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MEASUREMENT OF HIGHER-ORDER CORRELATION FUNCTIONS BY INTENSITY CROSS-CORRELATION LIGHT SCATTERING

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Abstract - We describe the principles and practice of the study of higher-order correlation functions in suspensions of colloidal particles by intensity cross-correlation light scattering.

I - INTRODUCTION

In this paper we describe the application of the technique of quasi-elastic light scattering to the study of higher-order correlation functions (HOCF) in suspensions of colloidal particles. This is a relatively new subject though one which shows promise for further development. Emphasis will be on qualitative aspects and the reader will be referred to the literature for more quantitative details.

The basic principle underlying the measurement of HOCF by quasi-elastic scattering methods is simple. The field amplitude E of radiation singly scattered by a sample is simply the sum of the fields scattered by the individual elements (atoms or colloidal particles, for example). The intensity I of scattered radiation is the square of the field amplitude $I = |E|^2$, and its average $\langle I \rangle$ depends on the spatial correlations of pairs of scattering elements: the structure factor is essentially the spatial Fourier transform of the radial distribution function $g(r)$. Thus to measure correlation functions of higher order than two it seems clear that one should study, for example, the mean-square intensity $\langle I^2 \rangle$ or, more generally, the cross-correlation $\langle I_1 I_2 \dots I_n \rangle$ of intensities scattered in different directions. However in attempting to follow this apparently simple prescription one immediately encounters difficulties.

Firstly to obtain $\langle I^2 \rangle$ one must be able to measure an intensity in a time short compared to its characteristic fluctuation time. For X-ray or neutron scattering by simple liquids this time is of the order of typical liquid relaxation times, namely picoseconds, much too short to be handled by conventional electronics. Secondly, as we will see in section II, higher-order intensity correlation functions only contain information on irreducible HOCF of the scattering medium if the volume of the sample from which the detectors receive scattered radiation is not much larger than the volume of spatial correlation within the scattering medium. In a simple liquid these spatial correlations have a typical range of a few Å. It is, at present, not possible to focus a reasonable flux of neutrons or X-rays into such a small region. (See, however, the paper in this volume by Howie, McGill and Rodenburg who have studied small regions of an amorphous solid with a focussed beam of electrons.)

Light scattering by suspensions of colloidal particles overcomes both these difficulties. There now exist quite well-characterised liquid suspensions of spherical colloidal particles which can, at high concentrations, exhibit "liquid-like" and crystalline arrangements of the particles which therefore mimic real liquids and solids with "lattice spacings" comparable to the light wavelength. (More detailed descriptions of these colloidal systems will be given in section II.2.) It is simple to focus laser beams into regions of spatial dimension of a few wavelengths. Furthermore characteristic fluctuation times of light scattered by these colloidal systems are in the range of μ s to ms which can easily be handled electronically.

In the next section II.1 we discuss, largely qualitatively, the theory underlying the measurement of HOCF in suspensions of interacting spherical colloidal particles by light-scattering intensity cross-correlation spectroscopy. In section II.2 we describe two experiments in which higher-order effects have been observed. The first involves a "two-dimensional colloidal liquid" composed of charged particles whereas in the second case a three-dimensional system of uncharged particles was studied.

In the systems discussed in section II.2 correlations between the positions of spherical particles develop because of inter-particle interactions at relatively high concentrations. The light-scattering technique can also be used in studying HOCF, or, more loosely, the spatial distribution of scattering material, within individual complex or "supramolecular" entities such as aspherical particles and random-coil polymers. Since it is the structure of individual particles (intra-particle structure) which is of interest here measurements are made on dilute suspensions where the effect of inter-particle interactions can be neglected. This area is reviewed in section III.

A few concluding remarks are made in section IV.

II - HIGHER-ORDER CORRELATION FUNCTIONS IN SUSPENSIONS OF INTERACTING SPHERICAL COLLOIDAL PARTICLES

II.1 Summary of Light Scattering Theory

A detailed formal theory of the measurement of HOCF by intensity cross-correlation spectroscopy has recently been given by Ackerson, Taylor and Clark /1/. Useful earlier work is summarised in references /2-6/. Here we will give a largely qualitative description leaving the reader to consult these references for detail.

First consider a suspension in which the scattering volume V (the region of sample defined by the profile of the incident beam and the detection optics) contains a large number of non-interacting spherical particles. Generally the particles will have a different refractive index from the liquid and will scatter much more light than the liquid. Because laser light is coherent, phase relationships are maintained in the scattering process. The light singly scattered into the far field forms a random diffraction or speckle pattern, composed of bright spots where a degree of constructive interference between the light scattered by different particles occurs and dark regions corresponding to destructive interference, which reflects the instantaneous random spatial arrangement of the particles. As the particles move under Brownian motion this speckle pattern evolves from one random configuration to another. Thus, as the speckle pattern changes, the signal registered by a detector with small sensitive area will fluctuate randomly in time at a rate determined by the particle motions. A typical speckle has size determined by the diffraction of the whole scattering volume and subtends an angle $\lambda/V^{1/3}$ (where λ is the wavelength of the light) at the scattering medium; (compare the case of a perfect crystal illuminated by coherent X-rays where the angular extent of a Bragg reflection is determined by the size of the crystal). If the particles have radius R comparable to λ the whole speckle pattern will show a spatial variation in intensity with angular scale λ/R (generally $\lambda/R \gg \lambda/V^{1/3}$, the speckle size, for large V) due to intra-particle interference, described by the form factor $P(Q)$ (see below).

Now consider "turning on" an interaction between the particles by, for example, taking a more concentrated suspension. Correlations will develop between the particle positions and the concept of a "correlation volume" is useful. One can loosely identify a correlation length in a system showing short-ranged order as the distance over which the radial distribution function is significantly different from one. The cube of this length defines a correlation volume v within which particle positions are spatially correlated. For the moment we will assume that the scattering volume V contains many correlation volumes v i.e. $V \gg v$. Then the speckle pattern of scattered light shows two differences from the case of non-interacting particles. Firstly, in addition to spatial modulation of the intensity by the form factor (intra-particle interference, above), it is also modulated, with feature angular scale $\lambda/\sqrt{v}^{1/3}$, by the structure factor $S(Q)$ which reflects inter-particle correlations. Secondly, though of less interest here, the time evolution of the pattern is altered, sometimes markedly, due to the coupling by the interaction of the Brownian motions of different particles.

