Master Thesis

Double Pulse Correlation Spectroscopy with Visible Light

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Abstract

In this master thesis the setup for Double Pulse Photon Correlation Spectroscopy (DPPCS) has been developed. A novel sample environment has been constructed that includes 3D-printed sample holders and four electric motor stages to translate the sample and rotate the detector. The beam size and particle size have been determined by autocorrelation and static light scattering. Then speckle patterns have been measured in continuous mode and pulsed mode. The stability of the setup was verified with a static sample. The beam size of the focused laser beam at the sample has been measured from the speckle patterns recorded as a function of time. Various concentrations of silica and polystyrene samples with radii ranging from 25 nm to 5 μm have been dissolved in water and used to verify the performance of the setup. Static Light Scattering (SLS) measurements showed the expected size of the investigated particles. The dynamics of the sample was investigated in sequential and double pulse mode. The fastest dynamics at the highest angles were measured in pulsed mode, the lowest characteristic time measured for r=25 nm polystyrene at 40° was $\tau_c = 2.3 \pm 0.1 ms$. In sequential mode a comparable $g_2$-curve was limited to a r=407 nm particle size at 20°. Both methods are in good agreement showing the good performance of the DPPCS setup.
Zusammenfassung

In dieser Masterarbeit wurde ein Aufbau zur Photon Korrelationsspektroskopie mit Doppelpulsen (DPPCS) erstellt. 3D-gedruckte Probenhalter und vier elektrische Motoren zum Bewegen der Probe und des rotierenden Detektorarms ergänzen und vereinfachen die Variation von Parametern während einer Messung.

Strahlgröße und Teilchengröße wurde mit Autokorrelation von Specklemustern und statischer Lichtstreuung als Charakterisationsmessung bestimmt. Anschließend wurden Streumuster im kontinuierlichen Modus und mit Doppelpulsen gemessen. Im gepulsten Modus konnten dabei weit schnellere Dynamiken unter höheren Winkel betrachtet werden als im kontinuierlichen Modus. Die kleinste charakteristische Zeit für eine r=25 nm Polystyrolprobe bei 40° wurde mit DPPCS auf $\tau_c = 2.3 \pm 0.1 \text{ ms}$ bestimmt. Im kontinuierlichen Modus konnten $g_2$-Funktionen mit einem vergleichbaren Kurvenausschnitt nur bis 20° und mit r=407 nm Silicaproben beobachtet werden. Die Übereinstimmung beider Methoden belegt die gute Leistung des DPPCS Aufbaus.
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Chapter 1

Introduction

This master thesis presents Double Pulse Photon Correlation Spectroscopy (DPPCS) as a novel tool to characterise dynamics of colloidal systems with visible light. Conventional Photon Correlation Spectroscopy (PCS) [1] allows to investigate dynamics of colloidal suspensions from about microseconds to seconds (as shown in Fig. 1.1) by using a point detector at a single scattering angle per measurement. DPPCS extents the PCS technique by employing a double pulse laser time structure and a 2D detector. In this way fast dynamics of the sample can be traced simultaneously at different scattering angles. In this work the pulses were generated from a CW laser ($\lambda=633$ nm) by an acusto-optic modulator (AOM). The time resolution is no longer restricted by the detector frame rate but by the time spacing between the two pulses. In contrast to PCS the minimum time delay is limited to the pulse length of each of the two pulses.

The Photon Correlation Spectroscopy technique can be also applied with x-ray sources (so called XPCS). Then it is allowing access to length scales close to a few angstrom (see Fig. 1.1). However, the implementation of the double DPPCS in the x-ray range brings high complexity. It requires ultra-intense, ultra-short and coherent x-ray pulses. These requirements are fulfilled by X-ray Free Electron sources (XFEL) [2, 3, 4]. Existing double pulses schemes include XFEL accelerator based techniques of crystal optics split-and-delay lines [5, 6]. In the latter case the XFEL pulse is split into two pulses and travels through pathways of different length. X-ray optical components for split-and-delay lines are highly sophisticated and very often have to be developed. Optics for visible light are not a limiting factor and are conventional.

This thesis is organized as follows: Chapter 2 contains the theory behind conventional PCS that employs a continuous beam and the double pulse approach DPPCS using discreet pulses. The experimental setup including specifications about motorisation, sample holders and sample systems is described in chapter 3. The following chapter contains details about the software which was written exclusively to analyse data taken with the built setup. In chapter 5 the results from the measurements are presented and in chapter 6 an outlook to possible further applications is given. At the end the work is summarized.
Figure 1.1: PCS probes length scales from few millimeters to several 100 nanometers while XPCS can go down to a few angstrom [7].
Chapter 2

Theory

2.1 Static Light Scattering from Colloidal Suspensions

In a light scattering experiment a monochromatic laser beam illuminates a colloidal sample and is elastically scattered under an angle $2\Theta$ into a detector. The magnitude of the incident wave vector $\vec{k}_i$ and the emerging wave vector $\vec{k}_e$ is defined by

$$\vec{k}_i = \frac{2\pi n}{\lambda_i} \quad \text{and} \quad \vec{k}_e = \frac{2\pi n}{\lambda_e}$$ (2.1)

where $\lambda_i$ and $\lambda_e$ denote the wavelength of the incident and outgoing wave respectively and $n$ denotes the refractive index of the scattering medium. In the elastic scattering case the magnitude of the incident wave vector $\vec{k}_i$ equals the emerging wave vector $\vec{k}_e$. Subtracting $\vec{k}_e$ from $\vec{k}_i$ (see Fig. 2.1) defines the scattering vector $\vec{q}$:

$$\vec{q} = \vec{k}_i - \vec{k}_e$$ (2.2)
When single particle scattering is assumed the absolute value of the scattering vector $\vec{q}$ is calculated as

$$|q| = \frac{4\pi n}{\lambda} \sin(\Theta)$$  \hspace{1cm} (2.3)$$

where $2\Theta$ is the angle between $\vec{k}_i$ and $\vec{k}_e$. The intensity of an electromagnetic wave is the product of the amplitude $A(q)$ and its complex conjugate.

$$I(q) = A(q) \cdot A^*(q)$$  \hspace{1cm} (2.4)$$

$$A(q) = \int \rho(r)e^{-qr}dr$$  \hspace{1cm} (2.5)$$
is the Fourier transformation of the charge density $\rho(r)$.

