Characterisation of Particle Assemblies by 3D Cross Correlation Light Scattering and Diffusing Wave Spectroscopy

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ABSTRACT

To characterize the structural and dynamic properties of soft materials and small particles, information on the relevant mesoscopic length scales is required. Such information is often obtained from traditional static and dynamic light scattering (SLS/DLS) experiments in the single scattering regime. In many dense systems, however, these powerful techniques frequently fail due to strong multiple scattering of light. Here I will discuss some experimental innovations that have emerged over the last decade. New methods such as 3D static and dynamic light scattering (3D LS) as well as diffusing wave spectroscopy (DWS) can cover a much extended range of experimental parameters ranging from dilute polymer solutions, colloidal suspensions to extremely opaque viscoelastic emulsions.

Keywords: Light Scattering, Diffusing Wave Spectroscopy, Microrheology, Colloids.

1. INTRODUCTION

To characterize the structural and dynamic properties of soft materials and small particles, information on the relevant mesoscopic length scales is required. Such information is often obtained from traditional static and dynamic light scattering (SLS/DLS) experiments in the single scattering regime[1-3]. In many dense systems, however, these powerful techniques fail due to strong multiple scattering of light. Here I will discuss some experimental innovations that have emerged over the last decade[4,5] with the aim to overcome such limitations. New concepts and technological advances[6] have led to a more widespread application of methods such as 3D static and dynamic light scattering (3D LS)[4,6] as well as diffusing wave spectroscopy (DWS)[4-7]. To illustrate their use and range of applications I refer to some examples from our own research such as the study of thermosensitive microgel particles[8], strongly interacting charged colloids[9], dense colloidal gels[10], the microrheology of wormlike micelle solutions[11] and the glassy dynamics and elasticity of monodisperse emulsions[12].

2. METHODS, RESULTS AND DISCUSSIONS

I will focus my attention on two complementary light scattering techniques in their most advanced realizations. The first method I'll discuss is *Modulated 3D cross-correlation light scattering*. This technique is based on a traditional goniometer based light scattering design for static and dynamic measurements as it has been used for several decades[1,3]. Multiple-scattering suppression can be achieved by using a beam-detector pair displaced symmetrically in a third dimension, instead of the standard single beam/detector configuration, Figure 1 a). This extended configuration is known as the 3D cross-correlation geometry[13] and is routinely used by a number of laboratories around the world since it's commercial introduction in the early 2000's. However, one important drawback of the 3D-technique is that one photon detector measures the scattered light intensity at the desired scattering vector, but also receives a contribution at a second undesired scattering vector. The latter leads to a fourfold reduction in the cross-correlation intercept due to cross-talk between the two simultaneous scattering experiments executed in this way. This in turn adversely affects the accuracy and precision when fitting models to the measured data. For strongly scattering samples, where only a small component of the detected light is singly scattered, the signal-to-noise ratio of the measurement becomes unacceptably low as the magnitude of the cross-correlation intercept falls into the noise of the baseline fluctuations.

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We recently demonstrated a significant improvement to this method in which the two scattering experiments are temporally isolated by modulating the incident laser beams and gating the detector outputs at frequencies exceeding the timescale of the system dynamics (inset Figure 1 a). This robust modulation scheme eliminates crosstalk between the two beam-detector pairs and leads to a fourfold improvement in the cross-correlation intercept, Figure 2a). Alternate shuttering of the laser beams is accomplished using acousto-optic modulators (AOM's, Figure 1 b)) as described in detail in reference[6].

