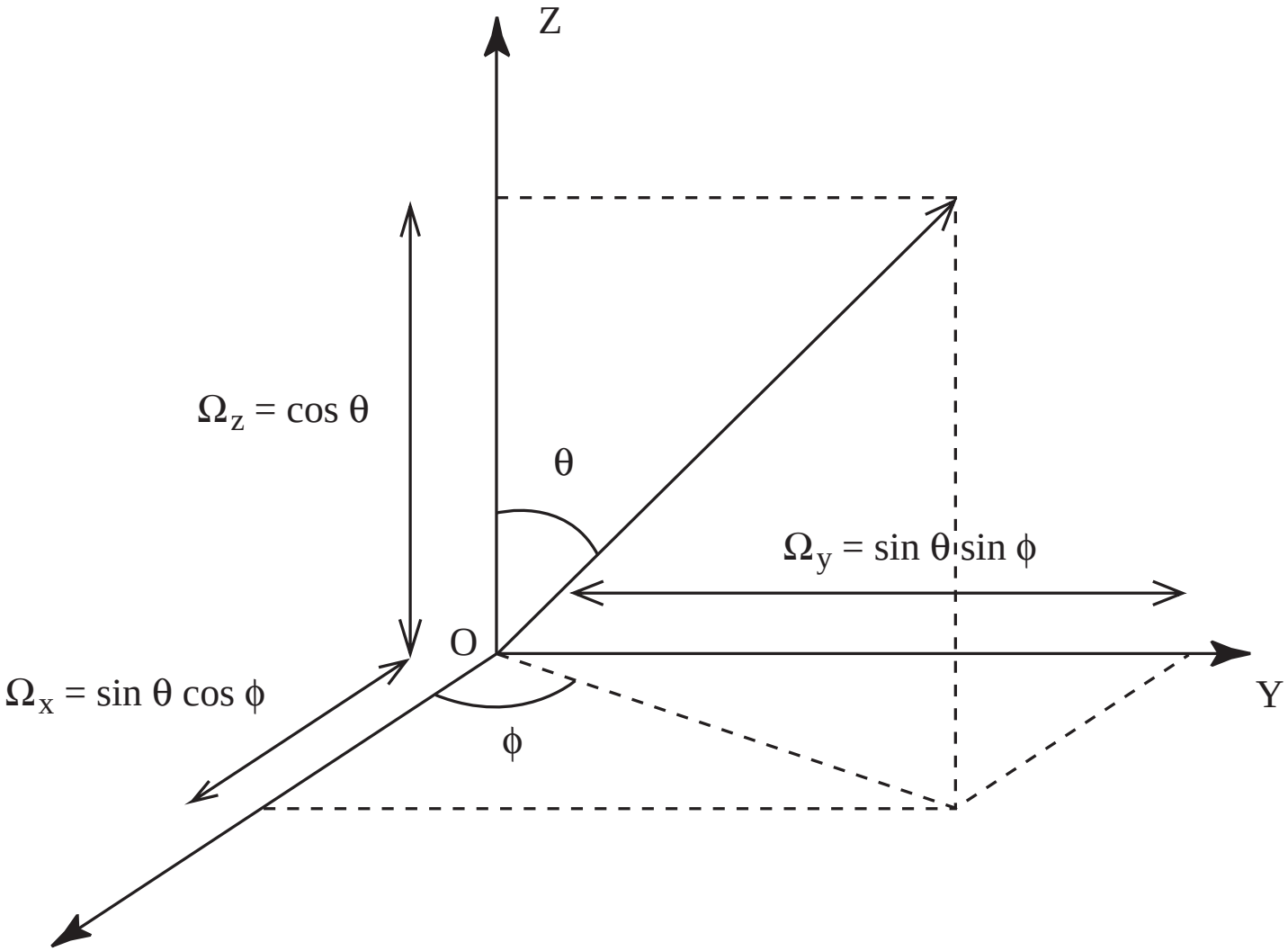

Figure 3: **Ilustration of the relationship between Cartesian and spherical coordinates. The rectangular components of the unit vector $\hat{\Omega}$ are $\Omega_x = \sin\theta\cos\phi$, $\Omega_y = \sin\theta\sin\phi$, and $\Omega_z = \cos\theta$.**

The Scattering Phase Function (3)

To determine the scattering cross section as a function of Θ, we form the following scalar product:

$$\hat{\Omega}' \cdot \hat{\Omega} = \cos\Theta = \Omega_{x'}\Omega_x + \Omega_{y'}\Omega_y + \Omega_{z'}\Omega_z.$$

The rectangular components Ω_x, Ω_y and Ω_z are illustrated in Fig. 3.