For scattering from more than one particle the measured intensity $I(q) = F(q)S(q)$ is made up of the form factor and the structure factor $S(q)$. The structure factor defines interparticle interactions and becomes 1 for high $q$-values or dilute systems without interactions between the particles [8]. The distribution of light scattered form a single spherical particle to a specific angle (scattering wave vector) is given by the form factor $F(q)$:

$$F(q) = \frac{I(q)}{I(0)} = 9\left(\frac{\sin(qr) - qrcos(qr)}{(qr)^3}\right)^2$$  \hspace{1cm} (2.6)$$

The radius $r$ of the particles defines the width of the oscillations given by the sinus and cosine function. If the system is dilute and there are no interactions between these particles, the size of the the particles can be calculated by analysing the intensity pattern. It should be noted that at large wave vector transfers the intensity follows the Porod law $I(q) \propto \frac{1}{q^4}$ [9].

Polydispersity

In reality the size of the particles varies from particle to particle. Polydispersity $\delta$ is a measurement of the distribution of particle sizes within one suspension. Size distribution is described with $\Delta r$ over the mean radius $r_0$ by the Schulz-Flory Distribution Function [10]:

$$a(r) = \frac{r^Z}{\Gamma(Z+1)}\left(\frac{Z+1}{r_0}\right)^{Z+1}e^{-\frac{r}{r_0}(Z+1)}$$  \hspace{1cm} (2.7)$$

where $\Gamma(\ldots)$ is the gamma function and $Z$ the coupling degree, the number of independent chains that are coupling to a discontinued chain.

With this the form factor changes into $F_p(q)$:

$$F_p(q) = \int_0^\infty a(r)F(q,r)\left(\frac{r}{r_0}\right)^6dr \quad \text{with} \quad \delta = \frac{1}{\sqrt{Z+1}}$$  \hspace{1cm} (2.8)$$
A comparison between $F(q)$ and $F_p(q)$ for particles of radius $2 \mu m$ is shown in Fig. 2.2. Unlike the symmetrical Gaussian Distribution, Schulz-Flory favours small polymer chains [11].

![Graph showing intensity vs qr with different colors for different particle sizes and polydispersity.]  

Figure 2.2: Simulation of the form factors of $r=5 \mu m$ particles with polydispersity $\delta=2.3\%$ (red) and without polydispersity (blue). Additionally the form factor for $r=407$ nm particles (green) is shown without polydispersity.

### 2.2 Coherence

Interference does only occur with coherent light. Coherence is defined as a set phase relation and a similar direction of propagation between two waves. The time in which the first condition is fulfilled is called transversal coherence length. The period before the first phase jump is in the angular range $< \frac{\lambda}{4D}$:

The spatial coherence of the beam is described by transvers coherence length $\xi_t$ given by:

$$\xi_t = \frac{\lambda R}{2D}$$  \hspace{1cm} (2.9)

where $\lambda$ is the wave length of the light source and $D$ is the expansion of the source. While transverse coherence length depends on the wavelength $\lambda$ and the angular source size (see Fig. 2.3b), the longitudinal coherence length is a measure of the monochromy of the light (see Fig. 2.3a). It can be described by

$$\xi_l = \frac{\lambda^2}{2\Delta\lambda}$$  \hspace{1cm} (2.10)
where $\Delta \lambda$ is the wavelength bandwidth. For a HeNe laser laser with $\lambda=633$ nm from LUMENTUM [12] the longitudinal coherence length is 1.2 m while for a mercury-vapour lamp it is $\xi_l=12.4$ mm [13].

Laser sources are capable of producing fully coherent beams. A third generation storage rings like PETRA III is a partically coherent source. Free electron lasers like the european XFEL have full transverse coherence. But the self-amplified spontaneous emission is a chaotic source with many temporal modes that causes low longitudinal coherence [14].

### 2.3 Speckle Patterns of Colloidal Suspensions

Colloids, a mixture of insoluble particles and a solvent, e.g. gas bubbles in a solid or sand in water, can be found in everyday life as foam, ink or mayonnaise [15]. They are in an intense focus of the photon science community. The dynamics of colloids in suspension are strongly dependent on temperature, pressure, concentration and chemical coating. The behaviour of disordered systems is a topic of current research [7].

When laser light shines upon a colloidal suspension of a disordered material, a speckle pattern can be observed. This pattern is a Fourier transformation of the spatial arrangement of colloids in real space. A characteristic spiky speckle structure can be seen by a line along the q-vector (as shown in Fig. 2.4a). With circular integration of a larger q-region the pattern can gain more statistical information.

The motion of each speckle contains information about the dynamic of the sample system [16]. The spatial extension $\delta_{x,y}$ of a single speckle depends on the wavelength, the sample-detector distance $L$ and the illuminated area $D_{x,y}$ at the sample position:
Figure 2.4: a) A linecut (black) and a circular integration region (magenta) of a speckle pattern for polystyrene 5 µm radius particles. b) Intensity analysis with a linecut (black) and circular integration (magenta dots).

\[ \delta_{x,y} = \lambda \frac{L}{D_{x,y}} \]  \hspace{1cm} (2.11)

With measurements of the speckle size and speckle distribution the experimental setup can be characterised. The beam size and contrast \( \beta^2 \) given by

\[ \beta^2 = \frac{\sigma^2(I)}{\langle I \rangle^2} \]  \hspace{1cm} (2.12)

qualify the alignment and long-time stability.

