MULTIPLE LIGHT SCATTERING IN COLLOIDAL SUSPENSIONS : CROSS-CORRELATION PHOTON COUNTING SPECTROSCOPY

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MULTIPLE LIGHT SCATTERING IN COLLOIDAL SUSPENSIONS : CROSS-CORRELATION PHOTON COUNTING SPECTROSCOPY

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Résumé - Les principes de base et la théorie sont donnés pour une expérience de diffusion dynamique de la lumière dans laquelle les diffusions multiples sont éliminées. Cette nouvelle technique utilise deux faisceaux laser se recouvrant et traversant l'échantillon en provenant de directions opposées. A angle droit avec les faisceaux laser on dispose deux photomultiplicateurs dont les compteurs sont corrélés. Cette technique sera illustrée par des résultats expérimentaux obtenus sur des dispersions colloïdales de silicates. Nous montrons que les effets de diffusions multiples peuvent être éliminés par cette méthode.

Abstract - The basic principles and theory are given for a dynamic light scattering experiment in which multiple scattering is eliminated. This new technique uses two spatially overlapping laser beams travelling through the sample cuvet from opposite directions. At right angles to the laser beams two photo-multipliers are positioned. Their photon counts are cross-correlated. The feasability of the technique will be illustrated by experimental results from colloidal silica dispersions. It is shown that the effects of multiple scattering can indeed be eliminated in this way.

1. INTRODUCTION

In the study of static and dynamic interactions in colloidal suspensions, light scattering is one of the powerful applied experimental techniques. The development of lasers in the 1960's and of digital correlators in the first half of the preceding decade have resulted in an extensive application (1-3) on so-called, laser beat spectroscopy, photon counting spectroscopy (PCS), quasi-elastic scattering spectroscopy (QELS) or dynamic light scattering spectroscopy (DLS). As it is a relatively new technique it still has many names, but they all refer to a technique where time correlations on fluctuations of intensities in scattered laser light are related to the diffusive properties of the (colloidal) scatterers, or more generally to number density fluctuations. In dilute solutions the technique is then used to determine colloidal size from the Stokes-Einstein relation while with increasing volume fraction the effects of static and hydrodynamic interactions come into play.
A limitation of the theory coupling light scattering and number density fluctuations is that in the light scattering process considered, double and multiple scattering are excluded. Therefore it is necessary to do experiments either on very dilute suspensions or on suspensions where

the solvent has practically the same index of refraction as the dispersed phase. This is called optical matching, but as usual new problems and possibilities arise. For instance, when there is a polydispersity in scattering power a careful interpretation of the measurements is required. The optical matching ($\Delta n < 0.01$) fails when suspended particles are inhomogeneous in index of refraction, for instance when they have a core and peripheral layer with different refractive index. These prerequisites and limitations exclude therefore many colloidal systems of practical and theoretical interest from experimental investigation wiht QELS.
It is the purpose of this paper to present the basic principles and theory for a dynamic light scattering experiment in which double and multiple scattering are eliminated. The feasibility of the technique will be illustrated by means of experimental results recently obtained. They show that the effects of multiple scattering can in fact be eliminated. We start with a short outline of single scattering and indicate what kind of information is obtained from the intensity fluctuation correlation function. Without going into details we assume that the Rayleigh-Gans-Debye light scattering regime holds and that we work with spherically symmetrical scatterers.

2. SINGLE SCATTERING

Consider a plane wave propagating in the $\vec{K}_0$- direction and polarized in the $\vec{E}_0$ -direction with amplitude $|E_0|$, scattered elastically at position $\vec{r}$ by a (spherical) scatterer, see figure 1.

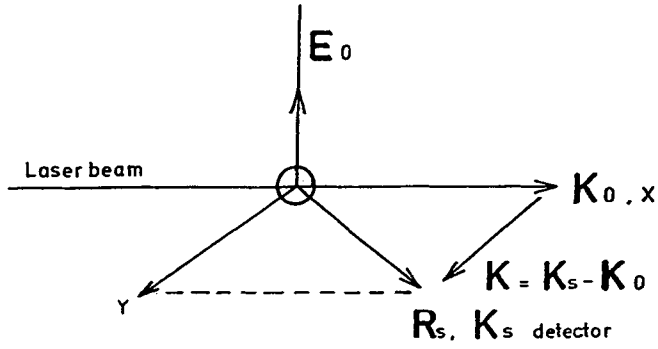


Figure 1. Scattering process, laser light is scattered at the origin. At position $\vec{R}_s$ in the direction $\vec{K}_s$ is a detector (photomultiplier).

