ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 122 (1997) 83–87

COLLOIDS AND SURFACES A

Probing dynamics of dense suspensions: three-dimensional cross-correlation technique

Ekkehard Overbeck, Christian Sinn, Thomas Palberg, Klaus Schätzel †

Institut für Physik der Johannes-Gutenberg-Universität, Staudingerweg 7, D-55099 Mainz, Germany

Received 20 March 1996; accepted 10 August 1996

Abstract

We describe the realization of a novel three-dimensional (3D) cross-correlation scheme, which provides the possibility to measure dynamic structure factors of highly concentrated colloidal samples without contributions of multiply scattered light. The apparatus is easier to align and more compact than the two-colour cross-correlation apparatus, which is commercially available. This should make the 3D cross-correlation set-up more convenient for routine applications, for example in industrial laboratories. We describe the set-up and discuss some special features of the optical components. © 1997 Elsevier Science B.V.

Keywords: Colloidal physics; Cross-correlation; Dynamic light scattering; Multiple scattering

1. Introduction

Light scattering has been shown to be a powerful tool for the investigation of colloidal samples. The conventional optical set-up, however, limits measurements to moderately concentrated suspensions, because increasing particle concentration leads to increasing multiple scattering contributions.

The strategy therefore is to isolate singly scattered light by performing two scattering experiments simultaneously on the same scattering volume and cross-correlating the signals obtained. If both experiments share the same scattering vector $\boldsymbol{q}$, but use different scattering geometries, only singly scattered light will produce correlated intensity fluctuations on both detectors. In contrast, multiply scattered light, scattered in a succession of generally different $\boldsymbol{q}$ vectors, results in uncorrelated fluctuations, which contribute to the background only.

Here we describe a technical implementation of a novel cross-correlation scheme, which has been proposed by Schätzel [1]. Since then, many ideas have been exchanged in the community about the feasibility of such an experiment. We demonstrate that the components compiled in our set-up are working. This contribution will therefore give an outline of our work in progress.

2. Two-colour cross-correlation technique

A cross-correlation technique was first described by Phillies [2] and later implemented in a more versatile way by Drewel et al. [3] as two-colour dynamic light scattering (TCDLS); the latter apparatus is now commercially available (ALV Laser–Vertriebsgesellschaft, Langen, Germany). In this scheme the condition of equal scattering vec-

---

† Deceased.

PII S0927-7757(96)03842-3

tors in different geometries is realized by using beams of two different wavelengths (the blue and green main lines of an Ar^+ laser), scattered under two slightly different scattering angles θ_1, θ_2 (see Fig. 2(b)). For each chosen $q_1=(4\pi n/\lambda_1)\times\sin(\theta_1/2)=q_2$, the small difference angle $\delta_{2C}=(\theta_1-\theta_2)/2$ has to be carefully adjusted for every new scattering angle $\theta=\theta_1-\delta_{2C}=\theta_2+\delta_{2C}$ in both transmission and receiving optics, because $\boldsymbol{q}_1=\boldsymbol{q}_2$ leads to the condition $\tan(\delta_{2C}/2)=[(\lambda_1-\lambda_2)/(\lambda_1+\lambda_2)]\tan(\theta/2)$; cf. Eq. (3) of Ref. [4]. This symmetrical alignment is rather difficult and requires complex optomechanical components.

Figs. 1(a) and 1(b) compare the dynamic structure factor of polystyrene spheres in aqueous solution measured in two samples of strongly different turbidities [4]. The particle radius $R=56$ nm, and the measurements were performed at $q=18\ \mu m^{-1}$. The open symbols refer to a conventional (autocorrelation) dynamic light scattering (DLS) experiment, while the full symbols refer to the two-colour experiment (TCDLS). In the dilute sample almost identical structure factors are measured in both experiments. In the concentrated sample (transmission only 1%, compared with 90% of the diluted sample) DLS reveals an apparent fast relaxation, which is an artefact due to multiple scattering. This contribution can be suppressed almost completely, which can be seen in the straight line measured by TCDLS. The intercept of the correlation function of a scattering experiment reflects the coherence of the detection. The reduced intercept in Fig. 1(a) of TCDLS compared with DLS is due to the incomplete overlap of the scattering volumes of the two light paths, which demonstrates the previously mentioned difficult alignment experimentally. Multiply scattered light is decorrelated by the cross-correlation technique and reduces the intercept further, which is also clearly visible in Fig. 1(b). These effects are already documented in the literature; for details cf. Schätzel [1] for a theoretical discussion and Segrè et al. [4] for the experimental point of view.