In this limit, where the scattering volume contains many particles or many independent correlation volumes, the scattered light field at a point in the far field is composed of many independent contributions and is therefore, through the central limit theorem, a (complex) Gaussian random variable. This property has two important consequences for light scattering. The first follows from well-known factorization properties of correlation functions of a Gaussian variable namely that all its higher-order correlation functions are reducible and can be written in terms of the second-order function. Thus, although one can measure higher-order correlation functions of the scattered light field (for example the intensity cross-correlation function $\langle I_1 I_2 \rangle$), in the limit $V \gg v$ where "conventional" quasi-elastic light scattering is performed they only contain information on the second-order field correlation function which, in turn, depends only on two-point correlations in the scattering medium. Secondly, in this limit, different speckles evolve independently in time. Thus if two detectors are placed in the scattered light field a non-trivial cross-correlation between their outputs will only be observed if they are effectively superimposed i.e. if they observe the same speckle.

It should be clear from the above that light scattering performed in the limit $V \gg v$ provides no information about irreducible spatial correlations in the scattering medium of order higher than two. Therefore we now consider the case where the illuminated volume V of the sample seen by the detector is comparable in size to the correlation volume v . Here light is scattered by a single or a small number of clusters of particles which, in a strongly-interacting system such as a colloidal liquid near freezing, will be strongly correlated in position. Thus the central limit theorem no longer applies, the scattered field is no longer Gaussian and there is no reason not to expect correlations between the intensities scattered in more than one direction. Crudely one can think of this process as scattering from small transient crystallites which, in certain orientations, can provide diffraction-broadened Bragg reflections in two or more directions simultaneously. Since a Bragg reflection requires correlated scattering from more than two particles it is not surprising that the full analysis of the $V \approx v$ case, performed by Ackerson et al /1/, shows that the cross-correlation of intensities scattered to spatially-separated detectors contains information on HOCF of the scattering medium.

With the foregoing discussion as motivation we now write down a few more quantitative results and discuss briefly a typical cross-correlation experiment. The amplitude of the electric field of light singly scattered by a suspension of spherical particles can be written as the sum of the fields scattered by the individual particles

$$E(\underline{Q}, t) = \sum_{i=1}^N a_i(\underline{Q}) \exp[i\underline{Q} \cdot \underline{r}_i(t)] \quad (1)$$

Here \underline{Q} is the usual scattering vector, the vectorial difference between the propagation vectors of scattered and incident light, having magnitude

$$Q = (4\pi/\lambda) \sin(\theta/2) \quad , \quad (2)$$

where λ is the light wavelength and θ the scattering angle; $\underline{r}_i(t)$ is the position of the centre of particle i at time t and $a(Q)$ the amplitude of the light scattered by a single particle. The summation runs over the N particles in the scattering volume. The instantaneous scattered intensity is given by

$$I(Q,t) = |E(Q,t)|^2 \quad (3)$$

so that its average is

$$\langle I(Q,t) \rangle = NP(Q) S(Q) \quad (4)$$

where the form factor $P(Q)$ is

$$P(Q) \equiv a^2(Q) \quad (5)$$

and the structure factor $S(Q)$ is

$$S(Q) \equiv \frac{1}{N} \sum_i \sum_j \langle \exp[i\underline{Q} \cdot (\underline{r}_i - \underline{r}_j)] \rangle \quad (6)$$

In terms of the discussion above equations (1) and (3) represent the instantaneous speckle pattern and equations (4)-(6) describe the scattered intensity averaged over all positions of the particles in the scattering volume or, equivalently, over many configurations of the speckle pattern so that only spatial modulations due to intra-particle ($P(Q)$) and inter-particle ($S(Q)$) interference remain.

In principle there is no reason why one cannot cross-correlate the outputs of many detectors obtaining thereby intensity moments and cross-correlation functions of arbitrary order. However here we will concentrate on what is probably the simplest useful quantity namely the cross-correlation function $\langle I(Q_1,t) I(Q_2,t+\tau) \rangle$ of intensities detected at two positions described by scattering vectors \underline{Q}_1 and \underline{Q}_2 . High-gain photomultiplier tubes are placed in the scattered light field. These are usually operated in a photon-counting mode so that their outputs consist of trains of pulses of charge modulated in rate by the temporal fluctuations in the intensities falling on their photocathodes. These digital signals are fed to a standard "photon correlator" which performs the time-delayed multiplication and accumulation operations required to obtain a good experimental estimate of the intensity cross-correlation function introduced above.

From equations (1) and (3) we have

$$\begin{aligned} \langle I(\underline{Q}_1,0) I(\underline{Q}_2,\tau) \rangle &= \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \sum_{\ell=1}^N a^2(Q_1) a^2(Q_2) \\ &\langle \exp i\{\underline{Q}_1 \cdot [\underline{r}_i(0) - \underline{r}_j(0)] + \underline{Q}_2 \cdot [\underline{r}_k(\tau) - \underline{r}_\ell(\tau)]\} \rangle \quad (7) \end{aligned}$$

Equation (7) can be reduced by a cluster decomposition which we now outline briefly. If scattering at small angles, within the diffraction lobe of the scattering volume, is neglected one-particle clusters do not contribute to equation (7) /1/. Two-particle clusters always contribute to equation (7) but the ratio of higher-order contributions to two-particle contributions is of order v/V /1,3,5/. Thus in the limit $V \gg v$, where $E(Q,t)$ is Gaussian, these higher-order contributions are negligible. One then gets the usual (Gaussian) result for the normalised intensity (cross) correlation function

$$g^{(2)}(Q_1, Q_2, \tau) \equiv \frac{\langle I(Q_1, 0) I(Q_2, \tau) \rangle}{\langle I(Q_1) \rangle \langle I(Q_2) \rangle} \quad (8a)$$

$$= 1 + \left[\frac{F(Q_1, \tau)}{S(Q_1)} \right]^2 \quad " \delta(Q_1 - Q_2) " \quad (8b)$$

where the intermediate scattering function F is given by

$$F(Q, \tau) = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \langle \exp i\mathbf{Q} \cdot [\mathbf{r}_i(0) - \mathbf{r}_j(\tau)] \rangle \quad (9)$$

Equation (8) shows the features anticipated above for the Gaussian, $V \gg v$, regime. The function $g^{(2)}(Q_1, Q_2, \tau)$ depends only on pair correlations through $F(Q, \tau)$ (equation (9)). Furthermore the "delta function" in equation (8) implies that intensity correlations different from the accidental rate 1 (the first term in equation (8)) are only observed when the two detectors lie within the same speckle i.e. $Q_1 \approx Q_2$.

