The Scattering of Light by Small Particles

Advanced Laboratory, Physics 407
University of Wisconsin
Madison, Wisconsin 53706

Abstract

In this experiment we study the scattering of light from various size small dielectric spheres suspended in water. When the spheres have radii small compared to the wavelength of the scattered light, the process is called Rayleigh Scattering with the familiar scattering probability proportional to the inverse fourth power of the wavelength resulting in the blueness of the daytime sky. When the spheres have radii comparable or large compared to the wavelength, the theory of classical optics diffraction will apply. In this experiment measurements of the angular distribution and polarization dependence of small sphere light scattering are made in the Rayleigh limit and beyond and compared to theory. The scattering, valid for spheres of any size, is called Mie Scattering.

1. Introduction

Scattering of light is part of our everyday experience. The blue sky, red sky at sunset, white light from clouds, scattering from surfaces, and Thompson Scattering are all manifestations of the scattering of light. Rayleigh scattering is the elastic scattering of light by particles much smaller than the wavelength of the light in transparent liquids and gases. The general case for scattering of particles of any size is called Mie scattering. The scattering in the Rayleigh limit can be readily derived in closed form.

In 1909 Gustav Mie developed a rigorous method to calculate the intensity of light scattered by uniform spheres of any size compared to the wavelength of the incident light. The solution is considerably more complicated than the Rayleigh approximation although it is simply a case of using the Maxwell equations to satisfy the boundary conditions at the surface of the scattering spheres. The system has spherical symmetry so the incident wave is expanded as an infinite series of vector spherical harmonics subject to the boundary conditions at the surface of the sphere. After considerable manipulation the scattered fields are determined and the differential and total cross sections can be calculated. This formalism was rarely used until the 1980s when large mainframe computers became available. However, in the present day, the calculations can be done on personal computers and the Mie scattering code is readily available.

The term 'light scattering' also applies to the case of scattering from density fluctuations. It is these density fluctuations which give rise to scattering in optically dense media. Although the mathematical expressions are similar, the underlying physics is somewhat different since scattering by fluctuations involves thermodynamic arguments whereas scattering by particles does not. Scattering by density fluctuations in ideal gases has the same functional form as scattering by dilute suspensions of particles small compared with the wavelength in an otherwise homogeneous medium. By homogeneous is meant that the atomic or molecular heterogeneity is small compared to the wavelength of the incident light.

We denote by Rayleigh scattering the scattering by dilute suspensions of particles small compared with the wavelength although in the literature there are many ways in which the term Rayleigh scattering is used and misused. There are also other light scattering phenomena that are inelastic: the scattered light has a different frequency than the incident light. Inelastic molecular scattering processes are usually associated with the names Brillouin and Raman. See Ref. [1] for a very nice historical account of Rayleigh Scattering.

2. Cross Sections and Mean Free Path

The relevant size parameter for light scattering of wavelength λ_0 from dielectric spheres of radius a is:

$$x = \left(\frac{2\pi a n_{med}}{\lambda_0}\right)$$

Here n_{med} is the index of refraction of the scattering medium. The Rayleigh limit is when $x \ll 1$. When this condition is satisfied, the driven oscillating polarization P of the dielectric sphere can be approximated as uniform throughout the sphere reducing the problem to that of the classic problem of a dielectric sphere in a uniform field.

The Rayleigh unpolarized light total cross section is given by:

$$\sigma = 8/3\pi a^2 x^4 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2$$

and the unpolarized light differential cross section is:

$$d\sigma/d\Omega = \frac{1}{2}a^2 x^4 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 (1 + \cos^2\theta)$$

Here λ_0 is the laser wavelength in vacuum, n_{sph} is the index of refraction of the scattering spheres, and $m = (\frac{n_{sph}}{n_{med}})$. The dependence of the scattering on the inverse fourth power of the wavelength is clearly seen. The polarization dependence of the scattering is evident in the $(1 + \cos^2\theta)$ term. The $\cos^2$ term is from the incident light linearly polarized in the scattering plane while the 1 term is the contribution from the incident light polarized perpendicular to the scattering plane.

