Polarized Light Scattering by Small Particles

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All of the polarized light scattering properties of single particles and suspensions of particles are contained in the 16-element Mueller matrix. For single-particle studies the particle is electrostatically suspended, the light scattering functions are measured, and the particle is then extracted from the suspension chamber by placing it on the point of a needle. The particle is examined subsequently with an electron microscope to determine precisely its size and shape. Results will be presented for single polystyrene spheres, sphere multiplets, approximately cubic NaCl crystals, and cubes of MgO. Recent studies of suspensions have concentrated on oceanic hydrosols. Some results and general features of these hydrosols will be presented.

INTRODUCTION

The single most important entity in radiative transfer theory is the Mueller matrix. If one wants to determine the transfer of radiation, for both single and multiple scattering, through fogs, smokes, etc., this 4×4 matrix is essential for a complete understanding of the scattered radiation field. The matrix measured at all scattering angles contains, in effect, the result of every elastic light scattering experiment that could be performed.

Measurement of the matrix requires, in principle, determining the linear and circular polarization intensities of the scattered light for all possible independent linear and circular polarization states of the incident light. We have developed an instrument that multiplexes this information in such a way that each matrix element appears as the amplitude of a different frequency component in the photomultiplier signal produced by the scattered light. The instrument has been previously described in detail by Thompson (1978) and Thompson et al. (1980).

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The first matrix element f_{11} is the scattering function; it is the quantity generally measured in light scattering studies and corresponds to the situation in which the incident light is unpolarized and the scattered light is detected without regard to polarization. To make absolute measurements of it, which we have not done, one must determine calibration factors such as detector sensitivity, absolute radiances, and in the case of particulate suspensions, the size of the observed scattering volume. Our instrument automatically normalizes the other 15 elements to f_{11}, and thus these calibration factors, as well as the errors associated with their determination, are eliminated. Consequently, the 15 matrix elements will be presented on a scale on which they are restricted to values between $+1$ and -1.

Two general comments about the form of the matrices are in order. First, Van de Hulst (1957) has pointed out that for a single particle in fixed orientation there are only seven independent matrix elements. Thus there are nine independent equalities relating the 16 matrix elements; these are given by Fry and Kattawar (1981). Second, Van de Hulst (1957) has shown that if the particle has a plane of symmetry and the matrix is averaged over particle orientations, as

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in our data, the matrix has the form

$$\begin{pmatrix} f_{11} & f_{12} & 0 & 0 \\ f_{21} & f_{22} & 0 & 0 \\ 0 & 0 & f_{33} & f_{34} \\ 0 & 0 & -f_{34} & f_{44} \end{pmatrix}. \quad (1)$$

There are only six independent matrix elements, and further, all matrix elements in the upper-right ($f_{13}, f_{14}, f_{23}, f_{24}$) and lower-left ($f_{31}, f_{32}, f_{41}, f_{42}$) quadrants must vanish. The vanishing of these quadrants is a necessary but not sufficient condition for random particle orientations; i.e., if these quadrants vanish, it is a strong indication but not a guarantee that the data have been properly averaged over all particle orientations.

In our measurements single particles are studied by suspending them in air using an electrostatic leviation chamber constructed along the lines described by Fletcher (1914) and by Wyatt and Phillips (1972). While suspended a particle is subject to Brownian motion and is free to tumble, so the measurements represent in general an average over all orientations. Particle extraction is accomplished by inserting a needle through the side of the levitation chamber. The needle is insulated and shielded so that only the tip is exposed. When the tip is near the suspended particle, polarities are changed to force the particle onto the tip of the needle. The needle is then taken to the electron microscope and the particle is examined to determine size and shape. Bottiger (1980) has given an analysis of the levitation chamber and a detailed description of the particle extraction system.

RESULTS

Measured matrix elements are presented as a function of scattering angle, with measurements typically from 15° to 160°. All data to be presented here were taken using incident light from a He–Cd laser (441.6 nm). The upper-right and lower-left quadrants vanish in all the following data. This indicates that we are probably getting a good orientation average. We do have some data, not presented here, with nonzero elements in these quadrants, but this has only occurred with large, multiparticle aggregates that do not have a plane of symmetry and might be expected to have some mean orientation in the levitation chamber.

Polystyrene Sphere

Results for a single polystyrene sphere are shown in Figure 1. These data are presented in the form of a matrix with the graph of each matrix element in its respective position. The crosses are data points, and the smooth curve is a Mie calculation in which the diameter and index of refraction have been adjusted to give the best fit. Their values are 1.112 μm and 1.6146, respectively. A change of 0.003 μm in the diameter clearly degraded the fit. The data for f_{11} are in arbitrary units and are on a log scale.

This is such an accurate method for absolute measurement of small dimensions that we now routinely use a polystyrene sphere to find the absolute calibration of the electron microscope when we measure dimensions of other particles.