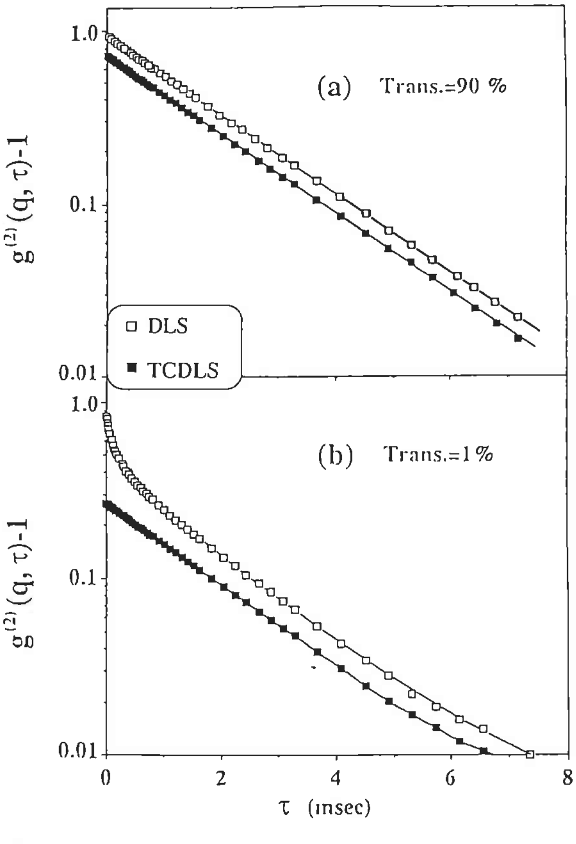


Fig. 1. Dynamic structure factor of aqueous suspensions of polystyrene spheres of radius $R=56$ nm, measured by a DLS set-up (open symbols) and the two-colour scheme (full symbols) ($q=18\ \mu m^{-1}$): (a) dilute sample, transmission $T=I/I_0=90\%$; (b) concentrated sample, $T=1\%$.

3. Three-dimensional cross-correlation scheme

On the basis of our experience with TCDLS and Schätzel's considerations [1], we are currently realizing an alternative approach to the cross-correlation technique.

We here propose a scheme which avoids the disadvantage of the complex alignment of the TCDLS by making use of the third dimension, while applying the same principle as the TCDLS. The different experiments, which are necessary for the suppression of multiple scattering, are performed by placing two lasers (and two detectors) at an angle $\delta_{3D}/2$ over and below the plane of symmetry of the scattering experiment. The same $\boldsymbol{q}$ vector is obtained by using two lasers having the same wavelength. Fig. 2 shows the succession in complexity of the scattering experiments as sketches of the wavevector arrangements, begin-