The general case for an arbitrary value of x is called Mie scattering. However, the cross section in the limit of $x \gg 1$ is the limiting case of classical optics and the total cross section will be geometric tending toward $\sigma = \pi a^2$. If the forward scattering diffraction peak can be observed, the cross section will be become twice the geometric limit.

The forward diffraction peak can be quantified in several respects since as $x \gg 1$ we are in the classical optics regime. The angular full width half maximum of the forward peak approaches:

$$\Delta\theta \simeq \frac{\lambda}{2a},$$

and secondary maxima and minima develop in the angular distribution separated by:

$$\Delta\left(k_d a\right) = \Delta\left(2ka\sin\frac{\theta}{2}\right) = \pi.$$

3

Here k_d is the magnitude of the scattering vector difference between the incoming $\vec{k_i}$ and outgoing $\vec{k_s}$ waves $\vec{k_d} = (\vec{k_s} - \vec{k_i})$.

Given a cross section σ and a volume density of scatterers ρ, the mean free path ℓ is defined to be that thickness of scattering target that gives a scattering probability of one. This condition is $\sigma \rho \ell = 1$, thus $\ell = 1/(\rho \sigma)$. It is important to keep the target thickness less than ℓ to ensure that the scattered light is due to a single scatter in the target. Significant multiple scattering will make it very difficult to compare measurement with theory. A comprehensive discussion of the scattering of light by small particles may be found in the book [2].

3. Apparatus

The apparatus consists of an angular spectrometer arrangement consisting of a light source, scattering cells containing a solution of different diameter polystyrene nanospheres in water, and a photomultiplier detector. The general layout is shown in Fig. 1 In order to use a Lock-In amplifier technique, the laser beam must be pulsed. the laser beam can be run in pulsed mode internally or the laser can be run CW and pulsed by a mechanical optical chopper. In the latter mode Fig. 1 should also show the optical chopper after the linear polarizer. A block diagram of the detection system is shown in Fig. 2.
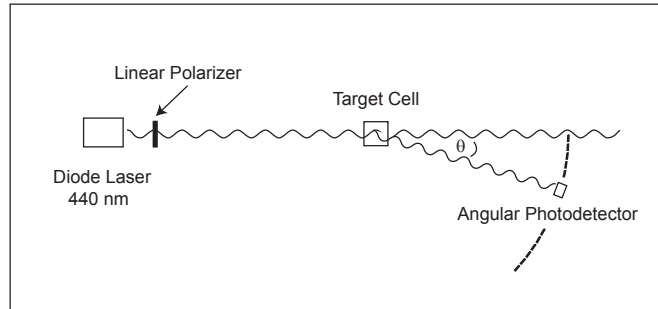

Figure 1: General Layout of the Scattering Spectrometer

The laser light source

The laser is a PicoQuant pulsed diode laser (PDL 800-D) with a 440 nm wavelength head. The repetition rate and intensity can be varied. The maximum average power

at 10 MHz is 0.69 mW giving a peak energy per pulse of about 70 pJ. The laser light is almost 100% linearly polarized.

The Photomultiplier Detector

The detector is a Hamamatsu R580 1.5 in photomultiplier which can be operated up to -1500 V. The photocathode quantum efficiency peaks at a wavelength of about 420 nm, a very good match to the diode laser wavelength. The photocathode face is masked to a 0.25 in diameter circular aperture in order to define the angular resolution.

PreAmp and Pulse Shaping Amplifier

The photomultiplier signal is amplified in two stages. The first stage is a fast, fixed gain X10 preamp (LeCroy) followed by a variable gain pulse shaping Ortec amplifier. The fast photomultiplier pulse (≈ 10 ns) is shaped to about 1 μs by the Ortec amplifier to match the input requirements of the Lock-In amplifier.

Function Generator

The Stanford Instruments function generator provides the external trigger for the diode laser controller and the reference input for the Lock-In amplifier. The normal settings are f = 100 kHz and a square wave output.