Then the field amplitude at a position $\vec{R}_s$ in a plane perpendicular to $\vec{E}_0$ and through $\vec{K}_0$ is given by

$$\vec{E}_1(R_s,t) = \frac{2\pi^2 K_0^2 \vec{E}_0}{(2\pi)^3 R_s} e^{(i\vec{K}_s.\vec{R}_s - i\omega t)} \sum_{j=1}^{N} \int_{V_j} \frac{\Delta\varepsilon_j(r')}{\varepsilon} e^{i(\vec{K}_0-\vec{K}_s).(\vec{r}_j+\vec{r}')} d\vec{r}' \quad (1)$$

$$= \frac{2\pi^2 K_0^2 \vec{E}_0}{(2\pi)^3 R_s} e^{(i\vec{K}_s \cdot \vec{R}_s - i\omega t)} \sum_{j=1}^{N} \frac{\Delta\varepsilon(K)}{\varepsilon} \cdot e^{-i\vec{K}\cdot\vec{r}_j} \qquad (2)$$

Or briefly

$$\vec{E}_1 = \sum_{j=1}^{N} \vec{b}_j e^{-i\vec{K}\cdot\vec{r}_j} = \sum_{j=1}^{N} \vec{b}_j e^{i(\vec{K}_0 - \vec{K}_s)\cdot\vec{r}_j} \qquad (3)$$

in this expression $\vec{b}_j$ is called the scattering strength of particle j, K_0 is the incident wave vector $|\vec{K}_0| = \frac{2\pi}{\lambda}$, $\vec{K}_s$ is the scattered wave vector $|\vec{K}_s| = \frac{2\pi}{\lambda}$ and $(\vec{K}_0 - \vec{K}_s) = -\vec{K}$; $|\vec{K}| = \frac{4\pi}{\lambda}$ (sin $\theta/2$) where θ is the angle between $\vec{K}_0$ and $\vec{K}_s$ and λ the wave length of the coherent laser light used. In other words, $\vec{E}_1$ gives the instantaneous field amplitude (as a function of scattering angle, expressed as a function of $\vec{K}$ which is the direction of a stack of (Bragg) planes of equal phase each separated by a distance $\Lambda = 2\pi/K$), of a large number N of scatterers whose position is given by $\vec{r}_j$ relative to the origin of the cell. Because the particles undergo Brownian motion, the field strength will fluctuate with time and so $\langle \vec{E}_1 \rangle_t = 0$. The time scale on which $\vec{E}_1(t)$ changes considerably must be connected with the time needed for the particles to wander from one Bragg plane to the next one over a distance Λ. From this and Brownian diffusion theory it follows that $t = (\frac{1}{2}\Lambda)^2/2D$. For a typical particle D is of the order $10^{-11} m^2 s^{-1}$ and so t is of the order 10^{-2}-10^{-4}s.

Another way of visualizing the scattering process is to say that concentration fluctuations can be decomposed into spatial Fourier modes, from each of which the incident light is refracted into predetermined angles given by the Bragg condition $\Lambda = 2\pi/K = \lambda/(2\sin\theta/2)$. This condition implies that at small K (thus small θ or large λ) large spacings are observed, the so called ($K \Rightarrow 0$) collective diffusion.
In practice one measures of course $E(t)E^*(t) \equiv I(t)$ the scattered intensity. For studying the statistics of the Brownian diffusion motion the intensity-time auto correlation is measured

$$G^2(K,\tau) \equiv \frac{\langle I(t).I(t+\tau)\rangle}{\langle I\rangle^2} \qquad (4)$$

with the help of the Siegert relation, stating that for a Gaussian process

$$\langle x(0)x^*(0)y(t)y^*(t)\rangle = \langle xx^*\rangle\langle yy^*\rangle + |\langle x(0)y(t)\rangle|^2 + |\langle x(0)y^*(t)\rangle|^2. \qquad (5)$$

The intensity correlation function is thus written in terms of the field correlation functions and reads after normalization on $\langle I\rangle$:

$$G^2(K,t) = 1 + \frac{|\langle E(0)E^*(t)\rangle|^2}{\langle I\rangle^2} + \frac{|\langle E(0)E(t)\rangle|^2}{\langle I\rangle^2} \qquad (6)$$

The last term on the right hand side of equation (6) averages out to zero and is therefore eliminated. Incorrectly however, it is often not included in the Siegert relation. The second term is coupled to the diffusion of the colloidal particles.

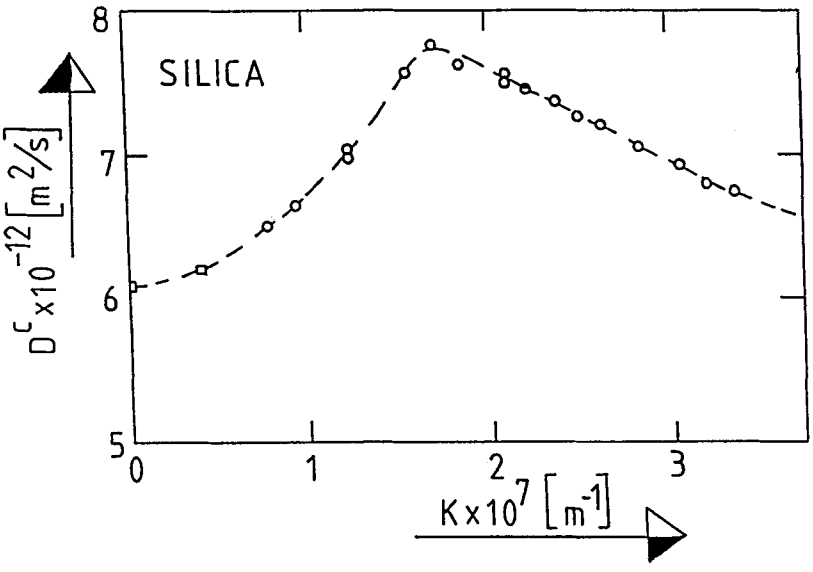


Figure 2. Apparent diffusion coefficient plotted against scattering angle expressed in K^2.

