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Development of the Temperature-Controlled Sample Environment for Double Pulse Photon Correlation Spectroscopy

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Abstract

A temperature-controlled sample environment was developed and verified for a Double Pulse Photon Correlation Spectroscopy (DPPCS) setup. Various polystyrene and thermoresponsive Poly(N-Isopropyl Acrylamide) (pNipam) samples were characterized in Dynamic Light Scattering (DLS) measurements. The thermoresponsive properties of the pNipam sample were investigated in a Small Angle X-Ray Scattering (SAXS) experiment at the beamline P10 of PETRA III. At $q \approx 0.005 \text{ \AA}^{-1}$, an increase in scattered intensity with increasing temperature was observed, indicating volume (radius) transition of the particles. To verify the performance of the DPPCS setup in measuring dynamics, the polystyrene samples were used in Single Pulse Photon Correlation Spectroscopy. The fastest sample's radius was determined to $R_h = 27 \pm 3 \text{ nm}$, which agrees well with the size provided by the manufacturer ($R = 25 \pm 4 \text{ nm}$). The pNipam sample was measured at temperatures from $T = 20^\circ\text{C}$ to 50°C both with Single and Double Pulse Photon Correlation Spectroscopy to verify the performance of the newly developed temperature-control. Both measurements showed the characteristic decrease of the radius at a transition temperature of $T \approx 32^\circ\text{C}$, demonstrating reliable functionality of the temperature-controlled sample environment.

Zusammenfassung

Es wurde eine Probenumgebung mit integrierter Temperaturkontrolle für einen Aufbau zur Photonenkorrelationsspektroskopie mit Doppelpulsen (DPPCS) entwickelt und seine Funktion nachgewiesen. Verschiedene Polystyrol- und temperaturempfindliche Poly-*N*-isopropylacrylamid (pNipam) Proben wurden mit dynamischen Lichtstreuexperimenten charakterisiert. Die temperaturabhängigen Eigenschaften von pNipam wurden in einem Röntgenkleinwinkelstreuexperiment an der Beamline P10 von PETRA III untersucht. Im Bereich von $q \approx 0.005 \text{ \AA}^{-1}$ wurde mit steigender Temperatur auch eine steigende gestreute Intensität beobachtet, was auf einen Übergang zu größeren Volumina (Radien) hinweist. Um die Funktionalität des DPPCS Aufbaus bei dynamischen Messungen zu überprüfen, wurden die Polystyrolproben für Einzelpuls Photonenkorrelationsspektroskopie genutzt. Der Radius der schnellsten Probe war hierbei $R_h = 27 \pm 3 \text{ nm}$, was sehr gut mit dem vom Hersteller angegebenen Radius von $R = 25 \pm 4 \text{ nm}$ übereinstimmt. Um die Leistung der neu entwickelten Temperaturkontrolle nachzuweisen, wurde pNipam bei Temperaturen von $T = 20^\circ\text{C}$ bis $T = 50^\circ\text{C}$ mit Einzel- und Doppelpuls Photonenkorrelationsspektroskopie gemessen. Bei beiden Messungen ist die für pNipam charakteristische Abnahme des Radius bei einer Übergangstemperatur von $T \approx 32^\circ\text{C}$ zu beobachten, was das zuverlässige Funktionieren der Probenumgebung mit Temperaturkontrolle belegt.

Contents

1	Introduction	5
2	Theory	7
2.1	Coherence	7
2.2	Static Light Scattering	8
2.3	Speckle Patterns	9
2.4	Photon Correlation Spectroscopy	10
2.5	Double Pulse Photon Correlation Spectroscopy	12
3	Experimental Setup	14
3.1	Temperature-controlled sample environment	18
3.2	Sample Systems	19
4	Data Analysis	20
5	Results	22
5.1	Dynamic Light Scattering	22
5.2	Small Angle X-Ray Scattering	25
5.3	Single Pulse Contrast Measurements	26
5.4	Photon Correlation Spectroscopy	27
5.4.1	Single Pulse Measurements	27
5.4.2	Double Pulse Measurements	30
6	Summary and Outlook	32
	Appendix A DPPCS Setup	33
	Appendix B Beam Center	34

Chapter 1

Introduction

Photon Correlation Spectroscopy (PCS) [1] is a technique to examine the dynamics of colloidal suspensions. The scattered intensity of a laser illuminating a colloidal suspension is measured by a detector at a fixed frequency. In most cases a point detector with only one pixel is used. It can measure at a high frequency but only at one fixed point in q -space which does not provide much statistics. If a detector with more pixels, for example a Charged-coupled device (CCD), is used, multiple points in q -space can be measured at the same time. However the frequency of the measurement is limited by the acquisition frame rate of the camera which may not be fast enough to capture the full dynamics.

To measure at a high acquisition rate and at multiple q 's at the same time a double pulse approach was introduced [2]. In Double Pulse Photon Correlation Spectroscopy (DPPCS) the sample is illuminated by two pulses at a very short time τ apart from each other. The scattering patterns from both pulses are recorded in the same exposure time of the detector as shown schematically in Fig. 1.1 .

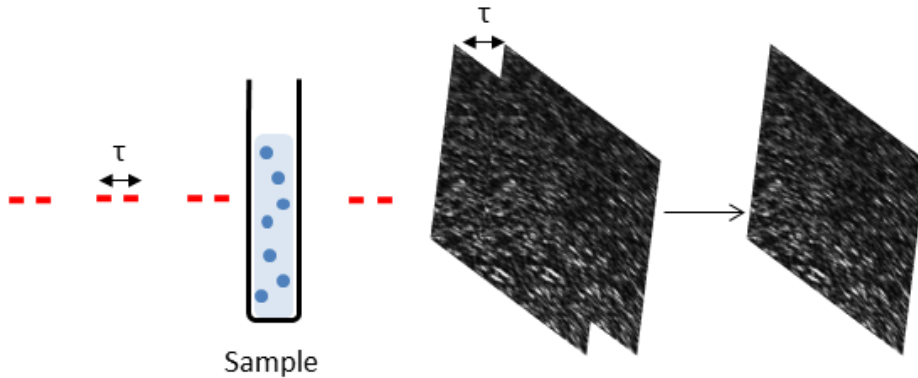


Figure 1.1: Schematics of Double Pulse Photon Correlation Spectroscopy. A sample is illuminated by two pulses, one of them delayed by τ . The scattering pattern from both pulses is recorded within the exposure time of the detector.

DPPCS is independent of the detector acquisition frame rate. It depends on the delay τ between the two pulses. For a dynamic sample the contrast of the speckle pattern decreases, the longer τ becomes. The contrast values for different delays τ can be related to the autocorrelation function used in PCS.

Colloidal systems like Poly(N-Isopropyl Acrylamide), pNipam, in an aqueous disper-

sion show a very strong thermoresponsive behaviour [3]. pNipam starts to shrink rapidly when heated to a temperature of approximately 32°C, which makes it very interesting for applications in biomedicine such as controlled drug delivery [4]. In order to study thermoresponsive samples, temperature-controlled measurement setups are needed.

For this bachelor thesis a temperature-controlled sample environment for a DPPCS setup was developed. It allows to investigate thermosensitive colloidal samples like pNipam both with PCS and DPPCS. Chapter 2 presents the theoretical background behind static light scattering, PCS and DPPCS. The experimental setup with the new temperature-controlled sample environment and the different sample systems are described in chapter 3. Chapter 4 explains how the measured data was analysed. The results of the measurements with the DLS setup, the measurements at PETRA and the DPPCS setup are shown in chapter 5. Chapter 6 summarizes the results and gives an outlook.

Chapter 2

Theory

2.1 Coherence

Fully coherent light is completely monochromatic and originates from a point source. To characterize the coherence of a light the longitudinal and the transversal coherence lengths are defined. If the wavelength of two waves propagating in the same direction is different by $\Delta\lambda$ the length in which they go from in phase to completely out of phase is the longitudinal coherence length L_L . The description of L_L is shown in Fig. 2.1a) and it can be calculated by:

$$L_L = \frac{\lambda^2}{2\Delta\lambda} \quad (2.1)$$

Fig. 2.1b) shows the transversal coherence length. Here the two waves propagate at angle $\Delta\theta$ and the transversal coherence length is the distance along the wave front where the two waves go from being in phase to being completely out of phase. This distance is given by:

$$L_T = \frac{\lambda R}{2D} \quad (2.2)$$

where D is the distance between the origins of the two waves and R is the distance between the observation point P and the origin of the waves.

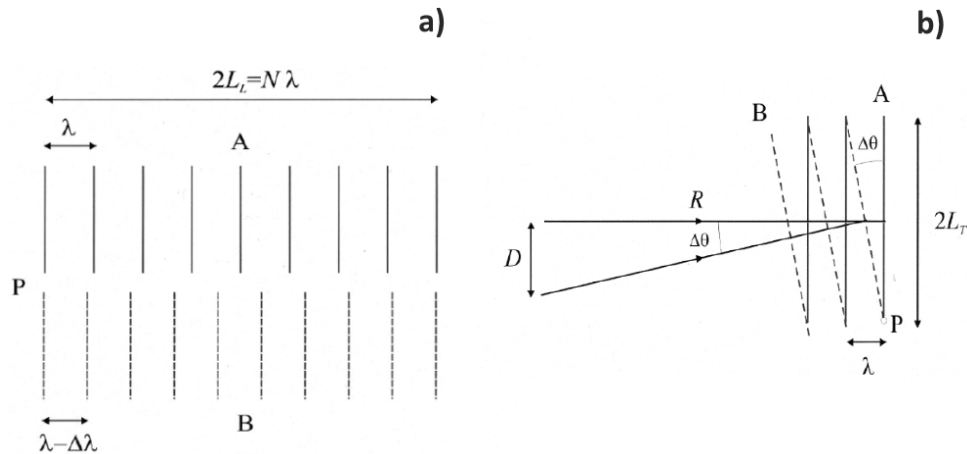


Figure 2.1: Description of longitudinal (a) and transversal (b) coherence lengths [5]

2.2 Static Light Scattering

In a Static Light Scattering experiment a sample is illuminated by a laser and the scattered intensity is measured at an angle 2θ at the detection plane. The schematics are shown in Fig. 2.2.

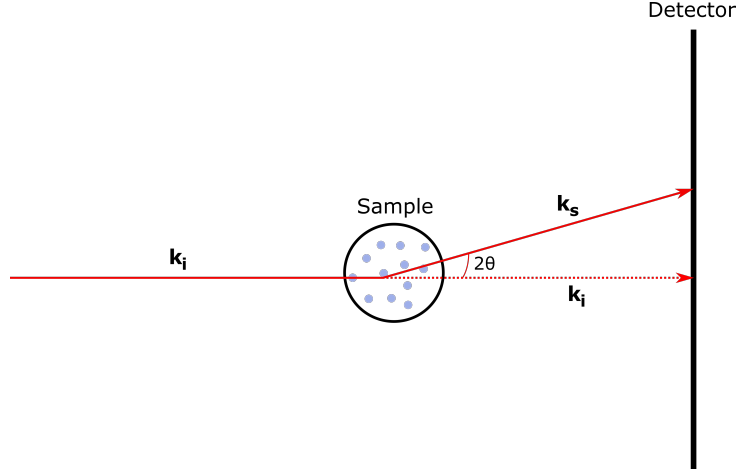


Figure 2.2: Schematics of a light scattering experiment

Considering elastic small angle scattering the magnitude of the incident wave vector $|\mathbf{k}_i|$ is equal to the magnitude of the scattered wave vector $|\mathbf{k}_s|$, $|\mathbf{k}_i| = |\mathbf{k}_s| = \frac{2\pi n}{\lambda}$. The scattering vector $\mathbf{q}$ is defined by the wave vectors:

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s \quad (2.3)$$

For single particle scattering the modulus of the scattering vector is given by:

$$|\mathbf{q}| = \frac{4\pi n}{\lambda} \sin(\theta) \quad (2.4)$$

where n is the refractive index, λ is the wavelength of the incident light and 2θ is the angle between $\mathbf{k}_i$ and $\mathbf{k}_s$. The scattered intensity $I(\mathbf{q})$ of a single particle can be calculated as:

$$I(\mathbf{q}) = |a(\mathbf{q})|^2 = a(\mathbf{q}) \cdot a^*(\mathbf{q}) \quad (2.5)$$

where a^* is the complex conjugate of a and the Fourier transform of the charge density $\rho(\mathbf{r})$:

$$a(\mathbf{q}) = \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (2.6)$$

The normalized scattered intensity for a single particle is given by the form factor $F(\mathbf{q})$ [6]:

$$F(\mathbf{q}) = \frac{I(\mathbf{q})}{I(0)} = \left(\frac{a(\mathbf{q})}{a(0)} \right)^2 = 9 \left(\frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right)^2 \quad (2.7)$$

Here R is the radius of the particles. A typical form factor is shown in Fig. 2.3. From the form factor the radius of the particles can be determined.

