Laboratory studies of scattering matrices for randomly oriented particles: potentials, problems, and perspectives

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Abstract

A number of issues relevant to laboratory studies of scattering matrices as functions of the scattering angle for randomly oriented particles in the visible part of the spectrum are discussed. The usefulness of experiments is compared with that of numerical computations, in particular, for ensembles of natural nonspherical particles with broad ranges of sizes and shapes. It is argued that measurements of the entire scattering matrix have considerable advantages over measurements of only the intensity and polarization of the scattered light for incident unpolarized light. Results of special test experiments are presented which show that our experimental results for scattering matrices are not significantly contaminated by multiple scattering and that the orientation of the particles can be adequately described as random. Some ways are pointed out to overcome the lack of measurements for very small and very large scattering angles. A possibility to reduce the amount of material needed in the experiments is indicated. Finally, characterizations of the particles in terms of sizes, shapes and refractive indices are discussed.

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1. Introduction

The scattering angle dependence of all 16 elements of the scattering matrix of an ensemble of randomly oriented (natural or artificial) particles in air (aerosols) or a liquid (hydrosols) can be measured in the laboratory by using lasers as light sources (see e.g., Ref. [1], and references therein, as well as Ref. [2]). An advanced experimental setup for such measurements at various wavelengths was described by Hovenier [3]. It was developed and located at the Free University in Amsterdam until February 2001. For the results of measurements with this setup we refer to Refs. [4–13]. In the meantime the setup has been moved to the Institute for Atomic and Molecular Physics (AMOLF) in Amsterdam where it is being employed and further developed in the framework of an official collaboration of AMOLF and the Astronomical Institute “Anton Pannekoek” of the University of Amsterdam. After the relocation several components of the setup were replaced by new ones and a number of improvements were introduced, but the setup (see Figs. 1 and 2) is still basically the same as before.

Fig. 1. Schematic picture of the experimental setup as used for aerosols. \( P \) = polarizer; EOM = electro-optic modulator; \( A \) = polarization analyzer; \( Q \) = quarter wave plate. The detector and monitor are photomultipliers. The detector can be moved on a goniometer ring (shaded) with an outer diameter of about 1 m. The aerosols move down in a jet stream through the nozzle of an aerosol generator in the center of the ring perpendicularly to the horizontal scattering plane.
Fig. 2. Photograph of the experimental setup as used for aerosols. The detector and the monitor are located on a goniometer ring with an outer diameter of about 1 m. The laser, the aerosol generator nozzle and the sample in the scattering volume are also indicated.

The main purpose of this paper is to discuss a number of issues that are relevant to the type of measurements under consideration.

2. Why measurements?

In recent years, a tremendous amount of progress has been made in analytical and computational methods for studies of electro-magnetic scattering by nonspherical particles (see, e.g., Refs. [1,14,15]). Nonetheless, it is important to conduct experiments in this field for the following reasons.

(i) The shapes and structures of many particles, in particular natural particles, are too complicated for calculating their light scattering properties with sufficient accuracy. This holds for a variety of aerosol particles, like sand and volcanic ashes, as well as for the so-called cosmic dust particles. The computational problems are usually exacerbated by the necessities to know the refractive index and to average over broad ranges of sizes, shapes, and orientations of the particles to get results for ensembles of natural particles in realistic situations. Similar complications occur in microwave analog measurements (see, e.g., Ref. [16]).

(ii) Computational results always rest on a number of assumptions and approximations and should, therefore, be tested by experimental data. Mie theory, for example, has been verified by light scattering experiments with latex spheres and water droplets, but a lot of similar work remains to be done for nonspherical particles.

(iii) Combining computational and experimental approaches can create synergy to the benefit of each of them. This yields more insight, data, and useful ideas than can be obtained from computational means alone. In particular, it is important to establish which non-sphericity effects of light scattering are general and which of these effects occur only for particular shapes, like spheroids and cylinders.
The intensity and state of polarization of a beam of light can be described by means of Stokes parameters [17,18]. The scattering matrix, \( F \), of an ensemble of particles is defined as follows. If the Stokes parameters of an incident beam, written as a column vector, are multiplied by \( F \) we obtain a scalar times the vector that consists of the Stokes parameters of the (once) scattered light. The value of the scalar depends on the normalization of \( F \). The 16 elements of the scattering matrix, \( F_{ij} \), with \( i, j = 1 \) to 4, depend on the properties of the particles, the wavelength of the radiation and the direction of the scattered light, which, for randomly oriented particles, is sufficiently described by means of the scattering angle, \( \theta \). When randomly oriented particles and their mirror particles are present in equal numbers in the ensemble the scattering matrix has the simple form

\[
F(\theta) = \begin{pmatrix}
F_{11}(\theta) & F_{12}(\theta) & 0 & 0 \\
F_{12}(\theta) & F_{22}(\theta) & 0 & 0 \\
0 & 0 & F_{33}(\theta) & F_{34}(\theta) \\
0 & 0 & -F_{34}(\theta) & F_{44}(\theta)
\end{pmatrix}.
\]

