

Ultrafast Dynamics of Nanoparticles in Highly Intense X-Ray Pulses

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Abstract

With the advent of lightsources of the fourth generation, such as the X-ray free electron laser (XFEL) the Linac Coherent Light Source (LCLS), structural studies on non-repetitive and non-reproducible nanoparticles such as single biomolecules appear imminent. A key challenge to increase the resolution of single particle imaging is radiation damage. Only a sound understanding of the underlying damage processes, such as the nanoplasma phase transition, can overcome this challenge and will ultimately lead to higher resolutions. Sacrificial tamper layers have been proposed to slow sample damage but this has not been shown experimentally in aerosol nanoparticles.

This work investigates the nanoplasma transition in superfluid He-, bulk Xe- and mixed HeXe-cluster using an ultrafast, XFEL accelerator-based X-ray pump – X-ray probe technique. Thereby triggers a first X-ray pulse the nanoplasma transition in the sample at intensities of $\sim 10^{17} \text{ W cm}^{-2}$ and a second X-ray pulse probes the system at a later time Δt at power densities of $\sim 10^{18} \text{ W cm}^{-2}$. Δt is varied from 0 fs to 800 fs delay. The probe creates a diffraction image of the ~ 30 to ~ 1000 nm sized objects with ~ 6 nm resolution and coincidentally ions are captured via time-of-flight (TOF) spectroscopy. He- and Xe-cluster are generated through a supersonic gas expansion into a vacuum. Mixed HeXe-cluster are created when He-droplets pickup Xe-atoms in a doping unit.

The study reveals single-shot snapshots of Xe-, He- and HeXe-cluster that undergo the nanoplasma phase transition. The reconstruction of a ~ 50 nm radius Xe-cluster with ~ 6 nm is shown. A large-scale structural analysis of the size and amount of scatterer in Xe-cluster show a rapidly expanding particle, thus structural damage. Expansion speeds and electron temperatures of the superheated nanoplasma are derived and compared to IR pump – X-ray probe studies. TOF spectroscopy reveals a time delay Δt depended ionization pattern in Xe-atoms and HeXe-cluster, while pristine He-droplets do not exhibit this dependency. The structural analysis of few hundred nm radius HeXe-cluster shows that the doped Xe-atoms arrange in small clusters to a plum-pudding type. The He-droplet acts thereby as shell and the Xe-cluster as sample. The X-ray pump – X-ray probe study on HeXe-cluster shows structural damage in the He-droplet, while Xe-cluster do not show structural damage 800 fs after the pump-pulse. Sample damage in pristine He-droplets is found and compared to Xe- and HeXe-cluster.

Contents

| | |
|---|-----------|
| 1. Introduction | 1 |
| 2. Fundamental Concepts | 3 |
| 2.1. Why X-ray free electron laser? | 3 |
| 2.1.1. From bending magnets to undulator | 5 |
| 2.1.2. Self amplification by spontaneous emission | 7 |
| 2.1.3. Soft X-ray self seeding | 9 |
| 2.1.4. Novel X-ray pump–probe techniques | 13 |
| 2.2. Rare gas clusters | 16 |
| 2.2.1. Creation of a homogenous cluster | 17 |
| 2.2.2. Formation of a heterogeneous cluster: The pickup principle | 22 |
| 2.3. Soft X-rays in matter | 24 |
| 2.3.1. Small angle X-ray scattering | 24 |
| 2.3.2. Ionization of matter | 28 |
| 2.3.3. Charge migration | 34 |
| 2.4. Ionization of clusters in intense X-ray pulses | 35 |
| 2.4.1. Formation and expansion of a nanoplasma | 36 |
| 2.4.2. Imaging of transient states | 38 |
| 2.4.3. Tampered layers to inhibit the nanoplasma expansion | 40 |
| 3. Experimental Setup | 44 |
| 3.1. The AMO instrument and FEE at the LCLS | 44 |
| 3.1.1. Focus characterization using a TOF spectrometer | 48 |
| 3.1.2. Focus characterization via imprint study | 49 |
| 3.2. The LAMP end-station at AMO | 49 |
| 3.3. The large area pn-CCD detectors | 53 |
| 3.4. Sample delivery | 55 |
| 3.4.1. Sample jet timing at LCLS | 58 |
| 3.5. Time of flight mass-spectrometer | 60 |

| | |
|--|------------|
| 4. Methods | 64 |
| 4.1. The computing environment at LCLS | 64 |
| 4.2. pnCCD photon detectors | 66 |
| 4.2.1. Combining multiple pnCCD detectors | 68 |
| 4.2.2. Impact of X-ray pump – X-ray probe on diffraction pattern | 72 |
| 4.3. Phase retrieval from a single diffraction pattern | 73 |
| 4.3.1. Principle of phase retrieval | 74 |
| 4.3.2. 2D reconstructions and image resolution | 74 |
| 4.3.3. 1D projections and phase reconstructions | 78 |
| 4.4. 2D electron density and diffraction image simulations | 79 |
| 4.5. Acqiris data sampling considerations | 81 |
| 4.6. Data filtering | 83 |
| 5. Results and discussion | 85 |
| 5.1. Structural damage in Xe-cluster induced by intense X-rays | 85 |
| 5.2. Time-dependend response of Xe-atoms due to a X-ray pump–probe beam . | 91 |
| 5.3. Time-resolved response of highly ionized He- and HeXe-cluster | 92 |
| 5.4. Condensation of xenon in helium cluster: Plum-pudding type cluster . . | 96 |
| 5.5. Understanding structural damage in plum-pudding type cluster | 99 |
| 5.6. Sacrificial layers: Comparison of structural damage in He- and HeXe-cluster | 102 |
| 6. Summary and outlook | 105 |
| 7. Appendix | 107 |
| 7.1. Matlab code on spherical integrations | 107 |
| 7.2. Python code on combining detectors | 108 |
| 8. Bibliography | 111 |
| A. Publications by the author | A |
| B. Disclaimer | C |
| C. Acknowledgment | D |

List of Figures

| | | |
|-------|--|----|
| 2.1. | Aerial view of the Linac Coherent Light Source. | 4 |
| 2.2. | Schematic setup of an undulator. | 6 |
| 2.3. | Undulator gain curve correlated to microbunching. | 8 |
| 2.4. | SASE single-shot and average spectra | 10 |
| 2.5. | Soft X-ray self-seeding spectra and brilliance of various lightsources. | 11 |
| 2.6. | Schematic setup of an undulator based pump–probe scheme. | 14 |
| 2.7. | Schematic setup of a bunch based pump-probe setup. | 16 |
| 2.8. | Schematic of a supersonic gas expansion into a vacuum. | 18 |
| 2.9. | Schematic of a pickup (gas-)source. | 22 |
| 2.10. | Principle of scattering rays of an atom. | 26 |
| 2.11. | Total absorption cross-sections for helium and xenon. | 29 |
| 2.12. | Schematic illustration of common charge transfer processes | 33 |
| 2.13. | Fluorescence spectra from xenon and neon K-LL Auger spectrum. | 34 |
| 2.14. | Schematic of the nanoplasma creation and expansion. | 36 |
| 2.15. | Measurement and simulation of the nanoplasma expansion in xenon cluster. | 39 |
| 2.16. | Experiment that shows early evolution of the nanoplasma transition. | 40 |
| 2.17. | Time of flight spectra of argon and xenon core-shell systems. | 42 |
| 3.1. | Schematic overview of the AMO beamline instrumentation. | 45 |
| 3.2. | Focal spot analysis using a time-of-flight ion spectrometer. | 47 |
| 3.3. | Focal spot analysis via an ex-situ microscope imprint study. | 48 |
| 3.4. | Overview of the AMO instrument in the LAMP end-station configuration. | 50 |
| 3.5. | Inside view of the C1 chamber showcasing the interaction region. | 51 |
| 3.6. | Rear and front pnCCD detector geometry in the LAMP instrument. | 52 |
| 3.7. | Geometry of a single pnCCD module. | 54 |
| 3.8. | Sideview of double sample jet configuration. | 56 |
| 3.9. | Schematic of the Parker-Hannifin Series 99 valve. | 57 |
| 3.10. | Schematic of LCLS EVR timing system. | 58 |
| 3.11. | Event receiver time delay at LCLS for supersonic gas jets. | 60 |
| 3.12. | Drawing of the time of flight spectrometer. | 62 |