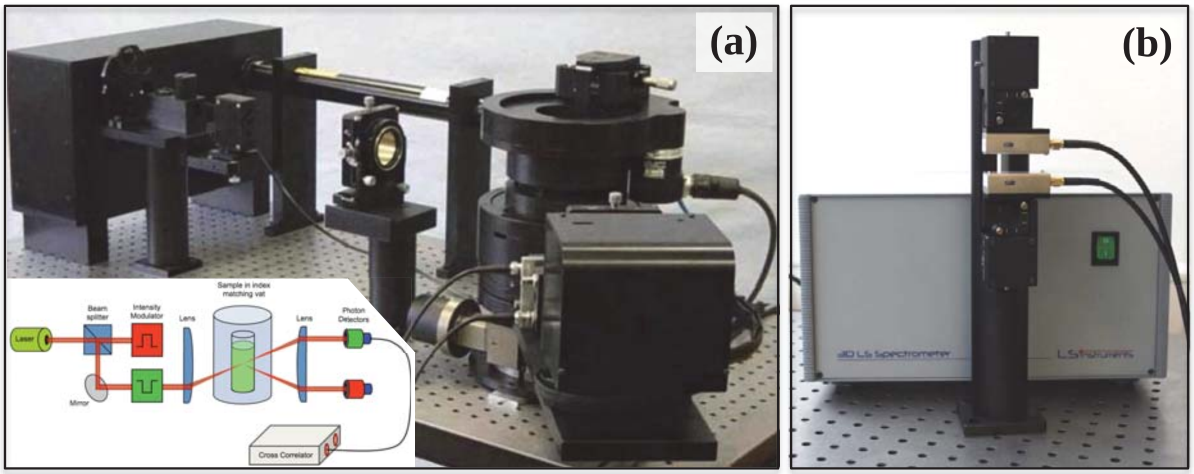

Figure 1. **Modulated 3D light scattering**. (a) 3D Cross Correlation Light Scattering Goniometer. Inset: Principle of time gating the beam-detector pair. (b) Pair of acousto-optical modulators (AOM) employed as MHz-frequency shutters when inserted into the beam bath (Pictures courtesy of LSInstruments AG, Fribourg, Switzerland).

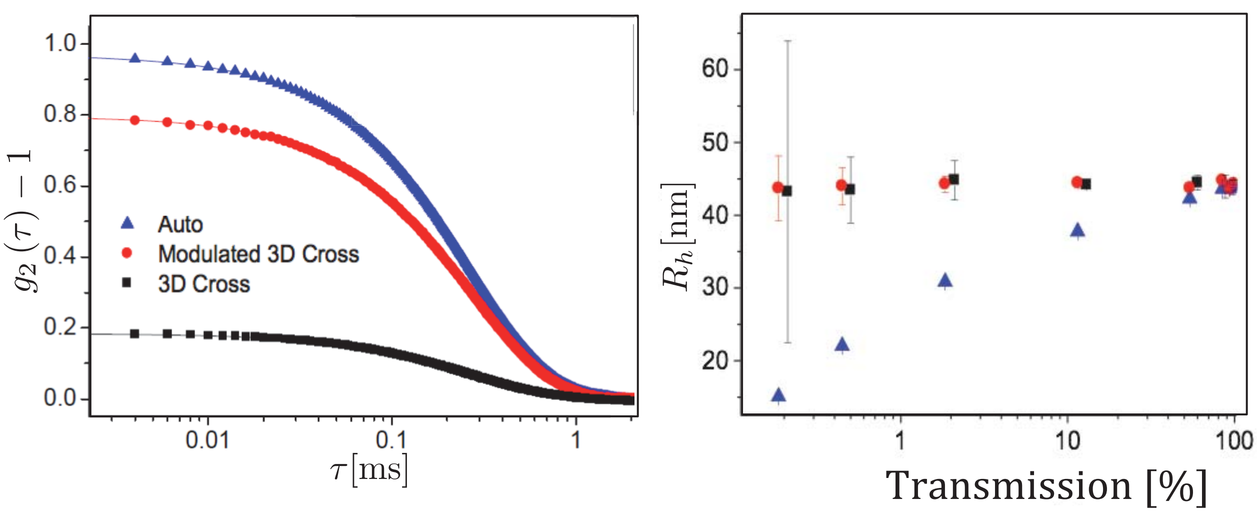

Figure 2. **Modulated 3D light scattering**. (a) Intercept of the correlation function for the three different cases (b) Hydrodynamic radius extracted from the measurements as a function of sample turbidity for each of the three correlation methods. Modulated 3D cross offers by far the highest accuracy and precision.