Carrying out the multiplications and noting that $\cos(\phi' - \phi) = \cos\phi' \cos\phi + \sin\phi' \sin\phi$, we find:

$$\cos\Theta = \cos\theta' \cos\theta + \sin\theta' \sin\theta \cos(\phi' - \phi). \tag{20}$$

This result is recognized as the familiar **cosine law** of spherical geometry.

For a medium consisting of just one type of particles of number density n [m^{-3}], $\sigma_n(\cos\Theta)$ [$\mathrm{m}^2 \cdot \mathrm{sr}^{-1}$] is the angular cross section per particle, and:

$$\sigma(\cos\Theta) = n\sigma_n(\cos\Theta) \qquad [\mathrm{m}^{-1} \cdot \mathrm{sr}^{-1}]$$

is the **angular scattering coefficient.**

The Scattering Phase Function (4)

It is convenient to introduce a dimensionless quantity which characterizes the scattering process. We define the **scattering phase function** as:

- the **normalized angular scattering cross section:**

$$p(\cos\Theta) \equiv \frac{n\sigma_n(\cos\Theta)}{n\int_{4\pi} d\omega\sigma_n(\cos\Theta)/4\pi} \qquad [\mathrm{sr}^{-1}]. \tag{21}$$

The normalization is:

$$\int_{4\pi} d\omega\,\frac{p(\cos\Theta)}{4\pi} = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\,\frac{p(\theta',\phi';\theta,\phi)}{4\pi} = 1. \tag{22}$$

Since $p(\cos\Theta)$ varies between 0 and 1, this suggests a probabilistic interpretation:

- Given that a scattering event has occurred, the probability of scattering in the direction $\hat{\Omega}$ into the solid angle $d\omega$ centered around $\hat{\Omega}$ is:

$$p(\hat{\Omega}',\hat{\Omega})d\omega/4\pi = p(\cos\Theta)d\omega/4\pi.$$

The Rayleigh Scattering Phase Function (1)

The radiation pattern for the far-field of a classical dipole is:

- proportional to $\Pi \sin^2 \theta$,

where

- θ is the polar angle as measured from the axis defined by the induced field, and
- Π is the induced dipole moment along that axis.

The scattered radiation therefore:

- maximizes in the plane normal to the dipole, and vanishes on the axis of the dipole itself.

How does this translate into a normalized angular scattering cross section or scattering phase function $p(\Theta)$? As defined above, $p(\Theta)$ is:

- the probability of scattering per unit solid angle, which depends upon the projection of the induced dipole moment in the direction Θ of the scattered radiation.

The Rayleigh Scattering Phase Function (2)

As usual we denote:

- the direction of propagation of the incident and scattered waves to be $\hat{\Omega}'$ and $\hat{\Omega}$, respectively.

It is convenient to use as a reference:

- the **scattering plane**, defined as the plane containing $\hat{\Omega}'$ and $\hat{\Omega}$.

For the present purpose it is sufficient to consider:

- two linearly polarized incident waves:
- one with its electric field **parallel with** (or in) the scattering plane, and the other with its electric field **orthogonal to** the scattering plane.

As indicated in Fig. 4:

- these incident waves give rise to induced dipoles ($\Pi_{\parallel}$ and $\Pi_{\perp}$) along the respective incident fields.