Actually this is done by solving, after Fourier transforming, the second law of Fick, and leads to an expression for the Fourier transform of the density probability distribution p(K,t). On inserting eq.(3) into eq.(6) and noting the similarity between this and the solution of Fick's law the basic equation of dynamic light scattering is found.

$$G^2(K,t) = b + ce^{-2DK^2t}. \qquad (7)$$

Where b and c are the result of experimental imperfections respectively called baseline and contrast. In case more than one type of fluctuation is present which decays (in)dependently, we will find the sum of several exponentials each with its own decay rate and amplitude.

3. MULTIPLE SCATTERING

It is not difficult to imagine that light from the laser beam is scattered through an arbitrary angle and subsequently scattered once more into the detector. It was shown by Van Rijswijk [4] that the statistics of that process is also Gaussian. As a rule of a thumb this double scattering contribution will become significant when the average Rayleigh ration $R > 1\ m^{-1}$ or when turbidity exceeds $10\ m^{-1}$. As the secondary scattering volume $\gg$ primary scattering volume these are upper limits. The effect of multiple scattering shows up in the experiments as shown in figure 2 where the apparent diffusion coefficient is plotted against K^2. At a certain K ($= \frac{4\pi n}{\lambda_0} \sin \theta/2$), D^{app} is found from the initial slope of ln $G^2(t)$ i.e.

$$\lim_{t \to 0} \frac{\delta\{\ln G^2(t) - b\}}{\delta t} \equiv -2D^{app}K^2. \qquad (8)$$

As the decay rate of the double scattering correlation function is larger than the single scattering correlation function it follows that $D_{app} > D_0$. Reliable data fitting and evaluation of D_0 from dynamic light scattering data "contaminated" with multiple scattering are not possible on the same grounds as it is difficult to interpret scattering data from a polydisperse system. A way out of the problem was proposed by Dhont [5]. He expressed the contribution of second and higher order scattering events to the field strength (intensity) at the detector in a recurrent expression containing the lower order scattering. In an iterative scheme the respective contributions are calculated and so the "pure" first order scattering contributions are evaluated. With careful experiments, and precise knowledge of the scattering geometry this scheme extends the useful turbidity or Rayleigh factor range by a factor 10 but relies on computational methods.

4. EXPERIMENTAL ELIMINATION OF MULTIPLE SCATTERING IN DYNAMIC LIGHT SCATTERING

An experimental elimination of multiple scattering is to be preferred whenever possible. Phillies [6,7] devised a measuring procedure in which he showed that multiple scattering can be suppressed. A quantitative theoretical treatment was given by Dhont [8]. A schematic diagram of our experimental set up is given in Figure 3. The scattering geometry consists of two anti-parallel laser beams and perpendicular to that two opposing photo-multipliers which signals are cross-correlated. The resulting correlation function contains to a very good approximation no multiple scattering contributions.

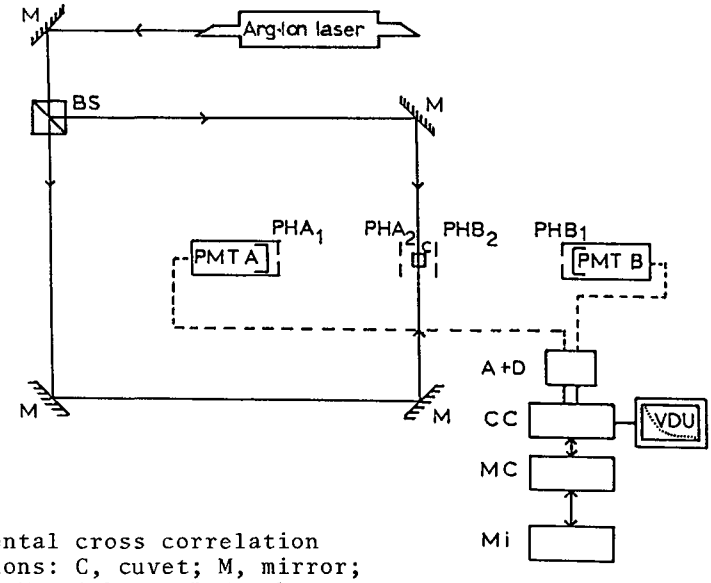


Figure 3

Scheme of experimental cross correlation set-up; abbreviations: C, cuvet; M, mirror; BS, beamsplitter; pH, pinhole; PMT, photomultiplier tube; A, amplifier; D. discriminator; VDU, visual display unit; CC, cross correlator; MC, micro computer; MI, mini computer.