| | |
|---|-----|
| 3.13. Sideview of the spectrometer showing ion, electron and photon trajectories. | 63 |
| 4.1. Diagram of the computing environment at LCLS and DAQ traffic. | 65 |
| 4.2. ADU histograms from electronic noise of not illuminated pnCCDs. | 67 |
| 4.3. Front and rear pnCCD arranged to combine measured diffraction image. | 70 |
| 4.4. Spherical projection of 2D diffraction image in 1D. | 71 |
| 4.5. Influence of X-ray pump– X-ray probe study in diffraction image. | 72 |
| 4.6. Example of a phase retrieval algorithm. | 74 |
| 4.7. Illustration of resolution enhancement and diffraction image cropping. | 76 |
| 4.8. Used electron densities in 2D real and Fourier space simulations. | 79 |
| 4.9. Comparison of analytical derived scattering and numerical simulations. | 80 |
| 4.10. First data point in Acqiris sampling. | 81 |
| 4.11. Using light peak to find absolute time zero in Acqiris traces. | 82 |
| 4.12. Average cluster size correlated to measured intensity on front pnCCD. | 83 |
| 5.1. Single Xe-cluster size distribution at varying time delay Δt . | 86 |
| 5.2. Time-resolved reduction of number of scatterer due to nanoplasma expansion | 87 |
| 5.3. Single-shot diffraction pattern of Xe-cluster at varying time delays | 88 |
| 5.4. Single-shot 1D reconstruction of ~ 30 nm radius Xe-cluster | 89 |
| 5.5. Recovered Amplitudes $ A $ and phase factor of 1D reconstruction | 90 |
| 5.6. Single-shot 2D reconstructions of ~ 50 nm radius Xe-cluster. | 91 |
| 5.7. Time-resolved answer of atomic xenon in TOF spectroscopy. | 92 |
| 5.8. Time-resolved answer of He-cluster in TOF spectroscopy. | 93 |
| 5.9. TOF spectra of HeXe-cluster with $\sim 0.6\%$ Xe-doping at various delays Δt . | 94 |
| 5.10. TOF spectra of HeXe-cluster with $\sim 0.06\%$ Xe-doping at various delays Δt . | 95 |
| 5.11. Potential arrangement of Xe-cluster within He-droplets. | 97 |
| 5.12. Reconstruction of HeXe-cluster and simulated electron densities. | 99 |
| 5.13. Simulated structural damage scenarios in HeXe-cluster | 100 |
| 5.14. Simulation and exp. data: Structural damage in He-droplet. | 101 |
| 5.15. Single-shot diffraction images of He-droplets at different time delays | 102 |
| 5.16. Single-shot diffraction patterns of HeXe-cluster at different time delays | 103 |

List of Tables

| | | |
|------|---|-----|
| 2.1. | Parameter K_{gas} values for rare gases. | 21 |
| 2.2. | Differential absorption cross-sections and ionization potentials for xenon. . | 31 |
| 2.3. | Absorption cross-sections and ionization potentials for xenon and helium . | 31 |
| 2.4. | Atomic scattering factors for helium and xenon. | 32 |
| 3.1. | Summary of LCLS beam parameter | 50 |
| 3.2. | pnCCD gain modes and typical ADU values at 1k eV photons. | 55 |
| 3.3. | Installed vacuum pumps in the experiment. | 56 |
| 3.4. | Applied voltages to the time of flight spectrometer. Ion side use only. . . . | 62 |
| 4.1. | Typical parameter used in the Hawk software package. | 75 |
| 5.1. | Relative comparison of measured scattering versus expected scattering. . . | 103 |

1. Introduction

At the end of the 19th century, Röntgen discovered the X-radiation [1] and quickly realized its impact due to its novel attributes. Soon, he was able to take the first medical X-ray image. Later, X-rays lead to the understanding of fundamental aspects of atoms [2] and crystals [3, 4]. The success story continues until today, where X-rays are being used to study the shape of proteins through crystallography. Proteins are the so-called “workhorse” in the human body and the shape of a protein defines its biological function. Unfortunately not all proteins can be grown as large crystal making the shape determination challenging. The advent of new lightsources, namely X-ray free electron laser (FEL) [5], enable new methods to study bio-molecules and other particles with intense and short pulsed X-rays [6, 7]. However, all matter irradiated by intense X-ray radiation disintegrates into its atomic components on ultrafast timescales¹ [8]. This process is a form radiation damage and is a major challenge for imaging methods with FEL [9].

The underlying principle of these imaging methods is that intense X-ray pulses diffract from a single macromolecular structure before they destroy it. In diffraction imaging, images of single, nanometer-sized particles can be taken for structural research. First experiments have successfully delivered single-shot diffraction images of biological particles, such as viruses [10] and non-biological particles, such as rare-gas cluster [11] and it has been a rapidly developing field enabling 3D images of nano-objects [12, 13].

A key driver of this success has been the development of new lightsources with more and more spectral brightness. The first hard X-ray FEL (XFEL) was built at Stanford University and is called the Linac Coherent Light Source (LCLS) [14]. It is a 4.1 km long machine² that produces X-rays (wavelengths from 4.6 nm to 0.1 nm), has a very high intense beam ($10^{18} \frac{\text{W}}{\text{cm}^2}$) and ultra short pulses (1 – 500 fs). LCLS is a user facility and scientists from around the world may apply to use this lightsource for their experiments. The Atomic, Molecular and Optical (AMO) physics instrument was the first of seven instruments that started operating and still is a focal point for biological imaging experiments to basic science [15].

Let us now imagine that we expose a nanoparticle to the highly intense X-rays from

¹Ultrafast timescales are on the order of atto- to nanoseconds.

²Measurement on Google maps from the injector building to the far experimental hall.

1. Introduction

LCLS (or any other XFEL). Within the first moment of interaction from the light and the nanoparticle, photons scatter distinctive to the shape of the particle that we are thus able measure. But the particle will also absorb the rays and lead to inner atomic-shell vacancies [16]. Subsequent processes, such as the Auger-decay, occur only few femtoseconds later and eventually the nanoparticle is transformed into a nanoplasm. The nanoplasm is very hot, comparable to the conditions of the surface of the sun and several forces will expand the plasma on the femtosecond timescale [17]. Finally, the nanoplasm disintegrates into its atomic components. The absorption process, which triggers this cascade of events in the nanoparticle, is unavoidable when the particle is exposed to intense X-rays and so is radiation damage in the sample.

The principle to *outrun* the radiation induced damage with femtosecond lightpulses is challenging for two reasons. One, it limits the intensity output of the lightsource, and two, sample damages due to photoionization and changing scattering factors are inevitable. Ultimately, these reasons will limit the achievable resolution in single particle imaging. But radiation damage can also be addressed in other ways. Computer models can account for known processes [18] and novel methods from AMO physics science such as molecule alignment [19] and sacrificial tamper layer [20, 21].

This thesis describes the nanoplasm phase transition in detail. A novel X-ray pump – X-ray probe method was employed to study the nanoplasm evolution in the testbed nanoparticles liquid He-, bulk Xe- and mixed HeXe-cluster. The pump-pulse initiates a cascade of X-ray induced effects in these particles and the probe-pulse creates a *snapshot* of the at a later time Δt . Coincident diffraction imaging and time-of-flight mass spectroscopy data is taken to answer the following questions:

- How compares X-ray induced damage to optical light induced damage?
- On what timescales change absorption cross-sections due to X-ray irradiation?
- How do mixed HeXe-cluster self-organize as a nanoparticle?
- Can tamper layer slow radiation damage in aerosol nanoparticles?

This document is organized as follows. Chapter 2 discusses fundamental aspects that are being used throughout this study. The focus of chapter 3 is the experimental setup at the AMO instrument at LCLS describing particularly the LAMP end-station and pnCCD detectors. In chapter 4, several computational methods are discussed in detail. Chapter 5 presents the results of the pump–probe study and finally 6 summarizes the present work and provides an outlook for further studies.