Finally, it should be noted that the Mie calculation predicts +1.0 for f_{22} at all scattering angles and 0.0 at all scattering angles for the eight elements in the upper-right and lower-left quadrants. While evidence of system noise at about a 5% level is apparent, overall agreement between the calculated matrix and the measured one is excellent.

Sphere Multiplets

Aqueous suspensions of polystyrene microspheres contain significant numbers of sphere multiplets. It is believed that the small but significant discrepancies between theoretical and experimental results for these suspensions may be due to the sphere aggregates. These were examined in our single particle scattering apparatus and their matrices measured. Results for the f_{43} matrix element for a singlet and three aggregates are shown in Figure 2. It can be seen that all the resonances appear at the same scattering angles for the singlet, doublet, triplet,

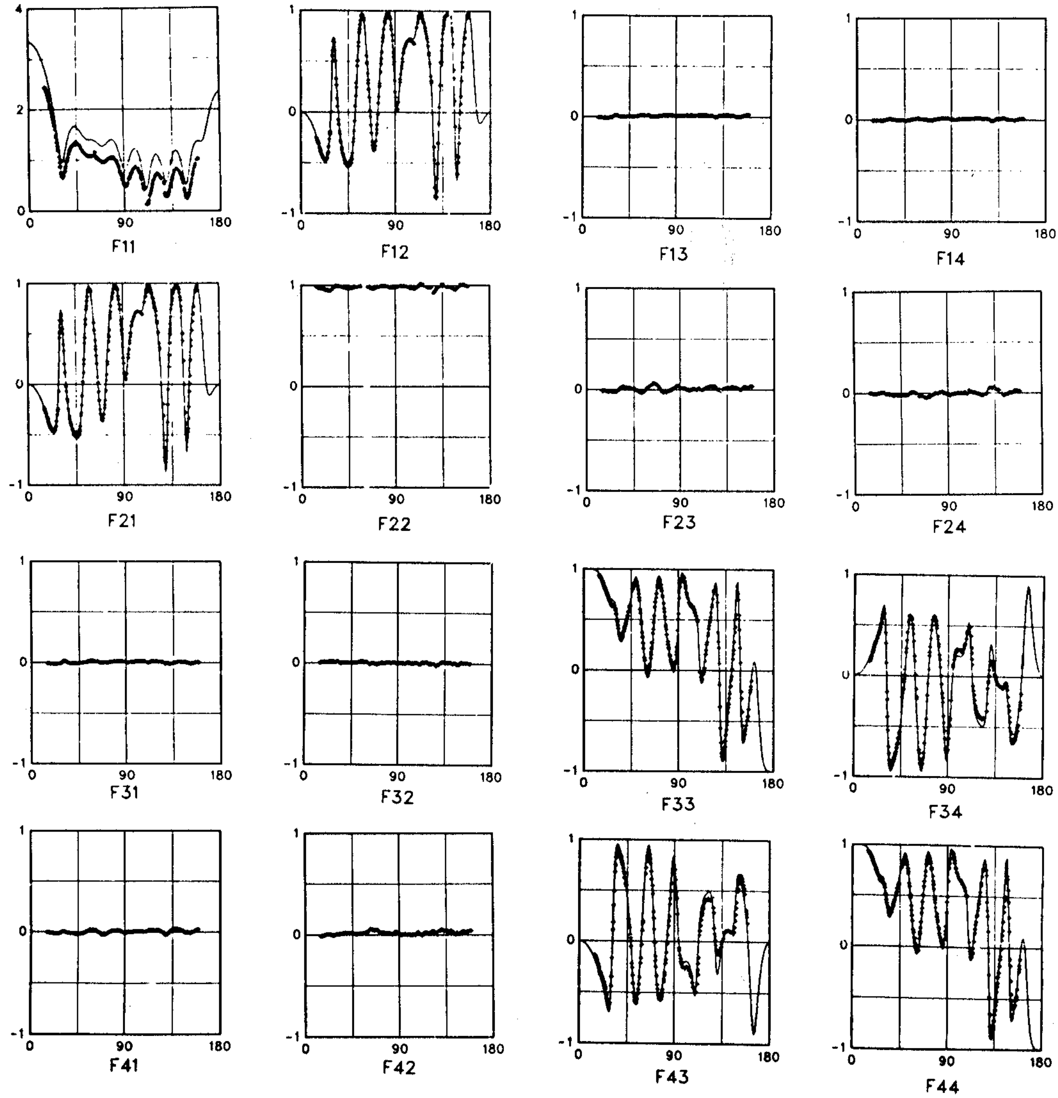

FIGURE 1. Complete matrix for a single polystyrene sphere of diameter 1.112 μm and index of refraction 1.6146. The crosses are the data points and the smooth curve is the Mie calculation.

and quadruplet. The major effect of increasing aggregate size is to wash out the amplitudes. The other nonzero matrix elements show this same effect, as can be seen in data presented by Bottiger et al. (1980).