5. THEORETICAL TREATMENT OF THE CROSS-CORRELATION

In order to understand and appreciate the underlying theory we give a treatment where only 90 degrees scattering of single and double scattering events are considered. This does not impose restrictions on the general validity of this treatment. The electric field strength of light scattered from laser beam A into detector A is:

$$E^A = E_1^A + E_2^A \tag{9}$$

where E_n represents n-fold scattered light. It was shown by Dhont(5) that

$$\vec{E}_1 = \frac{2\pi^2 K_0^2}{(2\pi)^3} e^{-\frac{1}{2}\tau l} \frac{e^{(-i\omega t + i\vec{K}_s.\vec{R}_s)}}{R_s} \sum_{j_0}^{N_0} \left(\int_{V_{j0}} \frac{\Delta\varepsilon(r'_{j_0})}{\varepsilon} e^{i(\vec{K}_0-\vec{K}_s).\vec{r}'_{j_0}} dr'_{j_0} \right) \times e^{i(\vec{K}_0-\vec{K}_s).\vec{r}_j} . \vec{T}(K_s)\vec{E}_0. \tag{10}$$

and

$$\vec{E}_2 = \frac{2\pi^3 K_0^3}{(2\pi)^6} e^{-\frac{1}{2}\tau l} \frac{e^{(-i\omega t + i\vec{K}_s.\vec{R}_s + i\pi)}}{R_s} \sum_{j_2}^{N_2} \sum_{j_1}^{N_1} \oint\int_{V_{j1}} \frac{\Delta\varepsilon(r'_{j_1})}{\varepsilon} e^{i(\vec{K}_0-\vec{K}_1).\vec{r}'_{j_1}} d\vec{r}'_{j_1} \times \int_{V_{j2}} \frac{\Delta\varepsilon(r'_{j_2})}{\varepsilon} e^{i(\vec{K}_1-\vec{K}_s).\vec{r}'_{j_2}} d\vec{r}'_{j_2} . e^{i(\vec{K}_0-\vec{K}_1).\vec{r}_{j_1}} e^{i(\vec{K}_1-\vec{K}_s).\vec{r}_{j_2}} . \vec{T}(K_s)\vec{T}(K_1)\vec{E}_0 dS_1. \tag{11}$$

The symbols have the following meaning (compare Figure 4).

$\vec{K}_0$ wave vector; length = $\frac{2\pi n}{\lambda_0}$ (m^{-1})

$\vec{K}_s$ scattered wave vector; length = $\frac{2\pi n}{\lambda_0}$ (m^{-1})

$\vec{K}_1$ scattered wave vector; length = $\frac{2\pi n}{\lambda_0}$ (m^{-1})

λ_0 wave length of laser light in vacuum (m)

n index of refraction of medium

ε dielectric constant of medium (= n^2)

$\Delta\varepsilon$ variation in dielectric constant

τ turbidity (m^{-1})

l length of light beam to reach edge of cell (m)

ω angular light frequency (0) $10^{14} s^{-1}$

$\vec{R}_s$ position of detector with reference to origin

N_0 number of particles in V_0

N_1 number of particles in V_1

N_2 number of particles in V_2

r'_{j_0} coordinate inside particle j_0 relative to its position coordinate $\vec{r}_{j_0}$

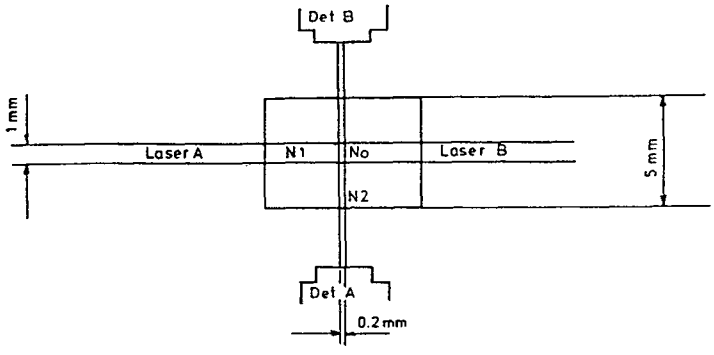
V_{j_0} volume of particle j_0

r_{j_0} position coordinate of particle j_0

$\vec{T}(K)$ $\vec{I} - \frac{\vec{K}\vec{K}}{|K|^2}$

$\vec{E}_0$ incident electric field strength

dS_1 infinitesimal element of half spherical surface with radius $|K_0|$ directed along the positive (or negative) z-axis in K_1 space.



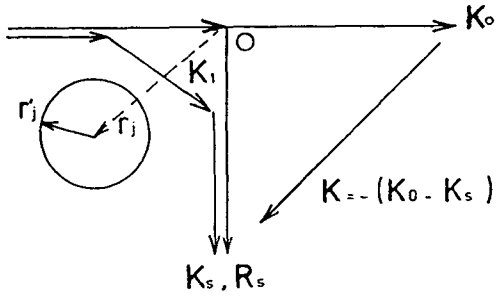


Figure 4. Scattering geometry and wave vectors.

As expressions (10) and (11) are rather lengthy and we are only interested in the relative magnitude of (contributions to) the correlation functions, we write :

$$E_1 \cong \sum_{j_0}^{N_0} e^{i(\vec{K}_0-\vec{K}_s).\vec{r}_{j_0}} \tag{12}$$

$$E_2 \cong \sum_{j_2}^{N_2} \sum_{j_1}^{N_1} \oint dS_1(\cdots)\, e^{i(\vec{K}_0-\vec{K}_1).\vec{r}_{j_1}}\, e^{i(\vec{K}_1-\vec{K}_s).\vec{r}_{j_2}} \tag{13}$$