If the scattering volume V is reduced in size to become comparable to v , terms similar to those in equation (8) remain. However an additional term of relative magnitude v/V now becomes important. This term arises in the cluster decomposition from the case when all four particles i, j, k and l lie in the same cluster or correlation volume. Thus this non-Gaussian contribution can be written

$$\sum_{i=1}^N \sum_{j \in v_i} \sum_{k \in v_i} \sum_{l \in v_i} a^2(Q_1) a^2(Q_2) \langle \exp i\{Q_1 \cdot [\mathbf{r}_i(0) - \mathbf{r}_j(0)] + Q_2 \cdot [\mathbf{r}_k(\tau) - \mathbf{r}_l(\tau)]\} \rangle \quad (10)$$

where the notation $j \in v_i$, for example, means that particle j lies with a spatial correlation length of particle i . Term (10) includes information not only on irreducible four-particle correlations but also on three-body and two-body correlations arising, for example, when $i=k \neq j \neq l$, $i=k \neq j=l$, etc.

The full formal cluster decomposition is given by equations (2.7)-(2.9) of Ackerson et al /1/ to which the reader is referred. These authors also include an "aperture function" or illumination profile in equation (1) and call their expressions "aper-tured correlation functions".

II.2 Experiment

II.2.1 Two-dimensional colloidal liquid

By far the best demonstration to date of the potential of cross-correlation light scattering in the measurement of HOCF is the elegant experiment of Clark, Ackerson and Hurd /7/ on a two-dimensional colloidal liquid. This experiment has been discussed in detail elsewhere /7/ and here we summarise the features relevant to the present paper.

The sample consisted of a suspension of polystyrene spheres of diameter about 220 nm in well deionised water. These particles carry a charge of several hundred elementary units which, in water without added electrolyte, is shielded only relatively weakly. Thus a repulsive interaction with energy many $k_B T$ persists to inter-particle separations equivalent to many particle diameters. The suspension was introduced into a wedge-shaped gap of about 10 μm between two quartz optical flats. The particles interact repulsively not only directly with each other but also with their images in

the quartz flats. Thus they tend to lie on the central plane between the flats. At a certain particle concentration a monolayer of particles is formed. In thicker regions of the gap the particles, under the influence of mutual repulsions, arrange themselves in a "two-dimensional crystal" where they are localised to the neighbourhoods of sites on a hexagonal lattice. In regions where the gap is narrower the particle concentration is lower, the inter-particle separation larger and the crystal is disrupted. Here, because a significant interaction still exists, the particles form a "two-dimensional colloidal liquid" in which they are able to diffuse over macroscopic distances but still show considerable short-ranged spatial order with typical spacing between neighbours of about $1 \mu\text{m}$.

The sample was illuminated with a laser beam normal to its plane, focussed to a spot of diameter about $5 \mu\text{m}$ which contained about 25 particles. Clark et al were then able to obtain photographic snapshots, as well as a video recording, of the scattered light patterns which showed relatively slow (timescale around tens of ms) temporal fluctuations. If the crystalline region was illuminated a relatively stationary diffraction pattern of six hexagonally-arranged Bragg spots was observed. However, if the liquid-like region was illuminated, a more complex fluctuating pattern was found. Frequently this showed six spots distributed hexagonally around the Debye-Scherrer ring (the first peak in the structure factor). A particular pattern only persisted for a few hundredths of a second after which it evolved into another pattern with different orientation. While six-spot patterns predominated, four-spot, two-spot and other more complex arrangements were also found. It should be noted that, because in this arrangement $v \approx v$, a single speckle or diffraction spot had angular size $\lambda/v^{1/3}$ comparable to the angular width $\lambda/v^{1/3}$ of the Debye-Scherrer ring (see section II.1).

Clark et al performed cross-correlation measurements on these scattered light patterns by placing, in the Debye-Scherrer ring, two fibre optic probes which fed photomultiplier tubes and a photon correlator. One probe was held fixed and the other moved to different locations around the ring where measurements of the normalised cross-correlation coefficient (equation (8a)) were made. The results are shown in Figure 1 where the equal-time (zero delay time) cross-correlation coefficient $g^{(2)}(Q_1, Q_2, 0)$ is plotted as a function of the angular separation ϕ of the probes in the Debye-Scherrer ring. Remember that totally uncorrelated intensities would provide a coefficient of one (section II.1). We see that positive correlations, $g^{(2)} > 1$, between the intensities at the two probes are found at $\phi = 0$ (essentially an autocorrelation) and at $\phi = 60^\circ, 120^\circ, 180^\circ$ etc whereas negative or anticorrelations, $g^{(2)} < 1$, are found at $\phi = 30^\circ, 90^\circ, 150^\circ$ etc. In view of the predominance of transient six-spot patterns observed in the photographs (see previous paragraph) these findings are not unexpected.

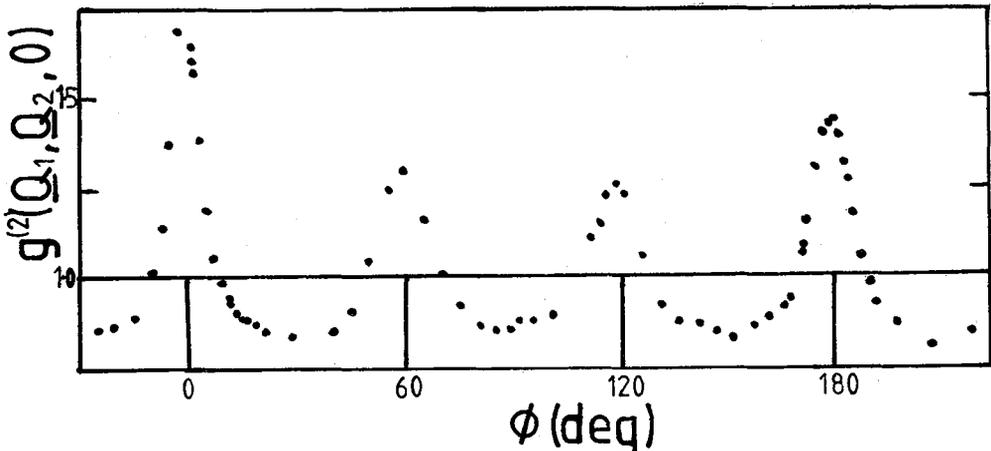


Figure 1. Normalised cross-correlation coefficient of a two-dimensional colloidal liquid as a function of angular separation ϕ of detectors in the Debye-Scherrer ring (taken from reference 7).

If a bright spot happens to fall on one probe another is likely to be found at relative angles around the ring of 60° , 120° etc thus providing, on average, a positive correlation. However if the probes are separated by 30° , 90° etc a bright spot on one will tend to be accompanied by a dark region on the other, leading to the anticorrelation.