Data for the f_{22} matrix element are shown in Figure 3. The important point to note here is that for a single sphere f_{22} is unity at all scattering angles and that deviation from unity is a conclusive indication of deviation from sphericity. The sphere aggregates clearly show this deviation in the total particle symmetry.

NaCl Cubes

In order to produce NaCl cubes, salt water was sprayed into a small chamber with an atomizer. The chamber contained a desiccant, and con-

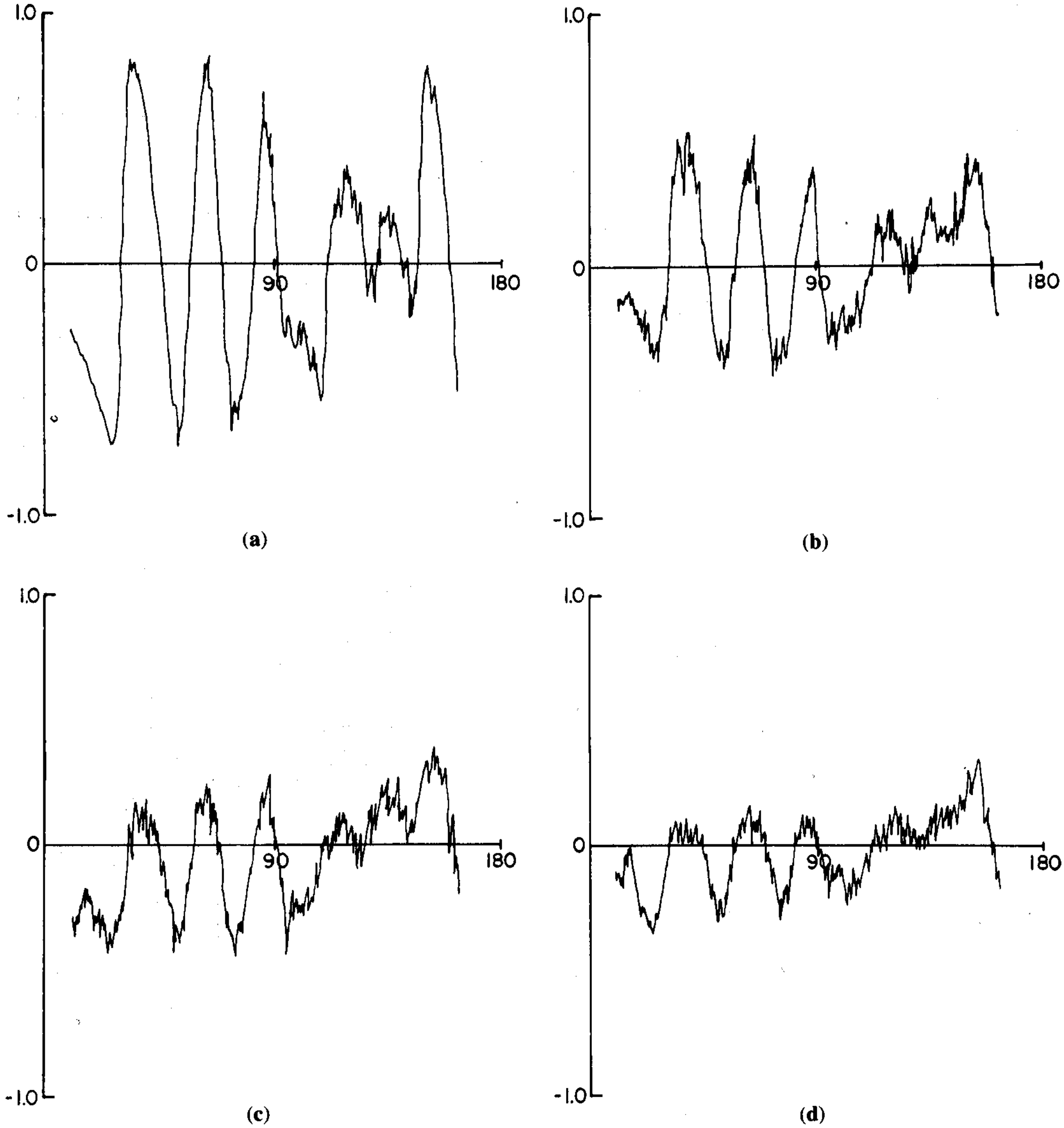

FIGURE 2. The f_{43} matrix element for aggregates of 1.1 μm diameter spheres: (**a**) singlet, (**b**) doublet, (**c**) triplet, and (**d**) quadruplet.

sequently the droplets quickly crystallized. The salt crystals then fell through a small hole in the bottom of this chamber and into the suspension chamber, where one crystal was suspended and its light scattering functions measured. Subsequent examination of these cubes with an electron microscope showed that, in general, all edges were not of equal length, the corners and edges were rounded, and the faces frequently had slight depressions in them. As before we present only a few matrix elements; complete data and photographs of the cubes have been given by Bottiger (1980). Figures 4 and 5 give the matrix elements f_{12} and f_{22}, respectively, for three cubes whose dimensions (in μm) are

G2: $0.75 \times 0.98 \times 1.05$;

G4: $1.01 \times 1.01 \times 1.07$; and

G6: $0.80 \times 0.90 \times 1.05$.