Here \( F_{11}(\theta) \) is the phase function and \( -F_{12}(\theta)/F_{11}(\theta) \) is the degree of linear polarization for incident unpolarized light. We always normalized experimental phase functions by making their values unity at a fixed scattering angle, namely 30°.

For some applications it suffices to measure only the two elements of the scattering matrix that provide the phase function and the degree of linear polarization of the scattered light for incident unpolarized light. This is true, for instance, for single scattering of sunlight, that is unpolarized, by cometary and interplanetary particles. Yet, we prefer to determine the complete scattering matrix, i.e., all 16 elements as functions of the scattering angle, for the following reasons.

(a) It is then possible to identify experimental errors by using all theoretical relationships valid for the elements of a scattering matrix [19,20],

(b) The complete scattering matrix provides the necessary information to determine the intensity and state of polarization of singly scattered radiation when the light source emits polarized radiation, as occurs in some lidar systems.

(c) It is often desirable or necessary to conduct multiple scattering calculations for polarized light for obtaining accurate results for scattering media, such as planetary atmospheres and circumstellar disks of dust particles. A variety of methods for performing such calculations exists [21–36]. In all of them one needs the scattering matrix of the ensemble of particles contained in a small volume element of the scattering medium considered. This matrix may depend on the location in the medium. However, the results of multiple scattering calculations do not only depend on the scattering and absorption properties of the medium, but also on the characteristics of the incident light as well as the size and shape of the medium.

3. Single or multiple scattering

It is clearly important that our measurements refer only to singly scattered light and are not significantly contaminated by multiple scattering. This means that, on the one hand, we should have enough particles in the scattering volume to be representative for an ensemble of randomly oriented
Fig. 3. The flux of the scattered light (arbitrary units) for unpolarized incident light versus the concentration of rutile hydrosol particles for a fixed position of the detector at 15° (squares) and at 90° (circles). The particles have a mean volume-equivalent-sphere diameter of 221 nm with standard deviation of 57 nm. As long as the data points lie on a straight line only single scattering is important.

particles of some material with various sizes and shapes, but, on the other hand, not so many particles that multiple scattering plays a significant role. However, it is possible to exclude multiple scattering contamination in our experimental determinations of scattering matrices by conducting some special tests in which the number of scattering particles is varied. For example, we can put the detector at a fixed angle and measure whether the flux of the scattered radiation for unpolarized incident light is proportional to the increasing amount of particles in the scattering volume. As long as this is the case only single scattering is important [17,37]. For hydrosol particles this can be routinely checked by changing the concentration of the particles in the cuvette in which the particles are located. An example of such a multiple scattering test is shown in Fig. 3 for two different fixed positions of the detector. For the detector fixed at a scattering angle of 15° the influence of multiple scattering appears at lower particle densities than for a fixed position of the detector at a scattering angle of 90°, since in the former case the amount of scattered light for unpolarized incident light is larger than in the latter case. For the scattering matrix measurements of hydrosols we always chose a particle density that clearly lies on the linear part of the curve for the smallest scattering angle used in those measurements.

For aerosols such a multiple scattering test is more complicated. To clarify this we should first explain how the particles of a particular sample are brought into the jet stream mentioned in the legend of Fig. 1. A compacted mass of powder is loaded into a cylindrical feed stock reservoir with a diameter of 14 mm and is fed onto a rotating brush by means of a piston that pushes the particles upward at a certain speed expressed in mm/h (see Fig. 4). Depending on this speed and the compactness of the sample the brush removes a reasonably well-defined quantity of powder
uniformly from across the whole exposed surface of the compacted powder. This powder is dispersed and is carried away from the dispersion head by an air stream to the nozzle of the aerosol generator right above the scattering volume. To check whether multiple scattering plays a significant role for the aerosol measurements we load the reservoir and perform a series of flux measurements.
Fig. 6. SEM image of the original green clay particles directly from the container and not processed by the aerosol generator. The complex layered structure of the highly irregular micron-sized clay particles is clearly visible.

