10 Polarisation Fluctuations in Light Scattered by Small Particles

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Abstract. Light which has been scattered by a suspension of particles contains information about particle motion, number, size and shape. One characteristic of such light which is particularly sensitive to shape is its polarisation state. If the particles are moving, then this will fluctuate in time and the statistical properties of the fluctuations can be used to deduce shape parameters. In this chapter a brief review of principles underlying this technique will be given together with the results of some preliminary experimental measurements

1 Introduction

Statistical analysis of light which has been scattered by systems of particles suspended in stationary or moving fluids forms the basis for many well established techniques designed to determine properties of either the particles themselves or the flows they seed. Laser anemometers and velocimeters are now commonly used to remotely measure wind velocity and other laminar and turbulent flows. Instruments for the measurement of particle size and dispersity have been commercially available for several years. In the case of very small particles the scattered light in these applications may be of such low intensity that the methods of photon counting and photon correlation spectroscopy are required [1].

One characteristic which appears to have received rather little attention is particle shape, despite the fact that it plays a significant role in many manufacturing processes. However, it is plain from standard texts on the subject that light scattering from particles is dependent on this quantity [2]. In the case of particles which are much smaller than the wavelength the dependence is manifest wholly in the polarisation state of the scattered light whilst for larger particles the situation is more complicated and information is additionally contained in other measures which vary with the orientation of the particles.

In this chapter a tutorial overview will be given of the principles which might be exploited in order to develop a practical technique for particle shape determination using light scattering. Quantitative calculations will be restricted to very small particles so that Rayleigh scattering theory is applicable. In this theory each particle is represented by a simple dipole at its centre. The approach can be generalised to larger particles but alternative methods then

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become available and interpretation of experimental measurements becomes more complicated. Even for the case of Rayleigh scatterers several different methods of analysing the scattered light are possible and optimisation will have to be made subject to the practical constraints of instrument design.

In the next section a scalar random walk model will be used to introduce the notion of Gaussian and non-Gaussian scattering, corresponding to a large or small number of particles being present in the scattering volume respectively [3]. Statistical measures which may be determined by experiment will be defined. In Sect. 3 polarisation will be introduced into the model and quantities of interest calculated for the case of randomly tumbling spheroidal particles. Section 4 will review the results of the calculations and a preliminary experiment will be described. Conclusions will be presented in Sect. 5.

2 Gaussian and Non-gaussian Scattering

When linearly polarised coherent light is scattered by a collection of particles which are dispersed over a volume which is much larger than the optical wavelength, the complex amplitude of one polarised component of the scattered light in the far field can be represented as the result of a random walk on a plane i.e. as a sum of random phasors:

$$E = \sum_{n=1}^{N} a_n \exp\left(i\varphi_n\right) \tag{1}$$

Here, N is the total number of particles present in the scattering volume, $\{a\}$ and $\{\varphi\}$ are the amplitudes and phases of the fields contributing at the receiving point. For a non-interacting particle system the latter quantities are statistically independent and the phases are uniformly distributed. Equation (1) is a two dimensional random walk and it is well known that as the number of steps becomes large the resultant vector will have statistically independent rectangular components which are Gaussian distributed. In this situation a homogeneous moving pattern of bright and dark regions known as Gaussian speckle may be observed in the far field of the scattering system. The quantity observed with the naked eye (or detected by a photomultiplier tube for example) is the intensity of the light, $I = |E|^2$. If it is assumed that the $\{a\}$ are statistically identical then the second moment and second order coherence function can be calculated from (1) [3]:

$$\frac{\langle I^2 \rangle}{\langle I \rangle^2} = 2\left(1 - \frac{1}{N}\right) + \frac{\langle a^4 \rangle}{N \langle a^2 \rangle^2} \tag{2}$$

$$\frac{\langle I_1 I_2 \rangle}{\langle I_1 \rangle \langle I_2 \rangle} = \left(1 - \frac{1}{N}\right)\left(1 + \left|g_{12}^{(1)}\right|^2\right) + \frac{\langle a_1^2 a_2^2 \rangle}{N \langle a_1^2 \rangle \langle a_2^2 \rangle} \tag{3}$$

where $g_{12}^{(1)} = \langle E_1 E_2^* \rangle / \sqrt{\langle I_1 \rangle \langle I_2 \rangle}$ and the subscripts refer to different spatial positions and/or times.