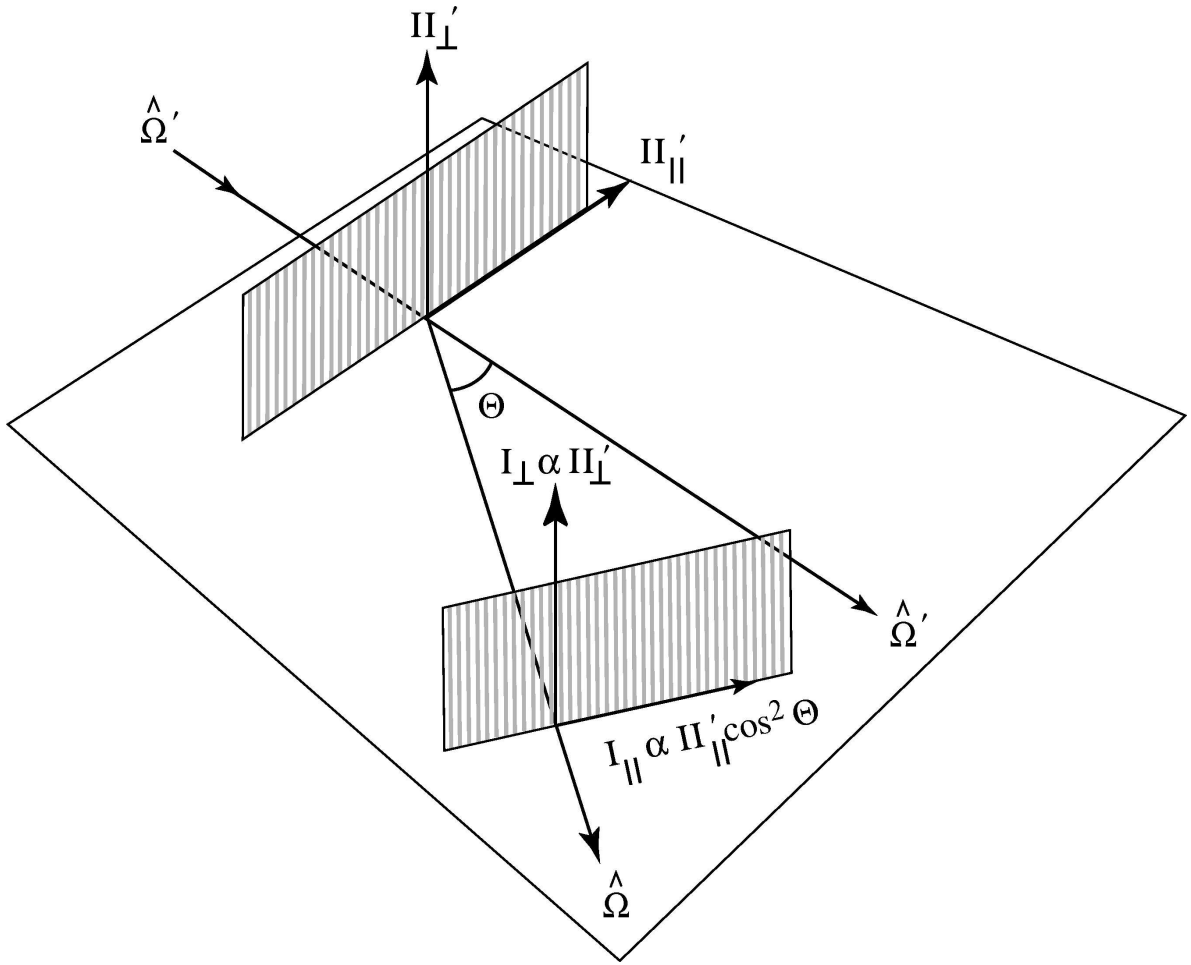

Figure 4: **Illustration of the two transverse components of Rayleigh-scattered light. $\hat{\Omega}'$ and $\hat{\Omega}$ are the incident and scattered propagation vectors, respectively. $\Pi_\perp'$ and $\Pi_\parallel'$ are the induced dipole moments for incident electric fields that are linearly polarized in the directions perpendicular to, and parallel with, the scattering plane (shown as the white rectangle), respectively. $I_\perp$ and $I_\parallel$ are the corresponding scattered radiances in direction $\hat{\Omega}$ associated with the induced dipoles. The plane defined by $\Pi_\perp'$ and $\Pi_\parallel'$ as well as by $I_\perp$ and $I_\parallel$ (both shown as shaded) are normal to the scattering plane.**

The Rayleigh Scattering Phase Function (3)

Referring to Fig. 4, we see that:

- if the incident electric field lies in the scattering plane, then the angle θ between the induced dipole and the direction of scattering is $(\frac{\pi}{2} + \Theta)$, where Θ is the scattering angle.