of the scattered light for unpolarized incident light with the detector at a fixed angle and with different speeds of the piston. Because small fluctuations in particle density in the reservoir and, consequently, in the aerosol jet occur, we integrate the signals over relatively long periods of time to get a reasonable accuracy. During the light scattering experiments piston speeds usually range between 20 and 100 mm/h. Fig. 5 shows the result of a multiple scattering test for a sample of green clay particles with a complex layered structure (see Fig. 6) at a wavelength of 632.8 nm in which we used much higher speeds, up to 190 mm/h, but still no significant deviation from a linear behavior was observed even at a scattering angle of 5°. A similar test in which we attained a piston speed of 400 mm/h gave the same result. To obtain information on the sizes of the particles that we used in the light scattering experiments we measured projected surface distributions of the particles. The sizes of the particles can thus be expressed in an effective radius \(r_{\text{eff}}\) and effective variance \(v_{\text{eff}}\) of projected-surface-equivalent spheres. The green clay particles employed in the multiple scattering tests have been used before [11]. Their sizes are characterized by \(r_{\text{eff}} = 1.55\mu m\) and \(v_{\text{eff}} = 1.4\). The composition and shapes of the green clay particles are quite representative for the other mineral aerosol samples we have used in the past [5,6,9–13]. Summarizing, we may be assured that none of our results for scattering matrices as functions of the scattering angle are significantly contaminated by multiple scattering.

4. Particle aggregation and separation

Since we are interested in studying the properties of natural irregular particles, we want to make sure that the method for producing the particle jet stream described in the preceding section does not
alter the sample, either by breaking up the particles in smaller parts or, conversely, by aggregating them into larger particles. To test this we made scanning electron microscope (SEM) images for the same sample of green clay particles as used for the multiple scattering tests. A piece of graphite tape was prepared with particles that had not been through the aerosol generator, but that came directly from the container in which the sample was stored. A second piece of graphite tape was prepared with particles collected directly in the jet stream by holding the tape briefly (less than a second) in the jet at the place where it intersects with the laser beam. Several SEM images made at different magnifications showed no evidence of a significant alteration of the particles due to the aerosol generator. As an example we compare the image of some particles directly from the container at a magnification of 5000 (Fig. 6), with an image of some particles collected from the aerosol jet at the same magnification (Fig. 7). Both images show similar irregular particles with dimensions of a few micrometers. Other SEM images at different enlargements gave similar results. It should be noted that the small (sub-micrometer) particles in the background of Figs. 6 and 7 are due to the graphite tapes.

5. Random orientation

Let us now address the question whether the orientations of the particles in our experiments can indeed be called random. As mentioned, the nozzle of the aerosol generator is located right above the scattering volume, so that the aerosol jet flows through the scattering volume perpendicularly to the scattering plane (see Fig. 2). Consequently, it is not expected that the particles in the scattering volume have any preferential direction of orientation, except possibly for the direction of the jet.
Fig. 8. Scattering matrix element $F_{11}(\theta)$, and element ratio $-F_{12}(\theta)/F_{11}(\theta)$ of a sample of green clay particles for different orientations of the jet stream for a wavelength of 632.8 nm. Open circles are the results for the jet stream oriented perpendicularly to the scattering plane, and solid triangles are the results for the jet stream oriented at approximately 45° with respect to the scattering plane.

However, we verified that the latter direction is irrelevant, by a test in which the jet stream was directed under an angle of 45° instead of 0° with the normal to the scattering plane. The two directions of the aerosol jet have been schematically indicated in Fig. 4. For the random orientation test measurements we used the same sample of green clay particles as used for the multiple scattering tests and a wavelength of 632.8 nm. The results of these test measurements are shown in Fig. 8 for the phase function and the degree of linear polarization for unpolarized incident light, and in less detail in Fig. 9 for the entire matrix. Open circles in Figs. 8 and 9 are the results for the particle jet oriented perpendicularly to the scattering plane, and solid triangles are the results for the jet directed under an angle of approximately 45° with respect to the scattering plane. The matrix element $F_{11}(\theta)$, and the element ratios $-F_{12}(\theta)/F_{11}(\theta)$, $F_{13}(\theta)/F_{11}(\theta)$, $F_{14}(\theta)/F_{11}(\theta)$, $F_{22}(\theta)/F_{11}(\theta)$, $F_{23}(\theta)/F_{11}(\theta)$, $F_{24}(\theta)/F_{11}(\theta)$, $F_{33}(\theta)/F_{11}(\theta)$, $F_{34}(\theta)/F_{11}(\theta)$, $F_{43}(\theta)/F_{11}(\theta)$, and $F_{34}(\theta)/F_{11}(\theta)$ have been measured.