The second method I'll discuss is *Echo Two Cell Diffusing Wave Spectroscopy*. The initial realization of Diffusing Wave Spectroscopy (DWS), introduced in the late 1980's[14], is based on the analysis of intensity fluctuations in the multiple scattering regime using a single beam/detector configuration analogous to the case of dynamic light scattering (DLS). Here, rather than trying to suppress multiple light scattering, the method allows to extract meaningful information directly from diffusely scattering light. In contrast to standard DLS the DWS method cannot provide q-dependent information and therefore a goniometer is normally not required. DWS is typically used for the study of highly opaque and concentrated samples such as particle dispersions, emulsions and foams. Many of these systems, however, are

viscoelastic liquids or solids that relax very slowly or do not relax at all over the typical time scale of a measurement. This severely complicates DWS since it prevents efficient time averaging by photon correlation spectroscopy.
Using a multi-speckle analysis scheme this problem can be solved[4]. By recording spatially averaged data instead of time averages a near real-time analysis can be performed even for viscoelastic samples. This can be achieved using a digital camera[15], or, as we could demonstrate, by putting a fast rotating diffuser in the optical path between laser and sample[16], Figure 3a). We could show that the recorded multi-speckle correlation echoes can be used to extract an ensemble-averaged signal that does not require additional time averaging, Figure 3 b). The advantage of our method is that it can be simply added to the traditional single beam/detector configuration and thus the possibility to access short and long relaxation times is preserved[4].

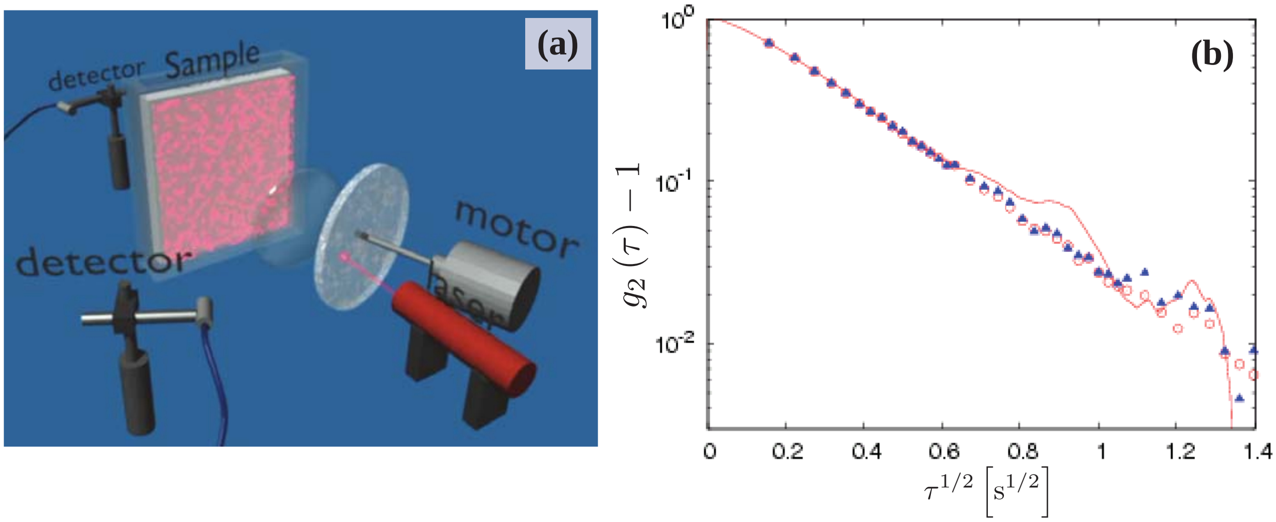

Figure 3. **Echo Two-Cell Diffusing Wave spectroscopy**. (a) Experimental setup for echo-two cell DWS in a schematic view (Graphics in panel a) by Dr Pavel Zakharov). (b) Intensity correlation function from backscattering DWS of titania suspended in glycerol[16]. Solid line: time averaging over 20 min., Symbols: echo analysis of a 12 s measurement using two different algorithms.

3. CONCLUSION

Recent advances in light scattering have enabled researchers to cover an extended range of experimental parameters. Significant progress has been made in particular concerning measurements on strongly scattering samples as well as systems that relax slowly or that are dynamically arrested (such as networks and gels). Here I have discussed two of our main recent contributions to this field of research on light scattering based technologies for the characterization of particle assemblies.

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