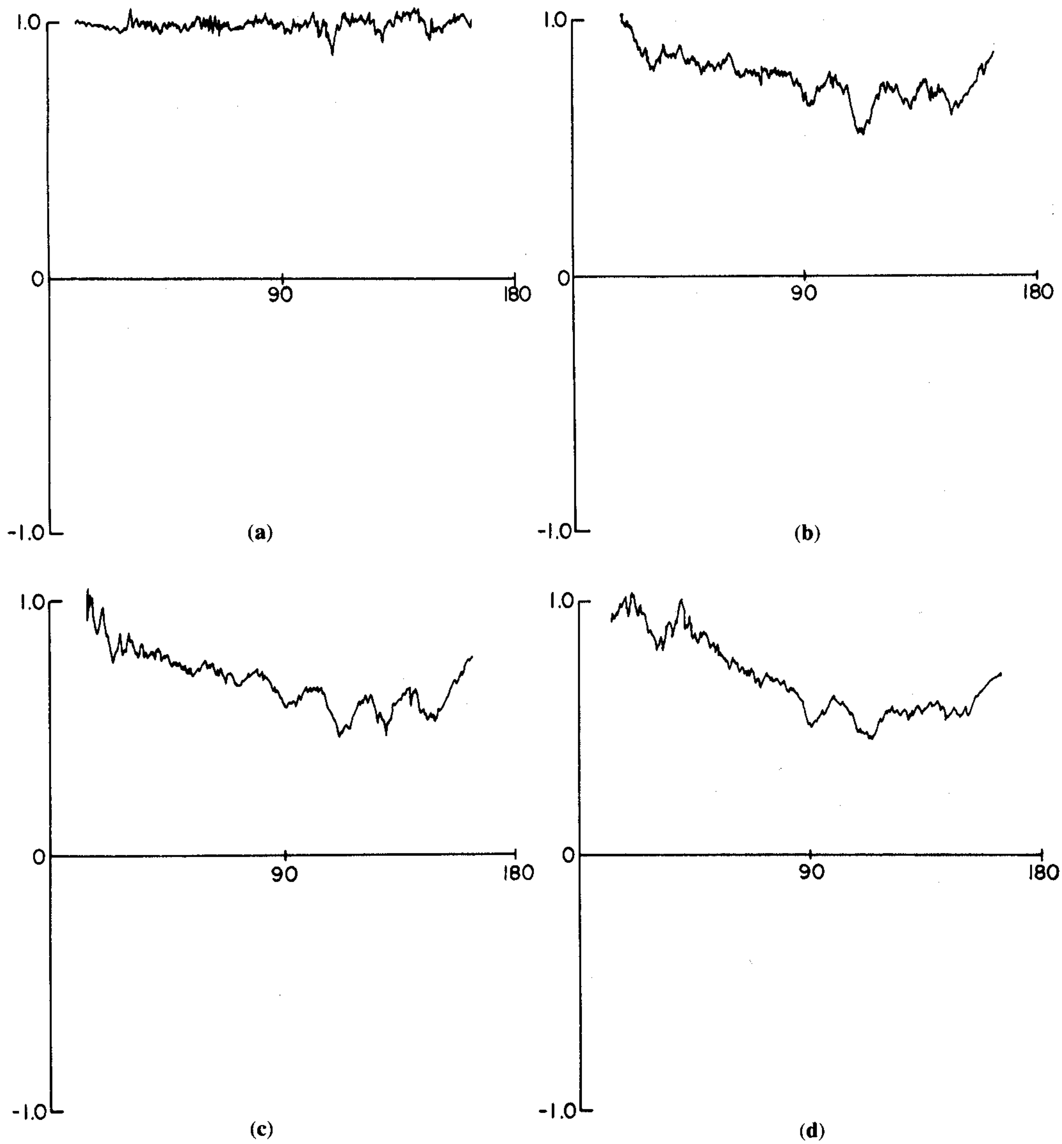

FIGURE 3. The f_{22} matrix element for aggregates of 1.1 μm diameter spheres: (**a**) singlet, (**b**) doublet, (**c**) triplet, and (**d**) quadruplet.

The measurements shown in Figures 4 and 5 are, like all the measurements presented in this paper except in Figures 2, 3, and 9, the result of averaging together five separate runs on the same particle. All individual runs clearly showed the same real features; averaging was done to suppress the random noise evident in Figures 2 and 3 (single sweeps).