Optical Chopper

The Stanford Instruments Optical Chopper is a mechanically rotating wheel with slits that chop the light beam. The beam can be chopped up to 4 kHz. A higher beam intensity can be obtained with this technique and in certain situations provides a better signal to noise compared to running the laser in the native pulsed mode. The chopper controller provides a sync output to connect to the Reference-In of the Lock-In amplifier.

Lock-In Amplifier

The amplified signal from the photomultiplier is synchronized with the repetition rate of the laser using a Lock-In amplifier. The locked-in output signal is read directly from the Lock-In amplifier.
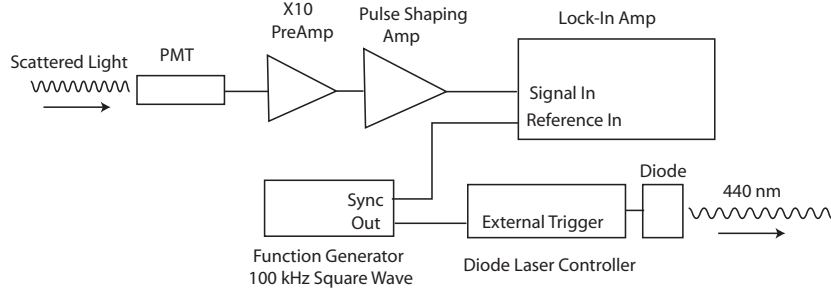
Figure 2: Block Diagram of the Detection Apparatus

Optical Components

A quarter wave plate (440 nm) is needed to provide an unpolarized beam since the laser beam is almost 100% linearly polarized. If the incident beam polarization is oriented at 45° an external linear polarizer can be used to select either horizontal or vertical beam polarization. This technique has the advantage that the beam profile will be identical for both polarizations. A linear polarizer is also needed to measure the scattered beam polarization.

The Target Scattering Cells

The scattering cells are 1 cm square quartz cells containing either 60 nm, 2 μ, or 4.17 μ diameter polystyrene spheres corresponding to size parameters x = 0.574, 19.1 and 39.8 respectively. The nanospheres have a density of 1.05 g/cm^3 and an index of refraction of 1.59 @ 589 nm. The nanosphere solution densities have been chosen to minimize multiple scattering effects by setting the scattering mean free path to be much less than the dimensions of the target cell. The nanospheres are in a water solution.

3. Procedure

The basic procedure consists of several well defined parts.

1. Start with samples that represent the long wavelength limit (d = 60 nm: Rayleigh Scattering region) and the short wavelength limit (d= 2000 nm: Diffraction Scattering region). Run the program MiePlot for each case to plan the angular scan.
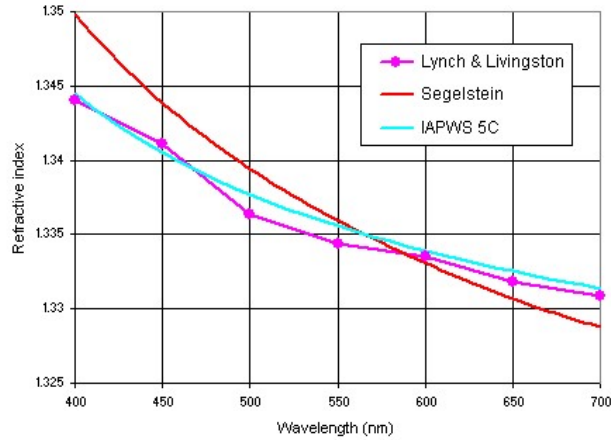
Fig. 1 *Refractive index of water as a function of wavelength*

Figure 3: The index of refraction of water as a function of wavelength

The index of refraction of water as a function of wavelength is shown in Fig. 3. You will find that scattering in the Rayleigh limit requires as much of a full angular range as the apparatus permits. In the short wavelength limit the cross section is close to zero before 90 degrees. The long wavelength limit will require separate measurements for each polarization direction (vertical and horizontal). The polarization dependence is not very large in the short wavelength limit. It is useful to measure at integer angles since the `mietable` and `snell` programs (see below) calculate at integer angles in one degree steps. The polarization direction can be varied by simply rotating the diode laser head. If the external linear polarizer is used, set the laser polarization (and beam profile direction) to 45° and select the polarization direction with the external polarizer.