In order to analyse a colloid the polydispersity δ of the particles has to be taken into account. This can be done by a size distribution function $P(R)$. The polydispersity is then defined as:

$$\delta = \frac{\Delta R}{R_0} \quad (2.8)$$

where ΔR and R_0 are the width and the mean of the distribution, respectively. The size distribution is given by the Schultz distribution function:

$$P_{(Z,R_0)}(R) = \frac{1}{Z!} \left[\frac{Z+1}{R_0} \right]^{Z+1} R^Z e^{-\frac{(Z+1)R}{R_0}} \quad \text{with} \quad \delta = \frac{1}{\sqrt{Z+1}} \quad (2.9)$$

The form factor then changes to:

$$F_P(\mathbf{q}) = \int_0^\infty d\mathbf{R} P(R) \cdot F(QR) \cdot \left(\frac{R}{R_0} \right)^6 \quad (2.10)$$

Simulations of both $F(\mathbf{q})$ and $F_P(\mathbf{q})$ for a 25nm particle are shown in Fig. 2.3.

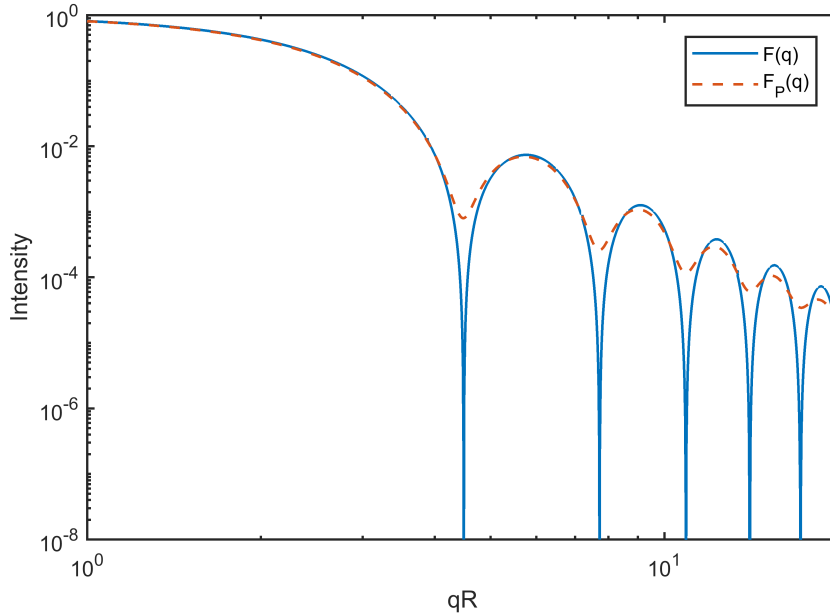


Figure 2.3: Simulation of $F(\mathbf{q})$ (blue) and $F_P(\mathbf{q})$ (red) with a polydispersity of $\delta = 4.5\%$ for $R = 25\text{nm}$ particles.

2.3 Speckle Patterns

A speckle pattern occurs when coherent light illuminates a disordered system, like a colloid. A typical speckle pattern for a pNipam sample at $T = 16^\circ\text{C}$ is shown in Fig. 2.4. It contains information about the dynamics of the investigated system. If a larger part of a

speckle pattern is recorded instead of a single point in q -space, more statistical information about the dynamics of the system can be gained.

The contrast of the speckle pattern recorded by the detector is given by:

$$\beta^2 = \frac{\text{var}(I)}{\langle I \rangle^2} \quad (2.11)$$

It depends on the coherence of the source, on the alignment of the setup and on the sample's dynamics. If the pulse width is longer than the time in which the particles rearrange themselves, the speckle pattern smears out. In the case of a fully coherent beam and a pulse width much shorter than the sample dynamics the contrast β is equal to 1.

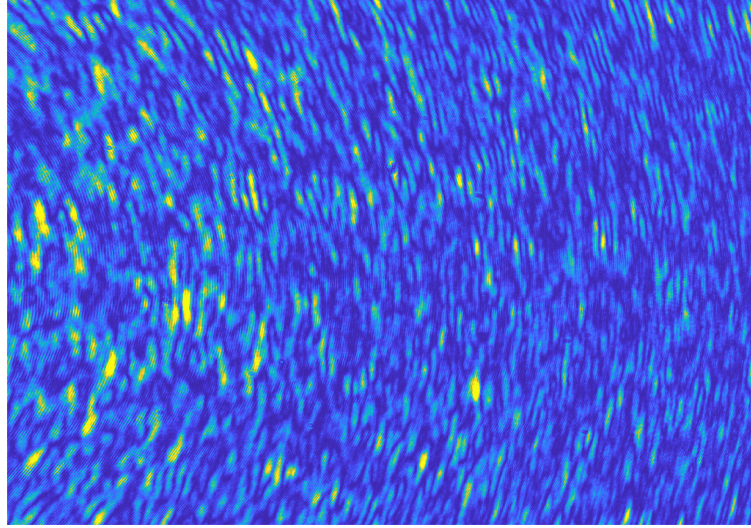


Figure 2.4: Speckle pattern from a pNipam sample measured at $T = 16^\circ\text{C}$ and an angle 2θ of 5° .

2.4 Photon Correlation Spectroscopy

Photon Correlation Spectroscopy (PCS) is a method to analyse the dynamics of a colloidal system. A sample is illuminated by a beam of coherent light. Then the intensity of the scattered light is measured by a detector. The schematics of a PCS measurement can be seen in Fig. 2.5.

Dynamics of the sample is measured by autocorrelating the intensity $I(t)$ of a scattered wave at a certain point in q -space $\mathbf{q}$ and a time t with the intensity $I(t + \tau)$ at a time $t + \tau$ and the same point in q -space. The normalized autocorrelation function of the scattered intensity is given by:

$$g_2(\mathbf{q}, t) = \frac{\langle |I(\mathbf{q}, t)| |I(\mathbf{q}, t + \tau)| \rangle}{\langle |I(\mathbf{q}, t)| \rangle^2} \quad (2.12)$$

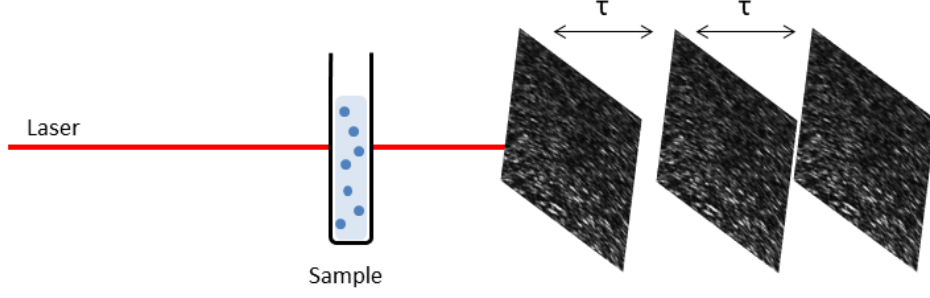


Figure 2.5: Schematic principle of a PCS experiment. The sample is illuminated by a beam of coherent light. The scattered intensity is recorded by the detector.

With the Siegert relation for Gaussian signals this can be rewritten as:

$$g_2(\mathbf{q}, t) = 1 + \beta^2 |f(\mathbf{q}, t)|^2 \quad (2.13)$$

where β is the contrast and $f(\mathbf{q}, t)$ is the normalized scattering function for Brownian motion:

$$f(\mathbf{q}, t) = e^{-\mathbf{q}^2 D_0 t} \quad (2.14)$$

where D_0 is the coefficient of self diffusion. The self diffusion coefficient D_0 is given by the Stokes-Einstein relation [1]:

$$D_0 = \frac{k_B T}{6\pi\eta R_h} \quad (2.15)$$

Here k_B is the Boltzmann constant, T is the temperature, η is the viscosity of the solvent and R_h is the hydrodynamical radius. The hydrodynamic radius is the radius of a spherical particle which is dissolved. The self diffusion coefficient is also related to the relaxation rate Γ and the characteristic time τ_c of the system:

$$\Gamma = q^2 D_0 = \frac{1}{\tau_c} \quad (2.16)$$

The characteristic time τ_c is defined as the time after the g_2 -function decays to $\frac{1}{e^2}$. The hydrodynamic radius R_h of a particle can be determined from the characteristic time of a system or the self diffusion coefficient, which can be determined by fitting the g_2 -function.

Simulations for g_2 -functions for particles of different sizes are shown in Fig. 2.6. If the contrast β is equal to 1, the g_2 -function goes from 2 to 1. The smaller the particle, the lower the characteristic time τ_c .

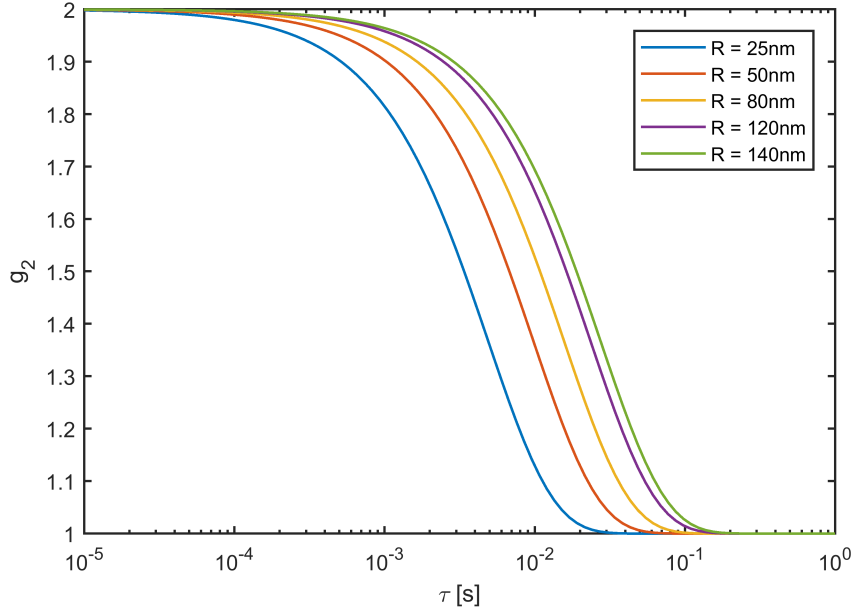


Figure 2.6: Simulation of g_2 -functions for particle sizes from 25nm to 140nm and $\beta^2 = 1$.

2.5 Double Pulse Photon Correlation Spectroscopy

Photon Correlation Spectroscopy often uses a point detector, which only captures a very narrow portion of q -space. Therefore the g_2 -function calculated for only one q -value provides very limited statistics. If a detector with more pixels is used, the data acquisition rate is limited by the frame rate of the detector. To measure at fast time scales and multiple q 's a double pulse approach was introduced [2]. Two pulses are generated at a short time τ apart from each other. Both illuminate the sample and are then recorded within one exposure time of the detector. The detector measures the summed up intensity of the two pulses $S(\mathbf{q}, t)$:

$$S(\mathbf{q}, \tau) = I(\mathbf{q}, t) + I(\mathbf{q}, t + \tau) \quad (2.17)$$

This technique is limited by the minimum distance between the two pulses and the minimum width of a single pulse. The correlation function for the summed intensity $S(\mathbf{q}, t)$ is:

$$c_2(\mathbf{q}, \tau) = \frac{\langle S^2(\mathbf{q}, \tau) \rangle - \langle S(\mathbf{q}, \tau) \rangle^2}{\langle S(\mathbf{q}, \tau) \rangle^2} \quad (2.18)$$

For very short time delays τ , the correlation function $c_2(\mathbf{q}, \tau)$ is equal to the single shot contrast. Simulated c_2 -functions for particles with $R = 50\text{nm}$ and different contrast β are shown in Fig. 2.7. In case of perfect contrast $\beta = 1$, the c_2 -function decreases from 1 to 0.5.