In every case the cubes clearly show resonances in these orientation-averaged results (the off-diagonal quadrants were all zero for these particles). The values of f_{12} for all observed particles were relatively small; this is consistent with the small values of this matrix element observed by Perry et al. (1978) for a distribution of cube sizes. Since particle geometry is nonspherical, the decrease in f_{22} at intermediate

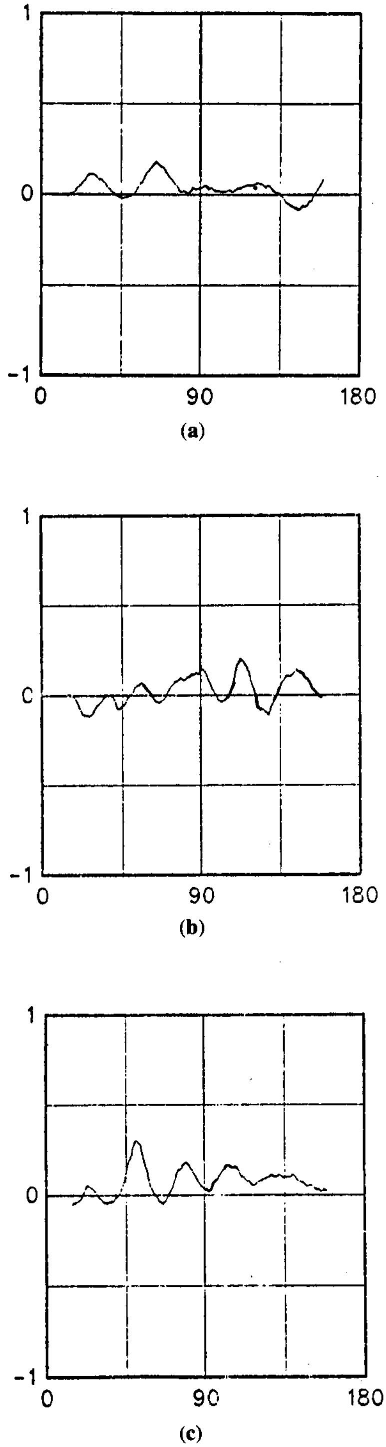

FIGURE 4. The f_{12} matrix element for the three NaCl cubes labeled (**a**) G2, (**b**) G4, and (**c**) G6, respectively.

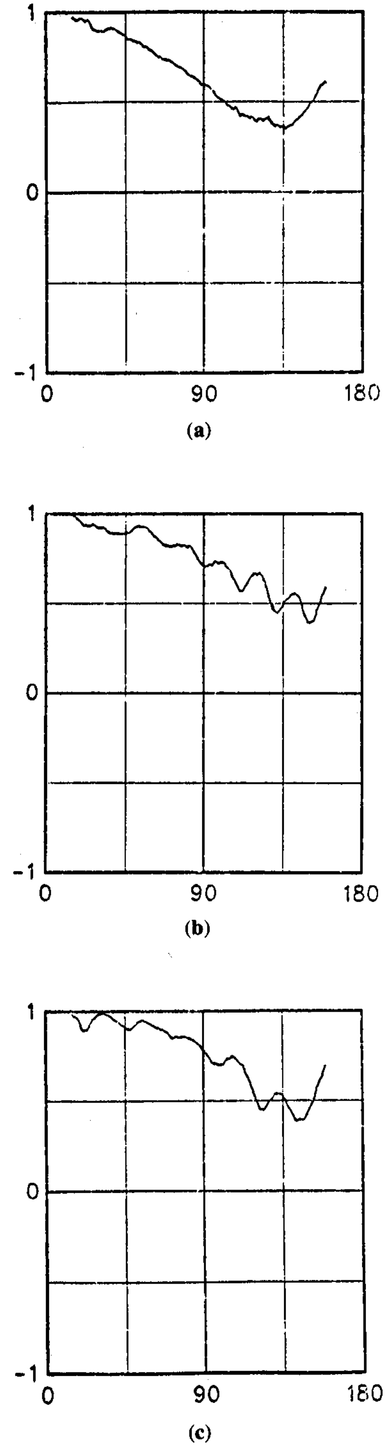

FIGURE 5. The f_{22} matrix element for the three NaCl cubes labeled (**a**) G2, (**b**) G4, and (**c**) G6, respectively.

FIGURE 6. Photograph of the MgO cube labeled P3.

scattering angles is, of course, observed with these cubes.

MgO Cubes

Nearly perfect cubes of NaCl can be produced (Gallily, 1977), but it is much easier to make essentially perfect cubes by simply burning Mg in air. Electron microscope photographs of these MgO cubes show that they typically have edge lengths in the range 0.3–2.0 μm. All edges of a given cube are equal in length within an accuracy of a few percent. The edges and corners appear very sharp in photographs; a cube of edge 1.0 μm is shown in Figure 7. As with NaCl, there are clearly resonances in these orientation-averaged data. The data of Figure 8 are from cube P6, 0.36 μm on an edge. This is the smallest cube we have observed. The results are beginning to approach those to be expected from a Rayleigh scatterer and are consistent with the small size of this cube.