2. Fundamental Concepts

This chapter condenses the theoretic concepts that will reoccur throughout the present thesis. We start off in section 2.1 with an introduction to the key aspects of X-ray free electron lasers (XFEL) including the beam operating modes self-amplified spontaneous emission (SASE), self-seeding and X-ray pump – X-ray probe. Section 2.2 is about the formation of rare gas clusters via supersonic jets and pickup sources. We then dive into the interaction of light and matter in section 2.3 that discusses coherent, elastic X-ray scattering, and inelastic processes in atoms. The chapter ends with section 2.4 describing the nanoplasma formation in pristine cluster and core-shell systems.

2.1. Why X-ray free electron laser?

X-rays were first created through *Bremsstrahlung*, where an electron beam with kinetic energies E_{kin} of 100eV - 100keV hit a block of copper and the deceleration of electrons in the copper led to the creation of X-rays. Since then, there has been tremendous progress in the creation of X-rays and are commonly created in synchrotron facilities for scientific purposes. In a synchrotron facility, electrons are accelerated near the speed of light $E_{\text{kin}} > \text{MeV}$ and then injected into a storage ring. The electrons are deflected at bending magnets to circle around the ring. The acceleration at the bending magnet leads to the emission of X-rays. Typically, electrons are bunched together to increase the amount of emitted photons and a synchrotron can store many electron bunches, thus a high repetition rate of light pulses on the order of megahertz. The X-ray pulses are characterized through the so called spectral brightness [22] or sometimes brilliance. We can define the spectral brightness as [23]

$$B = \frac{n}{A \Theta \Delta E}, \quad (2.1)$$

with n being the number of photons per second, A the source area, Θ the divergence of the beam, and ΔE being the spectral bandwidth of the light pulse. The spectral brightness is an overall measure of the quality of a light source. The development of modern synchrotron light sources is hence often measured and compared to previous achieved

2. Fundamental Concepts



Figure 2.1.: Aerial view of the Linac Coherent Light Source (LCLS). LCLS uses the last third of the SLAC Linear Accelerator but is overall a 4.1km long machine. The accelerator and buildings are stretched far because of the process light is generated. From [24]

B values. The motivation to improve the spectral brightness is to let a sample interact with as many photons possible, in the shortest time as possible and with an energy resolution as best as possible. In other words, more brilliant light sources are needed to create images of even smaller particles, or investigate dynamics that are even faster. To give a numerical example and to get a better understanding of the improvements needed, let us look at non-linear absorption dynamics in atoms and molecules. One can conservatively estimate that a typical absorption cross section at soft X-rays¹ is around $\sigma = 1 \text{ megabarn (Mb)}$ [25]. Typical X-ray focii are² $A = 1\mu\text{m}^2$ such that the number of photons n_{in} needed to absorb just 1 photon per atom n_{abs} is

$$n_{in} = \frac{n_{abs}A}{\sigma} = \frac{10^{-8}\text{cm}^2}{10^{-18}\text{cm}^2} = 10^{10} \quad \text{photons.} \quad (2.2)$$

An example of a modern synchrotron source is NSLS-II and it produces 1.710^4 photons per pulse in the Si111 bandwidth at pulse durations of a few ten picoseconds [26]. That is far out of reach to investigate non-linear, or multi-photon, processes. While this back on the envelope type of calculation might be off by an order of magnitude or so depending on the specific case, it illustrates the order of magnitude improvement scientists were looking for to unravel entire new aspects of nature. As it is not possible to use conventional optical methods to control X-rays, a progressive United States defense program in the 80's ignited an atomic bomb to create an X-ray beam that was intended for use as

¹X-rays with wavelengths of 10nm to 0.2nm.

²Focus size at the AMO endstation at LCLS.

2.1. Why X-ray free electron laser?

anti-(space)missile defense [27]. In a similar time, it was also proposed to build free electron laser [28, 29] to increase the spectral brightness. Free electron laser, amplify the light along a straight line to create optical laser alike radiation and a FEL can be seen in birds eye view in figure 2.1. Construction of the first hard X-ray finished in 2009 and the FEL is called Linac Coherent Light Source (LCLS). X-ray free-electron lasers (XFEL) are able to create 10^{12} photons per pulse and achieve pulse lengths of a few femtoseconds and allow the study of ultrafast processes, for example the movement of electrons in chemical reactions [14, 16]. The beam parameters of FEL increased the spectral brightness by many orders of magnitudes³ and we will explore this topic in detail in the next few subsections. Few XFEL exist today, LCLS at SLAC National Accelerator Laboratory in the United States, SACLAC at RIKEN in Japan but more are being build. The European XFEL near DESY⁴ in Germany, the SwissFEL at Paul Scherrer Institut and the PAL-XFEL at Pohang Accelerator Laboratory in South Korea.

2.1.1. From bending magnets to undulator

In synchrotron lightsources as well as free electron lasers, X-rays are generated using (bending) magnets. The first improvement to creating X-rays at a bending magnet was through a *wiggler*. Wigglers consist of magnets that are arranged in an alternating order to force the electron bunch on a sinusoidal trajectory. An electron bunch that is traveling through a wiggler near the speed of light is wiggled along its path using magnetic fields, which causes the particles to emit radiation. Wigglers can be considered as a series of bending magnets, which is why the total emitted power $P_{emitted}$ is proportional to the number of magnets m [31]

$$P_{emitted} \propto m, \quad \text{in a wiggler magnet.} \quad (2.3)$$

The emitted radiation has a broad, continuous spectrum and the center of that spectrum can be controlled by changing the speed or kinetic energy of the electron bunch. Wigglers have been used at the Stanford Synchrotron Radiation Lightsource (SSRL) in 1979 to generate X-rays. Independently from wigglers, undulators were developed [32]. A schematic setup of an undulator can be seen in figure 2.2. Wigglers and undulators create radiation because of the same principle, an electron bunch is accelerated near the speed of light and then forced on a sinusoidal pathway. In undulators, the separation of magnets is named undulator period λ_U . The undulator period and magnetic fields

³See figure 2.5 for an illustration of the improvement in brilliance.

⁴abbreviation for Deutsches Elektron Synchrotron

2. Fundamental Concepts

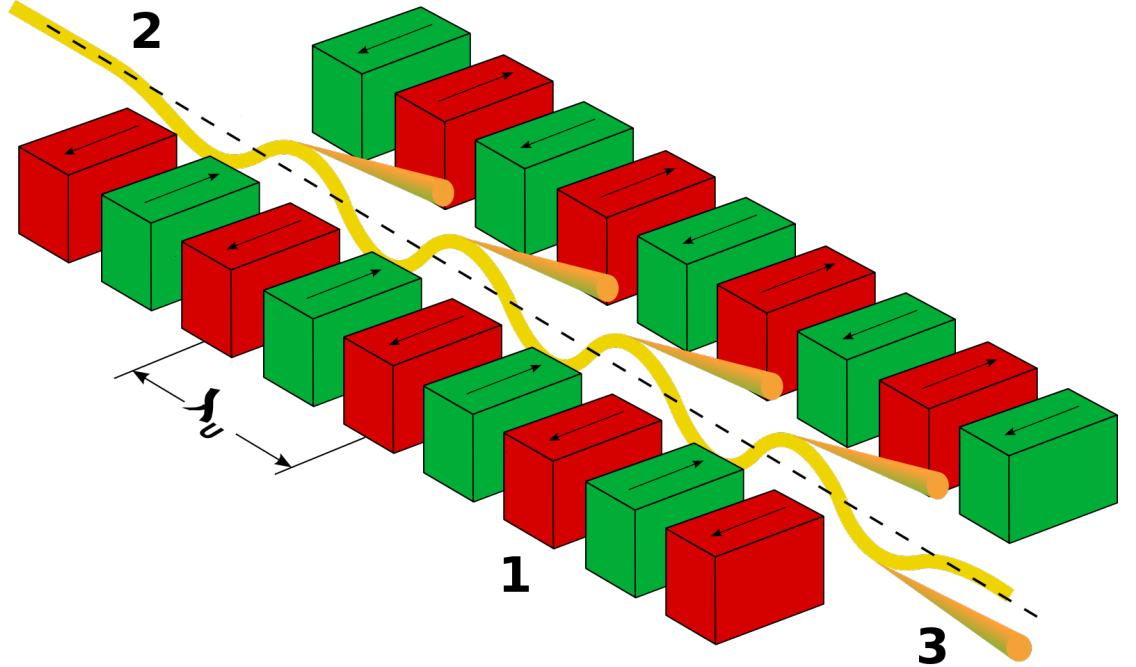


Figure 2.2.: Schematic setup of an undulator with a period of λ_U . (1) Magnets in alternating polarity; the arrows indicate the direction of the magnetic field. (2) Incoming electron bunch near the speed of light. (3) Emited light in beam direction due to sinusodial movement of the electron bunch. From [30].