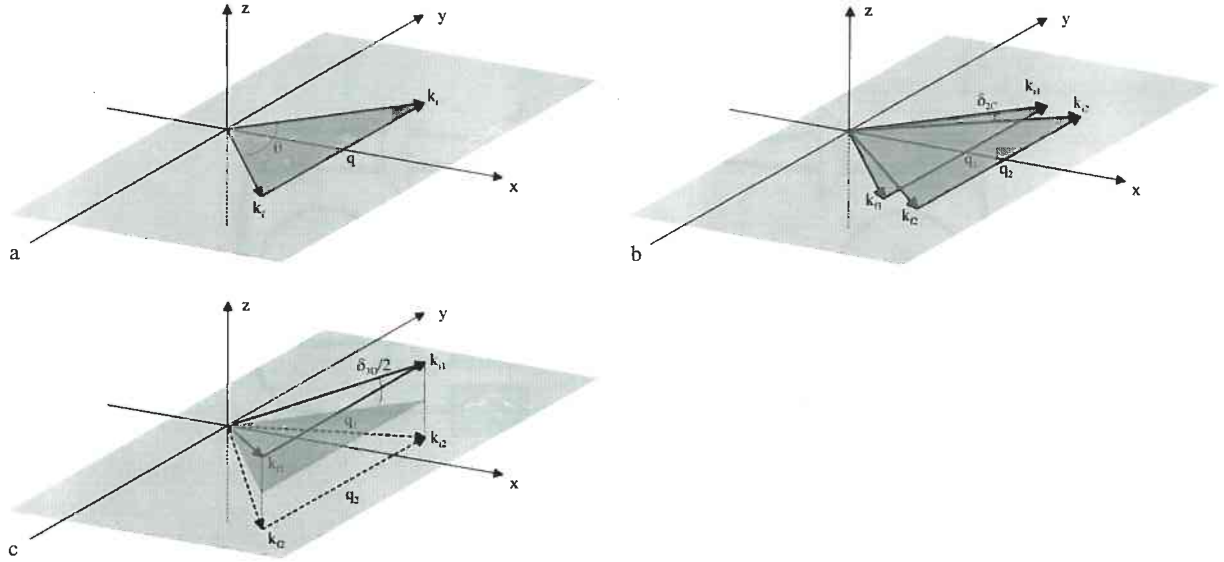


Fig. 2. Wavevector arrangements of three different scattering schemes. (a) Conventional (autocorrelation) technique: $\boldsymbol{k}_i$, incident wavevector; $\boldsymbol{k}_f$, final wavevector; θ, scattering angle; $\boldsymbol{q}=\boldsymbol{k}_i-\boldsymbol{k}_f$, scattering vector with $|\boldsymbol{q}|=(4\pi n/\lambda)\sin(\theta/2)$. (b) Two-colour cross-correlation technique; the numbers 1 and 2 refer to the different light paths; δ_{2C} is the difference angle between the two paths with different colour, on both the transmission and the receiving side; $\boldsymbol{q}_1=\boldsymbol{k}_{i1}-\boldsymbol{k}_{f1}=\boldsymbol{q}_2=\boldsymbol{k}_{i2}-\boldsymbol{k}_{f2}$; note that all vectors share the same (scattering) plane. (c) 3D cross-correlation technique; the numbers 1 and 2 refer to the different light paths, in this case, however, with the same colour; δ_{3D} is the difference angle between the two paths; note that the arrangement is symmetrical with respect to the shaded area; as in (b), $\boldsymbol{q}_1=\boldsymbol{k}_{i1}-\boldsymbol{k}_{f1}=\boldsymbol{q}_2=\boldsymbol{k}_{i2}-\boldsymbol{k}_{f2}$ is fulfilled.

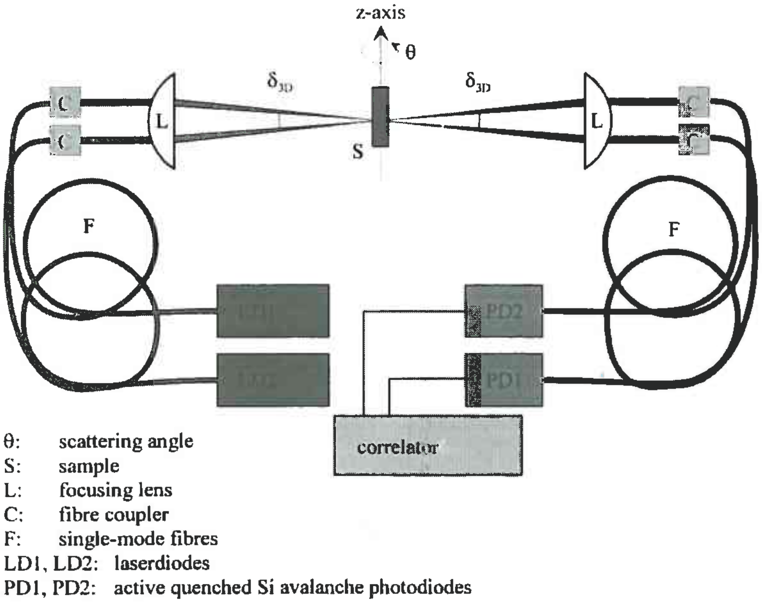
ning with the conventional technique (Fig. 2(a)) and ending with the three-dimensional (3D) set-up (Fig. 2(c)). The main advantage compared with TCDLS is that both lasers work with the same wavelength; thus no difference angle has to be re-adjusted. In fact, in this experiment the difference angle is only used to distinguish between the light paths and may adopt the appropriate value. This feature of the technique, however, bears in itself a loss in resolution power. Because, in principle, the experiment also detects the scattering events $\boldsymbol{q}_1=\boldsymbol{k}_{i1}-\boldsymbol{k}_{f2}$ or $\boldsymbol{q}_2=\boldsymbol{k}_{i2}-\boldsymbol{k}_{f1}$ neither of which equals $\boldsymbol{q}_1=\boldsymbol{q}_2$, the maximum intercept obtainable is only half the value of TCDLS [1].