It can be seen that when N becomes large the right hand side of the first equation reduces to the value 2. This is what would be expected for a complex Gaussian process for which the intensity I obeys a negative exponential distribution. In the same limit, the right hand side of (3) reduces to $1+\left|g_{12}^{(1)}\right|^2$ and is known as the Seigert relation or Reid theorem, being a useful factorisation property of Gaussian noise. In the present context the spatial structure described by this formula (i.e. the speckle size) is just the diffraction lobe width corresponding to the projected scattering volume whilst the temporal variations correspond to Doppler shifts determined by the *relative* scatterer motion.

When the number of particles is small additional terms proportional to $1/N$ must be retained in both expressions. Since the number of particles might be expected to scale in proportion to the scattering volume, it is evident that deviation from Gaussian statistics will arise when this volume becomes sufficiently small. In a laser light scattering experiment this can be achieved by focusing down the incident beam. Equation (1) indicates that the additional terms will depend on properties of the *individual* particles unlike the Gaussian limit where this information is lost. Equation (2) indicates that the corresponding intensity pattern will contain new length and time scales. These reflect the scattering properties of individual particles and their motion and are larger than those characterising the Gaussian term g.

In a real scattering configuration particles will continually move into and out of the scattering volume. This means that the number of particles N will be continually changing. The simplest model for this phenomenon is that the number fluctuations are purely random being governed by a Poisson distribution. If, in calculating (2) and (3), averages are carried out over such a distribution before normalisation then the terms in N within the first expressions on the right hand side vanish, whilst in the final terms N is simply replaced by its mean value. This implies that the intensity scattered by a small volume of suspension will in practice always fluctuate *more* than that scattered by a large volume.

In some light scattering configurations particle clustering will be encountered; this may be caused by aggregation or turbulent mixing of species, for example. It has been shown that this can lead to enhanced non-Gaussian fluctuations even when the mean number of particles is asymptotically large [4]. A particularly useful non-Gaussian limit distribution occurs if the number fluctuations obey a negative binomial distribution. This distribution is associated with the bunching of populations governed by a simple birth-death-immigration process. The limiting probability density of the random walk (1) is in this case a K-distribution and describes a Gaussian speckle pattern with a mean value which is varying in time or space according to a chi-square (Gamma) distribution [5].

As mentioned in the introduction, for the case of very small particles, the amount of scattered light may be so small that photon counting methods are required for detection [1]. In the case of classical light fields which concern us here, the measured signal can be interpreted as discrete photo-electron pulses which would be emitted at random by the detector if the incident light had a constant intensity. When the incident intensity varies, the pulse rate is modulated and the train of photo-electric events constitutes a doubly stochastic Poisson process:

$$p(n) = \frac{1}{n!}\int_0^\infty dEP(E)(\alpha E)^n \exp(-\alpha E) \tag{4}$$

where

$$E(T) = \frac{1}{T}\int_0^T dtI(t) \tag{5}$$

is the *integrated* intensity, T is the time interval containing the number n of photo-electron counts and α is the detector quantum efficiency. The factorial moments and correlation function of these counts are related in a simple way to the analogous statistical properties of the intensity:

$$\frac{\langle n(n-1)(n-2)\cdots(n-r+1)\rangle}{\langle n\rangle^r} = \frac{\langle E^r\rangle}{\langle E\rangle^r}, \frac{\langle n_1 n_2\rangle}{\langle n_1\rangle\langle n_2\rangle} = \frac{\langle I_1 I_2\rangle}{\langle I_1\rangle\langle I_2\rangle} \tag{6}$$

However, it is clear that the measured distribution of counts is related rather indirectly to the intensity fluctuation distribution. This has important implications for the choice of measuring technique. Note that if I is constant over the integration time then $E = I$.