The contrast function $c_2(\mathbf{q}, \tau)$ can be rewritten as [2]:

$$c_2(\mathbf{q}, \tau) = \frac{\beta^2}{2}(1 + |f(\mathbf{q}, \tau)|^2) \quad (2.19)$$

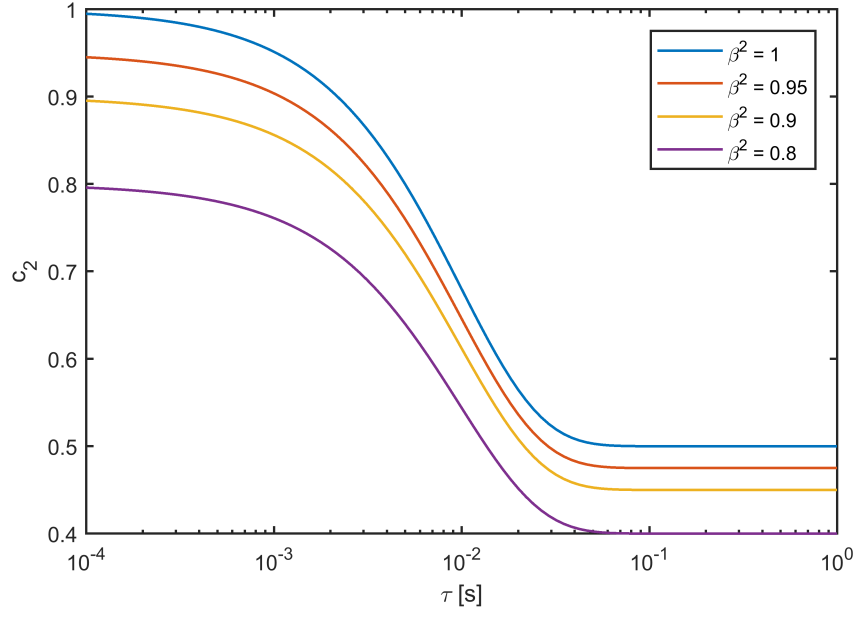


Figure 2.7: Simulation of c_2 -functions for β^2 from 1 to 0.8 and $R = 50\text{nm}$.

where β is the contrast of the speckle pattern. Equation 2.11 can be rewritten with Eq. 2.13:

$$g_2(\mathbf{q}, \tau) - 1 = 2c_2(\mathbf{q}, \tau) - \beta^2 \quad (2.20)$$

Using this relation, it is possible to calculate the g_2 -function from a c_2 -function.

Chapter 3

Experimental Setup

The schematics of the used Double Pulse Photon Correlation Spectroscopy (DPPCS) setup are shown in Fig. 3.1. A corresponding photo of the setup can be found in Appendix A.1. Details of the setup can be found elsewhere [7]. The setup is build on a $150\text{cm} \times 90\text{cm}$ optical table and is shielded by 2mm thick bead-blasted anodized aluminium barriers from *THORLABS* [8], black cloth and cardboard.

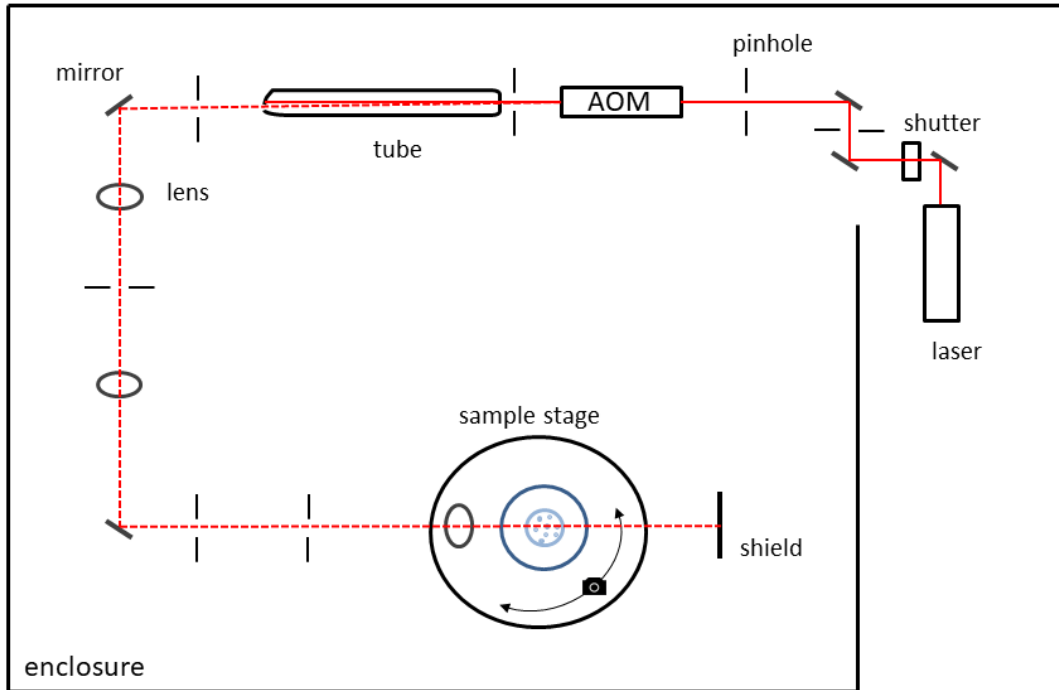


Figure 3.1: Schematics of the Double Pulse Photon Spectroscopy setup. The red line shows the path of the main beam. The dotted red line is the pulsed beam, defined by first order diffraction of the AOM.

The laser contained in the setup is a *LUMENTUM* HeNe Laser [9]. The specifications of the laser are listed in Tab. 3.1. An attenuator is placed behind the laser to adjust the intensity for example for finding the beam centre which is explained in Appendix B.

Parameter	HeNe Laser
Model	1145P
Wavelength	632.8nm
Power	21.0mW
Beam diameter ($\frac{1}{e^2}$)	0.7mm
Polarization	linear
Beam divergence	1.15mrad

Table 3.1: Specifications of HeNe laser from *LUMENTUM*.

The beam is then directed with mirrors through a safety shutter and two pinholes into the acusto-optic modulator (AOM). The AOM splits the beam into several diffraction orders, by initiating sound waves of radio frequency in a quartz crystal as shown in Fig. 3.2. The radio frequency driver (RF driver) initiating the sound waves is controlled by a wave function generator (WFG) triggering a digital delay generator (DDG), as shown in Fig.3.3. The main beam is blocked and only the first diffraction (pulsed) beam illuminates the sample. The number and length of the pulse is controlled by the DDG.

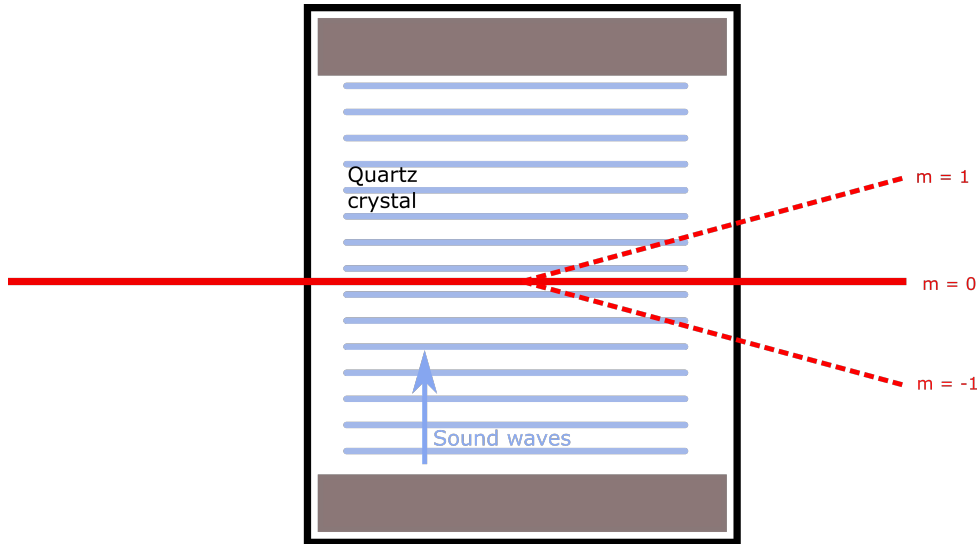


Figure 3.2: Schematic principle of the AOM. The laser beam is diffracted on the sound wave and split into several diffraction orders.

The beam is directed through a series of lenses and pinholes before arriving at the sample stage. The first lens ($f = 100\text{mm}$) focuses the beam. At the focal point a $200\mu\text{m}$ pinhole is placed to clean the beam from unwanted scattering artefacts. To keep the beam from diverging a second lens ($f = 100\text{mm}$) is placed behind the pinhole, collimating the beam. The beam goes through two more pinholes before it arrives at the sample stage. An image of the sample stage with the temperature-controlled sample environment can be seen in Fig. 3.4. The sample stage is motorized with four stepping motors, two for moving the sample along vertical and horizontal axes, one for rotating the detector around the sample and one for moving a focusing lens ($f = 100\text{mm}$). The motors are operated by *Sardana* based on a Tango server [10]. Before hitting the sample the beam is focused again. The scattering from the sample can be measured at an angle ranging from 0° to 100° with the 2D detector, here a *BASLER avA1000-120km*. The specifications of the

camera are listed in Tab. 3.2. The camera is operated with *LabVIEW NI Vision Assistant* [11]. The options of the camera are set with *Pylon Viewer* [12]. The distance between the sample and the detector is 8.3cm, so the BASLER avA1000-120km covers a range of 3.87° [7].

Parameter	Basler avA1000
Pixels	1024x1024
Pixel Size	5.5x5.5 μm^2
Max. frame rate	120fps
Sensor type	Kodak KAI-1050
Input/output trigger	yes

Table 3.2: Specifications of *BASLER avA1000-120km* [13].

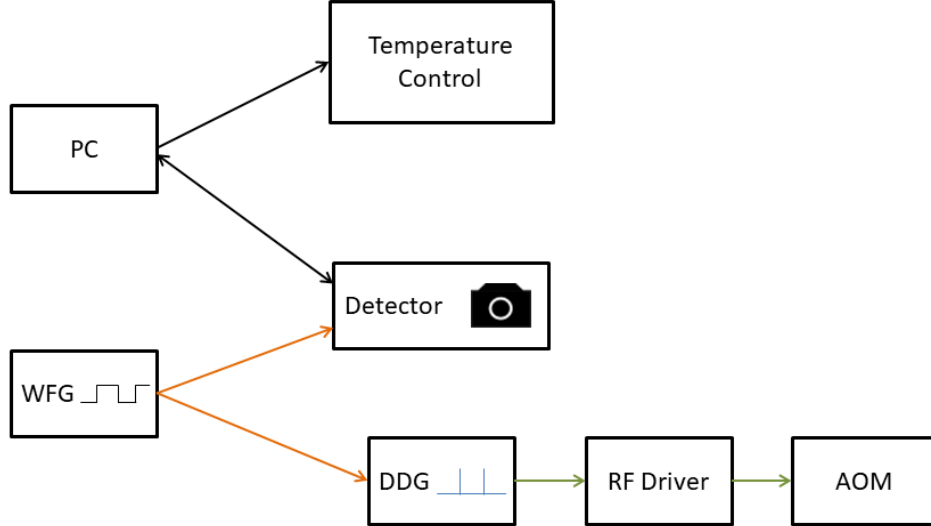


Figure 3.3: Communication between the various parts of the DPPCS setup. The Wave function Generator (WFG) triggers the Detector and Digital Delay Generator (DDG) (orange arrow). The double pulse signal from the DDG is sent to the AOM via the RF Driver (green arrow). The PC controls the temperature and the detector.