The observation, as revealed quantitatively by cross-correlation spectroscopy, of six-fold symmetries in the diffraction pattern provides, in principle, information on the HOCF of the positions of the particles in the two-dimensional colloidal liquid. Crudely, as anticipated, it implies that the sample contains small transient crystallites with hexagonal symmetry. However, as noted in section II.1, the general expression for the cross-correlation coefficient is very complicated, containing two-, three- and four-particle contributions. Extraction from the data of the various terms to provide detailed information on the higher-order distribution functions g_3 , g_4 etc (in the same manner that the structure factor $S(Q)$ can be inverted to give the two-body function $g(r)$) appears very difficult. For this reason Clark et al considered various theoretical models, eg a vibrating, rotating lattice /7/, and performed a hard-disk computer simulation /1/. These physically plausible approaches could provide results very similar to the data of Figure 1.

To complete the story we describe what Clark et al observed as the size of the laser spot illuminating the sample was increased. When the linear dimension of the spot was increased to be larger than the range of spatial correlation of the particles several "correlation regions" were illuminated. Thus several independent transient diffraction patterns were observed. Because the laser light was coherent over the whole illuminated region instantaneous interference between these different diffraction patterns still occurred leading to a deeply-modulated instantaneous speckle pattern. However because the individual patterns were in different orientations the transient six-fold symmetries became less obvious. In the Gaussian limit, where many independent correlation regions were illuminated, the pattern of scattered light consisted of a Debye-Scherrer ring (angular width $\sim \lambda/v^{1/3}$) composed of small independently-fluctuating speckles (angular width $\lambda/v^{1/3}$, $\ll \lambda/v^{1/3}$ for $v \gg v$) with no transient symmetries apparent. In this limit a cross-correlation measurement similar to that shown in Figure 1 would show an autocorrelation at $\phi = 0$ (the second term in equation (8b)) decaying rapidly to, and remaining at, one as ϕ was increased.

Clearly a measurement of, for example, the height of the $\phi = 60^\circ$ cross-correlation coefficient as a function of laser spot size would provide information on the range of spatial correlation in the sample /1/.

II.2.2 Three-dimensional colloidal liquid

The experiment of Clark et al on a two-dimensional colloidal liquid, described in the previous section, demonstrates vividly the principles underlying the measurement of HOCF by cross-correlation spectroscopy. For several reasons cross-correlation experiments on three-dimensional systems are technically much more difficult to perform. Firstly, whereas for the two-dimensional system a small volume is defined simply by using a focussed laser beam, in the three-dimensional case it is necessary to use, in addition, high-resolution detection optics (see below and Figure 2). Furthermore both detection systems must be accurately aligned to observe the same very small volume in the sample. Secondly, even in a strongly-interacting three-dimensional system, the magnitudes of measured cross-correlations are expected to be small. As pointed out by Ackerson et al /1/ the reciprocal lattice of a two-dimensional crystal consists of lines whereas that of a three-dimensional crystal consists of points. Lines are more likely to intersect the Ewald sphere to provide Bragg reflections simultaneously in several directions, leading therefore to strong cross-correlations.

Despite these difficulties we have recently studied by cross-correlation spectroscopy a three-dimensional colloidal liquid and here we describe briefly some preliminary observations. The sample consisted of spherical colloidal particles of poly-methyl-methacrylate (PMMA) of diameter about $0.65 \mu\text{m}$ stabilised sterically by a thin coating

of a different polymer. They were suspended in a mixture of two liquids, decalin and carbon disulphide, in a proportion chosen to match closely the refractive index of the particles (about 1.51). Thus it was possible to obtain quite transparent samples, suitable for light scattering, at high particle concentrations. The properties of these samples have been described in detail elsewhere /8/. The inter-particle interaction appears to be steep and repulsive so, to a first approximation, the particles can be regarded as hard spheres. The samples showed phase behaviour similar to that found in computer experiments on hard spheres ranging, with increasing concentration, from a liquid-like arrangement of particles through co-existence of liquid and colloidal crystal to all crystal and, at the highest concentrations, a glass-like phase. We studied the upper, liquid-like, phase of a sample in the co-existence region (at a volume fraction of particles of about 0.50) in which spontaneously nucleated crystallites had settled under gravity.

The structure factor of this "co-existing colloidal liquid" was measured by conventional light scattering (i.e. by measuring $\langle I(Q) \rangle$ as a function of Q , equation (4)) and was found to be in reasonable agreement with the results of computer experiments. At a laser wavelength of 647 nm (the red line of a krypton ion laser) the first peak in the structure factor occurred at a scattering angle of about 45° and the second peak around 90° . A plan view of the experimental arrangement used for the cross-correlation measurements is shown in Figure 2. Light from the laser was focussed into the sample cell by a microscope objective L1 of numerical aperture 0.35 and magnification 25:1. Similar microscope objectives L2, set at scattering angles of $\pm 90^\circ$, cast images of the focal region of the laser beam on slits S of width $50 \mu\text{m}$ placed in front of photomultiplier tubes PM1 and PM3. After initial alignment, fine adjustment of the various optical components was made to maximise the cross-correlation between the outputs of the detectors. This optical set-up provided a scattering volume with a typical linear dimension of about $5 \mu\text{m}$. In addition to the arrangement shown in Figure 2 (where detectors were set at the opposite ends of a diameter of the second Debye-Scherrer ring) we also used the arrangement shown in the inset to study light scattered at $\pm 45^\circ$ i.e. at opposite ends of a diameter of the first Debye-Scherrer ring. The 45° prisms glued to the cell allowed the scattered light to emerge normally thereby minimising aberration of the imaged scattering volume.

The measured cross-correlation functions obtained in these two arrangements are shown in Figures 3 and 4. For the $\theta = \pm 45^\circ$ configuration we observed an anti-correlation, $g^{(2)}(Q_1, Q_2, 0)$ being less than one, whereas for $\theta = \pm 90^\circ$ a positive correlation was found. Note that the magnitudes of the effects are very small, less than one per cent. Even to obtain the level of accuracy shown in Figures 3 and 4 it was necessary to accumulate data for several hours. As a "null" check, a measurement was also performed with one set of detection optics displaced slightly so that the detectors observed totally different scattering volumes. Here, as expected and as shown in Figure 5, essentially no cross-correlation was found i.e. $g^{(2)}(Q_1, Q_2, 0)$ has the "accidental" value of one.

From these results we conclude that we have observed cross-correlation effects related to higher-order spatial correlations in the sample. However the effects are small and it is clearly impossible to obtain from these data detailed information on the HOCHF. Nevertheless, as in the two-dimensional case, one can adopt a "transient crystallite" picture. The $\pm 90^\circ$ configuration is degenerate for a crystallite with cubic symmetry (the hard-sphere crystal is face-centred cubic) in that if the crystallite happens to be in an orientation which provides a Bragg reflection in the direction $\theta = +90^\circ$ there will also be a set of lattice planes which provides a Bragg reflection at $\theta = -90^\circ$. Thus, as is found (Figure 4), a positive correlation is expected. By contrast if the crystallite is in an orientation which gives a Bragg reflection (from the 111 fcc planes) at $\theta = 45^\circ$ it will not reflect at $\theta = -45^\circ$. Thus at least no correlation, or perhaps an anticorrelation as is found (Figure 3), is expected for this configuration.