3 Polarisation in the Random Walk Model

The scattering amplitudes $\{a\}$ appearing in (1) for the two dimensional random walk are associated with the measurement of a particular polarisation component which should be more generally identified by an additional label. Thus it is possible to think of correlating the outcome of random walks corresponding to two polarisation states of the measuring apparatus. Assuming,

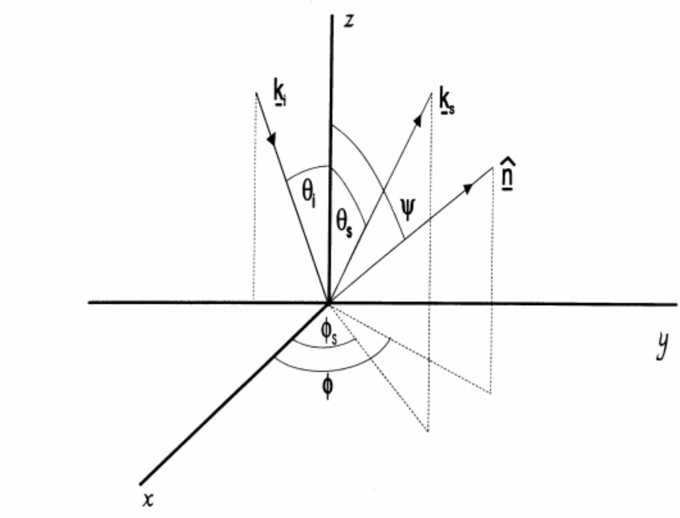

Fig. 1. Scattering geometry. The particle axis of rotation is along **n**.

as before, that the particle scattering amplitudes are statistically identical it is not difficult to demonstrate that [6]

$$\frac{\langle I_j I_k \rangle}{\langle I_j \rangle \langle I_k \rangle} = 1 + |g_{jk}|^2 + \frac{f_{jk}}{\langle N \rangle} \tag{7}$$

where

$$|g_{jk}|^2 = \frac{|\langle a_j a_k^* \rangle|^2}{\left\langle |a_j|^2 \right\rangle \left\langle |a_k|^2 \right\rangle} \tag{8}$$

and

$$f_{jk} = \frac{\left\langle |a_j a_k|^2 \right\rangle}{\left\langle |a_j|^2 \right\rangle \left\langle |a_k|^2 \right\rangle} \tag{9}$$

Here the intensities are measured at the same space-time points and the subscripts now label the *polarisation states* of the incident and detected optical field. Defining subscript p for polarisation vector in the scattering plane and s for the case when it is normal to the scattering plane $j, k \equiv ss, pp, sp, ps$ for linearly polarised initial and final states.

The single particle fluctuation factor f and Gaussian fluctuation factor g can be calculated exactly for very small particles (Rayleigh scatterers) by representing them as simple dipoles[2]:

$$a \propto \hat{e} \cdot \left(\underline{\underline{\alpha}}\boldsymbol{E}\right) \tag{10}$$

where $\boldsymbol{E}$ is the incident electromagnetic field, $\hat{e}$ defines the measured state and $\underline{\underline{\alpha}}$ is the polarisability tensor. Only the case of spheroidal particles will be considered here, for which