Thus, the scattered light radiance is:

$$I = I_{\parallel} \propto \Pi_{\parallel} \sin^2(\frac{\pi}{2} + \Theta) = \Pi_{\parallel} \cos^2 \Theta.$$

On the other hand:

- If the incident plane wave is linearly polarized perpendicular to the scattering plane, then the angle θ between the induced dipole and the direction of scattering is $\frac{\pi}{2}$, and the scattered radiance is simply proportional to the strength of the induced dipole, i.e.:

$$I = I_{\perp} \propto \Pi_{\perp}.$$

The Rayleigh Scattering Phase Function (4)

Since:

- natural, unpolarized incident light can be treated as a sum of two orthogonal, linearly-polarized waves (having no coherent relationship),

and since:

- they are of equal magnitude: $I_\perp = I_\parallel = I/2$,

we find that for incident unpolarized light:

- the scattered **radiance** and the **linear polarization** become:

$$I_{\mathrm{RAY}}(\Theta) \propto (I_\perp + I_\parallel) = I(1 + \cos^2\Theta)$$

$$P_{\mathrm{RAY}}(\Theta) \equiv \frac{I_\perp - I_\parallel}{I_\perp + I_\parallel} = \frac{1 - \cos^2\Theta}{1 + \cos^2\Theta}. \tag{23}$$