The other ratios have been obtained using the following reciprocity relations $F_{21}(\theta) ≡ F_{12}(\theta)$, $F_{31}(\theta) ≡ -F_{13}(\theta)$, $F_{41}(\theta) ≡ F_{14}(\theta)$, $F_{32}(\theta) ≡ -F_{23}(\theta)$, and $F_{42}(\theta) ≡ F_{24}(\theta)$ [17].

No significant differences in the elements of the scattering matrix as functions of the scattering angle were found for the two orientations of the particle jet (see Figs. 8 and 9). The largest discrepancy is found for the element ratio $F_{43}(\theta)/F_{11}(\theta)$ at small angles, but this ratio is notoriously sensitive to small alignment errors in the optical elements of the setup. In conclusion, the orientation of the jet stream plays no significant role in our experimental results and the orientation of the particles in our experiments can be adequately described as random. Fig. 9 also shows that, given the experimental errors, the measurements are consistent with the theoretical relations $F_{13}(\theta)/F_{11}(\theta) ≡ F_{14}(\theta)/F_{11}(\theta) ≡ F_{33}(\theta)/F_{11}(\theta) ≡ F_{24}(\theta)/F_{11}(\theta) ≡ 0$ which hold for an ensemble consisting of randomly oriented particles with equal numbers of mirror particles. Since these elements are zero at all scattering angles for all of our measured aerosol results so far, we usually omit these scattering matrix elements from figures.
6. Range of scattering angles

Virtually all measurements in Amsterdam were restricted to scattering angles in the range 5–173° for aerosols and to 20–160° for hydrosols. Recently, however, the range for aerosols has been expanded slightly to 3–174° (see Figs. 8 and 9). The main problems for small angles are that very close to zero degrees the scattered light cannot be separated from the much stronger incident light. Also, the strength of the scattered light in the smallest 3° often ranges over several orders of magnitude. To measure this requires a detector with a huge dynamical range, and a high angular
resolution. Finally, the finite size of the detector implies that around 3° it starts to move into the incident beam, producing stray light which increasingly disturbs the measurements, when going to smaller angles.

For large scattering angles we have a similar problem due to the finite size of the detector. Beyond 174° the detector is hit by the incident beam and no measurements are possible. An additional problem is that the signal here is often so low that contamination by stray light may disturb the measurements.

To overcome the lack of measurements for small scattering angles one may conduct a simple extrapolation, but it seems better to use a light scattering theory (e.g., Lorenz–Mie theory or Geometric Optics) to fit the measured angular distributions as well as possible, at least in the range containing the smallest angles for which experimental data were determined. For example, there are indications that strong forward peaks in phase functions of randomly oriented particles may depend little on the shape of the particles. Hence, assuming that this is also true for the particles used in the measurements, one can use Lorenz–Mie theory to compute this part of the phase function, provided the refractive index is known and size distribution data are available. Furthermore, phase functions for randomly oriented nonspherical particles are often rather flat for large scattering angles, so that a simple extrapolation to 180° may suffice to get a complete synthetic phase function in the range 0–180°, which equals unity when averaged over all scattering directions [38–40].

However, it is clear that measurements of the entire scattering matrix for very small and large scattering angles are coveted. It should be possible to modify our present setup for that purpose, using optical elements like beam splitters.

7. Samples

If we wish to measure light scattering by, e.g., phytoplankton, volcanic ash particles or cosmic dust analogs, one of the first problems to solve is, how to get samples of such particles. At present we need of the order of 100 g of aerosols to measure the scattering angle distributions of the entire scattering matrix at one wavelength and of the order of 10 g to do this for the two elements that yield the phase function and the degree of polarization for unpolarized incident light. Furthermore, we lose the material after the measurements have been conducted. The amounts needed may vary depending on the type of particle and in particular on the size distribution of the particles. In general, the smaller the particles are, the smaller the amount that is needed. For measurements of hydrosol particles, which are located in a cuvette, less material (of the order of a few grams) is needed to measure $F(\theta)$ at two wavelengths.