are chosen such that the emitted radiation per period constructively interferes with each other. Thus the emitted power P_W now scales with [33]

$$P_{\text{emitted}} \propto m^2, \quad \text{in an undulator magnet} \quad (2.4)$$

The emitted wavelengths of undulators have a more narrow spectrum and a higher flux than wigglers. We can further characterize undulator (and wiggler) by the strength parameter K , which is given by [34]

$$K = \frac{e B_{\max} \lambda_U}{2\pi m_e c}, \quad (2.5)$$

2.1. Why X-ray free electron laser?

with e being the elementary charge, B_{\max} being the maximum magnetic field in the undulator (wiggler), m_e being the mass of an electron and c being the speed of light, we can write in convenient units

$$K \approx 0.934 B_{\max} \lambda_U \quad [\text{T cm}]. \quad (2.6)$$

Undulator typically have $K < 1 \text{ Tcm}$ (and wiggler $K \gg 1 \text{ Tcm}$). Undulator magnets are large constructs of a few meters and their undulator period is on the order of centimeter. The electrons emit radiation in the nanometer wavelength regime because the electrons near the speed of light have to be considered relativistic and in view of the electrons the undulator period λ_U appears shorter. We can account for the relativistic effects and express the resonantly amplified wavelength λ_r by [34]

$$\lambda_r = \frac{\lambda_U}{2\gamma} \left(1 + \frac{K^2}{2} + \gamma^2 \Psi^2 \right), \quad (2.7)$$

with the kinetic energy γ of the electron bunch in the undulator and the electrons observation angle Ψ . Summarizing, modern lightsources use undulators to generate radiation as these magnets create more photons that have a narrow spectral bandwidth compared to bending magnets and wiggler. Undulators are characterized by the strength parameter given in equation 2.6, which is only dependent on the undulator gap λ_U and the magnetic field B . The fundamental amplified wavelength is given by the resonance condition equation 2.7.

2.1.2. Self amplification by spontaneous emission

If an electron bunch travels through just one undulator, the emitted power scales with linearly with the number of electrons N_e , which is due to the finite size and random electron density distribution of an electron bunch. If the electrons emit light from the same point or separated by $n \lambda_r$ ($n = \{1, 2, 3, \dots\}$) the emitted photons would constructively interfere and would be coherent. FEL use this idea to generate their light pulses. FEL have a straight and long undulator section⁵, where multiple undulators are connected in series. As the electron bunch travels through the FEL undulator section, microscopic effects play a role that could be neglected in typical synchrotron radiation sources. In vacuum, light will always be faster than electrons near the speed of light. This slight velocity difference means that the co-propagating photons and electrons have a phase

⁵LCLS has a 112m long undulator section.

2. Fundamental Concepts

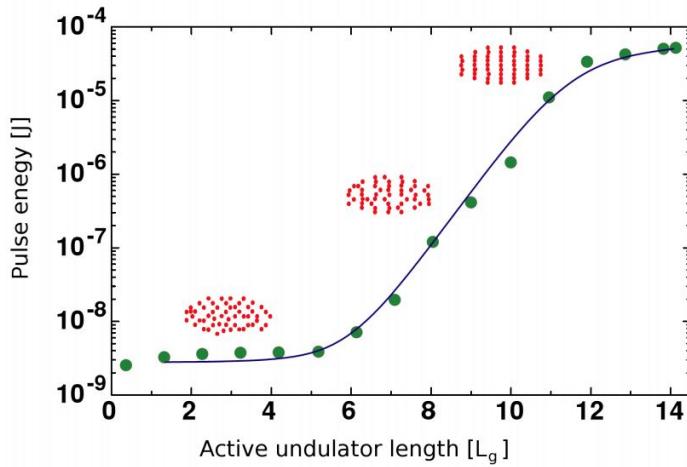


Figure 2.3.: Undulator gain curve correlated to microbunching. The X-ray pulse energy is plotted algorithmically over the undulator length L_g (blue curve, green dots) and shows an exponential growth until saturation. The electron bunch (red dots) starts with a random density distribution, as the bunch travels through the undulator modulates the electron density and the electrons are microbunched. Upon optimal microbunching, the X-ray lasing process saturates. From [35, 36]

2.1. Why X-ray free electron laser?

difference and interact with each other. Depending on the phase, an electron will either gain or loose velocity. Over each undulator period, we can describe this *slippage* with $\lambda_r(\Psi = 0)$. As a result, the initial uniform electron density is periodically modulated. The modulated electron bunch structure is called *microbunching*. The creation of microbunching as it travels through undulators is illustrated in figure 2.3. The increasingly structured electron beam amplifies a more narrow wavelength bandwidth and the number of electrons that are in phase with the photons increases over the travel length through the undulator. The lasing process saturates when the microbunching is fully developed. Initially (random) created photons in the undulator define the microbunching as it travels through the undulators and amplifies these photons through subsequent spontaneous emission. Hence, this type of radiation (or FEL operation mode) is called *Self Amplification by Spontaneous Emission* (SASE). SASE achieves laser alike amplification of the radiation power P_{SASE} scales [see 23, p. 61]

$$P_{\text{SASE}} \propto N_e^2, \quad \text{SASE operation} \quad (2.8)$$

SASE spectra can be seen in figure 2.4. A SASE spectrum is different from shot-to-shot and has distinct peaks that are defined by the initial photons on top of a more broad background. The electrons interact with the light field because of their narrow spatial and kinetic energy distributions that define the so called *emittance* of an electron bunch. Only the linear accelerator of FEL are able to compress an electron bunch in space and energy, i.e. create a low emittance electron bunch, such that it can interact with the photons and microbunch. Since the creation of X-rays affects the kinetic energy of the electron bunch γ and the lack of optics, XFEL use one (compressed) electron bunch⁶ in a long set of undulators to create one light pulse. This is also called a *single-pass high-gain* FEL. Without going into much detail, optics can be used to build *multi-pass low-gain* FEL that are able to reuse electron bunches [38], which leads to higher repetition rates and more narrow spectrum but fewer photons per pulse.

2.1.3. Soft X-ray self seeding

Another FEL beam mode is the seeded type. In contrast to the SASE operation, where the initial photons are randomly emitted and further amplified, a seeded FEL starts with a given *seed* of photons. If the set of initial photons is monochromatic, mostly this wavelength is amplified as the bunch travel through the undulator. The initial photon seed

⁶the European XFEL uses a so called bunch train, where multiple electron bunches are accelerated in series.