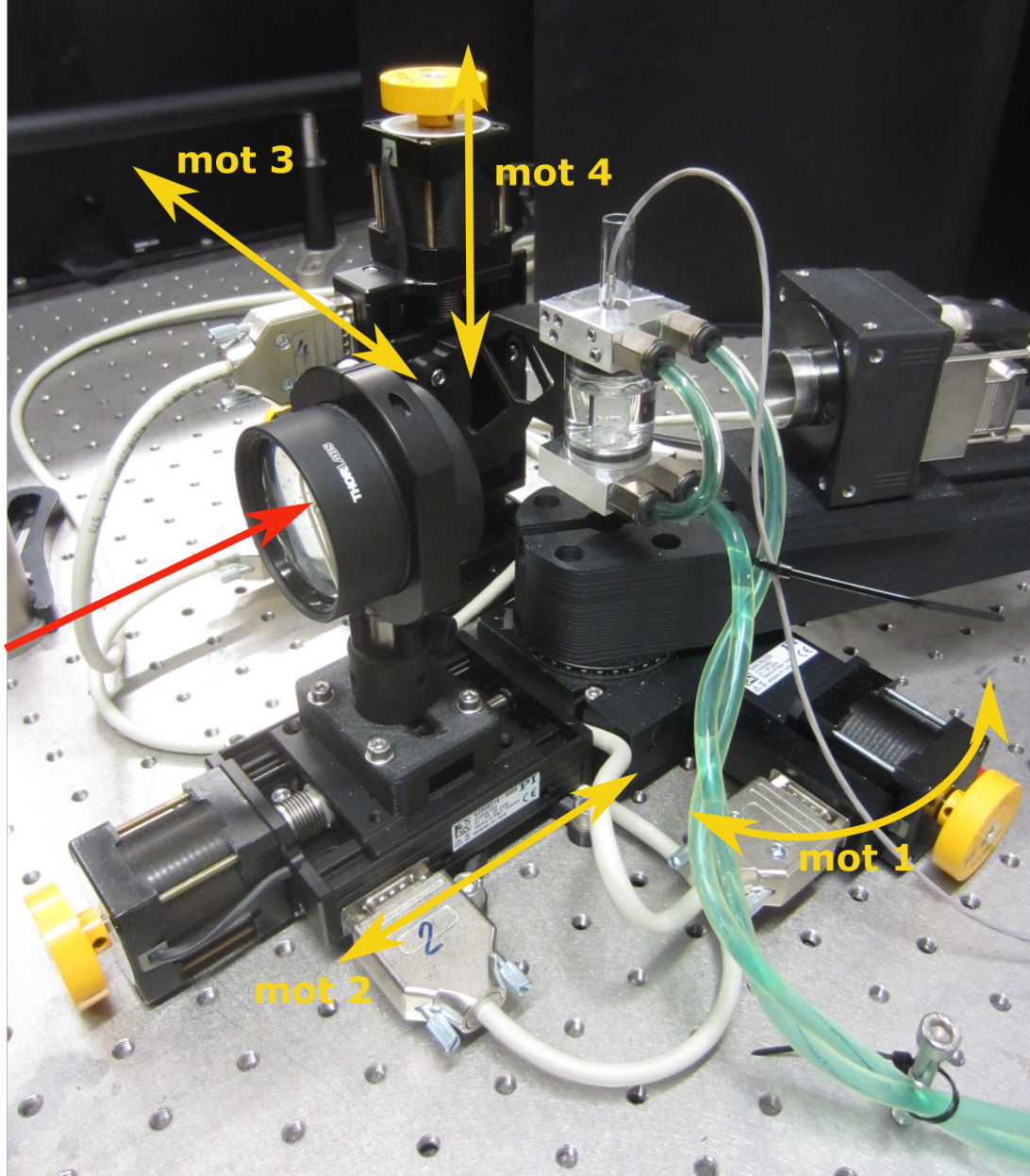


Figure 3.4: Sample stage of the DPPCS setup. Yellow arrows show in which direction the respective motor moves. The red arrow indicates the beam direction. The sample holder is connected the *Julabo F25-ME*. External temperature sensor is put directly into the sample.

An overview over the different timing signals can be seen in Fig. 3.5. The time flow of the WFG, DDG and Camera exposure signals is shown as a function of time. The WFG triggers the DDG and the camera. The DDG is connected to the AOM via the RF Driver. The camera has an internal delay of $42\mu\text{s}$. To make sure the two pulses are captured by the camera the pulses from the DDG are delayed by $100\mu\text{s}$. The pulse delay time between the pulses is set at least as long as the pulse width.

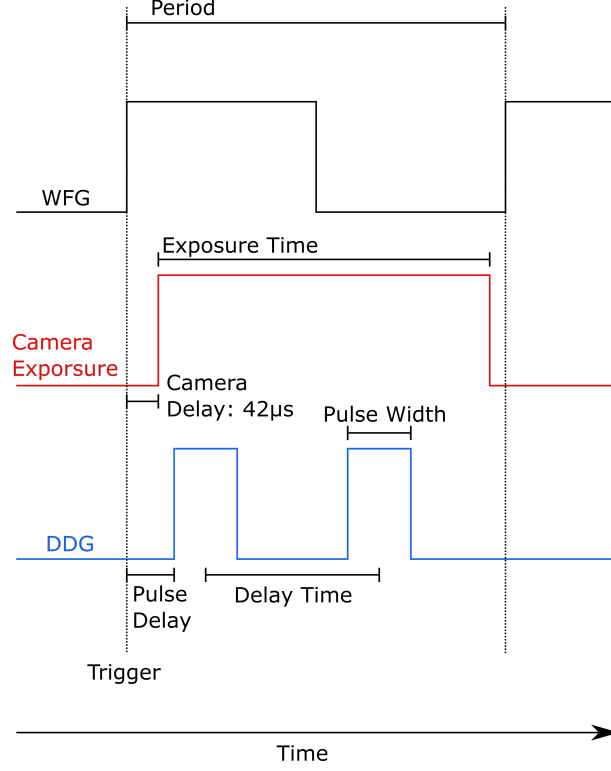


Figure 3.5: Overview over the signals of the WFG, the DDG and the camera exposure time. The WFG triggers the DDG and the camera.

3.1 Temperature-controlled sample environment

The temperature-controlled sample environment developed for the DPPCS setup can be seen in Fig. 3.4. To reduce background streaks the borosilicate glass capillarie [14] with the sample is placed in a bigger container filled with decalin. The refractive index of decalin is very similar to that of glass: $n_{\text{decalin}} \approx n_{\text{glass}} \approx 1.4$. The bigger glass container has metal plates at the top and bottom. Plastic hoses run through the metal plates connecting it to the *Julabo F25-ME Refrigerated/Heating Circulator*. Specifications of the *Julabo F25-ME* are shown in Tab. 3.3 [15]. The *Julabo F25-ME* can be controlled manually or by computer as shown in Fig. 3.3. It also has an external temperature sensor. The sensor can be used for temperature calibration measurements or to determine the temperature of the sample while measuring as shown in Fig. 3.4.

Parameter	Julabo F25-ME Refrigerated/Heating Circulator
Working temperature range	-28°C - 200°C
Temperature stability	$\pm 0.01^\circ\text{C}$
Setting / display resolution	0.01 °C

Table 3.3: Specifications of *Julabo F25-ME Refrigerated/Heating Circulator*.

3.2 Sample Systems

Two different sample systems were used to verify the functionality of the DPPCS setup, polystyrene microspheres and Poly(N-Isopropyl Acrylamide) (pNipam), both are shown in Fig. 3.6. PNipam is a thermoresponsive nanogel which undergoes a strong decrease in particle size at a temperature of $T \approx 32^\circ\text{C}$. The pNipam used in this experiment was diluted in water and has been fabricated inhouse.

Two different sizes of *Polybead* polystyrene microspheres were used, $R = 25\text{nm}$ and $R = 50\text{nm}$. Specifications are shown in Tab. 3.4.

Before measurements, the samples were diluted with ultra-pure water and filled into borosilicate glass capillaries. The capillaries were closed with a stopper to prevent the sample from evaporating.

Parameter	Polystyrene Microspheres
Manufacturer	Polyscience, Inc.
Description	<i>Polybead</i> non-functionalized microspheres
Diameter	100nm and 50nm
Coefficient of Variance (CV)	15%

Table 3.4: Specifications of *Polybead* polystyrene microspheres [16].



Figure 3.6: Polystyrene and pNipam sample systems. Left: pNipam and polystyrene spheres with $R = 50\text{nm}$ and $R = 25\text{nm}$. Right: Strongly diluted pNipam samples in glass capillaries.

Chapter 4

Data Analysis

The analysis of the data has been done with *Matlab R2017a*. For each data set a specific program was written. For the single pulse measurements a set of 100 or 200 images was taken, with additionally 10 or 20 dark frames respectively. The dark frames were taken by switching off the laser. Even though the detector can measure at frequency's of up to 120Hz, it can only store a very limited number of frames at a high speed. To ensure good statistics and to capture the whole g_2 -function the measurements were done at a frequency of 50Hz.

Each recorded image was divided into 18 different q -stripes and the g_2 -function was determined for each stripe via XPCSGUI [17]. XPCSGUI is a matlab based program to analyse X-Ray Photon Correlation Spectroscopy data. It can also be used to analyse PCS data. The g_2 -functions were then fitted. From the results for different fits the particle radius can either be determined directly for each q -stripe or via a linear fit over the relaxation rate Γ and the q -values with Eq. 2.16. In both cases the error is estimated as the error of the fit.

For the double pulse measurements there were 10 measurements with various pulse delays at each temperature. The delays ranged from 40 μ s for a pulse width of 30 μ s to 850ms for a pulse width of 300 μ s. Each of the 10 measurements included 100 frames. For each temperature a set of 100 darks was taken.

For the analysis a q -map was calculated with XPCSGUI for each temperature. The rest of the analysis was done using *Matlab*. The dark frames were added and an average dark frame was calculated. The images were corrected for darks and divided into 5 q -stripes with a Δq of 1.4 μm^{-1} . For each stripe the speckle contrast was calculated. From this contrast the c_2 -functions were calculated with Eq. 2.18. From the c_2 -functions the g_2 -functions were calculated with Eq. 2.20 and fitted. The radius of the particles was calculated by a linear fit over the relaxation rates Γ for different q 's. The error of the radius was estimated as the error of the linear fit.

An example of a frame taken by the detector with a selected q -stripe is shown in Fig. 4.1. The measurements of the small polystyrene particles ($R = 25\text{nm}$ and $R = 50\text{nm}$) were done at very low angles ($2\theta \approx 5^\circ$). At the small angles more parasitic scattering occurs compared to larger angles. Measurements with pure decalin and no sample were done to find motor settings with minimal parasitic scattering from the sample holder. Regions of high parasitic scattering or static background were masked out in the analysis as shown in Fig. 4.1.

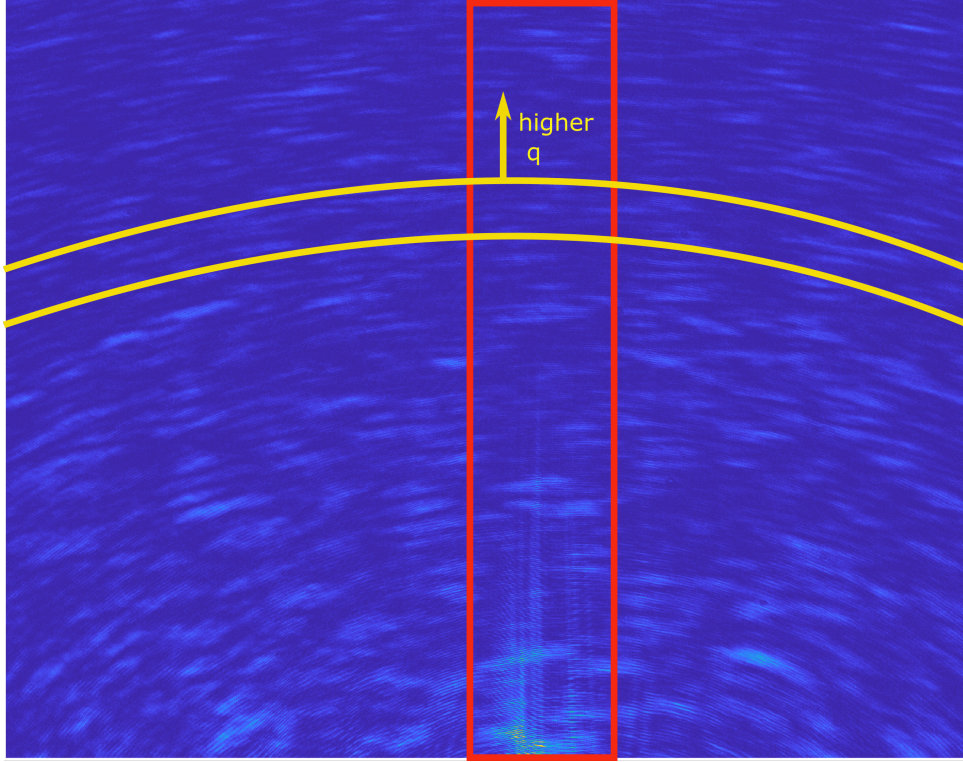


Figure 4.1: Speckle pattern of pNipam sample at $T = 38^\circ\text{C}$ and an angle of 3° . The yellow marked area shows a q -stripe. The red area is masked out and excluded from analysis due to parasitic scattering.

The measurements with the DLS setup were analysed with *LS Spectrometer* software [18]. It determined the g_2 -functions and the particle's radii for the measurements with polystyrene. For the pNipam measurement the g_2 -functions were determined by the *LS Spectrometer* software and then fitted with a *Matlab* program. A big difference between the DLS setup and the DPPCS setup is that the DLS uses a single pixel detector whereas the DPPCS setup uses a CCD camera. The image from the CCD can be divided into q -stripes while multiple measurements have to be done with the DLS to analyse several q 's.