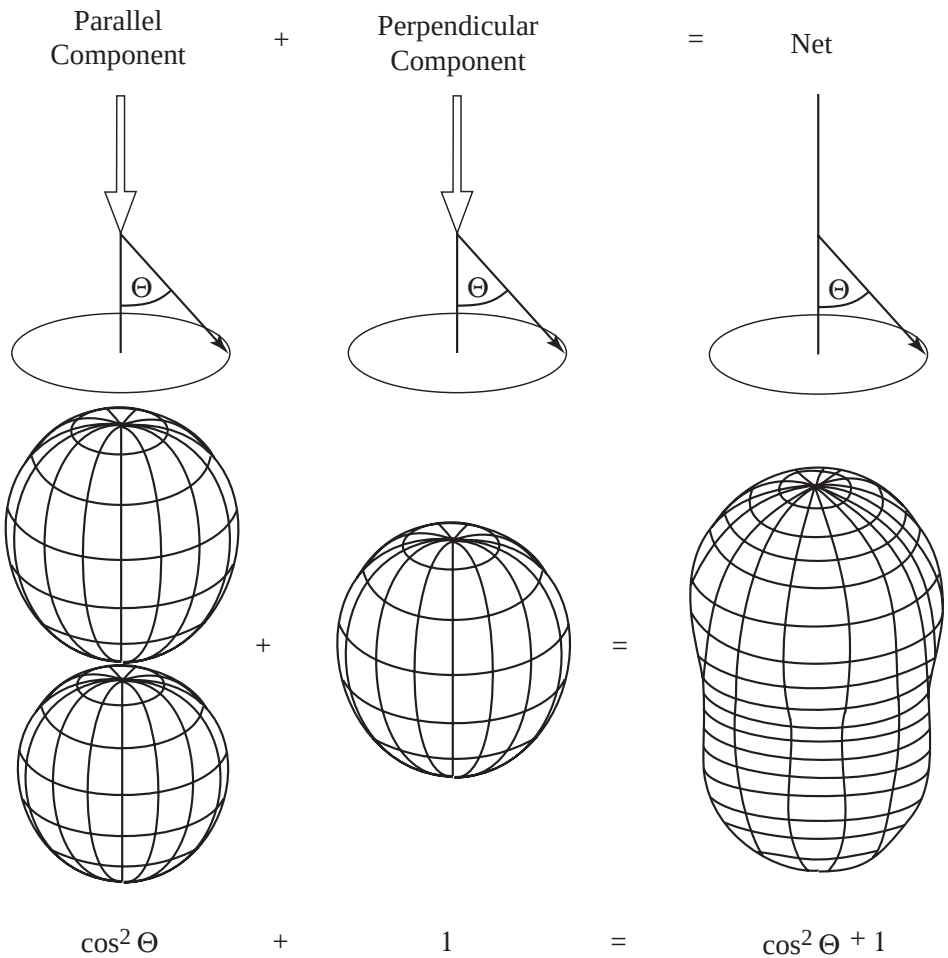

Figure 5: **Schematic three-dimensional diagram of the Rayleigh-scattered phase function, or scattering pattern, for the case of incident unpolarized light. The radiance of the parallel component of the incident light is scattered according to the pure dipole ($\cos^2\Theta$) law, as a result of the projection of the induced dipole along the scattered light direction Θ (see previous Figure). In contrast, the radiance of the scattered component perpendicular to the scattering plane is the same for all Θ and thus is isotropic. The sum of the two patterns yields the scattering pattern for the unpolarized light.**

The Rayleigh Scattering Phase Function (5)

The proportionality constant follows from noting that:

- $d\omega = d\phi \sin\theta d\theta$ in a polar coordinate system where $\hat{\Omega}'$ is along the z-axis.

Therefore:

$$\frac{1}{4\pi}\int_{4\pi} d\omega(1+\cos^2\Theta) = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\Theta \sin\Theta(1+\cos^2\Theta) = \frac{4}{3}$$

which implies that:

$$p_{\mathrm{RAY}}(\Theta) = \frac{3}{4}(1+\cos^2\Theta). \tag{24}$$

Figure 5 illustrates how:

- the two components, one isotropic, the other a dipole, combine to yield the Rayleigh scattering phase function.

The Rayleigh Scattering Phase Function (6)

It should be kept in mind that:

- even though we assumed that the incident light beam is unpolarized, the scattered light from a Rayleigh-scattering medium is polarized.
- This follows from Eq. (23) and the fact that $I_{\parallel}$ is not usually equal to $I_{\perp}$.

In fact, Eq. 23 shows that:

- for $\Theta = 90°$, the scattered light is 100% polarized, in the $\perp$-direction.

However:

- the polarization is diminished in the presence of multiple scattering, which mixes light beams of many polarization states.

In practise, if our interest lies primarily in the flow of energy through a Rayleigh-scattering medium:

- errors in methods which ignore polarization, and which use Eq. 24 for all orders of scattering are small, typically less than a few %.

The Rayleigh Scattering Phase Function (7)

However:

- angular distributions are subject to more severe errors, depending upon the optical thickness, among other factors.

Another consideration for air molecules is:

- the non-spherical shapes of N_2 and O_2.

This non-spherical shape introduces:

- a small anisotropic correction to the above formulas, since the two induced moments are slightly unequal ($\Pi_{\parallel} \neq \Pi_{\perp}$).

One consequence of anisotropy is that:

- the light scattered from air molecules through 90° is slightly depolarized (i.e. only 96% polarized).

The Rayleigh Scattering Phase Function (8)

The Rayleigh scattering phase function applies in general to scattering by small particles. Thus:

- Whenever the size d of the scattering particle is small compared with the wavelength of light ($d < \frac{1}{10}\lambda$), the Rayleigh scattering phase function gives a good description of the angular distribution of the scattered light.
- The Rayleigh scattering phase function for unpolarized light is given by

$$p_{\mathrm{RAY}}(\cos\Theta) = \frac{3}{3+f}(1 + f\cos^2\Theta) \tag{25}$$

where the parameter f is given by

$$f = \frac{1-\rho}{1+\rho}$$

and ρ is the depolarization ratio, attributed to the anisotropy of the scatterer (molecule).