Furthermore we will use:

$$E(t) = E_1(t)+E_2(t);\ \langle E(t)\rangle = 0;\ \langle E_1(t)\rangle = 0;\ \langle E_2(t)\rangle = 0 \tag{14}$$

and

$$I^A(t) = E^A(t)E^{*A}(t) \tag{15}$$

$$I^B(t) = E^B(t)E^{*B}(t)\ . \tag{16}$$

Then the intensity cross-correlation function is given by

$$\underline{\text{ICCF}} \quad G_c^2(t) \equiv \langle I^A(0).I^B(t)\rangle \tag{17}$$

while the intensity auto-correlation function is defined as:

$$\underline{\text{IACF}} \quad G_a^2(t) \equiv \langle I^A(0).I^A(t)\rangle \equiv \langle I^B(0).I^B(t)\rangle. \tag{18}$$

Substitution of the expressions (12) and (13) working out the ensemble averages and applying the "full" Siegert-relation leads after some algebra to the intensity correlation functions

$$\underline{\text{IACF}}: \quad \langle I(0)\ I(t)\rangle = \langle I\rangle^2 + \left|\langle E_1(0)E_1^*(t)\rangle + \langle E_2(0)E_2^*(t)\rangle\right|^2 \tag{19}$$

$$\underline{\text{ICCF}}: \quad \langle I^A(0)\ I^B(t)\rangle = \langle I^A\rangle\langle I^B\rangle + \left|\langle E_1^A(0)E_1^B(t)\rangle + \langle E_2^A(0)E_2^B(t)\rangle\right|^2 \tag{20}$$

Cross-terms containing terms like $\langle E_1.E_2\rangle$ are zero. Most strikingly is the apparent symmetry in the relations except that in the ICCF the non-complex conjugate products survive. This is a result of the fact that in the ICCF the intermediate scattering wave vector-$(K_0-K_s)=K^A$ is just anti parallel to K^B in contrast to the IACF. It may be emphasized that in using an incomplete Siegert relation the second term of the right hand side of (20) is not found at all, leading to the wrong conclusion that in the cross-correlation experiment no correlation is present.
Furthermore it follows that when double and higher order scattering are absent, the IACF = ICCF, which could also be argued on grounds of symmetry. It remains to be shown that the second order field strength correlation gives different contributions in the respective experiments. Substitution of (13) leads to

$$\langle E_2^A(0).E_2^B(t)\rangle = \sum_{j_4}^{N_4}\sum_{j_3}^{N_3}\sum_{j_2}^{N_2}\sum_{j_1}^{N_1}\oint dS_1 \oint dS_2\ (\ldots)^{*}(\ldots)$$

$$\times \langle e^{i\vec{K}_1^A.\vec{r}_{j_1}(0)}\ e^{i\vec{K}_2^A.\vec{r}_{j_2}(0)}\ e^{i\vec{K}_1^B.\vec{r}_{j_3}(t)}\ e^{i\vec{K}_2^B.\vec{r}_{j_4}(t)}\rangle . \qquad (21)$$

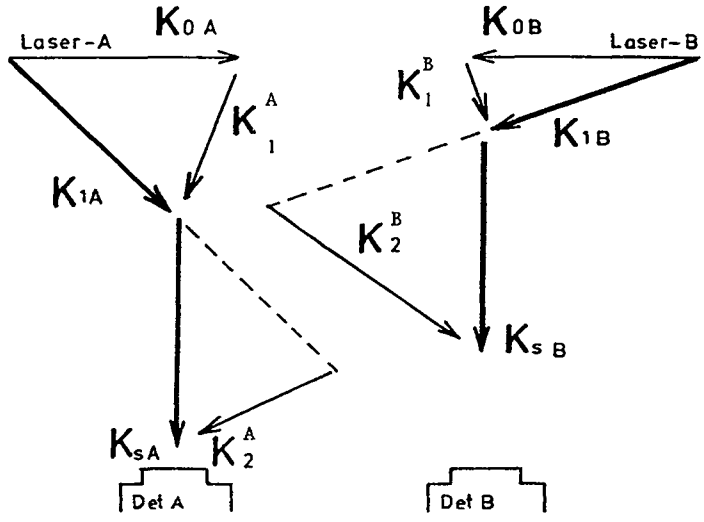


Figure 5. Definition of wave vectors.

In working out the ensemble average, we see that for $j_1 \neq j_2 \neq j_3 \neq j_4$ the net result is zero. So the following terms of the ensemble average remain

$$\text{I.}\quad \sum_{j_{1234}}^{N_{1234}} \langle e^{i\vec{K}_1^A.\vec{r}_{j_1}(0)}\ e^{i\vec{K}_1^B.\vec{r}_{j_3}(t)}\rangle \langle e^{i\vec{K}_2^A.\vec{r}_{j_2}(0)}\ e^{i\vec{K}_2^B.\vec{r}_{j_4}(t)}\rangle$$

+

$$\text{II.}\quad \sum_{j_{1234}}^{N_{1234}} \langle e^{i\vec{K}_1^A.\vec{r}_{j_1}(0)}\ e^{i\vec{K}_2^A.\vec{r}_{j_2}(0)}\rangle \langle e^{i\vec{K}_1^B.\vec{r}_{j_3}(t)}\ e^{i\vec{K}_2^B.\vec{r}_{j_4}(t)}\rangle$$