The contrast becomes 1 for full coherence when the variance \( \sigma^2 \) equals the normalised mean intensity \( \langle I \rangle \).

The intensity probability distribution depends on the number of modes \( M \) with the contrast \( \beta^2 = \frac{1}{M} \) and shows an exponential decay [17]:

\[ P(I) = \left( \frac{M}{\langle I \rangle} \right)^M \frac{\exp(-M \times I/\langle I \rangle)}{\Gamma(M)} \]  \hspace{1cm} (2.13)

In case of full coherence with \( M=1 \) the probability density function has a monotonically decreasing form (Fig. 2.5). For a partial coherence and incoherence case the width of the distribution decreases compared to the full coherence case as the characteristic speckle oscillations get smaller.

Furthermore noise (e.g. from the background) increases the value of the mean intensity \( \langle I \rangle \) which is used to calculate the contrast in Eq. 2.11. To reduce the influence on the contrast the background \( \langle I_b \rangle \) has to be subtracted from the experimental data \( \langle I_{ex} \rangle \) (see Fig. 2.6):

\[ \langle I \rangle = \langle I_{ex} \rangle - I_b \]  \hspace{1cm} (2.14)
Figure 2.5: The probability density function for full coherence $M=1$, partial coherence $M=4$ and incoherence $M=16$.

Figure 2.6: The background influences the mean intensity. The real mean intensity is given by the measured mean intensity (blue dotted line) subtracted by the intensity of the background (red dotted line).
2.4 Photon Correlation Spectroscopy

The dynamics of an investigated system can be analysed by measuring time correlations of intensity I recorded as a function of time t at the scattering wave vector q. The temporal correlation between two times \( t \) and \( t + \tau \) is calculated via the normalized intensity correlation \( g_2 \):

\[
g_2(\vec{q}, t) = \frac{\langle |I(\vec{q}, 0)| |I(\vec{q}, \tau)| \rangle}{\langle |I(\vec{q})|^2 \rangle} \tag{2.15}
\]

The Siegert relation [1] for Gaussian signals rewrites this to

\[
g_2(\vec{q}, \tau) = 1 + \beta^2 |f(\vec{q}, \tau)|^2 \tag{2.16}
\]

With a fully coherent source and a detector resolution smaller than one speckle \( \beta^2 \) is 1 and \( g_2 \) becomes 2. It decreases to 1 at larger time differences \( \tau \), when the system becomes uncorrelated.

\( f(\vec{q}, \tau) \) is the normalized intermediate scattering function:

\[
f(\vec{q}, \tau) = e^{-2\Gamma \tau} \tag{2.17}
\]

In case of no interaction between the particles, the displacement between the particles follows Brownian motion. Diffusion is related to the particle hydrodynamical radius \( r_h \). It is expressed in the self diffusion coefficient \( D_0 \). \( \Gamma \) is the relaxation rate with the characteristic relaxation time \( \tau_c \), after which the \( g_2 \) function decays to \( \frac{1}{e} \):

\[
D_0 = \frac{k_b T}{6\pi \eta r_h} \tag{2.18}
\]

\[
\Gamma = q^2 D_0 = \frac{1}{\tau_c} \tag{2.19}
\]

where \( \eta \) is the viscosity of the solvent, T is the temperature and \( k_b \) the Boltzmann constant. For a given radius the corresponding particle can be calculated and the relaxation time determined. Fig. 2.7 shows a typical \( g_2 \)-curve with the corresponding relaxation time \( \tau_c \).

For diffusive motion \( \tau_c \) has experimentally shown a behaviour proportional to \( q^{-2} \) [18].
Figure 2.7: Simulation of a $g_2$-function falling from 1 to 0 and the characteristic time $\tau_c$ after the decay to $\frac{1}{e}$.

2.5 Double Pulse Photon Correlation Spectroscopy

Conventional methods for the Dynamical Light Scattering technique (DLS) can detect colloidal dynamics on a nanosecond time scale. But they are limited by their point detector to a single point in q-space. Limited statistics are recorded due to the single pixel detection. Furthermore a q-dependant measurement is not realisable at the same time and therefore no decaying processes are measurable. A double or multiple pulse approach for Photon Correlation Spectroscopy (PCS) is limited by pulse width and the distance between to pulses to colloidal dynamics in a microsecond regime. But it presents a possibility to provide statistics and measure q-dependant. It is a measure of contrast for two images with the summed up intensity $S(\vec{q}, \tau)$ in the charged coupled device (CCD) of a 2-dimensional camera.

$$S(\vec{q}, \tau) = I(\vec{q}, t) + I(\vec{q}, t + \tau)$$  \hspace{1cm} (2.20)

Thereby each pulse illuminates the system for a short time, creating an image of a speckle pattern. The camera records both patterns within one exposure time. The shortest $\tau$ becomes dependent on how fast the two pulses can be generated (see Fig. 2.8). With an acusto-optic modulator (AOM) a pulse width of 1 $\mu$s with a delay time of 1 $\mu$s can be generated.

The correlation function corresponding to the intensity $S(\vec{q}, \tau)$ is $c_2$:

$$c_2(\vec{q}, \tau) = \frac{\langle S(\vec{q}, \tau)^2 \rangle - \langle S(\vec{q}, \tau) \rangle^2}{\langle S(\vec{q}, \tau) \rangle^2}$$  \hspace{1cm} (2.21)
Figure 2.8: Double Pulse Photon Correlation Spectroscopy (DPPCS). Two pulses record the state of the system with a time difference $\tau$. Both images are summed up within the same exposure time of the detector.