In order to obtain a complete picture of electromagnetic scattering by cubes, data must be obtained over a range of particle sizes or, equivalently, over a range of incident wavelengths. At the present time no theoretical solutions to this electromagnetic scattering problem have been found.

Oceanic Hydrosols

Extensive measurements of the Stokes matrix for oceanic hydrosols have been made by Kadyshevich et al. (1976). They observed a great deal of structure in their measurements. This contrasts with our results, which, when normalized to f_{11}, have general features very similar to those of Rayleigh scatterers. A typical result is shown in Figure 9. This particular sample was taken from the surface of the Gulf of Mexico near Houston, but results from other areas of the Gulf and of the Atlantic Ocean, as well as from various depths, have the same general characteristics. Of course, the magnitude of the unnormalized f_{11} varies greatly for samples from various areas. There are several features that consistently appear in the ocean water data:

1. f_{12} is a very accurate reproduction of f_{21}, as is f_{33} of f_{44} and f_{43} of $-f_{34}$.
2. At 90° f_{12} and f_{21} generally reach minima between -0.5 and -0.8.
3. f_{22} always drops below $+1.0$ at intermediate scattering angles.
4. f_{33} and f_{44} generally cross zero at scattering angles slightly above 90°.

These features were also qualitatively observed in the Kadyshevich data. However, they observed appreciable nonzero values for matrix elements in the off-diagonal quadrants, whereas we find good zeros. The reasons for this disagreement are presently unknown. However, two points should be made. First, their data were obtained at 546 nm, whereas ours were taken at 442 nm. Second, the basic concept of our measuring system is significantly better. We require approximately 1.0 min for a complete measurement of the matrix, whereas they require 1–2 hr. We also routinely measure the matrix for a known suspension of polystyrene