+

$$\text{III.}\quad \sum_{j_{1234}}^{N_{1234}} \langle e^{i\vec{K}_1^A.\vec{r}_{j_1}(0)}\ e^{i\vec{K}_2^B.\vec{r}_{j_4}(t)}\rangle \langle e^{i\vec{K}_2^A.\vec{r}_{j_2}(0)}\ e^{i\vec{K}_1^B.\vec{r}_{j_3}(t)}\rangle$$

II is independent of t, hence does not give rise to a time-correlation. Transforming the position coordinates $\vec{r}_i$ into $\vec{p}_{ij}(t) = \vec{r}_i(0)+r_j(t)$ and $\vec{q}_{ij}(t) = \vec{r}_i(0)-\vec{r}_j(t)$ and using the definitions

$$G_V(K,t) = \frac{\frac{1}{8}\int_V e^{i\frac{1}{2}\vec{K}.\vec{p}}\,d\vec{p}}{V}, \quad \text{form factor of scattering volume} \qquad (22)$$

$$F^{(i,j)}(K,t) = \frac{1}{\sqrt{N_i N_j}} \sum_i^{N_i} \sum_j^{N_j} \langle e^{i\vec{K}.(\vec{r}_j(0)-\vec{r}_i(t))} \rangle \qquad (23)$$

which we will call dynamic structure factor, leads after some algebra to the following expressions for I and III.

$$\text{I.} \quad \rho^2 V_1 V_2\, G_{V_1}\{(K_1^A + K_1^B)\}\; F_1^{(1,3)}\{(K_1^A - K_1^B),t\}$$

$$\times\, G_{V_2}\{(K_2^A + K_2^B)\}\; F_2^{(2,4)}\{(K_2^A - K_2^B),t\}$$

$$\text{III.} \quad \rho^2 V_1 V_2\, G_{V_1}\{(K_1^A + K_2^B)\}\; F_1^{(1,4)}\{(K_1^A - K_2^B),t\}$$

$$\times\, G_{V_2}\{(K_2^A + K_1^B)\}\; F_2^{(2,3)}\{(K_2^A - K_1^B),t\}.$$

Each term (I,III) is seen to contain the product of two form factors and two "dynamic structure factors". The form factors differ significantly from zero when their argument $(K^A + K^B) \to 0$. If particles are independent, of the structure factors only those terms in the double summation survive for which $j_i = j_j$.
These conditions are summarized as follows:

$$\text{I.} \quad K_1^A + K_1^B \approx 0;\ j_1 = j_3 \qquad\qquad \text{III.} \quad K_1^A + K_2^B \approx 0;\ j_1 = j_4$$

$$K_2^A + K_2^B \approx 0;\ j_2 = j_4 \qquad\qquad K_2^A + K_1^B \approx 0;\ j_2 = j_3$$

with $\vec{K}_{0A} = -\vec{K}_{0B}$; $\vec{K}_{sA} = -\vec{K}_{sB}$ it follows that both for I and III

$$\vec{K}_{1A} = -\vec{K}_{1B} \qquad \text{and} \qquad \vec{K}_{2A} = -\vec{K}_{2B}.$$

and state that, the scattering process must be completely antisymmetrical in A and B otherwise the contributions I and III average out to zero. We may visualize one situation (structure) occurring in the ensemble averages I and III as in Figure 6.
As we see the condition of an antiparallel scattering process is easily fulfilled in both cases. The condition for I that particle j_1 at r_{j1} coincides with particle j_3 at rj_3 can be fulfilled. However the condition that $j_4 = j_2$ cannot be met when we require $K^A = -K^B$ and $j_1 = j_3$.

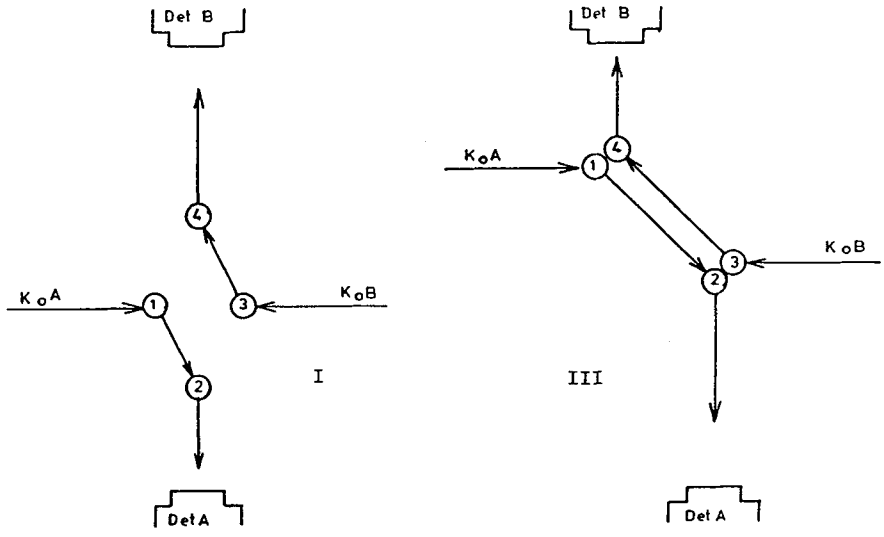


Figure 6. Schematic picture of double scattering process

Intuitively one suspects the scattering process in Figure 6.I not to be correlated. This is in contrast to the situation in Figure 6. III with $j_1 = j_4$ and $j_2 = j_3$. Now particles j_1 and j_3 are positioned in the spatially overlapping laser beams while j_3 and j_4 must be "visible" for the opposing detectors, compare Figure 4. The requirement that, at least for independent particles, $j_1 = j_4$ and $j_2 = j_3$ can therefore only be fulfilled in the intersection volume $V_1 \cap V_2 = V_0$.