It is related to the $g_2$ function through equation 2.13:

$$c_2(\vec{q}, \tau) = \frac{\beta^2}{2} (1 + |f(\vec{q}, \tau)|^2)$$

$$g_2(\vec{q}, \tau) - 1 = 2c_2(q, \tau) - \beta^2$$

The ratio between the intensity of two pulses reduces the amplitude of the contrast drop. For pulses of equal intensity ($\rho=1$) it is falling from 1 to 0.5 [19]:

$$c_2(\vec{q}, \tau) = \beta^2 \frac{\rho^2 + 1 + 2\rho |f(\vec{q}, \tau)|^2}{\rho^2 + 1 + 2\rho}$$

Typical $c_2$-curves at different contrasts and with varying $\rho$ are shown in Fig. 2.9. The contrast is a value not only dependent on the source, but also on the alignment of the setup and the duration of the pulses. A pulse longer than the time in which a moving particle changes position smears out the speckle pattern. But at the same time the pulse needs a finite length to create intensity. The calculation of $\beta^2$ is the variance in an area divided by the mean intensity and a certain number of counts is needed to overcome the noise.
Figure 2.9: Simulation of a $c_2$-function for particles with $r=1\mu m$ at $q=5.14\mu m^{-1}$. The dependence on the ratio $\rho$ and the contrast $\beta^2$ is shown.
Chapter 3

Experimental Setup

The setup was built in the DLS Laboratory in the basement of building 25f on the DESY campus. The room is darkened from natural light. Laser, optical components, sample holder and detector are placed on a 150 cm × 90 cm optical table, shielded by 2 mm thick bead-blasted anodized aluminum barriers and 5 mm thick plastic-coated cardboard panels with foam core from THORLABS [20, 21] (see Fig. 3.2 and Appendix C).

Figure 3.1: Schematic view of the setup including the acousto-optic modulator (AOM) and the LUMENTUM HeNe laser. Blue circles indicate motorised sample stage and rotational arm with detector. Lenses, mirrors, shield, black tube and 200 µm pinhole have been purchased from THORLABS, Inc.
Figure 3.2: PCS setup (without usage of the AOM, with THORLABS HeNe laser). The red line denotes the laser path.
Two different lasers has been used in the experiments. Their properties are listed in Tab. 3.1 and the setup can be seen in Fig. 3.1 and Fig. 3.2. The HeNe laser HEL020R-EC form THORLABS [22] with a power of 2mW was used for the alignment and characterisation of the setup with the large $r=5\mu m$ polystyrene samples. With the LUMENTUM [12] HeNe Laser (21mW) a higher intensity provided more counts on the detector at smaller pulse length so the delay time between the pulses could get smaller. Thereby it cannot be smaller than the pulse width itself. This laser was used to measure smaller polystyrene samples down to $r=25\text{ nm}$ with faster dynamics.

Table 3.1: Specification of the 2 mW THORLABS and the 21 mW LUMENTUM HeNe laser.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>THORLABS HeNe Laser</th>
<th>LUMENTUM HeNe Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>HEL020R-EC</td>
<td>1145P</td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>632.8</td>
<td>632.8</td>
</tr>
<tr>
<td>Power (mW)</td>
<td>2.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Beam diameter ($\frac{1}{e^2}$) (mm)</td>
<td>0.81</td>
<td>0.7</td>
</tr>
<tr>
<td>Polarization</td>
<td>random</td>
<td>linear (vertical)</td>
</tr>
<tr>
<td>Beam divergence (mrad)</td>
<td>1.0</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Downstream the laser, the unfocused light was first directed via aluminium-coated plano mirrors into an acusto-optic modulator (AOM). This device was used for the second set of experiments, where it chopped the light into pulses of controllable number and length. Before hitting the sample, the beam was focused with an array of three focussing lenses. The first lens with a focal point at $f=100\text{ mm}$ focuses the beam into a 200 $\mu\text{m}$ pinhole which cleans the beam from unwanted artefacts. The second lens ($f=100\text{ mm}$) refocuses the beam onto the sample. The third lens ($f=100\text{ mm}$) is mounted on the motorised sample stage. It focuses the beam onto the volume of the sample and can be moved by 2.6 cm on the focus axis.

One of the main emphases of this theses has been the implementation of a motorised sample enviroment into the experimental setup. The sample stage includes two translation stages VT-80 [23] with the travel range of 2.6 cm each. They translate the upright standing sample in perpendicular directions to the beam. An additional motor shifts the focussing lens in axis with the beam. A rotation stage DT-80 [24] moves the detector in plane horizontal from $2\Theta=0^\circ$ to $110^\circ$ (see Fig. 3.3). The motors are operated by Sardana based on a Tango [25] server while the detector is controlled with the program LabVIEW [26].

With the detector at a distance of 8.3 cm, the angular range of the BASLER avA1000 covers 3.87$^\circ$. Holders for capillaries and cuvettes were 3D-printed with PLA on an Ultimaker 2+ and a RAISE 3D N2plusk. The platform on the rotation stage was printed with ABS on a Stratasys Dimension (details to particular components can be found in Appendix A).

Two types of two-dimensional detectors were used in the measurements, the USB 2.0 CMOS Camera for the characterisation of the setup with a continuous beam and a BASLER avA1000-120km otherwise (see Tab. 3.2) [27, 28].
Figure 3.3: Motorised sample stage. Mot1 denotes the rotation arm at $\sim 30^\circ$ with the BASLER CCD mounted, mot2 to mot4 are the translation stages moving the focus lens and the cuvette containing the sample, respectively. The red line denotes the laser path and the translation plane of the motor movement is denoted by the yellow arrow.
Table 3.2: Specification of the *THORLABS* CMOS and the *BASLER avA1000* detectors.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>THORLABS CMOS</th>
<th>BASLER avA1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pixels</td>
<td>1280 × 1024</td>
<td>1024 × 1024</td>
</tr>
<tr>
<td>Pixel Size (µm)</td>
<td>5.2 × 5.2</td>
<td>5.5 × 5.5</td>
</tr>
<tr>
<td>Max. frame rate (fps)</td>
<td>25</td>
<td>120</td>
</tr>
<tr>
<td>Sensor type</td>
<td>CMOS</td>
<td>Kodak KAI-1050</td>
</tr>
<tr>
<td>Input/output trigger</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

### 3.1 Double Pulse Generation via AOM

The principle operation of the acusto-optic modulator (AOM) can be seen in Fig. 3.4. A radio frequency driver (RF driver) initiates sound waves in a quartz crystal, on which the beam diffracts into several diffraction orders. For the first order of diffraction the intensity is much weaker than for the incident beam. Measurements with a powermeter [29] show an intensity of 20 nW (0.5‰) for the laser from *THORLABS* and 7.3 mW (35%) for the *LUMENTUM* laser at the site of the sample.