4. Special features of the experimental set-up

Fig. 3 shows the experimental set-up. The layout of the apparatus is optimized towards measurements at the highest possible sample turbidity. In order to reduce the scattering cross-section of the samples, the wavelength of both of the laser diodes used is chosen to be in the near-IR region. For practical reasons we use GaAlAs laser diodes having a wavelength $\lambda=790$ nm, which is just perceptible to the naked eye. The diodes (Mitsubishi ML 64114R) emit approximately 50 mW of power, which should be sufficient to compensate for the coupling losses into a polarization-maintaining fibre. Single-mode fibres are used, in the illuminating as well as in the receiving light paths, because they guarantee a perfect Gaussian beam profile, which in turn allows a high intercept of the correlation function to be obtained [5,6].

The small fibre-optical components allow for a very compact set-up, which in addition is easier to align compared with the TCDLS apparatus; one alignment feature, for example, is the common large lenses for both light paths on the transmission and the detection sides, which fix the maximum difference angle δ_{3D} via their aperture used.

In view of the low quantum efficiency of photomultipliers in the near-IR spectral region, we side view for θ = 0:



top view for arbitrary θ:

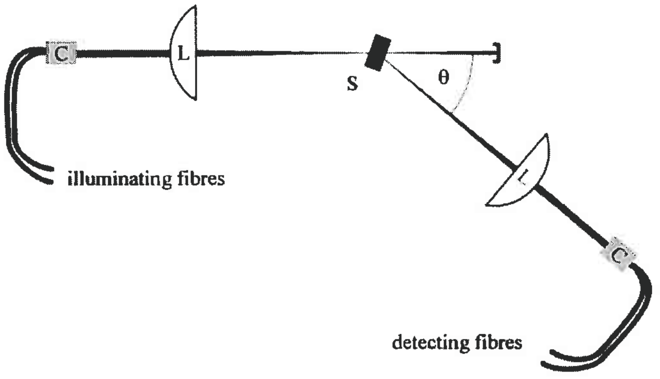


Fig. 3. Side view and top view of the experimental set-up.

choose avalanche photodiodes (EG & G C30921S) as single-photon counters. An active quenching circuit is realized in order to single-photon events to be detected. As commercial modules have only recently become available (EG & G Optoelectronics, Ottawa, Canada), the electronics is homebuild. While its general principle is straightforward, its realisation bears its own challenge.

Neither laser diodes nor avalanche photodiodes belong to the standard equipment of a light scattering experiment. The technical characterization of the equipment has therefore been of primary importance. We hope to demonstrate the advantages of our approach for the investigation of concentrated colloidal suspensions in the near future.

5. Conclusion

We have developed a novel scheme for the measurement of dynamic structure factors by photon correlation spectroscopy in concentrated samples free from multiple scattering contributions. The proposed set-up is easier to align and more compact than the available two-colour technique, but will provide the same experimental possibilities.

References

[1] K. Schätzel, J. Mod. Opt., 38 (1991) 1845–1865.
[2] G.D.J. Phillies, Phys. Rev., 24 (1981) 1939–1943.
[3] M. Drewel, J. Ahrens and U. Podschus, J. Opt. Soc. Am. A, 7 (1989) 206–210.
[4] P.N. Segrè, W. van Megen, P.N. Pusey, K. Schätzel and W. Peters, J. Mod. Opt., 42 (1995) 1929–1952.
[5] J. Rička, Appl. Opt., 32 (1993) 2860–2875.
[6] T. Gisler, H. Rüger, S.U. Egelhaaf, J. Tschumi, P. Schurtenberger and J. Rička, Appl. Opt., 34 (1995) 3546–3553.