Chapter 5

Results

5.1 Dynamic Light Scattering

Prior to the DPPCS experiments all the samples were characterized via Dynamic Light Scattering (DLS) experiments. For this a 3D LS Spectrometer from LS Instruments [18] was used. Both pNipam and Polystyrene samples were measured at various temperatures. The temperature was first increased from $T = 15^\circ\text{C}$ to 40°C and then decreased back to $T = 15^\circ\text{C}$ again. To assure the sample is at a stable temperature while measuring, there is a waiting time after changing the temperature. Two polystyrene measurements with the radii vs temperature directly determined by *LS Spectrometer* are shown in Fig. 5.1. The measurements have waiting times of 100s and 50s. As expected, the radius increases only a few nanometres with rising temperature.

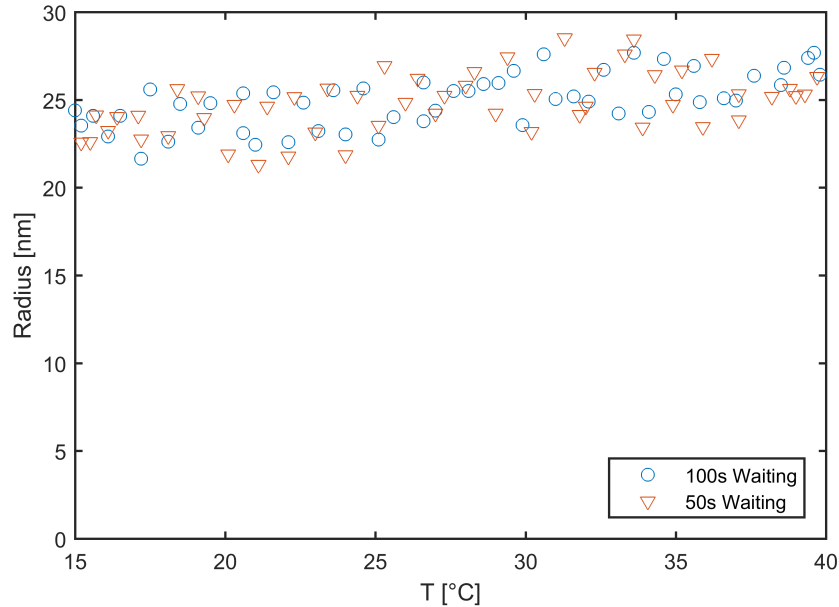


Figure 5.1: The radius of polystyrene spheres measured at temperatures from $T = 15^\circ\text{C}$ to $T = 40^\circ\text{C}$, with two different waiting time between measurements.

The DLS measurement for the pNipam sample is shown in Fig. 5.2. For this measurement the values for the g_2 -functions were taken from *LS Spectrometer* and fitted with Eq. 2.13, like shown for a g_2 -function at $T = 18^\circ\text{C}$ in Fig. 5.3. As expected, during the

heating process, the radius starts to decrease quickly at a temperature of approximately $T = 35^\circ\text{C}$. The radius increases again to about 75nm. This effect was not observed during decreasing the temperature. The radius started to increase from 75nm again at a temperature of $T = 42^\circ\text{C}$. This behaviour was not expected but occurred in several independent measurements [3].

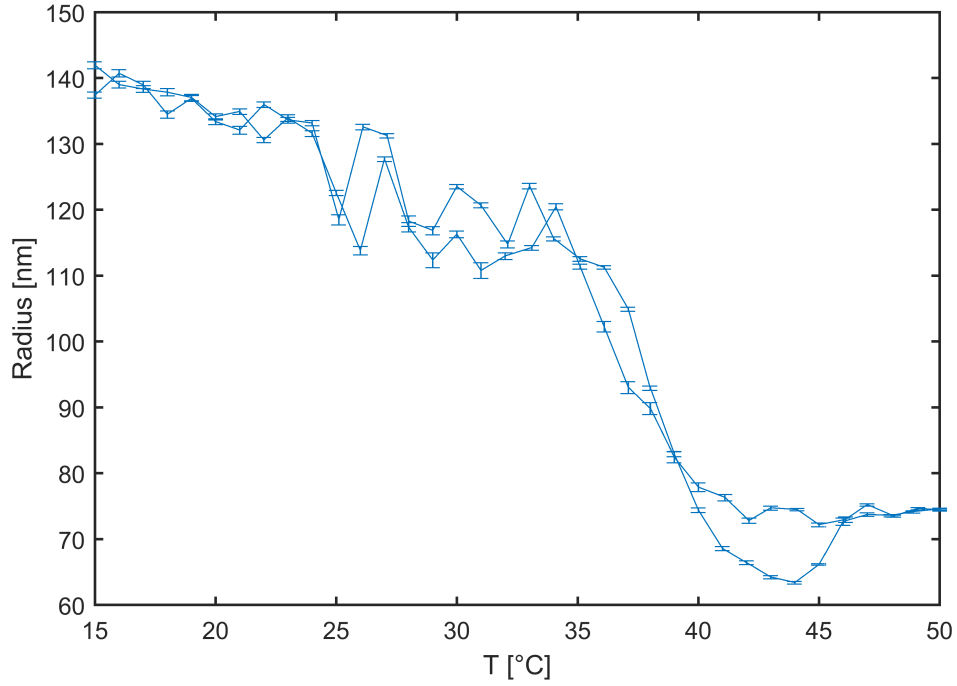


Figure 5.2: Radius of the pNipam sample for temperatures from $T = 15^\circ\text{C}$ to $T = 50^\circ\text{C}$ with 800s waiting time for temperature adjustment.

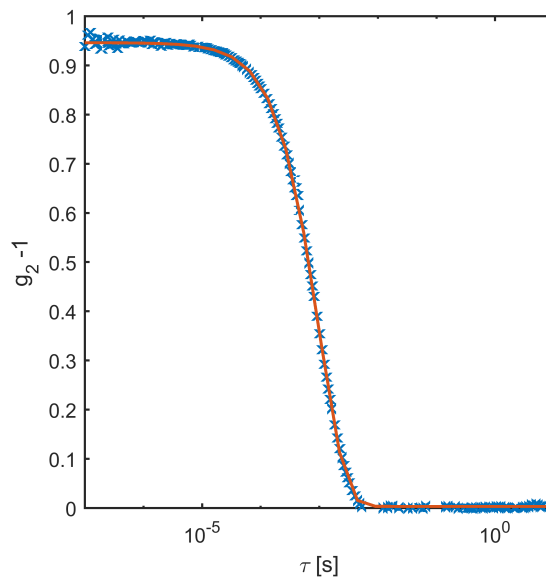


Figure 5.3: Example for a fitted g_2 -function at $T = 18^\circ\text{C}$. The fit determined $R = 134 \pm 1$ nm.

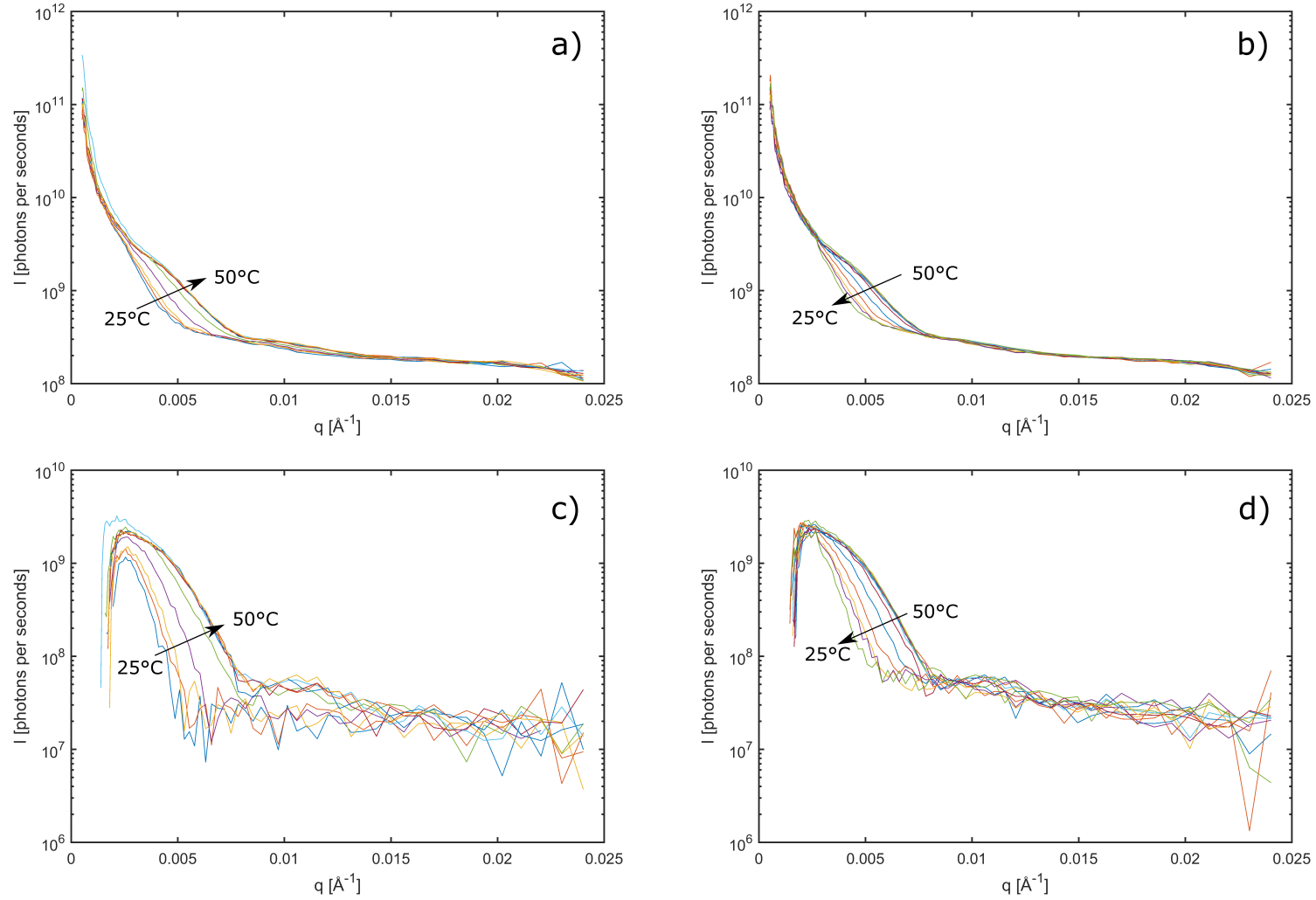


Figure 5.4: Measurements at PETRA III (beamline P10) at temperatures from $T = 25^\circ\text{C}$ to $T = 50^\circ\text{C}$. a) increasing temperature b) decreasing temperature c) increasing temperature, background subtracted d) decreasing temperature, background subtracted

5.2 Small Angle X-Ray Scattering

The pNipam sample was also investigated in a Small Angle X-Ray Scattering experiment at the beamline P10 of PETRA III. The scattered intensity was measured as a function of q , first while increasing the temperature from $T = 25^\circ\text{C}$ to $T = 50^\circ\text{C}$ and then decreasing it back to $T = 25^\circ\text{C}$ again. At each temperature point there were two measurements for the pNipam and one background measurement with water. The measurements for increasing and decreasing temperatures with and without background are shown in Fig. 5.4. At $q \approx 0.005\text{\AA}^{-1}$ the measured intensity changes more than one order of magnitude between temperatures from $T = 25^\circ\text{C}$ to $T = 50^\circ\text{C}$. This indicates that the pNipam is also temperature dependent.