2. With the photomultiplier voltage off, set the spectrometer to 0° and align the direction of the laser beam so that it is centered on the target cell and the center of the spectrometer aperture.

3. Before starting measurements, make sure that the spectrometer is out of the direct beam. The normal photomultiplier voltage is 1500 V. The instructor will show you how to use the Lock-In amplifier. Take measurements as a function of angle. Do not go below 2.5°. Use the wooden beam block to block the beam

7

every time you change the spectrometer angle.

4. The photomultiplier signal is obtained from the output of the Lock-In amplifier. The angular distribution of the measurements will be compared to geometry corrected Mie Theory.

5. A minimal set of measurements should include:

   - 60 nm: Intensity vs angle for horizontal and vertical beam polarization. A reasonable choice is 15° to 135° in 15° steps.

   - 60 nm: Polarization of the scattered beam for horizontal and vertical polarized incident beam.

   - 2 and 4 micron: Intensity vs angle for either horizontal or vertical beam polarization in 2.5° steps out to 60°. The horizontal and vertical beam polarization are almost identical but horizontal polarization results in a more narrow beam through the sample cuvette, resulting in less scattering from the side walls of the sample cuvette. Go as far out in scattering angle until you no longer see the secondary maxima.

   - Determine the nanosphere density ρ of each sample by measuring the sample absorption at zero degrees. To do this, a neutral density filter must be placed in front of the detector so that the laser beam can be directly incident on the detector obtaining a signal strength comparable to the normal scattering signals. Failure to provide suitable beam attenuation will damage the photomultiplier. The instructor will show you how to set this up.

     The calculation for obtaining the nanosphere density depends only on the thickness of the sample, the sample absorption, and the total cross section according to:

     $$I = I_0 e^{-t/\ell} \quad \text{with the mean free path} \quad \ell = 1/\sigma\rho$$

     Here t is the sample thickness, I is the measured intensity with the sample, and I_0 is the measured intensity with the water sample. The samples have been prepared so that the sample transmissions range from about 60 to 80 percent.

4. Analysis

0.0.1 Analysis Tools

Scattering in the Rayleigh limit leads to a simple formula readily derived [3]. The more general case of arbitrary wavelengths (Mie Theory) is well known but is not in a simple form since the electric fields inside and outside the scattering spheres must be calculated subject to the appropriate boundary conditions [5]. Fortunately there are several available programs that perform the calculation. The Windows based program **MiePlot** has entry points for all the relevant parameters and plots the scattering angular distribution.

A more detailed set of routines (**Mie Scattering Utilities**) calculates the Mie theory `mietable` as a function of angle in the form of column lists which can be entered into a program which provides plotting capability such as SigmaPlot or Excel. The utilities include a routine called `snell` which corrects for the cuvette refraction. Two other routines included with the utilities called `fitmie` and `fitdist` are available for fitting refraction corrected data to the the Mie theory [5]. A User's Guide contains all the relevant information needed to run the utilities. The Mie Utilities run as .exe routines in a terminal window. All the Mie routines are available on a laboratory CD.

0.0.2 Analysis Procedure

Be sure to read Ref. [5] first. the experiment described therein is similar to what is done in this lab. Compare the refraction corrected results to theory. The 60 nm nanospheres are close to the Rayleigh regime and so can be compared to the exact Rayleigh formulas. Since the laser intensity will be identical for both laser polarizations, the unpolarized cross section can be obtained by combining tha data from both polarization directions. The short wavelength data produces secondary maxima. Comparing data to theory, the nanosphere diameter can be determined.

5. Questions

1. Give a simple argument for the incident beam polarization dependence in the Rayleigh limit where the polarization parallel to the scattering plane gives a $\cos^2 \theta$ dependence and the polarization normal to the scattering plane is independent of scattering angle.

2. Explain the results for the polarization of the scattered beam in the Rayleigh limit for the three cases of horizontal, vertical, and unpolarized incident beam.