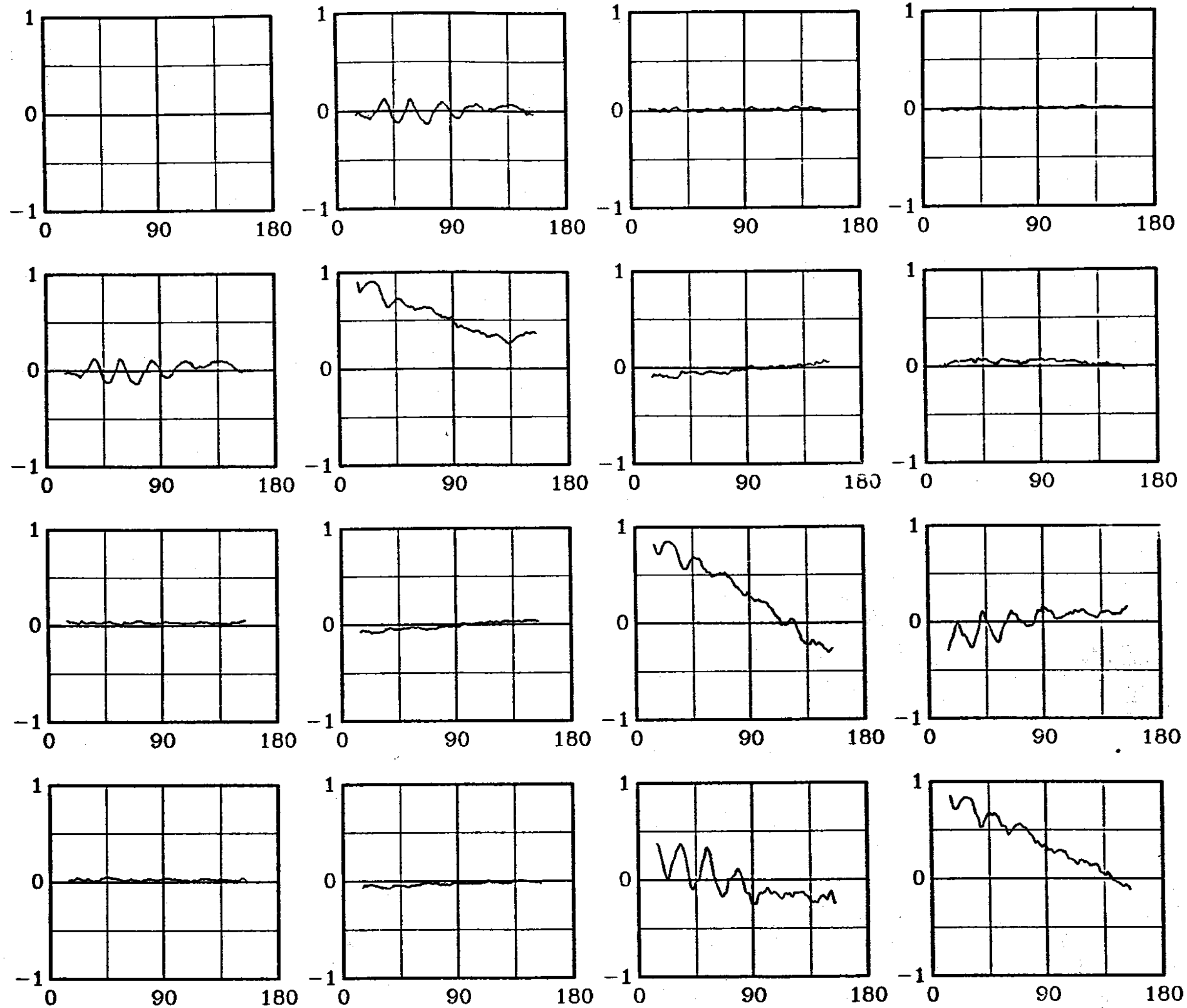

FIGURE 7. The complete normalized matrix for the MgO cube labeled P3. Edge length is 0.65 μm.

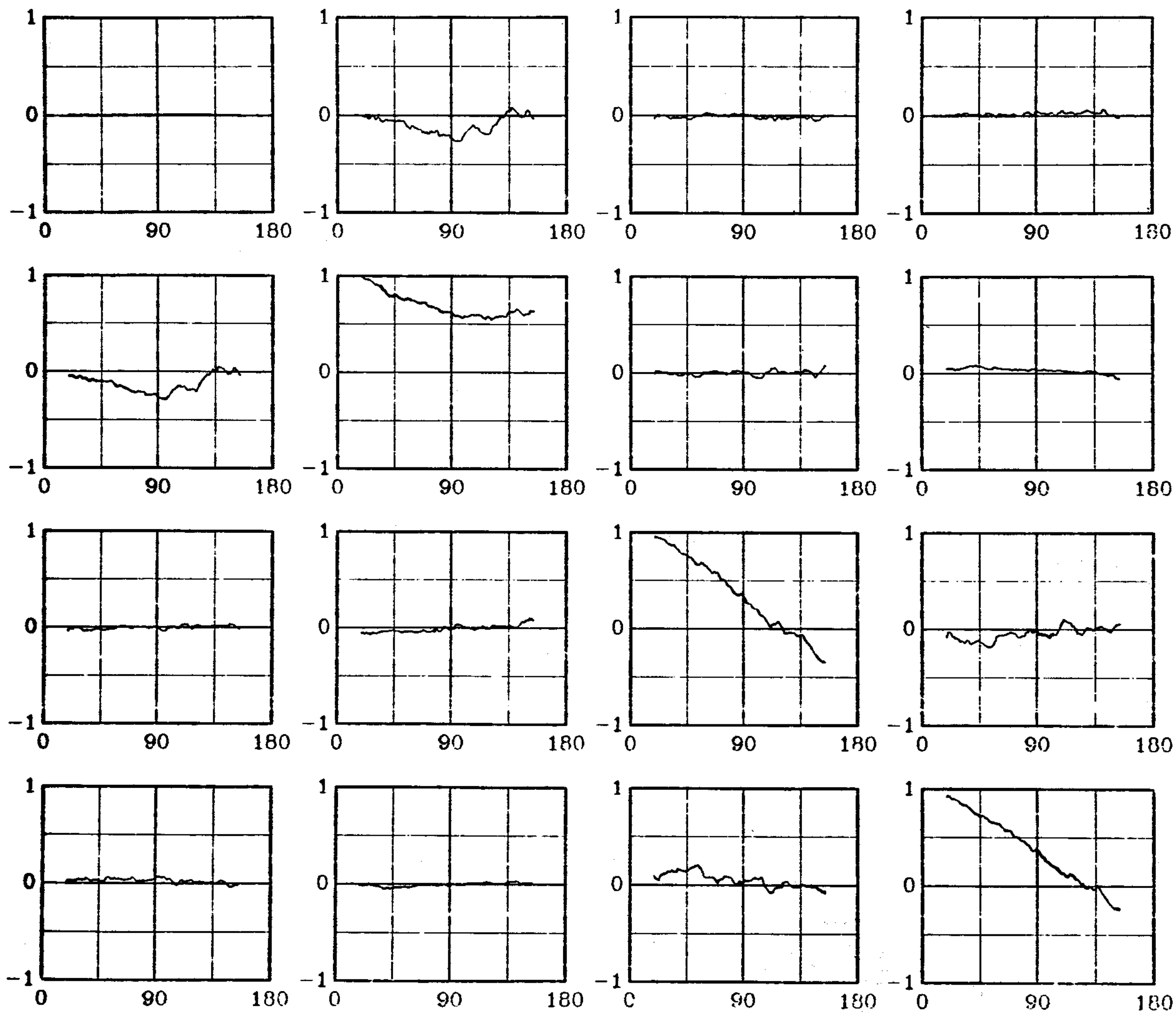

FIGURE 8. The complete normalized matrix for the MgO cube labeled P6. Edge length is 0.36 μm.