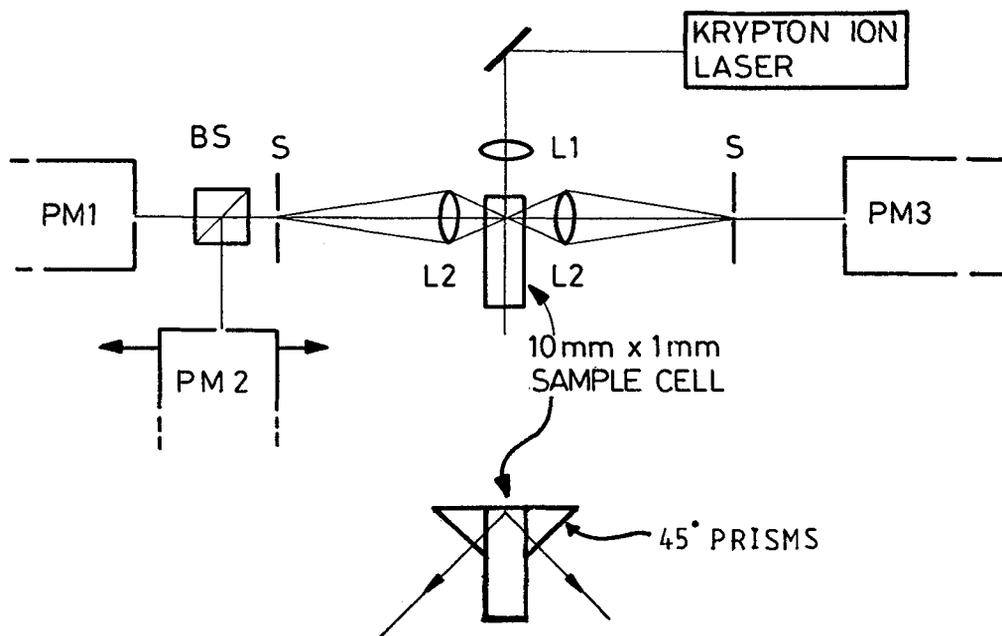


Figure 2. Plan view of the cross-correlation apparatus, described in the text. The apparatus can also be used with the detectors PM1 and PM2 viewing the same slit (and scattering volume) via the beam splitter BS (see section III).

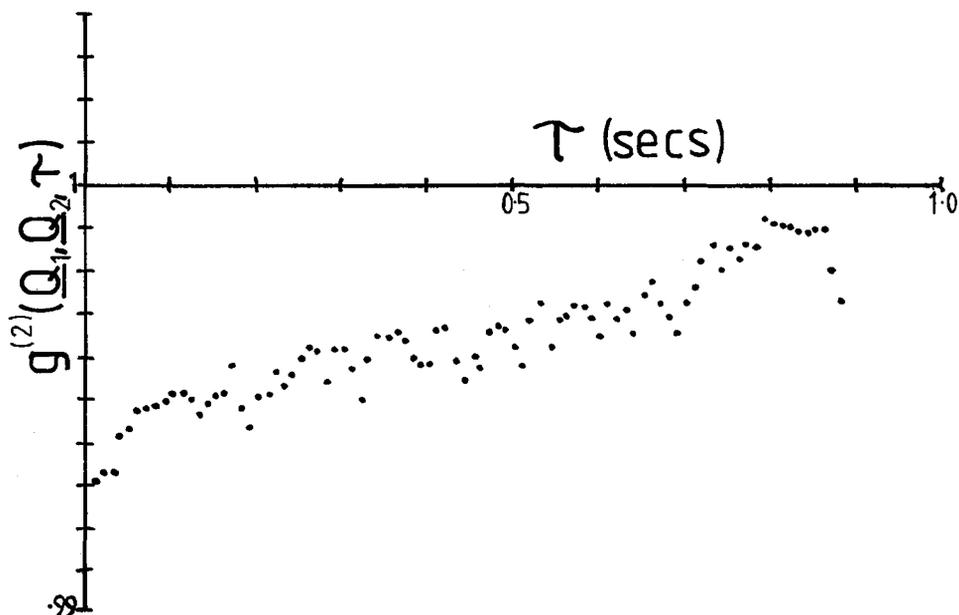


Figure 3. Normalised cross-correlation function of a three-dimensional colloidal liquid as a function of delay time τ in the $\theta = \pm 45^\circ$ configuration.

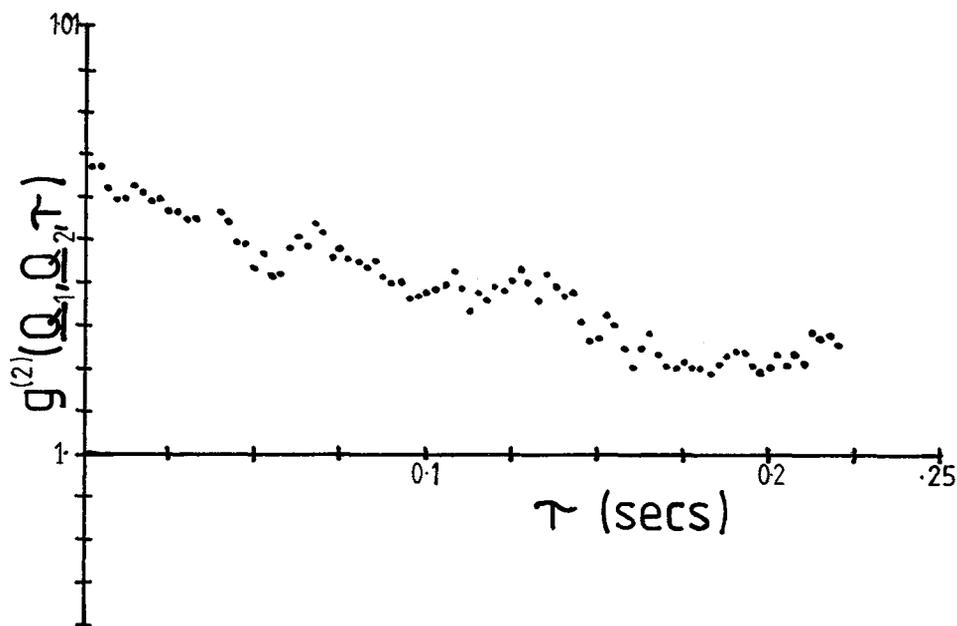


Figure 4. Normalised cross-correlation of a three-dimensional colloidal liquid as a function of delay time τ in the $\theta = \pm 90^\circ$ configuration.