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_2 \end{pmatrix} \tag{11}$$

For an isolated spheroid with its axis of symmetry aligned along the direction (Fig. 1) $\hat{n} = (\sin\psi\cos\phi, \sin\psi\sin\phi, \cos\psi)$ it may then be shown that [6]

$$\begin{aligned}
a_{ss} &= E_s\left[(\alpha_1-\alpha_2)\sin^2\psi\cos^2\phi + \alpha_2\right] \\
a_{pp} &= E_p\left[(\alpha_1-\alpha_2)\sin\psi\cos\phi(\sin\psi\sin\phi\cos\theta + \cos\psi\sin\phi) + \alpha_2\cos\theta\right] \\
a_{ps} &= E_p\left(\alpha_1-\alpha_2\right)\sin^2\psi\sin\phi\cos\phi \\
a_{sp} &= E_s\left(\alpha_1-\alpha_2\right)\sin\psi\cos\phi(\sin\psi\sin\phi\cos\theta + \cos\psi\sin\theta)
\end{aligned} \tag{12}$$

where θ is the scattering angle i.e. the angle between the direction of the incident plane wave and that of the detector. In many cases of interest the particles will be tumbling so that their orientation is random and governed by the distributions:

$$\begin{aligned}
p(\phi) &= (2\pi)^{-1} \qquad & 0 < \phi < 2\pi \\
p(\psi) &= \tfrac{1}{2}\sin\psi \qquad & 0 < \psi < \pi
\end{aligned} \tag{13}$$

These distributions may now be used to calculate the statistical properties of the scattering amplitudes (12). For example [6]

$$\begin{aligned}
\frac{\langle a_{ss}^4\rangle}{\langle a_{ss}^2\rangle^2} &= \frac{5}{7}\frac{35r^4+40r^3+48r^2+64r+128}{(3r^2+4r+8)^2} \\
p(a_{ss}) &= \left[2\sqrt{E_s(\alpha_1-\alpha_2)(a_{ss}-\alpha_2 E_s)}\right]^{-1}
\end{aligned} \tag{14}$$

Here r is the polarisation ratio α_1/α_2 which, for homogeneous small spheroids, is equal to the ratio of their major to minor axes.

4 Discussion of Theoretical Predictions

The behaviour of the fourth amplitude moments is illustrated in Fig. 2. Note that over some parameter ranges two values of the polarisation ratio give

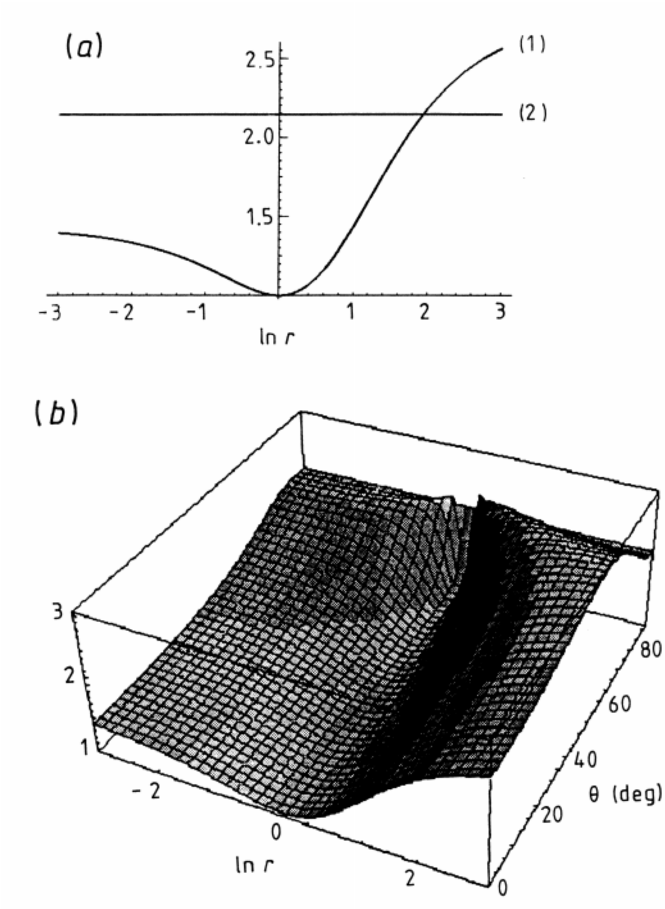

Fig. 2. Fluctuation enhancement factors f versus polarisability ratio r for a single spheroid. (a) s co-polar 1 and cross polar 2, all scattering angles. (b) p co-polar.