The condition $j_1 = j_4$ actually is the condition that the positions of particles j_1 and j_4 are correlated. For independent particles this requires their coincidence. For highly structured suspensions their correlation may extend through the scattered volume. This was shown in an elegant experiment by Clark [9]. He also cross-correlated two photo-multipliers but these were directed on different parts of a colloidal crystal, thus showing the spatial correlation in the position of particles.

As we consider relatively dilute suspensions with independent particles we thus find that the only contribution, if any, to the correlated part of $\langle E_2^A(0) E_2^B(t) \rangle$ comes from V_0 and is given by

$$\langle E_2^A(0) E_2^B(t) \rangle = \int\int (\ldots)(\ldots) \rho^2 V_0^2 \times G_{V_0}(K_1^A + K_2^B) \cdot F_1^{(1,4)}\{(K_1^A - K_2^B), t\} \times G_{V_0}(K_2^A + K_1^B) \cdot F_2^{(2,3)}\{(K_2^A - K_1^B), t\} dS_1 dS_2. \quad (24)$$

In order to compare this to the conventional set up in auto-correlation we must calculate $\langle E_2(0)E_2^*(t)\rangle$. Again inserting the equation (14) for $E_s(t)$, working out the ensemble averages will lead to the conclusion that the scattering process at t = 0 and t = t must be correlated with respect to the position of the particles while from the geometrical factors it follows that the scattering vectors must be parallel. This is found by replacing every K_B- wave vector in equation (21) and in the ensemble averages by $-K_A$ because for the autocorrelation part we have $E_2^*(t)$, the complex conjugate. Then of the ensemble averages (I,II,IIf), the term I is nonzero leading to:

$$\langle E_2^A(0)E_2^{*A}(t)\rangle = \int\int (\ldots)(\ldots)\rho^2 V_1 V_2 \times G_{V_1}(K_1^A - K_1^A) \cdot F_1^{(1,3)}\{(K_1^A + K_1^A), t\} \times G_{V_2}(K_2^A - K_2^A) \cdot F_2^{(2,4)}\{(K_2^A + K_2^A), t\} dS_1 dS_2. \quad (25)$$

Again we may visualize this contribution as in figure 7.

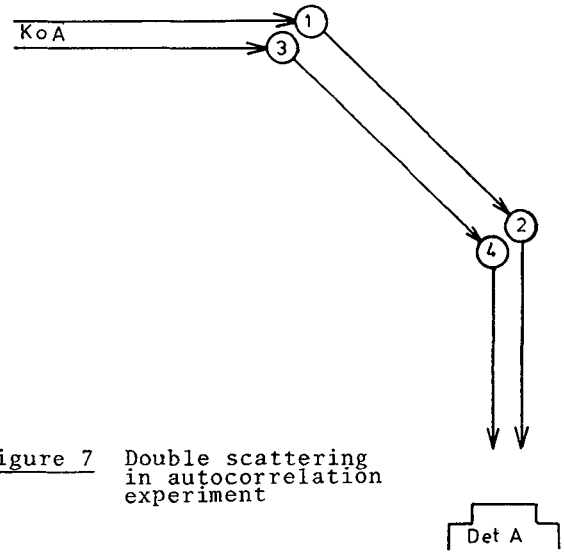


Figure 7 Double scattering in autocorrelation experiment

Expressing K_1^A, K_2^A, K_1^B and K_2^B in terms of K_{1A} and K_{1B} it follows that the relative contributions to the correlated part of the correlation functions are found as:

$$\underline{\text{IACF:}}\ \frac{\langle E_1(0)E_1^*(t)\rangle}{\langle E_2(0)E_2^*(t)\rangle} \sim \frac{V_0^2}{V_1 V_2} \qquad \underline{\text{ICCF:}}\ \frac{\langle E_1(0)E_1(t)\rangle}{\langle E_2(0)E_2(t)\rangle} \sim \frac{V_0^2}{V_0^2}$$

Hence the relative double scattering contribution is suppressed by a factor V_0^2/V_1V_2 in the ICCF relative to the IACF.

As similar result was given by Phillies[7,8] but based on a less rigorous treatment. The result may be interpreted by saying that double scattering is proportional to the number of scatterers "available"

for the first order scattering and for the second order scattering i.e. V_1V_2. In the cross correlation experiment this is confined to the square of the intersection of $V_1 \cap V_2 = V_0$.

A quantitative estimate of V_0^2/V_1V_2 is 2.10^{-3} as calculated from figure 4 where we give representative dimensions for a typical scattering experiment. For ease of calculation we consider a rectangular geometry.

It may indeed be argued that employing a very small scattering cell (V_0) would lead to the same result. In that situation however the presence of the cell walls will give an unwanted contribution to the dynamic structure factor. A marked example of that effect is found by Hurd [10] et al. On the other hand Pusey [11] uses the proportionality factor V_1V_2 in equation 25 to detect multiple scattering contributions to his measurements by varying the position of the scattering volume in the cell. In this way V_1V_2 is changed and accordingly the relative contribution of the multiple scattering.