![Figure 3.4: Schematic principle of the AOM operation. Light is diffracted on waves in the crystal. Intensity is split into different diffraction orders (m = -2, -1, 0, 1, 2).](image)

To control the timing of the pulses generated with the RF driver as shown in Fig. 3.5, a wave function generator (WFG) triggers a digital delay generator (DDG) and the detector at the rising edge of a square-wave signal. The DDG directly regulates the RF driver (Fig. 3.6). The WFG is modulated manually, but the DDG can be controlled via the SHH client *PuTTY* [30]
on the same computer as the detector. Detector options are set with *Pylon Viewer 4.0* [31] and frames are acquired by *Vision Assistant 2011* [32] (see Appendix B).

Figure 3.5: Trigger and signal time coordination for the 2 V square-wave signal from the WFG (black), the two pulses from the DDG (green) and the camera exposure time (yellow). The pulse width (dark blue) is set at least as long as half of the delay time. Due to a delay from the camera (red) the pulses from the DDG are also set with a pulse delay time (light green).

Figure 3.6: The communication between AOM crystal (Gooch& Housego I-M110-3C10BB-3-GH27), RF Driver (Gooch& Housego A35110-S-1/50-p4k7u), WFG (Tektronix AFG3022C), DDG (Stanford Research Systems Model DG645) and Oscilloscope (Rhode& Schwarz MHO3004) is controlled by signals given by the user (blue arrows) and secondary signals (grey arrows).
3.2 Capillaries & Cuvettes

Small curvatures of the borosilicate glass capillaries containing the sample have shown to produce streaks in the speckle pattern (see Appendix A). To avoid this static background, the curvature can be reduced by placing the capillary in a bigger glass container (Fig. 3.7) filled up with decalin ($C_{10}H_{18}$). Decalin has a refraction index very similar to glass [33][34]:

\[ n_{\text{glass}} \approx n_{\text{decalin}} \approx 1.4 \] (3.1)

For static light scattering experiments the round capillaries can be exchanged with rectangular cuvettes. The cuvettes used were 3500 µl CV10Q3500F-E quartz glass with four polished sides [35]. They are applicable for a limited range of detector positions, as the sample thickness deviates with the angle. Angles up to $\sim 40^\circ$ can be measured (see Fig. 3.8), while with capillaries in decalin there is no limitation in angular range.

Figure 3.7: Round cuvette and square capillary. a) 3D-printed sample holder for round capillaries in a decalin container. b) sample holder for rectangular cuvettes. c) the schematics of a bigger decalin container to lessen the curvature of the incident beam. This way streaks in the speckle pattern can be reduced.

3.3 Sample Systems

For characterisation of the setup and dynamic measurements two different sample systems were used (listed in Tab. 3.3 and shown in Fig. 3.9). Experiments were made at concentrations between 0.0016 and 0.08 $\text{w/v}$ for polystyrene and 0.1 to 0.01 $\text{mg/ml}$ for silica particles. With particle sizes from $r=25$ nm to $r=5$ µm a wide range of dynamics could be observed. All particles were dissolved in ultra-pure water. To prevent evaporation the capillaries and cuvettes were sealed with multiple layers of PARAFILM. Especially for the larger particles ($> 1$ µm) shaking the sample system before the measurement became necessary due to sedimentation.
Figure 3.8: The top view onto square cuvettes is shown. a) pathways within a rectangular cuvette. The distance between sample and detector stays constant ($A + B = C + D$), but the sample thickness varies with the angle ($4A < C$). b) top view onto a cuvette being hit to the left off center (case 1) and right off center (case 2) while the detector is positioned on the right. In case 1 the angle has a range from $0^\circ$ to $40^\circ$, in case 2 the range is further limited from $0^\circ$ to $20^\circ$ by the edge of the cuvette.

Table 3.3: Specification of the silica and polystyrene sample system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Radius (nm)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybead Polystyrene Microspheres</td>
<td>5000</td>
<td>Polyscience, Inc.</td>
</tr>
<tr>
<td>Polybead Polystyrene Microspheres</td>
<td>2250</td>
<td>Polyscience, Inc.</td>
</tr>
<tr>
<td>Polybead Polystyrene Microspheres</td>
<td>25</td>
<td>Polyscience, Inc.</td>
</tr>
<tr>
<td>Silica Spheres</td>
<td>407</td>
<td>inhouse</td>
</tr>
</tbody>
</table>

Figure 3.9: Sample systems (see Tab. 3.3). Left: Silica spheres $d=815$ nm at different concentration. Right: Polystyrene spheres $d=10$ µm, $4.5$ µm and $50$ nm.
Chapter 4

Data Analysis

The analysis of the data for this thesis has been done using Matlab R2016a. Various scripts were written for beam characterisation, static light scattering and double pulse correlation spectroscopy. The data recorded via double pulse correlation spectroscopy has been analysed with two scripts ‘sequentialmode.m’ for measurements without AOM and ‘doublepulsemode.m’ for those with AOM.

For the beam size analysis in the static measurements the frame size of $1280 \times 1024$ pixel of the THORLABS CMOS was reduced to a region of interest of $80 \times 80$ pixel. In this way a regions without overlapping speckles could be chosen. Characterisations for the dynamic setup and measurements has been done with the BASLER avA1000.

The static light scattering analysis requires a wide range of the $q$-value. Therefore 3-6 frames of $1024 \times 1024$ pixel with a $q$-range of $6.6 \mu m^{-1}$ each were stitched together.