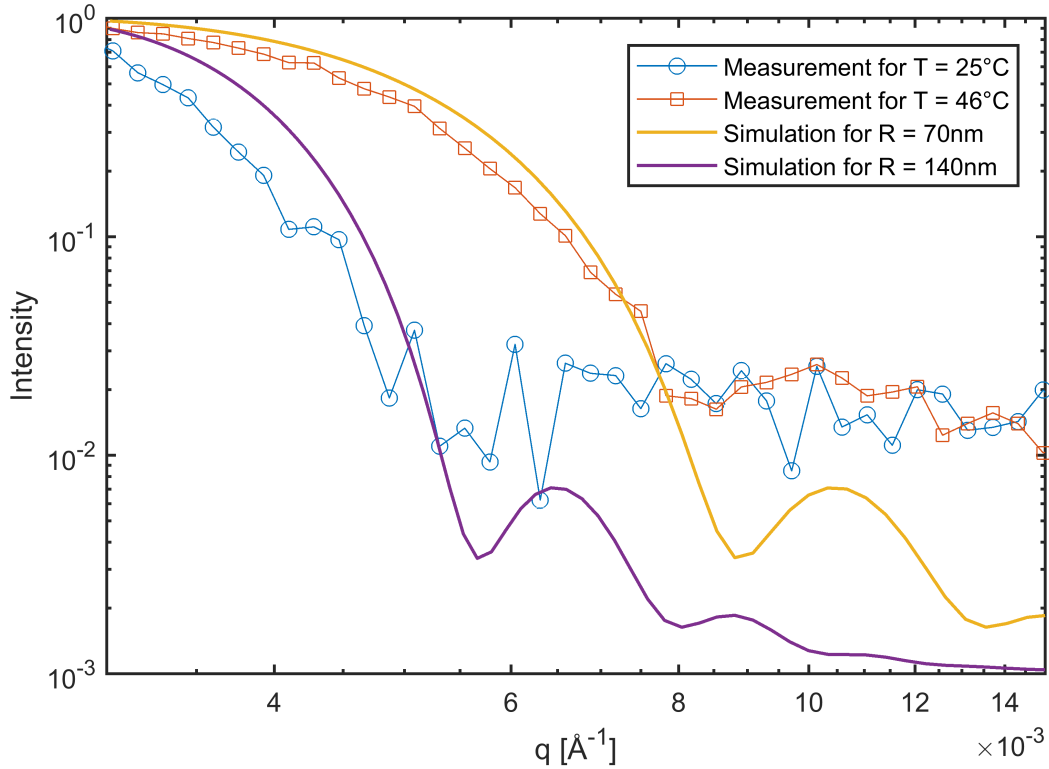


Figure 5.5: pNipam measurement at the beamline P10 of PETRA III for $T = 25^\circ\text{C}$ (blue) and $T = 46^\circ\text{C}$ (red), simulations of the form factor for $R = 70\text{nm}$ (yellow) and $R = 140\text{nm}$ (purple). For both simulations a polydispersity of $\delta = 8.1\%$ is used.

Fig. 5.5 shows two background corrected measurements for $T = 25^\circ\text{C}$ and $T = 46^\circ\text{C}$ while increasing the temperature and two simulations of the form factor with $R = 70\text{nm}$ and $R = 140\text{nm}$, respectively. The simulation for $R = 70\text{nm}$ is in good agreement with the curve for $T = 46^\circ\text{C}$ for q -values lower than $q = 0.008\text{\AA}^{-1}$, suggesting that the radius of pNipam is close to 70nm at $T = 46^\circ\text{C}$. The curve for $T = 25^\circ\text{C}$ is in agreement with the simulation for $R = 140\text{nm}$ for q -values lower than $q = 0.006\text{\AA}^{-1}$, suggesting that the radius of pNipam is close to 140nm at $T = 25^\circ\text{C}$. For q -values larger than $0.015\text{\AA}^{-1}$ the intensity in both simulated SAXS curves is an order of magnitude lower than the measured curves. This suggests that there is a significant amount of background scattering. In conclusion, a change in size depending on temperature was observed for the pNipam sample. A detailed analysis was not performed due to a significant amount of background scattering.

5.3 Single Pulse Contrast Measurements

To determine the maximum pulse width usable before the contrast measurements in DP-PCS, pNipam was investigated with different pulse widths at $T = 20^\circ\text{C}$. The measurements are shown in Fig. 5.6. The pulse widths ranged from 10ms to 850ms. For each pulse width a set of 100 images was taken and the contrast for different q 's within the images was calculated. The contrast for pulses longer than 100ms decreases fast because the particles move during the duration of the illumination and the speckle pattern starts to smear out. An image depicting this process i.e. speckles that are starting to smear out is shown in Fig. 5.7.

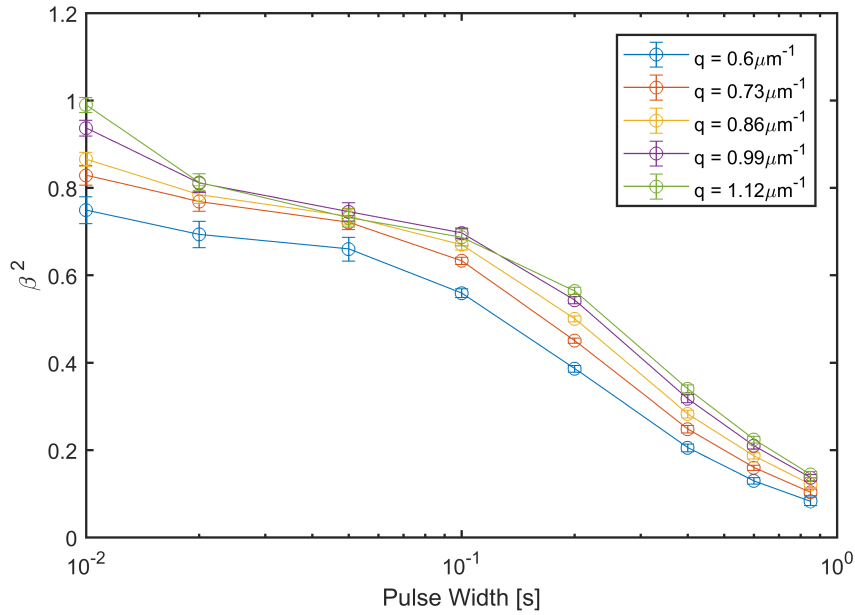


Figure 5.6: Contrast as a function of pulse width. The longer the pulse width, the lower the contrast.

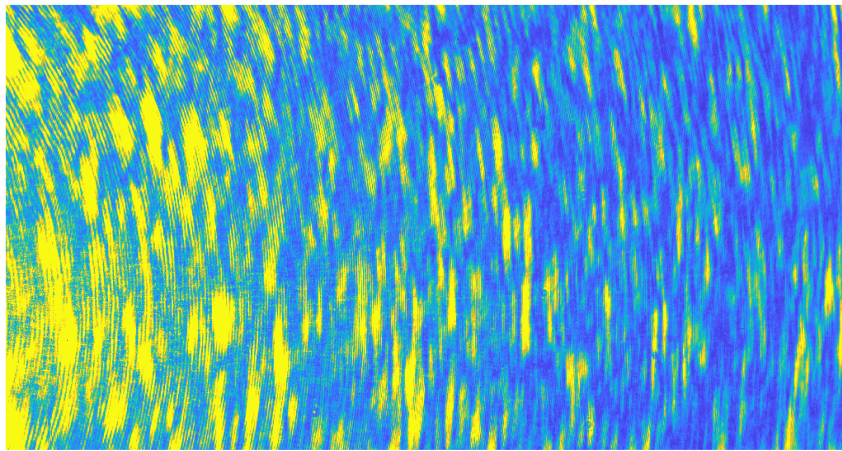


Figure 5.7: Speckle pattern of a pNipam sample at $T = 20^\circ\text{C}$, measured with a pulse width of 200ms. The speckles are starting to smear out.

5.4 Photon Correlation Spectroscopy

5.4.1 Single Pulse Measurements

Single Pulse Measurements were done for two different polystyrene samples ($R = 25\text{nm}$ and $R = 50\text{nm}$) and for a pNipam sample at temperatures from $T = 17^\circ\text{C}$ to $T = 46^\circ\text{C}$. Each taken image was divided into different q -stripes and for each q -stripe the g_2 -function was determined via XPCSGUI. The g_2 -functions for the 50nm polystyrene sample are shown in Fig. 5.8. The functions were then fitted and the result for the relaxation rate Γ for different q -values was plotted. From this plot one can determine the hydrodynamical radius of the particles with a linear fit, shown for the 50nm polystyrene sample in Fig. 5.8. For the linear fits only the values with a relatively low error were used. The resulting radii were $R_h = 27 \pm 3\text{nm}$ and $R_h = 52 \pm 5\text{nm}$. Both are in a very good agreement with the respective radii from the manufacturer, $R = 25 \pm 4\text{nm}$ and $R = 50 \pm 8\text{nm}$.

Fig. 5.8 also shows that for small particles it is no longer possible to measure the full g_2 -function because the acquisition rate is limited by the frame rate of the camera.

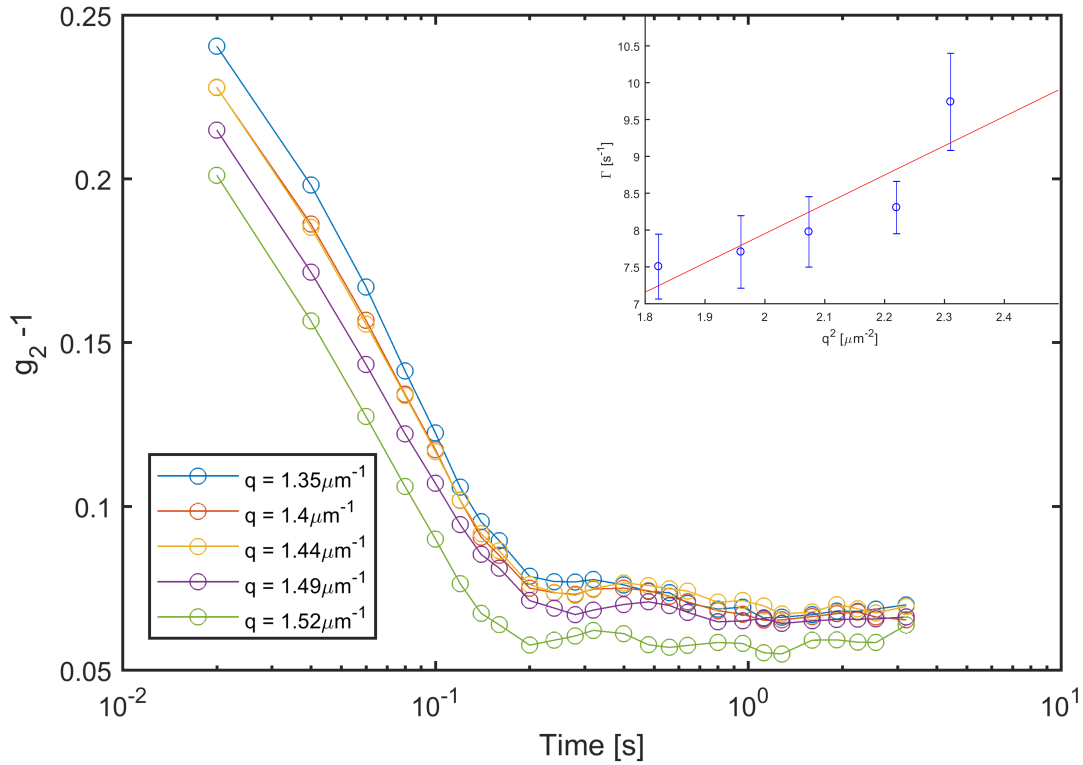


Figure 5.8: g_2 -functions for different q -stripes for the single pulse measurements of the $R = 50\text{nm}$ polystyrene sample. The inset shows the fit for the hydrodynamic radius R_h .

Before performing a temperature dependent measurement with the sample, there was a calibration measurement. The temperature in the bath and in the sample was measured, as shown in Fig. 5.9 along with the input temperature. This measurement shows that the temperature in the sample is always lower than the input temperature. It also shows that it takes approximately 40 minutes for the temperature to stabilize after a 3°C step.

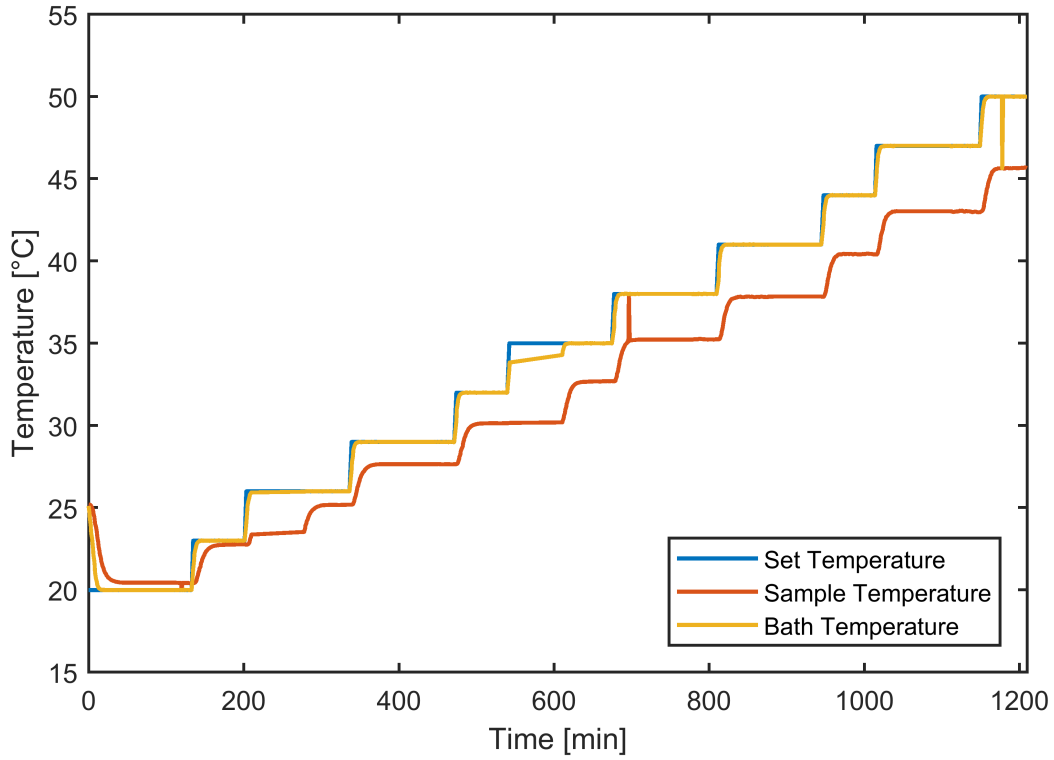


Figure 5.9: Calibration curve for the temperature dependent measurement. The temperature was increased in 3°C steps from 20°C to 50°C. The input temperature is plotted along with the temperature in the bath of the Julabo and the sample temperature.