2. Fundamental Concepts

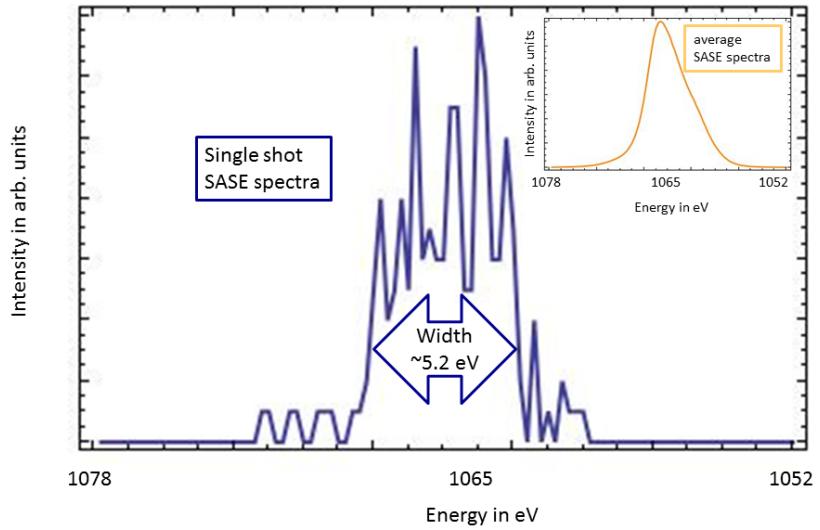


Figure 2.4.: Spectra of FEL SASE operation. The large blue spectra is a SASE spectra from a single FEL shot using a photoelectron spectrometer as described in [37]. Note the spiky peak structure on a background pedestal. Within the narrow bandwidth of a FEL pulse some energies are getting more strongly amplified due to the microbunching. The yellow graph in the inset is an average spectrum of several hundred single-shots and has a low energy tail, which is due to FEL-jitter.

2.1. Why X-ray free electron laser?

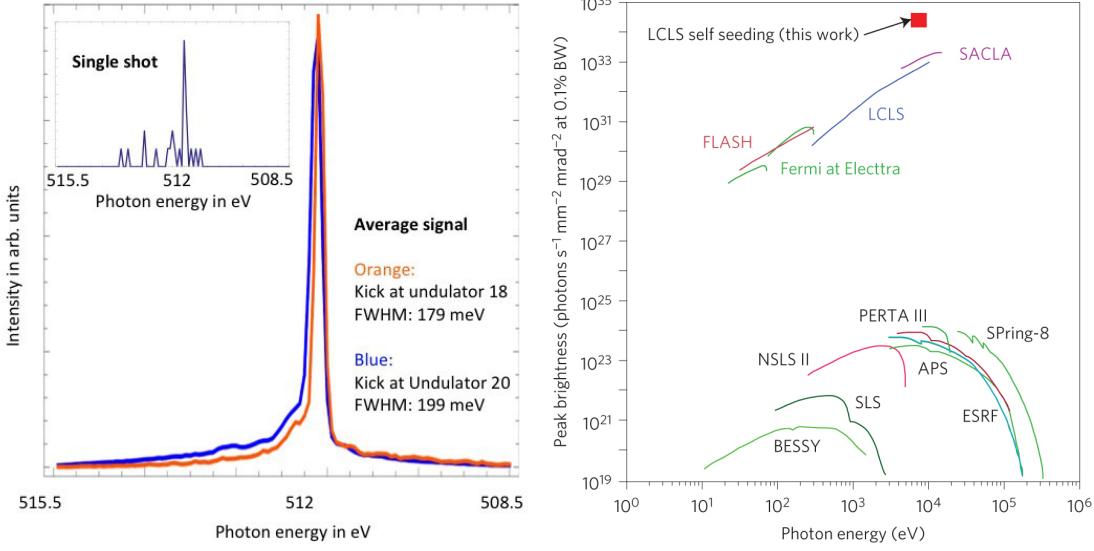


Figure 2.5.: Left, normalized average spectra of soft X-ray self-seeding operations using the SXRSS and AMO instrument at LCLS [37]. The self-seeding spectra is characterized by a sharp spectral peak around a desired energy accompanied by a SASE radiation type spectral pedestal. The often undesired SASE pedestal is suppressed, when the electron bunch travel through undulators is shortened, here kick at LCLS undulator 18 vs. 20. The right image shows the peak spectral brightness of various light sources over a wide photon energy range. Soft X-ray self-seeding has a spectral brightness that exceeds current SASE FEL sources. From [39].

2. Fundamental Concepts

can be created through various processes and the wavelength of the photon seed is the critical parameter in determining which method to choose. For example, in the infra red (IR) to extreme ultra violet (XUV) regime, conventional lasers can be used to place the initial photons seed. However, due to the lack of lasers available at X-rays wavelength regimes, the idea of *self-seeding* gained traction. In self-seeding, an electron bunch is first send through a few undulator magnets to generate a few SASE photons, the electrons and photons are then separated using a magnetic chicane, which also neutralizes the microbunching in the electron bunch. The monochromator selects a small wavelength slice from the comparably broad SASE spectrum of the initial photons. Photons exiting the monochromator are considered as *seed*. The seed and the electron bunch are overlapped again using the magnetic chicane and then send through more undulators. Here, the seed modulates the electron bunch and thus only a narrow spectral band is amplified. A typical spectrum of a soft X-ray self-seeded beam can be seen in the left figure 2.5. The characteristics of a self-seeded spectrum are an intense peak at the selected wavelength regime on top of a broad SASE background pedestal. The background is an artifact of the amplification of some spontaneous emission events and can be suppressed by using fewer undulator magnets. Self-seeded beams have a significantly reduced pulse energy by an order of magnitude, depending on the exact beam parameters, as compared to SASE operations. However, in their main peak, self-seeded beams have a higher spectral brightness when compared to a SASE spectrum. Using equation 2.1 the increase in spectral brightness compared to SASE is understandable and it is illustrated in the right figure 2.5. Self-seeded beam operations have recently been demonstrated at LCLS. At hard X-rays, the Hard X-Ray Self-Seeding (HXRSS) instrument uses a diamond crystal to select a wavelength slice [40]. At soft X-rays, the Soft X-ray Self Seeding (SXRSS) instrument uses a grating as dispersive element [41]. A seeded beam using an external laser generate photons as initial seed has been demonstrated at the extreme ultra violet (XUV) FEL FERMI at Ellettra-Sincrotrone in Italy [42]. The peak intensity in a narrow spectral band makes seeded beams interesting for a variety of applications particular in condensed matter physics, where it is instrumental to excite with narrow bandwidth photons. Of course there are also applications in atomic and molecular physics, ranging from linear absorption spectroscopy [43], to ultrafast photoemission spectroscopy on molecules [37], to non-linear stimulated Raman spectroscopy [44], to ultra-fast photoemission studies. Particular interesting for this work is the magnetic chicane from the SXRSS instrument that has been used as described in the next chapter.

2.1.4. Novel X-ray pump–probe techniques

In order to study X-ray induced phenomenon using X-ray imaging and spectroscopy techniques, as it is discussed in the present work, two X-ray pulses are needed. Here, a pump pulse is used to induce dynamics in the sample system and a probe pulse is used to probe them at a certain time delay Δt . Pump–probe experiments are commonly used as they allow a precise study of dynamics. The pump pulse gives a very controllable starting point, i.e. time zero in the dynamic process, and the probe pulse can perform a measurement at a later time delay Δt . Sometimes pump and probe pulse are switched, which is indicated by a negative time delay Δt , often to verify time zero or to probe the system before any dynamics have occurred.

Creating two X-ray flashes to create a pump–probe experiment is a technical challenge and again this challenge is due to the lack of X-ray optics. In order to overcome this challenge, two methods have been proposed. Method one, mirror based beam-split and delay systems [45, 46] that split one pulse into a pump and probe beam and allow the delay of the latter. These systems are typically limited to short times delays, as the optics have to fit into existing setups and have a low transmission of X-rays over the mirrors. Method two, uses accelerator based schemes [47, 48] that manipulate electron bunches to create two X-ray pulses. Limitations arise depending on the scheme, e.g. limited pulse delay Δt or pulse energy split through limited electron beam separation or length of magnetic chicane. Both methods have been demonstrated at LCLS and have found use to complement the more widely available optical laser pump – X-ray probe methods particularly in the chemical sciences [49–51].

Another aspect to pump–probe experiments is the tunability of wavelengths in each pulses, for example to resonantly pump and off-resonance probe or vice versa. Equation (2.7) indicates which parameters can be tuned to create two pulses of different color. One, the undulator parameter K can be tuned to change the emitted wavelength, or two, the lorentz factor γ can be different if there are two electron bunches. A potential third option are variable gap undulators that allow a change of period λ_U . At LCLS λ_U is fixed but future upgrade plans for LCLS-II include variable gap undulators [52]. As the accelerator based X-ray pump – X-ray probe method, let us describe these schemes in greater detail.