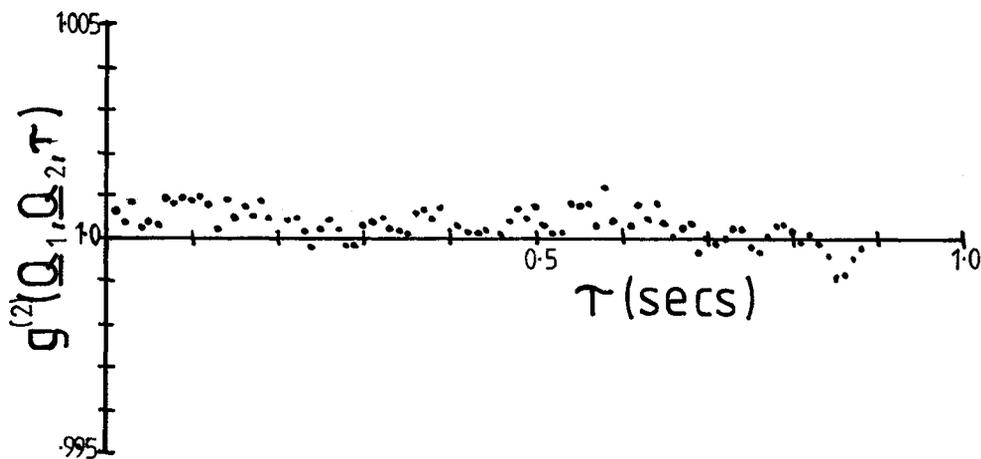


Figure 5. As Figure 3 but with one detection slit (see Figure 2) displaced so that the two detectors view different scattering volumes.

III - INTRA-PARTICLE STRUCTURE AND DYNAMICS OF COMPLEX PARTICLES IN DILUTE SUSPENSIONS

In this section we consider the case of dilute suspensions of complex colloidal particles where cross-correlation spectroscopy probes fluctuations in the number and scattering power of the individual particles.

The cross-correlation function (equation (8a)) of the intensities scattered by a dilute suspension, of complex particles can be written /5,9-12/

$$g^{(2)}(\underline{Q}_1, \underline{Q}_2, \tau) = 1 + [F_S(\underline{Q}_1, \tau)]^2 \delta(\underline{Q}_1 - \underline{Q}_2) + \langle N \rangle^{-1} g_{NF}(\tau) g_I(\underline{Q}_1, \underline{Q}_2, \tau) \quad , \quad (11)$$

the various terms arising, as before, from an ensemble average of four-fold products of the scattered fields. The second, Gaussian, term comes from the case where two pairs of fields are scattered from within two distinct particles whereas for the third, non-Gaussian, term all four fields arise from within the same particle. For identical particles with internal structure the self-intermediate scattering function $F_S(\underline{Q}, \tau)$ is defined by

$$F_S(\underline{Q}, \tau) \equiv \frac{\langle a(\underline{Q}, 0) a^*(\underline{Q}, \tau) \exp i\underline{Q} \cdot [\underline{r}(0) - \underline{r}(\tau)] \rangle}{\langle |a(\underline{Q})|^2 \rangle} \quad , \quad (12)$$

where $a(\underline{Q}, t)$ represents the amplitude of the field scattered by a particle at time t and $\underline{r}(t)$ is the position of its centre-of-mass. $F_S(\underline{Q}, \tau)$ can be expressed approximately as the product /13/

$$F_S(\underline{Q}, \tau) = \exp(-D_T \underline{Q}^2 \tau) \frac{\langle a(\underline{Q}, 0) a^*(\underline{Q}, \tau) \rangle}{\langle |a(\underline{Q})|^2 \rangle} \quad , \quad (13)$$

where D_T is the particle's translational diffusion coefficient. The amplitude $a(\underline{Q}, t)$ can be written as an integral over phase factors weighted by the time-dependent distribution $\rho(\underline{r}_p, t)$ of mass within the particle P

$$a(\underline{Q}, t) \equiv \int_P d^3 \underline{r}_p \rho(\underline{r}_p, t) \exp(i\underline{Q} \cdot \underline{r}_p) \quad . \quad (14)$$

As fluctuations in $a(\underline{Q}, t)$ only become significant when Q^{-1} is comparable to the spatial dimension of the particle the timescales of translational and intra-particle fluctuations are usually similar so that unambiguous separation of the two contributions from a measurement of the Gaussian term in equation (11) is difficult.

The third, non-Gaussian, term of equation (11) also contains components depending on translational and intra-particle motions. The factor $g_{NF}(\tau)$ ($g_{NF}(0) = 1$) describes fluctuations in the number of particles in the scattering volume V and decays on timescales reflecting the mean time taken by particles to diffuse across V ; since, typically, $V^{1/3} \gg Q^{-1}$ this time is usually large, of order seconds. The intra-particle factor

$$g_I(\underline{Q}_1, \underline{Q}_2, \tau) \equiv \frac{\langle |a(\underline{Q}_1, 0)|^2 |a(\underline{Q}_2, \tau)|^2 \rangle}{\langle |a(\underline{Q}_1)|^2 \rangle \langle |a(\underline{Q}_2)|^2 \rangle} \quad (15)$$

is a four-point correlation evaluated within individual particles and averaged over the ensemble of size and shape fluctuations; it essentially describes the cross-correlation of intensities scattered by the same particle in two directions. The function g_I generally decays in time much more rapidly than g_{NF} so that relatively unambiguous measurement of the intra-particle fluctuations can be made by study of the non-Gaussian term in equation (11). However, the amplitude of the non-Gaussian term is determined by the relative variance of the fluctuating number of particles

in V which, for a random (Poisson) distribution of non-interacting particles, gives the factor $\langle N \rangle^{-1}$. Experiments are best performed using dilute suspensions and, as before, small scattering volumes such that $1 \leq N \leq 10$. Suppression of the Gaussian term in equation (11) is again achieved by using two detectors separated in angle by more than the speckle size $\lambda/\sqrt{1/3}$.

As an aside we note that in the case of interacting particles considered in section II fluctuations in the number of particles in the scattering volume also occur. In the formal analysis they emerge naturally if a factor describing the illumination profile of V is included in equation (1) (/1/ and end of section II.1). In this case, however, number fluctuations are small both because of the relatively large number, $\langle N \rangle \approx 25$, of particles studied and because of their suppression by inter-particle repulsions /14/.