In sequential mode operation a continuous beam illuminated the sample and the detector recorded $N$ frames with a maximum frame rate of 120 Hz. The internal memory storage of the camera limited the number of frames at 120 Hz to 25. At lower frame rates higher numbers of frames could be recorded (80 Hz: 40 frames, 50 Hz: 100 frames). The contrast of each frame was analysed and a $g_2$-function over the corresponding time was measured. To increase statistics each measurements has been repeated up to five times.

For the analysis in the double pulsed mode the frames has already been summed up during the same exposure time of the detector. Burst periods ranged from 2 ms to 40 ms for the 2 mW laser and down to 200 $\mu$s for the 21 mW laser. Measurements with a constant time between two pulses were taken 100 times to ensure good statistics. Measurement series consistent of 100 single shots were taken to allow the calculation of the contrast for a single image. Averaging of a series was done after calculating the contrast of the images. The method of selecting the $q$-value is shown in Fig. 4.1.

The selected $q$-rings had a width of 50-200 pixel, corresponding to a $\Delta q$ of $0.35 \mu m^{-1}$ to $1.4 \mu m^{-1}$. Dark frames with ultra-pure water were taken and subtracted from each frame. Artefacts from the setup can be assumed to have larger sizes than the sample system and therefore they scatter in a small angle scattering region. Measurements at $> 30^\circ$ are assumed to have less
Figure 4.1: The q-ring area for integration was selected with a width of 100 pixel. The speckle pattern is a single shot image recorded at 96 ms exposure time.

parasitic scattering influences. A test measurement of a glass capillary at all angles > 30° with a toluene sample showed no significant scattering of the components of the setup. Additionally the PCS analysis with frames taken in the sequential mode was done with the program XPCSGUI [36]. A new detector type 101 for the BASLER camera has been added to the selection of XCPSGUI and the calculation for the detector position in this mode has been accommodated.
Chapter 5

Results

5.1 Characterisation of the Setup Stability

In this setup configuration the laser beam was illuminating the sample and the resulting speckle patterns were recorded as a function of time. A typical speckle pattern is shown in Fig. 5.1.

Figure 5.1: The method to determine beam size from the measured speckle pattern of a static sample. a) Typical speckle pattern from a static sample (diffuser) illuminated with the HeNe laser and recorded by a full frame CCD image. b) Selected region of interest (ROI) for the analysis. The region consists of $80 \times 80$ pixels and is depicted in a) by the red square. c) 2D correlation image of the speckle pattern shown in a). d) Line cut though the center of the autocorrelation function (blue circles) and the fitted Lorentzian function (magenta line).
The beam size of the sample is defined by the laser source and focussing. According to Eq. 2.11 the beam size can be calculated with speckle size, wavelength of the laser and distance of the detector from the static sample (diffuser). To measure the size of the speckles, first a 80×80 pixel region of interest (ROI) was chosen. After autocorrelating the intensity of the speckle pattern the vertical and horizontal cut through the center of the autocorrelation pattern (see Fig. 5.1(c)) has been fitted with a Lorentzian function $F_L(x)$:

$$F_L(x) = \frac{2A}{\pi} \frac{w}{4(x-x_0)^2 + w^2}$$

where $A$ is the area under the curve which is calculated from the peak height $P_{\text{height}}$ at $x=x_0$. The full width at half maximum (FWHM) $w$ of the speckle size was used to calculate the beam size.

![Figure 5.2: A long-time measurement of the laser stability results in a mean beam size of 2.69±0.52 mm.](image)

![Figure 5.3: The histogram of the beam size distribution shows asymmetrical shape.](image)
Fig. 5.2 shows a long-time study of the stability of the beam size over 18 min. The average of the beam size was found to be 2.69±0.52 mm. Larger deviations from the mean value are observed at the 15th min and 17th min. They are most likely associated with external disturbances like the air condition of the laboratory or instabilities of the experimental table. The histogram in Fig. 5.3 shows a more detailed distribution of the speckle size. The distribution is asymmetric and the mean beam size is 2.3 mm.

Fig. 5.4 shows the long time contrast measurements of the static sample. The contrast values have been determined from each speckle pattern according to Eq. 2.12. The measured mean value of the contrast is $\beta^2=0.733\pm0.024$. Similar to the beam size measurements the contrast values are affected at the 15th and 17th minute. However on the time scale of 12 minutes both beamsize and contrast remain sufficiently stable allowing to perform Photon Correlation Spectroscopy measurement with dynamical samples.

Figure 5.4: Long-time study of the contrast for a static sample system. The mean value of the measured contrast is $\beta^2=0.733\pm0.024$. 
5.2 Static Light Scattering

To examine size and polydispersity of the colloidal particles static light scattering (SLS) has been employed. This method has been applied to the polystyrene sample with a radius of 5 µm at a concentration of \( c = 0.025 \frac{w}{v} \). The intensity was recorded with the BASLER avA1000. A comparison was made between round capillaries and cuvettes (see Appendix A). The capillaries have shown to have a wider angular range and therefore easier handling for SLS measurements. Fig. 5.5 shows the recorded scattering patterns corresponding to four successive angles that are stitched together. The pattern shows the form factor oscillations as a function of scattering angle \( (q_{\text{WOL}}) \). With circular integration the decrease of intensity for higher angles is shown in Fig. 5.6.

Additionally the measurements were performed partially with a focusing lens (with the wave vector \( q_{WL} \)) \( (f=30 \text{ mm}) \) 4 cm in front of the detector. For this measurements the correction factor \( A = 1/2 \) for \( q_{WOL} = q_{WL} * A \) was found. The particle size \( r = 5.2 \pm 0.9 \mu m \) with a polydispersity \( \delta = 1.9 \pm 0.6 \) for the tested setup was fitted with Eq. 2.8 and is close to the expected value of \( r = 5 \mu m \). The obtained results allow to proceed with dynamic measurements.