For the pNipam sample the radius at each temperature was determined by fitting a single g_2 -curve, like shown in Fig. 5.10. The results of these fits are shown in Fig. 5.11. As expected the radius decreased with increasing temperature. However the measured radii decreased to only a few nanometres at higher temperatures. This result is not consistent with DLS measurements (see Fig.5.2), where the radius decreased to approx. 75nm. This discrepancy could be explained by the fits for the g_2 -functions. At higher temperatures they were no longer accurate because only a part of the g_2 -function could be measured.

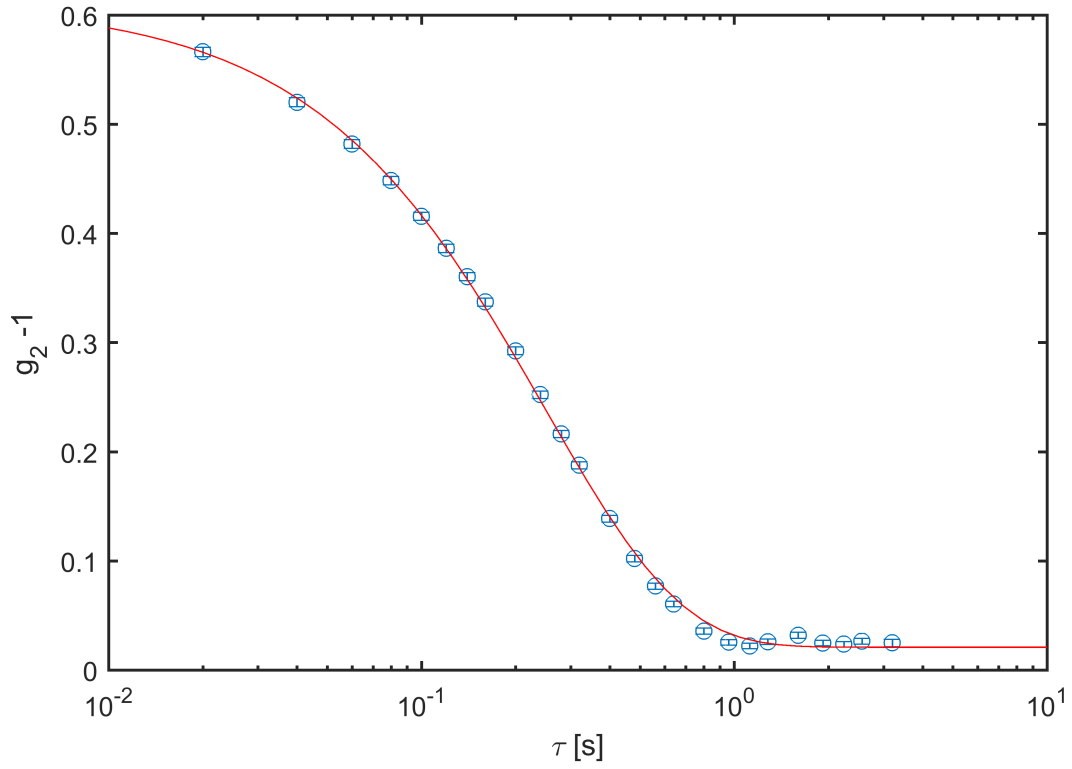


Figure 5.10: g_2 -curve and fit for the pNipam sample at $q=1.49 \text{ } \mu\text{m}^{-1}$ and $T = 23^\circ\text{C}$. The fit determined a radius of $R_h = 241\text{nm}$. The errors determined by XPCGUI lie within the data points.

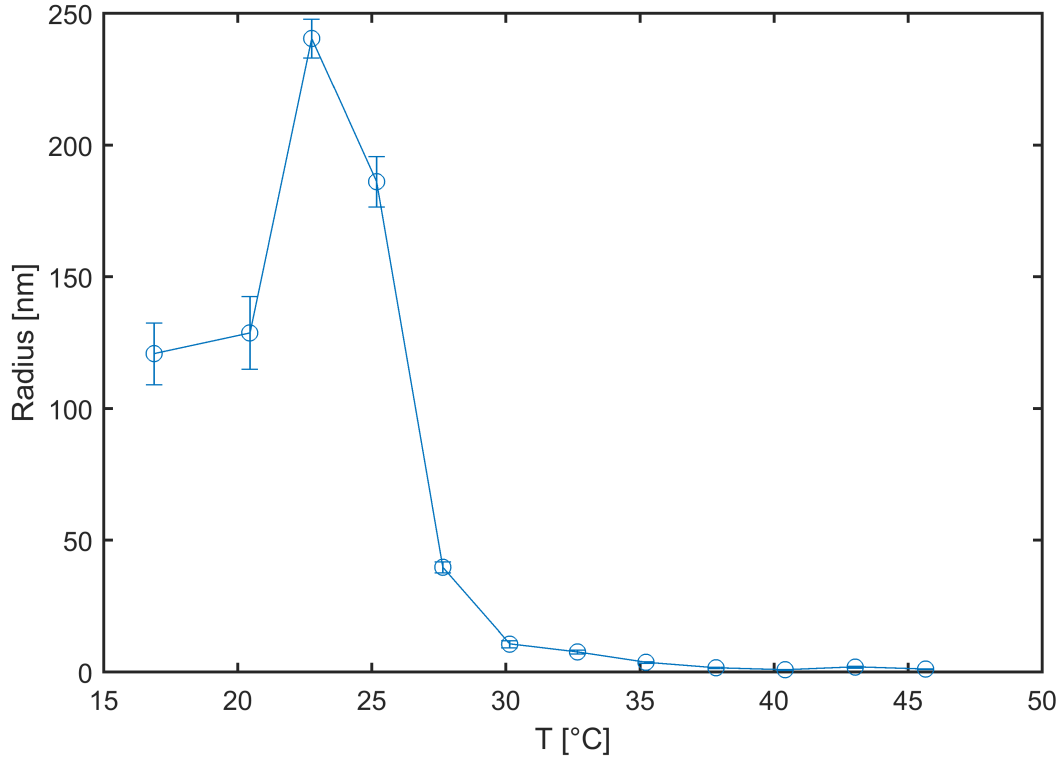


Figure 5.11: Radii of the pNipam sample determined by fitting single g_2 -curves at temperatures from 17°C to 46°C .

5.4.2 Double Pulse Measurements

Double Pulse measurements were done for the pNipam sample at various temperatures between $T = 20^\circ\text{C}$ and $T = 47^\circ\text{C}$. At each temperature there were 10 measurements with different times between the two pulses. The shortest time between two pulses was $40\mu\text{s}$ with a pulse width of $30\mu\text{s}$. From the measured c_2 data the g_2 -function was calculated using Eq. 2.20, the reconstructed g_2 -functions for $T = 26^\circ\text{C}$ and $T = 47^\circ\text{C}$ are shown in Fig. 5.12 and 5.13. The images were divided into 5 q -stripes, the g_2 -function was calculated for each of them. The g_2 -functions were fitted and the radius of the particles was determined via a linear fit of the relaxation rate Γ and the q -values from the different stripes. At $T = 26^\circ\text{C}$ a radius of $R_h = 125 \pm 9\text{nm}$ was determined, at $T = 47^\circ\text{C}$ the radius was $R_h = 26 \pm 1\text{nm}$. For faster dynamics at temperatures above 40°C the double pulse measurements still captured the whole g_2 -function as shown in Fig. 5.13.

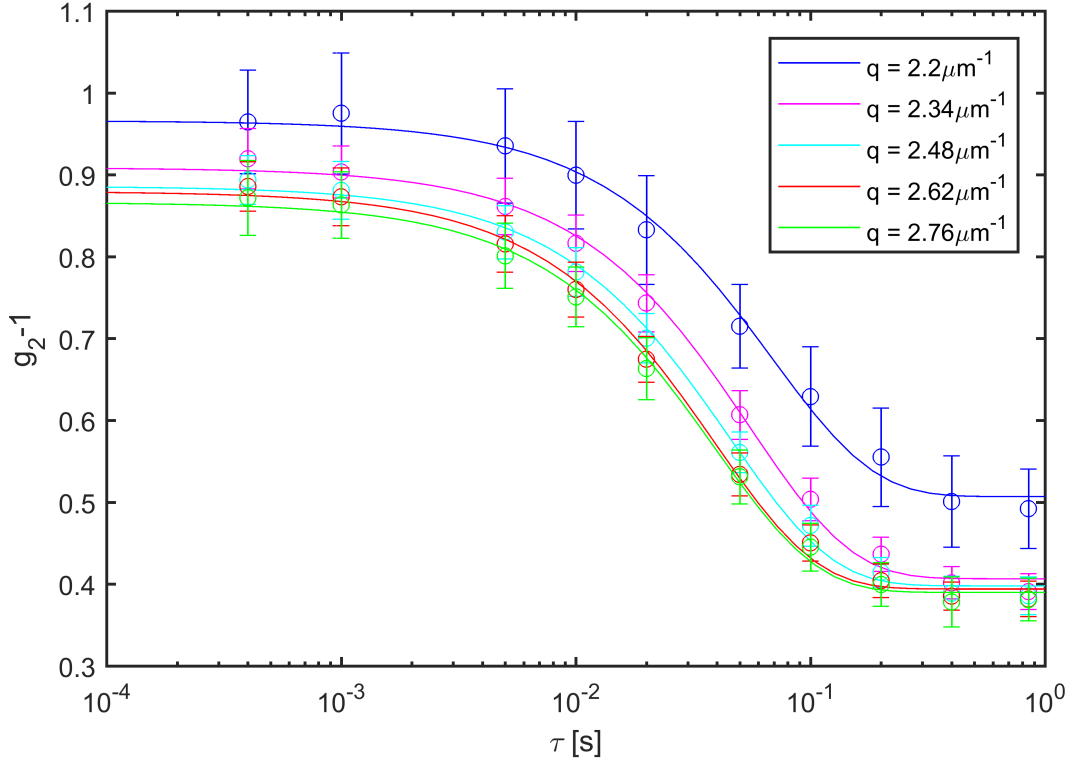


Figure 5.12: Double Pulse measurements for the pNipam sample at $T = 26^\circ\text{C}$ and an angle of 15° . The fits determined a radius of $R_h = 125 \pm 9\text{nm}$.

All of the fitted radii are plotted as a function of the temperature in Fig. 5.14. The radius of the pNipam decreases from $R_h = 140\text{nm}$ at $T = 20^\circ\text{C}$ to $R_h = 30\text{nm}$ at $T = 47^\circ\text{C}$, which is slightly smaller and at a lower temperature than in the DLS measurements. In conclusion, the results from the Double Pulse measurements are comparable to the results from the DLS measurements and the good performance of the temperature-controlled sample environment for the DPPCS setup has successfully been verified.