Cross-correlation measurements of the type described above are useful in the study of long chain polymers /10,15/, of large colloidal aggregates /16/ and particularly of the structure and rotational diffusion of rigid aspherical particles /9-12/. Here we use as an example some recent work on slightly aspherical colloids, approximately ellipsoids of revolution, where measurement of both the decay rate and amplitude of g_I has allowed estimation of particle size and axial ratio (J. G. Rarity, to be published).

In the analysis of the rotational diffusion of an asymmetric particle the single scattering (in the first Born approximation) is expressed as a series expansion of Legendre polynomials and ultimately as a series of spherical harmonic functions. Using solutions of the rotational diffusion equation expressed in analogous fashion the averages implied by equation (15) can be evaluated by exploiting the orthogonality properties of the spherical harmonics /11-13,17/. For dielectric particles with spherical top symmetry g_I (equation (15)) can be written as

$$g_I(Q_1, Q_2, \tau) = 1 + [A_0(Q_1, Q_2)]^{-1} \sum_{\substack{J=2 \\ \text{EVEN}}}^{\infty} A_J(Q_1, Q_2) P_J(Q_1 \cdot Q_2 / Q_1 Q_2) \exp[-J(J+1)D_R \tau] \quad (16)$$

where the A_J are coefficients dependent on the size and shape of the particle, $P_J(\cos\phi)$ is the Legendre polynomial of order J with argument the cosine of the angle ϕ between the scattering vectors Q_1 and Q_2 and D_R is the rotational diffusion coefficient of the particle. When the particles are small enough (typical maximum dimension $< 4\pi/(Q_1+Q_2)$) equation (16) can be approximated by

$$g_I(Q_1, Q_2, \tau) = 1 + B(Q_1, Q_2) P_2(\cos\phi) \exp(-6D_R \tau) \quad (17)$$

We have calculated B (and the higher A_J) in terms of the radius b and axial ratio q of ellipsoids of revolution. The rotational diffusion coefficient D_R can also be expressed in terms of b and q via Perrin's equation /18/

$$D_R = \frac{k_B T}{8\pi\eta b^3 q} P_R(q) \quad (18)$$

where $k_B T$ is the thermal energy, η the viscosity of the liquid in which the particles are suspended and $P_R(q)$ is a factor close to one for small q . Measurement of D_R and B allows estimation of b and q by graphical solution of equation (18) and the relationship between B , b and q .

The two simplest optical configurations for this type of experiment are shown in Figure 2. One involves (as in section II.2.2) the two detectors, PM1 and PM3, placed at scattering angles $\theta = \pm 90^\circ$. The scattering vectors for this case, shown in Figure 6a, are separated by an angle $\phi = 90^\circ$ so that, in equation (17), $P_2(\cos\phi) = P_2(0) = -0.5$. The second involves placing the two detectors, PM1 and PM2, behind the

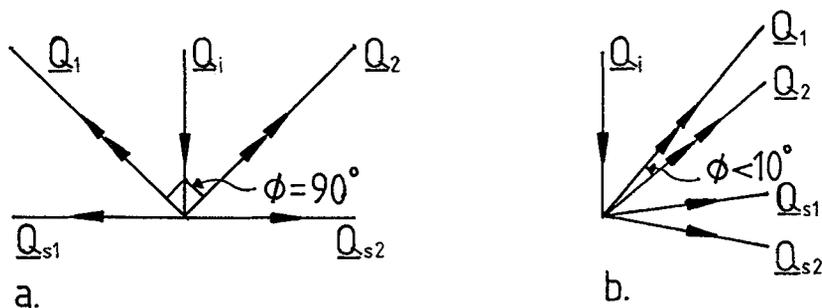


Figure 6. Scattering vector geometries for 90° cross-correlation. \underline{Q}_i : incident wavevector, \underline{Q}_{s1} and \underline{Q}_{s2} : scattered wavevectors, \underline{Q}_1 and \underline{Q}_2 : scattering vectors ($\equiv \underline{Q}_{s1}$ or $\underline{Q}_{s2} - \underline{Q}_i$). (a) "Opposed-detector" case, scattering angles $\pm 90^\circ$ with angle between scattering vectors $\phi = 90^\circ$. (b) "Same-side" detection, scattering angles $90 \pm \delta^\circ$, $\phi = \delta < 10^\circ$.

same image slit but set at slightly different scattering angles close to 90° . This can be achieved by using a beam splitter or fibre optic probes. The effective suppression of the Gaussian term in equation (11) due to the detector separation can be checked with a test sample containing many spherical scatterers in V. In this configuration the magnitudes of \underline{Q}_1 and \underline{Q}_2 are similar to those for the opposed-detector arrangement (see Figure 6) so that B in equation (17) has the same value; the typical angle ϕ between \underline{Q}_1 and \underline{Q}_2 required to suppress the Gaussian term is around 5° so that $P_2(\cos\phi) \approx 1$. Thus from equation (17) we see that in the "opposed-detector" arrangement (Figure 6a) an anti-correlation ($g_I(\underline{Q}_1, \underline{Q}_2, 0) < 1$) is predicted whereas in the "same-side" detector case (Figure 6b) a positive correlation, of twice the amplitude, is expected. The anticorrelation predicted in the first case has a simple physical interpretation /11/ which can be seen by reference to Figure 6a. If the longest dimension of an aspherical particle happens to lie in the direction of scattering vector \underline{Q}_2 , for example, this is the "mirror" orientation for scattering to detector 1 which will therefore register a high intensity. However, for this orientation of the particle, destructive interference will occur between light scattered into detector 2 from different regions of the particle along its long dimension; detector 2 will thus register a small intensity. This mechanism leads to an anti-correlation, which survives the average over particle orientation, between the detector outputs.

Examples of the cross-correlation functions of intensities scattered by a dilute suspension of roughly ellipsoidal particles are shown in Figure 7. For these measurements a similar cross-correlation apparatus to that described in section II.2.2 (Figure 2) was used with lower power lenses (x6 microscope objectives of numerical aperture .15) and wider slits (200 μm) creating a scattering volume roughly 40 μm long and 15 μm in diameter. The short timescale decays seen in Figure 7 arise from rotational motions (g_I in equation (11)) while the very much slower decays, appearing almost flat in Figure 7, represent the number fluctuations (g_{NF} in equation (11)); on longer timescales than shown here the correlation function $g^{(2)}$ decays to one. The anticorrelation and positive correlation effects for opposed and same-side detector configurations are clearly demonstrated. The slow component is fitted and divided into the measured $g^{(2)}$ to provide an estimate of g_I . Plots of $\ln[g_I(\tau) - 1]$ against τ (Figure 8) are roughly linear implying, as predicted by equation (17), exponential decays. The ratio of the amplitudes of $g_I - 1$ for the two configurations is about -1.65 although, averaged over several measurements, it was -1.92 ± 0.25 closer to the theoretical value -2 (i.e. $1/-0.5$). From a series of such measurements made with a range of laser wavelengths we obtain a particle radius of $b = 81 \pm 4$ nm and axial ratio $q = 1.52$ in reasonable agreement with the values 85 nm and 1.45 obtained by electron microscopy.