Figure 5.5: Speckle pattern of a 5 µm polystyrene samples single frame consisting of 4096×1024 pixel. The measurement was performed with a square cuvette with lens at 10°-46° detector position.
Figure 5.6: Measurements of the form factor (black circles) for different setups and fit with Eq. 2.8 (magenta line). a) round capillaries without a lens, $r_{fit} = 5.1 \, \mu m$ and $\delta_{fit} = 2.3\%$. b) square cuvettes without a lens, $r_{fit} = 4.4 \, \mu m$ and $\delta_{fit} = 2.5\%$. c) round capillaries with a lens, $r_{fit} = 6.5 \, \mu m$ and $\delta_{fit} = 1.4\%$. d) square cuvettes with a lens. $r_{fit} = 4.85 \, \mu m$ and $\delta_{fit} = 1.5\%$. 
5.3 Single Pulse Contrast Measurement

A study of the laser stability in a pulsed mode and the *LUMENTUM* laser shows a mean beam size of 2.7±0.4 mm. Furthermore the mean contrast of a static sample (diffuser) illuminated by a single shot with different pulse length has been measured at 94±3% (see Fig. 5.7). That the contrast stayed constant for the range of different pulse lengths indicates stability of the pulsed setup including the AOM.

![Figure 5.7: The speckle contrast of the static sample measured with different pulse lengths is $\beta^2=94\pm3\%$ on average. Each point is an average of 20 single frame measurements.](image1)

The speckle contrast at different pulse lengths for the dynamic 407 nm radius silica sample is shown in Fig. 5.8. In contrast to the static sample the contrast is not constant as a function of pulse width. For longer pulse lengths $\geq 500\,\mu s$ spacial arrangement of particles occurs on the time scale of illumination. Therefore the resulting speckle pattern begins to smear out. This behaviour becomes visible in the decreasing contrast of the dynamic sample system.

![Figure 5.8: The single shot contrast of the dynamic 407 nm radius silica sample at different pulse length is decreasing with the pulse length. Each point is an average of 20 measurements.](image2)
5.4 Photon Correlation Spectroscopy

Main objective of this master thesis was characterisation of colloidal dynamics with Photon Correlation Spectroscopy (PCS). Measurements have been done without acusto-optic modulator (AOM) as single pulse experiment and with the AOM as double pulse PCS. Sample sizes ranged from r=25 nm to 5 µm (see Tab. 3.3).

5.4.1 Single Pulse Measurements

When the laser beam continuously hits the sample and the detector operated at the highest frame rate (i.e. 120 Hz), the shortest correlation time is at 8.3 ms. With measurements at 120 Hz and 60 Hz combined (see Fig. 5.9) the smallest samples of r=407 nm were analysed. Different angles correspond to different q-values, ranging from 4-30 µm\(^{-1}\). The \(g_2\)-function (Eq. 2.17) was fitted to the data and provided a characteristic time \(\tau_c=41\) ms at 32°. As described in Eq. 2.19 the dynamic of a system is expected to get faster for higher q-values. In Fig. 5.9 (inlet) the \(\Gamma\) of the measurements is plotted versus \(q^2\). The slope of the fitted linear function provides the diffusion coefficient \(D_{0,f} = 8.9 \pm 1.1 \times 10^{-13} \text{ m}^2/\text{s}\) while the expected value was \(D_{0,ex} = 5.3 \times 10^{-13} \text{ m}^2/\text{s}\).

![Figure 5.9: PCS measurements in a single pulse mode at various angles. The 407 nm radius silica sample was illuminated with the 2 mW laser. \(\tau\) is limited thought the frame rate of the BASLER detector. The inset shows the q dependence of the correlation rate \(\Gamma\) determined from the correlation curves shown in the figure. The diffusion coefficient \(D_{0,f}\) is 8.9 ± 1.1 \times 10^{-13} \text{ m}^2/\text{s}\) (magenta line).](image-url)
Fig. 5.10 illustrates the limitation of the conventional PCS with 2D detectors. With the shortest time scale the autocorrelation function is 8.3 ms. The analysis was done with XPCS-GUI. The result for the characteristic time was calculated to $\tau_c = 101 \pm 3 \text{ms}$.

![Graph showing autocorrelation function](image)

Figure 5.10: 407 nm radius polystyrene sample at $q=2.6 \mu m^{-1}$ analysed with XPCSGUI.

### 5.4.2 Double Pulse Measurements

A double pulse time structure with a width between 200 $\mu$s and 40 ms were generated by the AOM to perform double pulse photon correlation spectroscopy. With this settings a minimum distance between the two pulses of 2 ms (pulse width 2 ms) could be reached with the 2 mW laser. With the 21 mW laser a distance of 200 $\mu$s (pulse width 200 $\mu$s) was possible. The scattering intensity is the limiting factor in a double pulse photon correlation source. The minimum time delay can be further decreased with an higher power laser. With the given setup settings the largest q-value of 11.4 $\mu m^{-1}$ could be measured with the largest sample $r=5 \mu m$. The fit in Fig. 5.11 yields $\tau_c = 191 \pm 35 \text{ms}$ while $\tau_c = 235 \text{ms}$ were expected.

The DPPCS method is especially suited to investigate fast dynamics down to a few milliseconds characteristic time. The smallest sample ($r=25 \text{nm}$) was measured up to an angle of 40° (see Fig. 5.12) and the fit yielded the characteristic time to 2.3 $\pm$ 0.1 ms. As the dynamics become faster also the fit becomes less precise, because the first plateau of maximum contrast cannot be detected. The diffusion coefficient was fitted to $D_{0,f} = 8.3 \pm 1.0 \times 10^{-12} m^2 / s$ and was expected at $D_{0,ex} = 8.6 \times 10^{-12} m^2 / s$ (Fig. 5.12(inset)).
Figure 5.11: For $r=5\mu m$ polystyrene sample at $70^\circ$ with a pulse width=$1ms$ $\tau_c = 191 \pm 35ms$ was measured.