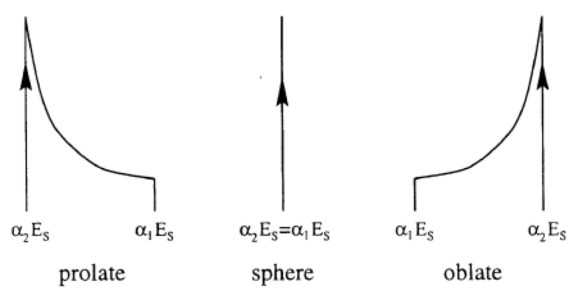

Fig. 3. Schematic diagram of the probability density of s co-polar returns from a single randomly tumbling spheroid.

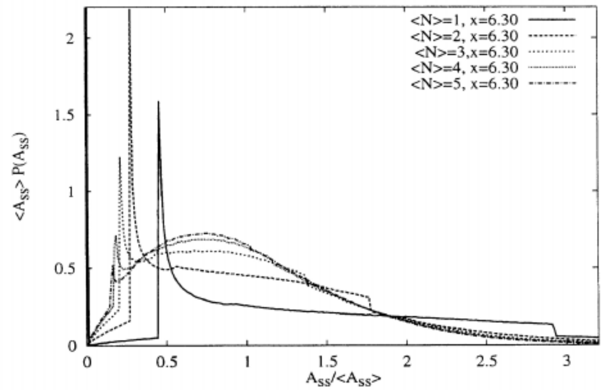

Fig. 4. Probability of s co-polar returns from an average number $< N >$ of randomly tumbling prolate spheroids.

rise to the same degree of fluctuation. However, the probability densities are unambiguous. For example, Fig. 3 shows schematically the distributions of s co-polar amplitudes returned from single spheroids [7]. Clearly prolate and oblate shapes could be distinguished by a measurement of this quantity. In practice it would not be possible to maintain a single spheroid in the illuminated volume. As mentioned before, the number of scatterers would fluctuate. Figure 4 shows that provided the *mean* number is less than about 5 the distribution of polarisation fluctuations might still provide an unambiguous means of shape determination. Unfortunately, in such a non-Gaussian configuration the intensity of the scattered light would be very low and photon counting methods would be required. The Poisson transform 4 would then tend to obscure the detailed shape of the intensity distribution.

Although all of the fluctuation factors, f, contain information about r, they can only be determined through measurements in the small N regime where the scattered intensity is low. Particle shaping methods based on non-Gaussian polarisation fluctuations are therefore possible but are likely to be susceptible to noise and imperfections in the measuring apparatus. On the other hand, the Gaussian speckle regime, where many scatterers are illuminated, is known to be robust and is used in existing particle sizing equipment, for example. Unfortunately, the fluctuation factors g are for the most part zero. However, there are a few exceptions such as the following cross-correlation coefficient between s and p co-polar returns [6]:

$$\frac{\langle a_{ss}a_{pp}\rangle^2}{\langle a_{ss}^2\rangle\langle a_{pp}^2\rangle} = \frac{\cos^2\theta\left[(r-1)^2+10(r-1)+15\right]^2}{(3r^2+4r+8)\left[(r-1)^2(2\cos^2\theta+1)+5(2r+1)\cos^2\theta\right]} \tag{15}$$

This formula could form the basis for a practical method for particle shaping but, in fact, is not directly measurable. However, equivalent information can be obtained by cross-correlating two Stokes parameters [8] and this has been tested using the experimental layout shown schematically in Fig. 5. This is described in detail elsewhere [9] but basically, laser light which is linearly polarised at 45^o to the scattering plane is incident on the sample. The scattered s and p components are then detected by two photo-multiplier tubes and cross-correlated , normalised and plotted as a function of scattering angle. No variation with angle is predicted for spherical scatterers but strong variations occur in the case of spheroids.