Undulator parameters $K_{1,2}$ based pump–probe scheme

The first developed accelerator based pump–probe technique at LCLS [47] uses a difference in undulator parameters $K_{1,2}$ to create two pulses of different wavelength, the time

2. Fundamental Concepts

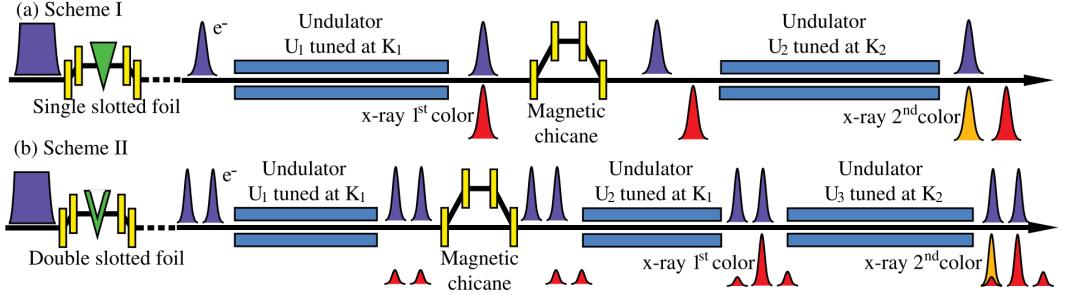


Figure 2.6.: Schematic setup at LCLS of undulator parameter K_i based pump–probe schemes. Scheme I creates one electron bunch using a single slotted foil and scheme II creates two electron bunches using a double slotted foil. The electron bunches emit radiation with a wavelength depending on K_i . A time delay Δt between pulses is introduced using a magnetic chicane. From [47]. Reprinted with permission from APS.

delay is introduced through a magnetic chicane and a schematic setup can be found in figure 2.6.

Following the figure, in scheme I, one electron bunch is created through a single slotted foil⁷ The use of the slotted foil enables control over the pulse duration. The electron bunch then travels through an undulator section U_1 tuned at strength parameter K_1 and is stimulated to lase but the process does not go into saturation such that the electron bunch can be reused in the second undulator section. A magnetic chicane removes the microbunching from section U_1 such that in undulator section U_2 , tuned to undulator strength parameter K_2 , the electron bunch lases again and the process is able to saturate. The maximal color separation between the two pulses is 1.9% in relative difference between K_1 and K_2 .

The time delay Δt between the two pulses is introduced by a magnetic chicane. At LCLS, a dedicated chicane, e.g. from the soft X-ray self-seeding instrument, can reach up to

$$\Delta t_{\max} = 800 \text{ fs}. \quad (2.9)$$

The minimal time delay can be achieved by setting the deflection in the magnetic chicane to zero in which case

$$\Delta t_{\text{drift}} = \frac{l}{v_{\text{el drift}}} - \frac{l}{c} \approx 0 \text{ fs}, \quad (2.10)$$

⁷A single slotted foil or emittance-spoiling foil works comparable to a monochromator. It leaves a certain energy band of the electron bunch within the slot unspoiled and Coulomb scatters or spoils (compare to apertures) the rest. The ‘dispersive’ element is a magnetic chicane. By narrowing the electron beam one also reduces its pulse duration [53].

2.1. Why X-ray free electron laser?

with $l \approx 4m$ being the length between undulator sections U_1 and U_2 and c being the speed of light and $v_{\text{el drift}}$ being the drift velocity of the electron bunch. As the electron bunch travels close to the speed of light t_{\min} is typically on the tens of attosecond timescale. The timing jitter between the two light pulses using only one electron bunch comes from the magnetic chicane due to the magnetic field jitter and the electron beam energy jitter. The total contribution to the timing jitter is less than 0.4% of the time delay Δt imposed by the chicane. Since the delay chicane does not significantly contribute to the delay Δt_{\min} a bigger factor is the velocity mismatch of the light pulse and the electron bunch. This mismatch can be estimated by

$$\Delta t_{\min} - t_{\text{drift}} = \frac{N_u \lambda_r}{c}, \quad (2.11)$$

with N_u being the undulator periods. Given the parameters in study [47], $t_{\min} = 3fs$ such that a partial overlap between the electron bunch and lightpulse could be achieved after the magnetic chicane. It should be noted that this technique has been used in the described experiment.

Scheme II uses a double slotted foil⁸ to create two electron beams. The two beams have a longitudinal separation that translates into the time delay Δt . The electron bunches travel through a first set of undulators U_1 that creates two pulses of the same wavelength, due to the shortness of the section U_1 the lasing process does not saturate. The electron bunches are then delayed using a magnetic chicane such that the leading electron bunch overlaps with the trailing light pulse. This light pulse now functions as a seed for the leading electron bunch such that this pulse saturates in undulator section U_2 . The electron bunches then travel through the magnets at U_3 , where the trailing electron bunch creates a second saturated pulse, the leading electron bunch barely emits radiation in U_3 since its energy spread has become too large after lasing in U_2 . Using this method, two saturated lasing pulses can be generated, however, temporal overlap cannot be achieved.

Twin bunch or Lorentz factor γ based pump–probe scheme

The second developed accelerator-based pump-probe technique at LCLS [48] uses two electron bunches of different energy. A schematic setup of this beam operation can be found in figure 2.7.

The electron bunches are created through a double laser pulse that impinges on a photo-

⁸A double slotted foil works as a single slotted foil but it leaves to parts of the electron beam unspoiled through the two slots.

2. Fundamental Concepts

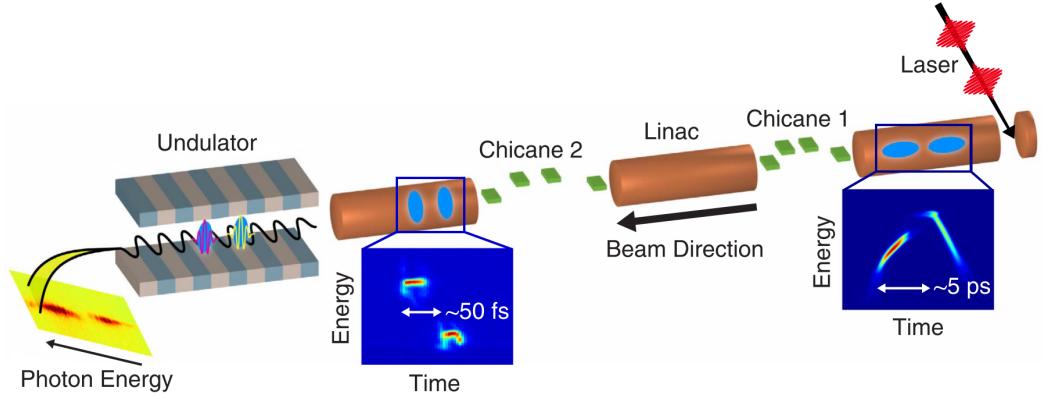


Figure 2.7.: Schematic setup of the two bunch, two color pump–probe setup at LCLS. Two laser pulses shot at a cathode create two electron bunches with a delay Δt on the picosecond timescale. Two magnetic chicanes compress the bunches such that a delay Δt on the up to the ten femtosecond timescale is achieved. Both pulses go through one undulator section and the lasing process is saturated. The relative color separation is on the order of 1% between the bunches. From [48, CC-BY].

cathode. Initially, these two bunches have a time delay of a few picoseconds, however, two magnetic chicanes compress the electron bunches in the time and intensity domain such that a time delay on the ten femtosecond timescale is achieved. The electron bunches then travel through one undulator section and both pulses saturate in their lasing process. At 8.3k eV, both pulses combined can reach pulse energies of $1.2mJ$, the color separation is 100 eV and the time separation ranges from $\Delta t_{min} = 0fs$ to $\Delta t_{max} = 100fs$. At hard X-rays, this method requires the pump pulse to have a higher photon energy than the probe pulse, although their respective intensities may vary. However, this method is not restricted to hard X-rays and can be utilized at soft X-rays. In the soft X-rays wavelength regime, where the slotted spoiler foil can be used. This allows a further control to tune the time delay of the electron bunches and enables scanning across time zero with both pulses.