We are seeking ways to work with smaller amounts of aerosol particles and a first step in that direction has already been made. During the aerosol measurements the particles are located in a jet stream that is blown through the scattering volume. Thus, no vials, vessels, or cuvettes are needed to contain the sample. This is a great advantage, since anything between the particles and the detector decreases the accuracy of the measurements and limits the angular range. However, a disadvantage of this method is that after being blown through the scattering volume the particles have to be removed and are lost. In an attempt to diminish this problem, we have constructed an aerosol collector. This device pumps the air containing the aerosol particles through water. After passage through the water,
the air escapes but the aerosol particles remain in the liquid and may be recovered for later use. We still have to find out whether this process changes the properties of the particles of the sample in any way.

A related problem is separating size effects from shape effects. For that purpose we would like to divide a certain sample of particles into a number of subsamples with different narrower size distributions, but without changing the original shape distribution. We have tried to do so by (wet) sieving a sample of olivine particles [9], but it appeared that it is extremely hard to separate the small particles from the large particles, because small particles show a strong tendency to stick to the surface of the larger particles. Another difficulty is that the large particles tend to clutter the sieves, so that small particles are even less likely to pass through the sieves. Further work on this problem is in progress.

Characterizations of the samples in terms of sizes, shapes and refractive indices of the particles are very desirable to study and document the scattering properties in a systematic way, to foster insight into these properties and to enable us to make comparisons with results of computations and experimental work of other investigators. Although many so-called particle sizers exist, we must keep in mind their limitations, especially for nonspherical particles. Often they cannot measure the sizes of very small or very large particles and their results are frequently based on the assumption that the particles behave like spherical particles.

Some indications of the shape and structure of the particles may be obtained from visual inspection of photographs, but a more detailed analysis is much more laborious. It is already helpful, however, to know the distribution of the aspect ratios, (largest over smallest dimensions) and this is often feasible, at least for more or less compact particles, e.g., by analyzing SEM images of the particles [8,41,42].

Reliable values of the refractive index of natural particles at the wavelengths needed can only seldom be found in the literature. Measurements of the refractive index at various wavelengths require samples that are identical to the samples we use for the light scattering experiments. So far, we have only used lasers with wavelengths of 441.6 nm (HeCd) and 632.8 nm (HeNe), but we intend to broaden the wavelength range, in particular, into the ultraviolet and infrared.

8. Epilogue

A variety of scattering matrices for randomly oriented particles has been measured over wide ranges of the scattering angle at two wavelengths in the visual range of the spectrum. Several possibilities for improving and extending the experimental techniques exist. Clearly there is still a lot of interesting work to do in Amsterdam and elsewhere. This may lead to a large collection of experimental scattering matrices. It is important to look for systematic characteristics in such data. One step in that direction has already been made by the discovery of preferential domains in plots of scattering matrix elements versus scattering angle for a variety of randomly oriented irregularly-shaped mineral particles [10]. This is shown in Fig. 10, which also illustrates that the scattering matrix elements of fly ash particles, consisting of aggregated spheres [11], exhibit a different angular scattering matrix behavior. The differences in comparison with the mineral particles must be due to differences in shapes since the refractive index and sizes of the fly ash particles lie within the range of values of the irregularly shaped mineral particles studied by Volten et al. [10]. More measurements with
Fig. 10. Average aerosol scattering matrix element $F_{11}(\theta)$, and element ratios $-F_{12}(\theta)/F_{11}(\theta)$, $F_{34}(\theta)/F_{11}(\theta)$, $F_{22}(\theta)/F_{11}(\theta)$, $F_{33}(\theta)/F_{11}(\theta)$, and $F_{44}(\theta)/F_{11}(\theta)$ (solid curves) for seven samples of irregularly shaped mineral particles measured at 441.6 nm and 632.8 nm. The $r_{\text{eff}}$ of the samples range between 1.0 and 8.2 μm and $\nu_{\text{eff}}$ between 1.0 and 12.3. The domains occupied by the measurements for the individual samples and wavelengths are indicated in grey. The phase functions, $F_{11}(\theta)$, equal unity at 30°. For comparison the matrix elements of randomly oriented fly ash particles with $r_{\text{eff}} = 3.65$ μm and $\nu_{\text{eff}} = 10.9$ have been plotted for both wavelengths.

different types of aggregates are needed in order to establish general scattering patterns of such particles.

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