Explicitly derive an expression for the scattered polarization for an unpolarized beam as a function of scattering angle.

3. Explain why the angular distribution becomes very forward peaked as the particle size becomes much larger than the incident light wavelength.

4. Why are there secondary maxima in the short wavelength limit?

5. What is the relation between scattering cross-section, the number of the scattering spheres, and the scattering mean free path?

6. Using the Mie scattering cross sections obtained from the program **Mie Calculator**, calculate the number density of a suspension of each of the three size spheres to give a mean free path of 1 cm.

Appendix - Scattering by a Bound Electron

The incident electric field excites a bound electron and forces the electron to vibrate at the frequency of incident wave. The bound electron reradiates energy at the same frequency and the problem reduces to finding the acceleration of the electron charge in terms of the electric field. The acceleration will then give the electron radiated energy and the resultant scattering cross section becomes:

$$\sigma = \sigma_0 \frac{\omega^4}{\left(\omega_0^2 - \omega^2\right)^2 + (\gamma\omega)^2},$$

where σ_0 is the Thompson (free electron scattering) cross section:

$$\sigma_0 = \frac{8\pi}{3} r_0{}^2; \quad r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2}.$$

Here r_0 is the classical electron radius and γ is the spectral line width. The maximum value of σ is when $\omega \simeq \omega_0$, i.e. when the frequency forms a resonance with one of the atomic spectral lines. In that case the the scattering cross section can become very large. For strong binding, $\omega \ll \omega_0, \gamma \ll \omega_0$, the cross section becomes:

$$\sigma = \sigma_0 \left(\frac{\omega}{\omega_0}\right)^4,$$

giving a cross section that depends on the inverse fourth power of the incident wavelength. A dielectric sphere with dimensions small compared to the wavelength scatters radiation with the same wavelength dependence. Rayleigh, in his investigation of
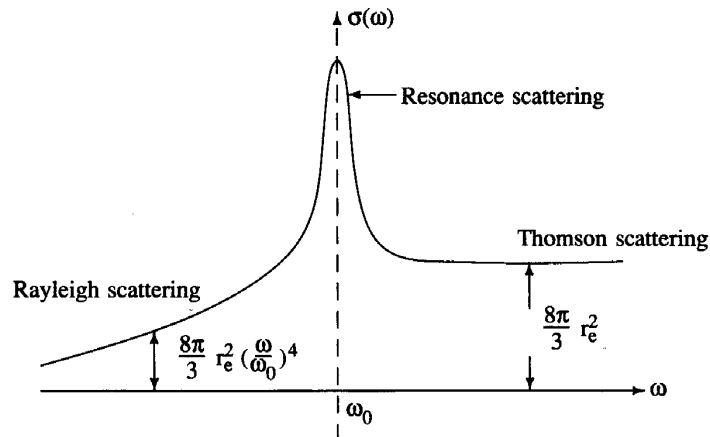
Figure 4: The total cross for elastic scattering from electrons as a function of frequency showing both the long and short wavelength limits

the blueness of the sky, assumed that individual molecules scatter light in a random fashion, so that the phases are random and just the individual intensities add. The above expression in the Rayleigh limit not only accounts for the blueness of the sky, but with empirical values of ω_0, leads to good agreement with observed atmospheric scattering, not only in intensity, but also in the scattered polarization.

Fig. 4 shows the transition from the Rayleigh limit to the short wavelength Thompson scattering limit. Thompson scattering is the non-relativistic limit to Compton Scattering.

References

[1] "Rayleigh Scattering", Andrew T. Young, Physics Today, Jan. 1982, 42.

[2] C.F. Bohren and D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).

[3] "An experiment to measure Mie and Rayleigh total scattering cross sections", A.J. Cox et al., Am. J. Phys. **70**, 620 (2002).

[4] "Mie Scattering", R.M. Drake and J.E. Gordon, Am. J. Phys. **53**, 955 (1985).

[5] Particle Size Determination: An undergraduate lab in Mie scattering", I. Weiner, M. Rust, and T.D. Donnelly, Am. J. Phys. **69**, 129 (2001).