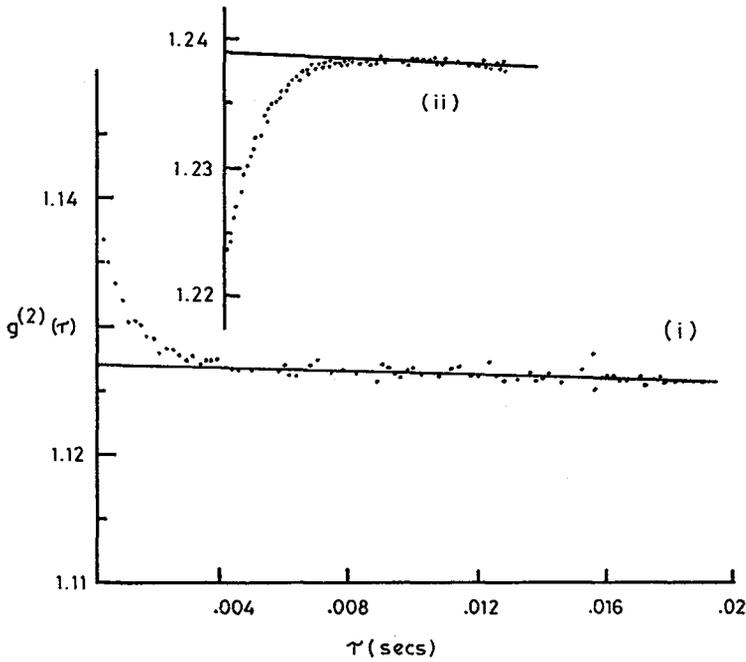


Figure 7. Cross-correlation functions $g^{(2)}(\tau)$ of intensities scattered by dilute suspensions of ellipsoidal particles. (i) "same-side" and (ii) "opposed-detector" arrangements. $g^{(2)}(\tau)$ decays to 1 at long times (seconds) due to slow number fluctuations.

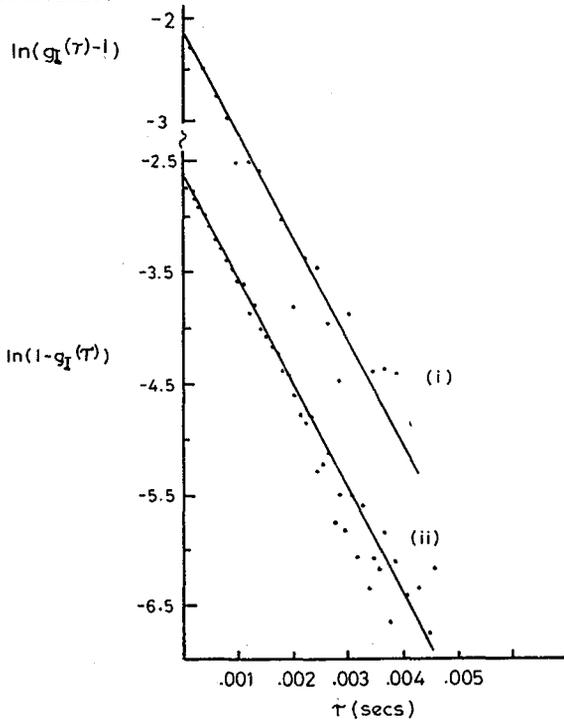


Figure 8. The logarithm of the fast component $\ln|g_I(\tau) - 1|$ estimated from the data in Figure 7. Labelling as in Figure 7.

We should emphasise that, in this type of experiment, any measured deviation of g_{\perp} from one is an indication of asymmetry of the scatterer and that in favourable cases the technique should be sensitive to asymmetries as small as $q = 1.025$. By contrast asymmetries as large as $q = 1.5$ cannot be detected unambiguously by measurements made in the Gaussian regime, that is by study of the second term in equation (11). This is an example of a four-point correlation function providing more information than a two-point function. We also note that the opposed-detector configuration probes correlations between orthogonal dimensions of a particle (since $Q_1 \cdot Q_2 = 0$, Figure 6a). For example, a random-coil polymer with Gaussian statistics should provide no modulation of g_{\perp} when studied in this configuration whereas with detectors on the same side (Figure 6b) a signal reflecting internal motions should be seen /15/.

IV - CONCLUDING REMARKS

We have described the use of cross-correlation light-scattering techniques in the study of higher-order correlation functions in suspensions of colloidal particles. The experiment of Clark et al on a two-dimensional colloidal liquid, discussed in section II.2.1, demonstrates clearly the principles and potential of the method in studying higher-order spatial correlations induced by strong inter-particle interactions. Our own experiments, section II.2.2, detected much smaller effects in a three-dimensional colloidal liquid. While the effects observed in both these experiments clearly depend on HOCF, analysis of the data to provide information on three- and four-body distribution functions still appears very difficult. A more promising, if less informative, approach to analysing the data is the construction of simple theoretical models and the use of computer simulation.

In describing these experiments we have concentrated on the behaviour of the equal-time correlation $g^{(2)}(Q_1, Q_2, 0)$. Useful information should also be contained in the time-dependence of $g^{(2)}$. In particular its initial decay,

$$\lim_{\tau \rightarrow 0} \frac{d}{d\tau} g^{(2)}(Q_1, Q_2, \tau) ,$$

has recently been analysed theoretically /19/. When hydrodynamic interactions between the particles can be neglected, as in the case of the relatively dilute charge-stabilised suspensions studied by Clark et al, this quantity is found to depend on three- rather than four-body correlations, a fact which could be exploited to assist in extracting from measurements the higher-order distribution functions.

Phillies /20/ has described another light scattering technique based on cross-correlating the outputs of three detectors each operated in the heterodyne mode (i.e. with a "reference" laser beam). While this experiment could be very difficult to set up it is sensitive to three-body correlations only and could therefore be simpler to analyse than the two-detector intensity cross-correlation method considered in this paper.

The study by intensity cross-correlation spectroscopy of dilute suspensions of (non-interacting) aspherical particles was described in section III. While these experiments are harder to perform than conventional (Gaussian-regime) measurements, already they can provide useful quantitative information (average shape, rotational diffusion, internal dynamics etc) and, in favourable cases, could be developed into a standard technique.

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