Figure 5.12: Correlation function $g_2 - 1$ as a function of the delay time $\tau$ for different angles. The measurement of the $r=25\text{ nm}$ polystyrene sample was done with the $21\text{ mW}$ laser and a pulse width of $200\mu s$. The inlet shows the fitted diffusion coefficient $D_{0,f} = 8.3 \pm 1.0 \times 10^{-12} \frac{m^2}{s}$ (magenta line), the expected value was $D_{0,ex} = 8.6 \times 10^{-12} \frac{m^2}{s}$. 
Chapter 6

Outlook

Future goals with the Double Pulse Photon Correlation Spectroscopy setup developed within this thesis work are further technical developments and pump-probe experiments. The temperature control is already present, only a fitting vat for the decalin container has to be purchased. Potential sample systems like Poly-N-isopropylacrylamid (PNiPAM), an aqueous thermosensitive nanogel [37], will be examined as a function of temperature and pressure. Another possible type of experiment are pump-probe experiments. Therefore the AOM could produce two pulses of different length. The longer first pulse would excite the system while the shorter second pulse would record the process of de-excitation simultaneously at various q-values. In this mode the few counts from the probe pulse for evaluation would be superimposed by the pump pulse. Easier to implement would be a system with two beams that have an angle to each other. When synchronised, one laser would function as pump laser while the other probes the sample. Only the scattered light from the probing laser would be detected by a camera (see Fig. 6.1).

The DLS Lab inventory contains a 200 mW laser which could further improve the DPPCS setup by providing higher intensity for shorter pulses. In a pump probe experiment it could also be used as a pump laser to gradually increase intensity in order to find the damage threshold for certain polymers.

Figure 6.1: Pump-probe experiment with two lasers.
Chapter 7

Summary

Double Pulse Photon Correlation Spectroscopy can extend the conventional PCS technique by employing a double pulse laser time structure and a 2D detector. In this master thesis a setup for DPPCS has been developed and tested. The characteristic correlation time of polystyrene samples with a radius down to 25 nm and silica particles of radius 407 nm have been measured. The results show that the double pulse technique with a minimum time delay that is not limited by the detector frame rate but the pulse length can characterise the dynamics of fast particles.
Nomenclature & Symbols

$\vec{q}$ scattering vector
$\lambda$ wavelength
$I(q)$ intensity
$A(q)$ amplitude
$F(q)$ form factor
$F(q)_p$ polydispersity form factor
$\delta$ polydispersity
$\beta^2$ contrast
$M$ number of modes
$\Gamma(...)$ gamma function
$g_2$ intensity correlation function
$f(\vec{q}, t)$ intermediate scattering function
$D_0$ diffusion coefficient
$\tau_c$ characteristical time
$\Gamma$ relaxation rate
$S(\vec{q}, \tau)$ summed up intensity
$c_2$ contrast correlation function
$\rho$ ratio between pulse lengths
$\tau$ distance between two pulses
AOM acusto-optic modulator
WFG wave function generator
DDG digital delay generator
RF driver radio frequency driver
SLS static light scattering
PCS photon correlation spectroscopy
DPPCS double pulse photon correlation spectroscopy
DLS dynamic light scattering
Appendix A

This chapter presents additional details of the DPPCS setup including various sample holders, motor designs and detector stages. Images of the control systems are shown as well.

Figure 7.1: Shown is the platform on the rotation stage, printed with ABS on a Stratasys Dimension 3D-printer.

Fig. 6.1 shows a close-up image of the 3D-printed rotation arm. Various versions of the sample holder were 3D-printed and tested. All measurements presented in chapter 5 were taken with the holders in Fig. 6.2(b) and (d). The temperature controlled holder in (a) could not be tested because the glass of the decalin vat produced strong streaks and no substitution was found in time. A speckle pattern with similar streak but measured with a round capillary without decalin is shown in Fig. 6.3. The holder in (c) is an improved version of the holder for capillaries. The decalin container no longer stands on the rotation stage but is mounted directly under the capillary. Therefore the sample is independent of the rotation of the detector. All capillaries were put into position thought an opening from above. To prevent scratches on the polished walls of the cuvette it was handled with gloves and mounted from below.
Figure 7.2: Depicted are 3D-printed sample holders. a) temperature controlled capillary holder, b) round capillary holder, the decalin vat stands under the holder on the rotation stage, c) round capillary holder with the decalin vat fixed to it d) square cuvette holder
Figure 7.3: Speckle pattern of silica particles in a round capillary without decalin container. The streaks produced are due to the unpolished curvature of the capillary walls.
Appendix B

Figure 7.4: Top: WFG; Bottom: Oscilloscope for visual assessment of the measurement control system: The square-wave function is shown in yellow, the two pulses (magenta) fit within the signal of the WFG and the camera (blue) opens at the rising edge of the square-wave function.
Figure 7.5: Shown is the Pylon Viewer 4.0 to set detector options and the Vision Assistant 2011 to acquire frames with the BASLER detector.

Fig. 6.4 shows the wave function generator (WFG) and an oscilloscope controlling the timing signals while operating the AOM. The square-wave signal from the wave function generator (yellow square function) has an amplitude of 2 V and was set to a frequency of 119.6 Hz. This number results from the 120 Hz maximum as well as the short delay time of the camera (blue square function). The default value for the delay of the pulses (magenta square function) was set at 1 µs. The screenshot of the GUI software for the detector control is shown in Fig. 6.5.
Appendix C

To avoid background light all the optical components of the setup were shielded from ambient light by black housing (Fig. 6.6). Aluminium barriers were fixed to the table. One barrier in front of the sample stage can be opened to allow easier access while changing samples. The cardboard laid on top is not fixed and can swiftly be removed to control beam pathways. It prevents dust from settling on the optical components. The positioning of AOM, sample and detector are depicted on top of the cardboard and the laser pathway is implied by the red line.
Bibliography


Ort, Datum

Unterschrift