In the above treatment we considered scattering of radiation from laser A into detector A only and similarly for B. Interchanging either detector A and B or laser A and B does give exactly the same contribution to the correlated part of the ICCF. All other scattering geometries do not contribute.

Alignment of the set-up requires a high degree of precision as follows from the following reasoning. The geometrical factors $G_{V_0}(K)G_{V_0}(K)$ already become very small when the product $|\vec{K}|a$ is only slightly different from zero. Allowing a 10-fold decrease in the product $G_{V_0} \cdot G_{V_0}$ from 1 to 0.1 gives $G_{V_0} \approx 0.3$. As a typical dimension of the scattering volume is $a=10^{-4}m$ we calculate $\Delta K \approx 10^4 m$. From $\Delta K = 4\pi n/\lambda \sin(\theta/2)$ where θ is the "misalignment"angle, we calculate $\theta = 6.10^{-4}$ (rad) or roughly 1 mm per meter. For this reason one should use small pinholes and a non-divergent laser beam.

6. EXPERIMENTAL RESULTS

As expected it appeared to be rather difficult to align all optical components of figure 3 in such a way that a cross correlation signal was observed. When using an argon-ion laser in the current-stabilized mode the correct positioning of the optical parts is manifested by a sharp upswing in light output of the laser. The reason for this is, that an extended cavity is made. Actually placing the cell in the cavity of a laser would be easiest, but then threshold will not be reached with turbid samples. To get things started we mainly used the following optical train, which can be applied with medium turbid samples and is easier to operate than the set-up of figure 3.

In figure 9 we plotted apparent diffusion coefficients (according to equation 8) as a function of sample turbidity. We made two series of measurements i) a square 1 cm optical cuvet is used and ii) a rectangular 2 x 5 mm inside measure cuvet is used. The scattering sample was a 40 nm radius sterically stabilized silica dispersed in toluene $|n_p - n_{solv.}| \approx 0.05$.

As the cells were not thermostated there is still some scattering in the cross-correlated data, especially as the measurements were made over a period of a few weeks. In our opinion figure 9 shows unambiguously that the experimental set-up is capable of suppressing very efficiently multiple scattering for rather turbid samples.

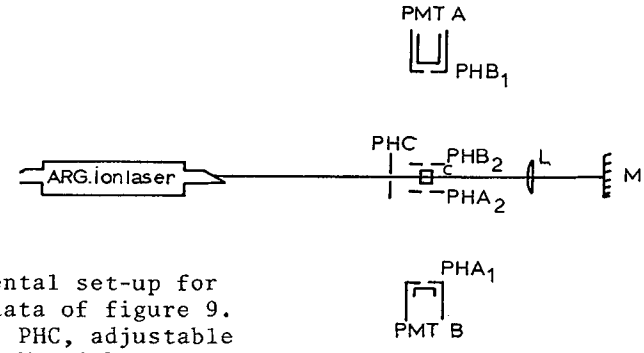


Figure 8 Actual experimental set-up for obtaining the data of figure 9. Components are: PHC, adjustable vertical slit; pH, pinholes; c, measuring cell; M, flat mirror; L. cylindrical lens; PMT, photomultiplier tube.

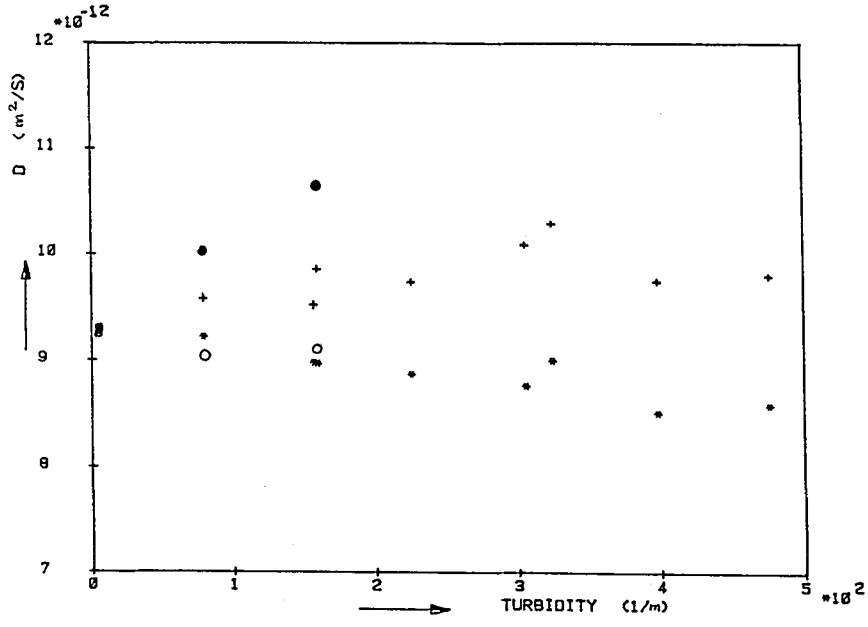


Figure 9. Experimental results. The apparent diffusion coefficient plotted against turbidity of the sample ; o, 1cm^2 cuvet ICCF ; •, 1cm^2 IACF ; *, 2x5mm^2 ICCF ; +, 2x5mm^2 IACF.

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