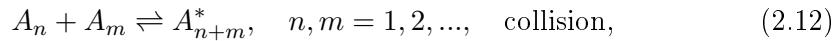
2.2. Rare gas clusters

Clusters have a long history to study light-matter interaction for a few reasons. Their characteristics are well known, they can form interesting states and often it has practical purposes [54]. Generally speaking, clusters are an aggregation of atoms or molecules and

vary in size. Their size ranges from a few atoms to mesoscopic sizes such that one can classify a cluster as a bulk material. Even though clusters can form exotic materials that are interesting to study, they can be simulated with computer models. Besides these testbed characteristics, clusters can be created comparably easily and are tunable in size. Rare gas clusters are a subclass of clusters and they are bound by van der Waals forces, thus are normally neutral-charged. Single van der Waals cluster typically form in an icosahedral⁹ shape when they are sufficiently small (up to nanometer sized) [55] and have mostly a fcc-crystal¹⁰ structure but exhibit also hcp-crystal¹¹ structures [56, 57]. In the present work, superfluid helium cluster (or droplets), solid xenon cluster and a mixture of both have been used as a sample. Therefore, we shall explore the creation of homogenous and heterogeneous rare gas clusters in the next sub-sections.

2.2.1. Creation of a homogenous cluster

Rare gas clusters, for example xenon clusters, can be generated in a variety of ways. Often, as in the described experiment, rare-gas clusters are created by releasing gas from a reservoir into a vacuum. Here, a nozzle connects the gas reservoir with the vacuum system and while the gas is expanding through the nozzle, many collisions take place. So, the cluster formation process can be explained intuitively through a kinetic model [58]. In other words, clusters grow through collisions with monomer, dimer and other clusters. We can express a collision mathematically through the following reaction formula



with n, m denoting the number of monomer assembling body $A_{n,m}$. A body A_n collides with another body A_m and form a metastable state A_{n+m}^* that will dissociate if not a subsequent collision deactivates it



M is a chaperone that can be any kind of third body that removes energy from the system. Note that a chaperone M can also activate the state again. The binding force behind rare-gas clusters is the Van der Waals force, hence these clusters are called Van der Waals cluster sometimes.

While the early stage of the cluster growth is driven by the monomer addition, cluster-

⁹An icosahedron is a polyhedron with 20 faces, i.e. a dice with 20 faces.

¹⁰fcc is short for face-centered cubic. A very common crystal structure.

¹¹hcp stands for hexagonal close-packed and is also a crystal structure.

2. Fundamental Concepts

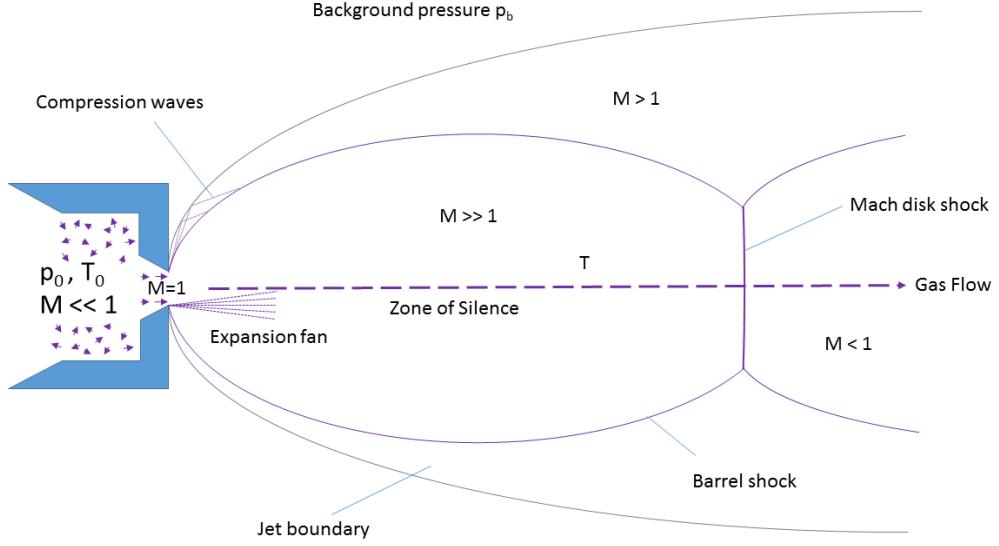


Figure 2.8.: Schematic of a supersonic gas expansion into the vacuum. Gas is stored in a reservoir at pressure p_0 , temperature t_0 and speed of the gas is thermal distributed ($M \ll 1$). As the gas enters the nozzle area, it is accelerated to the speed of sound ($M = 1$) and as the gas expands, the temperature T drops altering the speed of sound such that the gas now travels supersonic ($M \gg 1$). In this expansion, clusters are generated in the nozzle region, where $M = 1$ (see text for details). After [61]

cluster coagulation start to dominate the later growth processes [59, 60]. This is due to the quantitative increase in small clusters in the generation process that then start to collide, similar to above kinetic model. From empirical evidence, we know that clusters solely generated through monomer addition have a size distribution of an exponential decay, whereas larger clusters that grew through coagulation follow a log-normal distribution. So through coagulation, the density of smaller clusters (and monomers and dimers) decreases because of the cluster-cluster coagulation and larger clusters are formed. The most probable size of a cluster, i.e. the maximum of the log-normal distribution, is given by the parameters of the (supersonic) gas expansion, which is what we will discuss next.

Supersonic jet setups typically store gas in a reservoir at a certain stagnation pressure p_0 and temperature T_0 . The gas expands through a nozzle into a vacuum and figure 2.8 shows a schematic drawing of this process. Typical values for p_0 are 10 bars, where the mean free path of the atoms is much smaller than the nozzle diameter D . This is why many collisions occur during the expansion in the nozzle and the above described kinetic

theory explains the cluster formation. However, this holds not true in the supersonic molecular flow region, where no further cluster growth happens. To understand the expansion process in detail, we assume to work with an ideal gas and to describe the gas expansion itself, we further assume that no clusters are formed and that turbulence and effects of heat conduction are unimportant [54, 62].

To begin, the velocity distribution of the gas is thermally distributed at a set temperature T_0 . The movement direction of each atom is randomly orientated. For an ideal gas, we can define the enthalpy H_0 in the stagnation chamber

$$H_0 = c_p T_0, \quad (2.14)$$

with the specific heat c_p for atoms

$$c_p = \frac{5}{2} k_B, \quad (2.15)$$

where is the Boltzman constant k_B . The expansion of the gas through the nozzle is driven by the pressure difference p_{vac}/p_0 . In the nozzle, the (steady) gas flow becomes directed and the enthalpy H_0 is converted into kinetic energy $\frac{1}{2}mv^2$ and a rest enthalpy H . So, in the expansion process, we can use the conservation of energy, and equation (2.15) we can write down

$$H_0 = H + \frac{1}{2}m_{gas}v^2 = c_p T + \frac{1}{2}m_{gas}v^2, \quad (2.16)$$

with T being the local temperature along the gas flow and m_{gas} the atomic mass of the gas. To look at this in greater detail, let us define the Mach number M as the ratio of the stream velocity v and the local speed of sound c_s

$$c_s = \sqrt{\frac{\gamma k_B T}{m_{gas}}}. \quad (2.17)$$

With the ratio of specific heats $\gamma = \frac{c_p}{c_v}$ at constant pressure and volume, they can be regarded as independent of temperature for atomic gases, we can rearrange equation 2.16 to

$$T = T_0 \left(1 + \frac{1}{2} (\gamma - 1) M^2 \right)^{-1}. \quad (2.18)$$

Here the interplay between the Mach number M^2 and the local temperature T give insight into the directed mass flow versus the remaining thermal energy in the system.