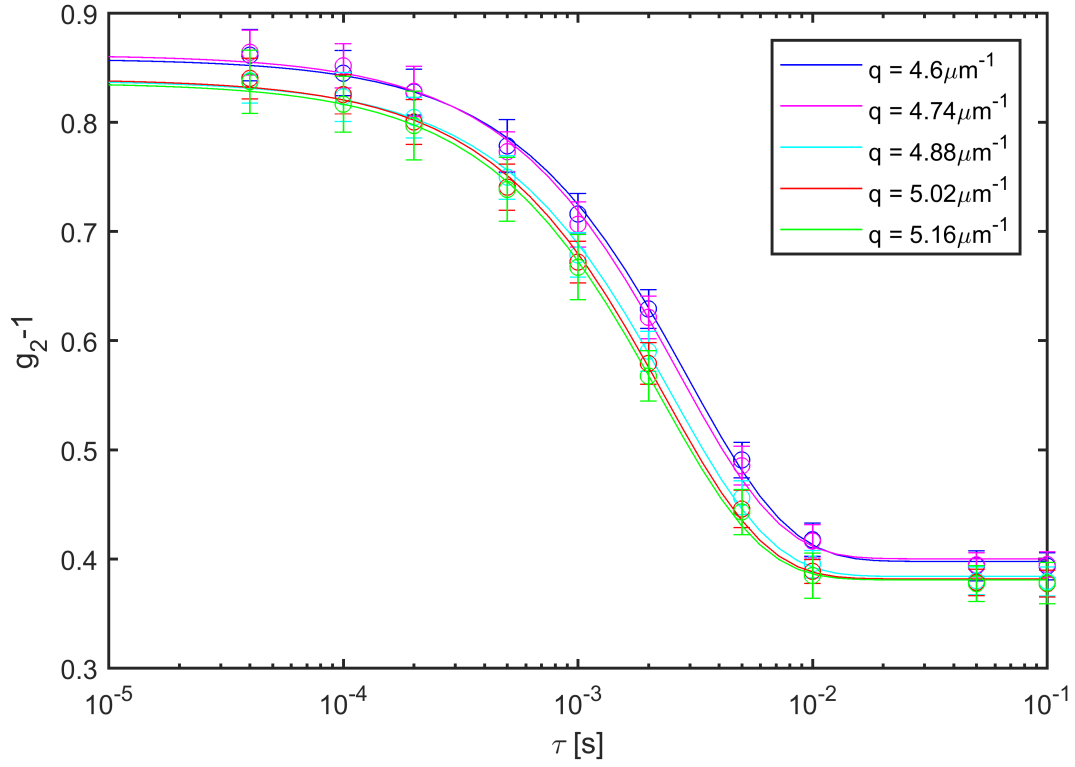


Figure 5.13: Double Pulse measurements for the pNipam sample at $T = 47^\circ\text{C}$ and an angle of 30° . The fits determined a radius of $R_h = 26 \pm 1\text{nm}$.

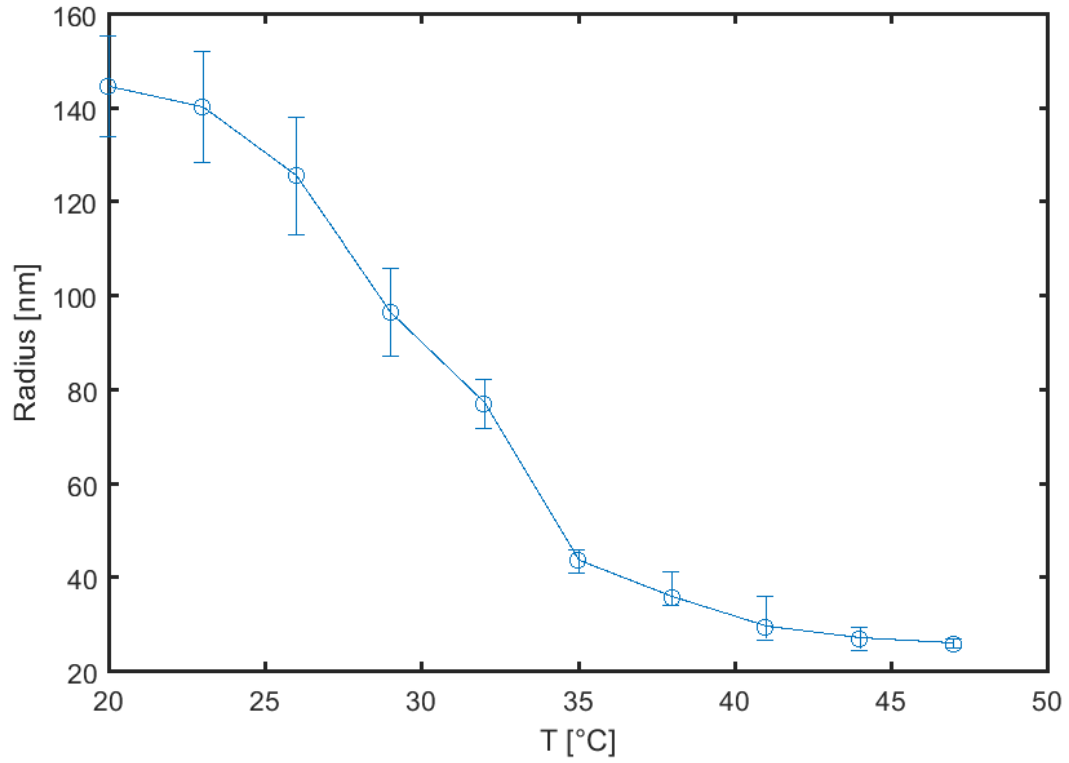


Figure 5.14: Fitted radii for the double pulse measurements at temperatures from $T = 20^\circ\text{C}$ to $T = 47^\circ\text{C}$. The radius decreases from $R_h = 145\text{nm}$ to $R_h = 25\text{nm}$ as a function of temperature.

Chapter 6

Summary and Outlook

A temperature-controlled sample environment for Double Pulse Photon Correlation Spectroscopy (DPPCS) has been developed. It was tested by Photon Correlation Spectroscopy (PCS) and DPPCS measurements with polystyrene samples with radii down to $R = 25\text{nm}$ and thermoresponsive Poly(N-Isopropyl Acrylamide) (pNipam), samples at temperatures from 20°C to 50°C . The pNipam was also investigated in a Small Angle X-Ray Scattering (SAXS) experiment at beamline P10 of PETRA III where a decrease in particle size with increasing temperature was observed. The results for the DPPCS setup show that the development was successful and the temperature dependent DPPCS is not limited by the detector frame rate but can measure the dynamics of nanometre sized particles with high statistics.

Future improvements on the DPPCS setup and the temperature controlled sample environment could be a sample holder with an integrated temperature sensor. Up to now the temperature in the sample is measured with the external temperature sensor of the *Julabo* by putting it inside the sample capillary. This means that either a temperature control measurement with water has to be done before the measurement to determine the actual temperature at each step or the sensor has to be inside the sample while measuring. This could lead to parasitic scattering and at higher temperatures to evaporation of the sample. The temperature sensor also produces a small amount of heat which can lead to heating of the sample.

Since the good performance of the setup was successfully verified more temperature dependent colloids like pNipam can now be investigated. The double pulse method provides a way to measure fast dynamics of nanometre samples at multiple q 's at the same time. The measurements are only limited by the minimum pulse width and the minimum delay between pulses. Measuring at multiple q 's at the same time also provides more statistics than a conventional one point detector.

Appendix A

DPPCS Setup

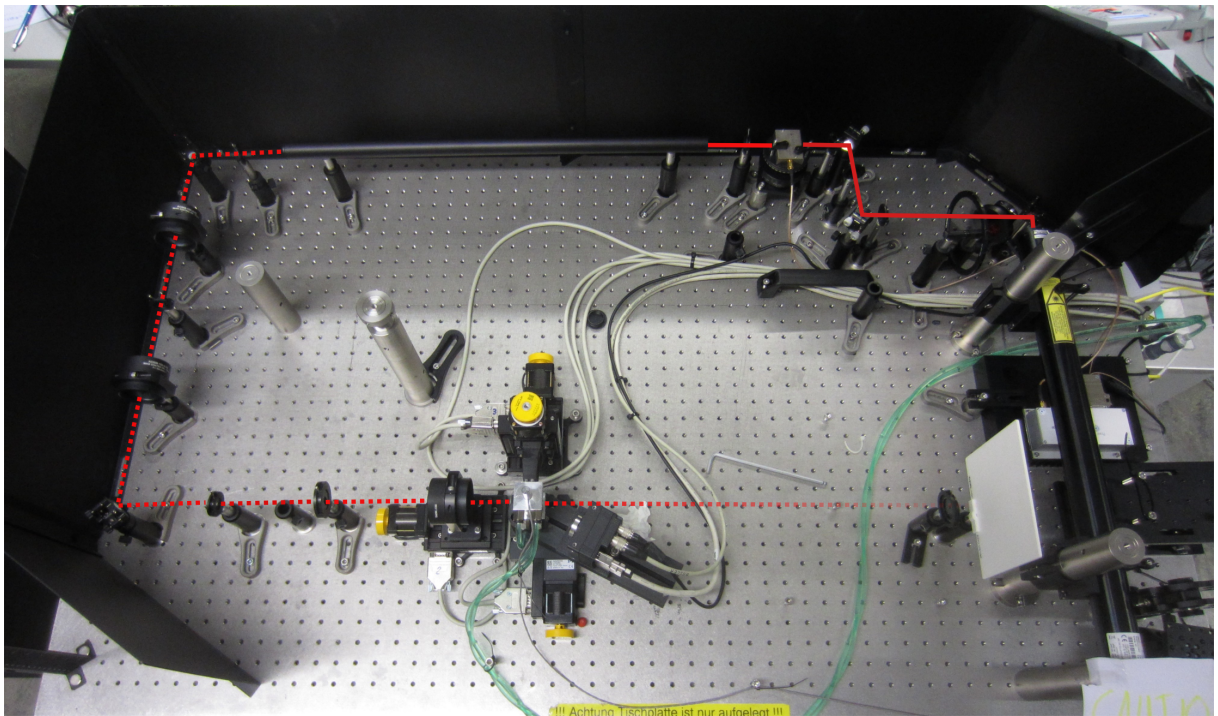


Figure A.1: Image of the DPPCS setup without most of the shielding. The red line shows the path of the direct beam, the dotted red line the path of the first order of diffraction.

Appendix B

Beam Center

To define an angle of 0° for the detector the intensity of the laser was reduced by placing an attenuator directly behind it. The detector was then placed in the direct beam and the beam was centred in the detector frame. A series of 100 images was taken and averaged with *Matlab*. The resulting image is shown in Fig. B.1. The position in which the images were taken, was set as zero point of the detector. From the image the exact position of the beam center was determined to [615,499].

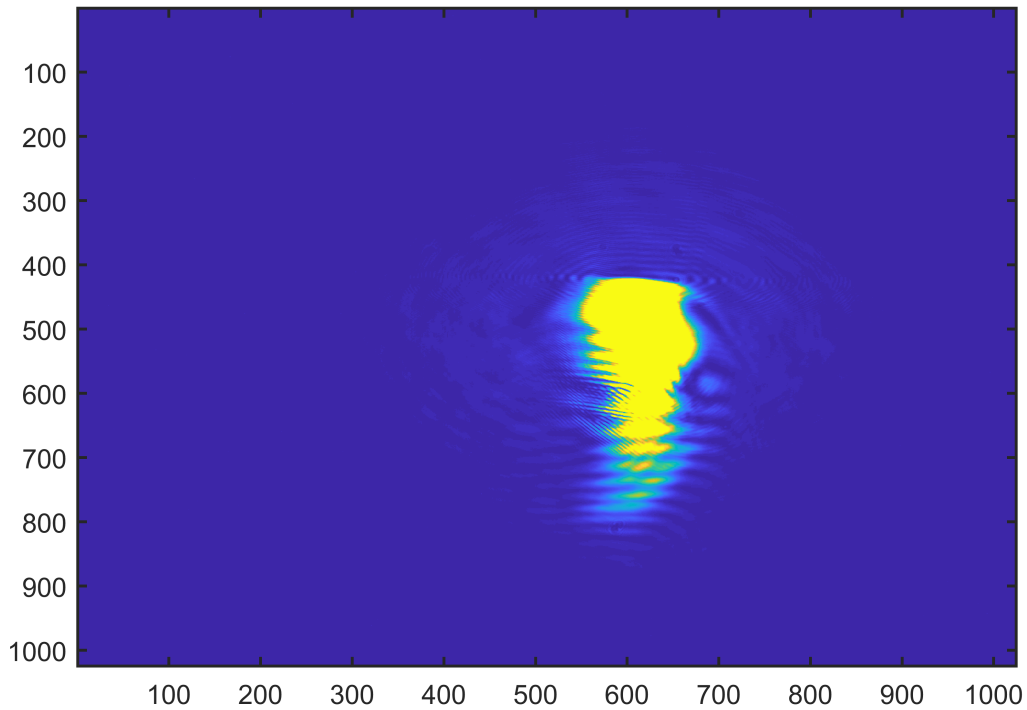


Figure B.1: Image of the direct laser beam. This position was set as zero point of the detector. The exact position of the beam center in the image was determined to [615,499].

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