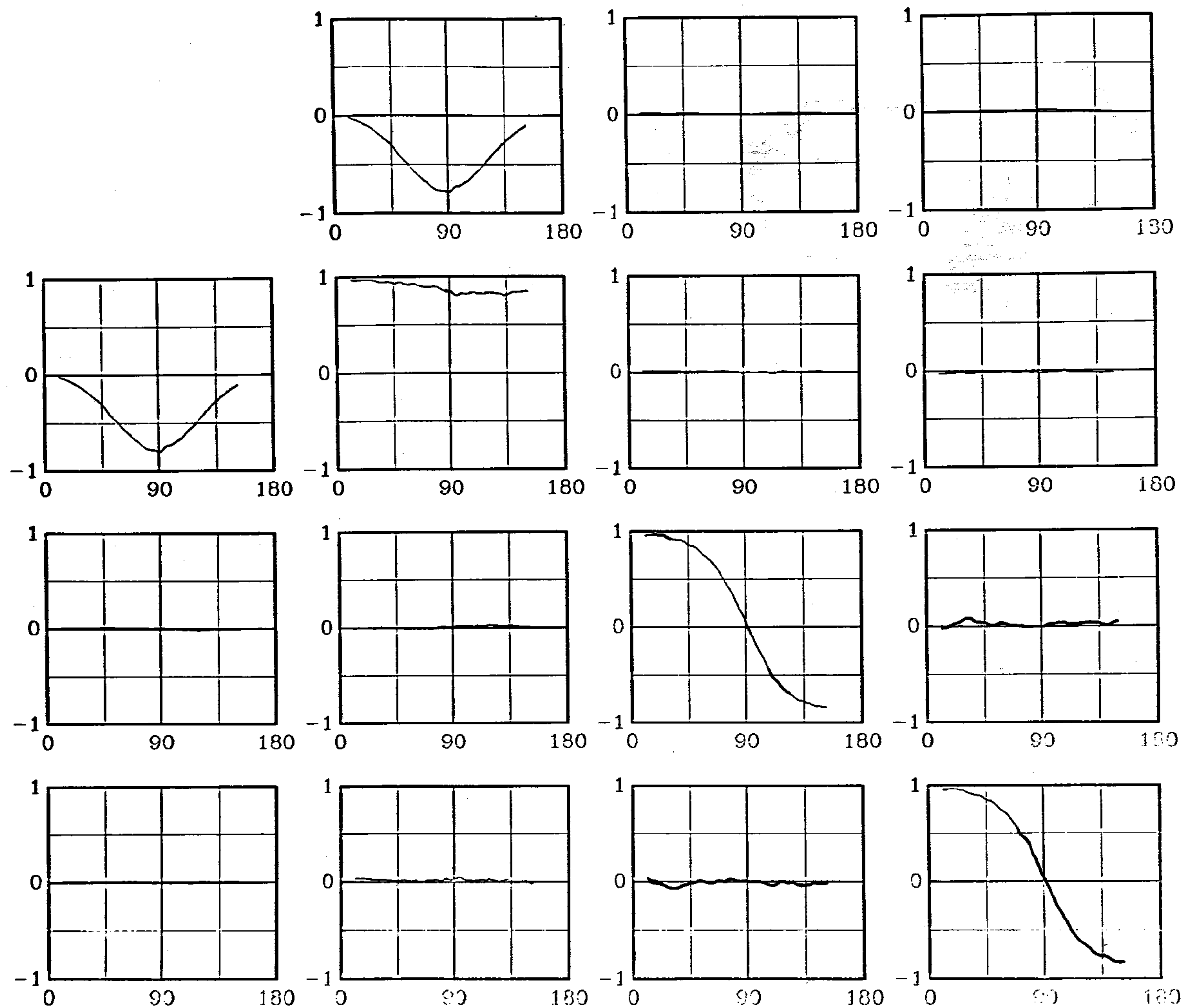

FIGURE 9. The complete normalized matrix for an ocean water sample taken from the surface of the Gulf of Mexico near Houston.

spheres before and after each ocean water measurement; this enables us to continually check for systematic effects.

SUMMARY

A powerful tool for studying electromagnetic scattering has been developed. Accurate determinations of the size and index of refraction of small polystyrene spheres have been made by fitting the measured scattering functions with Mie theory. It has been shown that the scattering functions of sphere aggregates clearly show the resonances due to their monodisperse substructure. The first complete results for electromagnetic scattering by a small cube have been obtained, and they clearly show size-dependent resonances even after orientation averaging. Finally, the normalized scattering functions for oceanic hydrosols at 442 nm have been found to be relatively independent of sampling location.

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