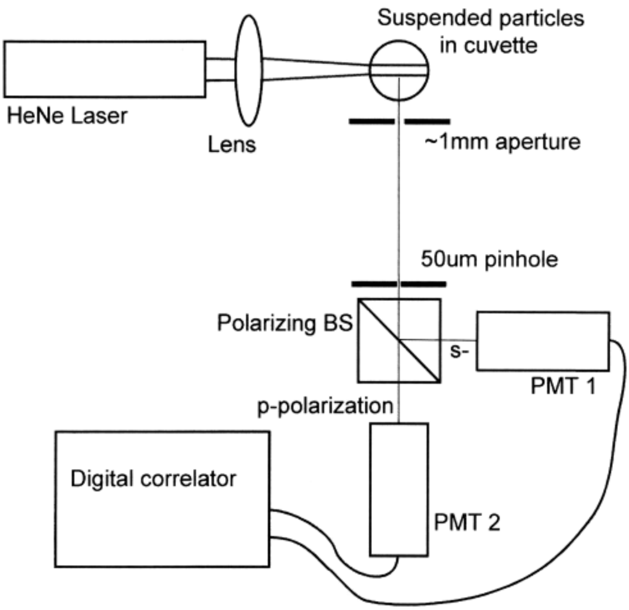

Fig. 5. Diagram of experimental arrangement.

Figure 6 shows some preliminary results obtained using specially prepared Haematite particles having an r value near 3. Since these were larger than the optical wavelength, the Rayleigh theory described above is not valid and the theoretical curves shown for comparison were calculated numerically using Mishchenko code [10]. Encouraging agreement between the measured and predicted behaviour was found.

The experimental method described above has a number of features which make it an attractive candidate technique for particle shaping. In particular, **it is independent of**

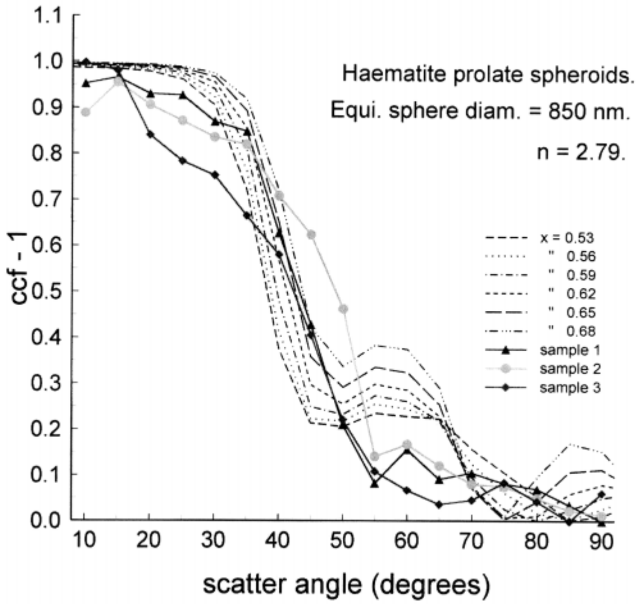

Fig. 6. Comparison of experimental results with theoretical predictions.

* the strength of the incident radiation and any variation during the measuring time

* the size and shape of the illuminated volume

* the absolute transparency of the polarising elements

* the relative strength of the intensity components after division

* the detector efficiencies

The performance characteristics of a number of other closely related configurations are currently being explored with a view to the development of a practical instrument.

5 Conclusions

It has been shown that polarisation fluctuations in light which has been scattered by non-spherical particles contains information about particle shape. When the particles are much smaller than the wavelength a simple theoretical development can be carried out which predicts quantitative relationships between statistical moments, probability densities and the aspect ratio of scattering spheroids. These properties can be all be measured in principle, but it has been argued that in practice measurements in the Gaussian regime, when the scattering volume contains many particles, are likely to prove more robust. Preliminary experimental measurements on characterised spheroids are in agreement with experimental predictions and provide encouragement for the development of a practical instrument for particle shaping.

6 Acknowledgements

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