2. Fundamental Concepts

As indicated the figure 2.8, M increases dramatically along the expansion axis and that is due to decrease in speed of sound c_s that is proportional to \sqrt{T} as indicated in equation (2.17). The gas quickly reaches the terminal velocity $v_\infty = \sqrt{\frac{2R}{m_{gas}} \left(\frac{\gamma}{\gamma-1} \right) T_0}$, with R being the universal gas constant, while the speed of sound is decreasing. This can be abused to calculate flight times $t_{\text{flight}} = \frac{d}{v_\infty}$, if the distance d from nozzle to interaction point is known (see sub-section 3.4.1). Finally, the expansion speed of the gas gives the name to such types of gas sources, namely supersonic jets.

Let us describe the appearance of the jet stream (see figure 2.8) next. Upon exiting the nozzle, the Mach number increases by a wide margin ($M \gg 1$), that means that the gas travels faster than information in this medium. Here, a *zone of silence* is formed, where the gas flow is not influenced by other particles, thus uninterrupted. As the supersonic flow is exiting the nozzle it has to turn around the edge of the nozzle to further expand and the supersonic flow turns by actually creating smaller Mach waves. At the borders of the *zone of silence*, M decreases drastically resulting in dense regions that are called *barrel shock* to the sides and *Mach disk* downstream the gas flow. For an unhindered transport of the gas and clusters to the interaction region, the interaction region needs to be within the *zone of silence*. We can express the distance from the nozzle to the Mach disk x_{MD} through

$$\frac{x_{MD}}{d} = 0.67 \sqrt{\frac{p_0}{p_b}}, \quad (2.19)$$

with the nozzle diameter d . So the competing stagnation pressure p_0 and the background pressure p_b define the distance of the otherwise static parameters. p_b needs to be low enough to drive the Mach disk downstream of the interaction region. By using skimmers and thereby physically separating the jet expansion into separately pumped compartments, the background pressure p_b can be reduced, hence x_{MD} increased.

While we have described a cooling gas in the expansion process it should be noted that the clusters are comparably hot. Through the kinetic process described above, they are efficiently heated. The two processes to loose energy are, one, collisions with a chaperone M that deactivates the cluster, or two, evaporation of monomers from the cluster. The evaporation process makes the temperature size-independent, after the clusters have reached a certain minimum size [63]. Typically, the jet reaches temperatures of a few Kelvin and the cluster temperature is heavily dependent on their material, particularly the dissociation energy. For this study relevant are mostly the temperature of Xenon cluster that is $75K^{12}$ and the fact xenon clusters are solid as their melting temperature

¹²To put this temperature in perspective, krypton clusters are $50K$ and argon cluster $40K$ [63, 64]. Note that in this study the cluster size was $\bar{N} > 800$, hence above the minimum value to be size

| Helium | Neon | Argon | Krypton | Xenon |
|--------|------|-------|---------|-------|
| 3.85 | 185 | 1646 | 2980 | 5554 |

 Table 2.1.: Parameter K_{gas} values for rare gases [65].

is higher [64]. For similar reasons, helium clusters are liquid, which is why they are often called (helium-)droplets. If helium droplets are produced using a cryogenic jet even superfluid helium-droplets can be observed.

At the current point of the discussion, it should shine out that the average cluster size is very much depended on the gas type, stagnation temperature T_0 , stagnation pressure p_0 and the nozzle type. Indeed, an empirically found scaling law named after Hagena [66–68], can be written down as

$$\Gamma^* = K_{\text{gas}} \cdot T_0^{0.25q-1.5} \cdot p_0 \cdot d_{eq}^q \quad \left[\frac{\mu\text{m mbar}}{\text{K}} \right], \quad (2.20)$$

with the gas specific parameter K_{gas} that can be found in table 2.1 for some rare gases, the gas specific parameter q that varies between 0.5 and 1 and is 0.85 for all rare-gases, and the equivalent nozzle opening d_{eq} that is $d_{eq} = d$ for pinhole sources and for conical nozzles d_{eq} reads [65]

$$d_{eq} = d \frac{\tan(\Phi_0)}{\tan(\Phi)} = 0.719 \frac{d}{\tan(\Phi)} \quad (2.21)$$

with the half opening angle of the nozzle Φ and the half opening of the free gas expansion Φ_0 . The Hagena scaling parameter Γ^* allows us to estimate the mean cluster size, i.e. amount of accumulated particles per cluster $\langle N \rangle$, as follows

- $\Gamma^* < 350$, no cluster formation observed.
- $350 < \Gamma^* < 1800$, in this region $\langle N \rangle$ reads

$$\langle N \rangle = 38.4 \left(\frac{\Gamma^*}{1000} \right)^{1.64} \quad (2.22)$$

- $1800 < \Gamma^*$, in this region $\langle N \rangle$ reads

$$\langle N \rangle = 33.0 \left(\frac{\Gamma^*}{1000} \right)^{2.35} \quad (2.23)$$

Supersonic jets generally create clusters of different sizes. This size distribution is cen-

independent. For the evaporative cooling process to settle at a given temperature, a certain flight distance (in the cited study 6.5cm) should also be taken into account.

2. Fundamental Concepts

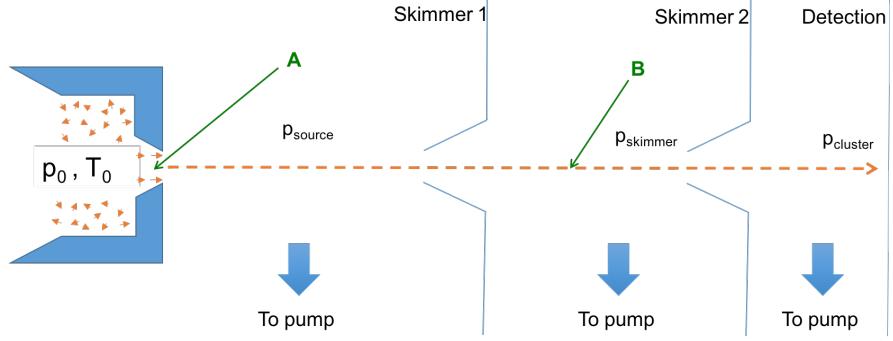


Figure 2.9.: Schematic setup to generate heterogeneous clusters through pickup. Thereby is a first cluster generated via a supersonic gas expansion, which is doped at regions marked A or B. In region A, the dopant gas is mixed in the nozzle such that it becomes part of the nucleus. In region B, the cluster condenses atoms on its surface and commonly gas cells are used to regulate the pressure p_{skimmer} effectively. p_{source} is the pressure in the source chamber. The cluster can be detected upon evaporation, i.e. by contact with the chamber, through the pressure p_{cluster} and the cluster doping can be determined through partial pressures (see text for details). After [54, 71].

tered around $\langle N \rangle$ and for solid rare gas clusters this distribution is a log-normal distribution. The size distribution can be an experimental challenge, especially when size dependent effects are investigated. Historically, electron diffraction [63, 69] has been used to determine the mean cluster size, mean temperature and mean geometry. Today, free electron laser allow the determination of the size of a single cluster through a diffraction image and by measuring enough single clusters, one can reproduce size distributions of a supersonic jet as shown in figure 5.1.

Experiments using supersonic jets for cluster generation are typically performed with pulsed valves to decrease cost and gas load in the overall system. Upon opening and closing of the valve, the gas density varies. This mostly affects the cluster size and one would expect to see smaller clusters. This remains true in the beginning of the pulse but in the *afterpulse* one finds giant clusters that exceed the above described scaling laws due to the effects when closing the valve [70].

2.2.2. Formation of a heterogeneous cluster: The pickup principle

A possibilities to create heterogeneous clusters is through the principle of picking-up atoms or molecules [54, 71]. Figure 2.9 illustrates pickup regions that are typically used in an experiment. Mainly, there are two different pickup places, one, monomers are added

to the cluster in region A of figure 2.9 that represents the nozzle of a supersonic source, or two, they can be picked up by a cluster in region B for example through an increased background pressure p_{b2} with the dopant material. If clusters pick up atoms or molecules in the nozzle region A, they can become part of the cluster formation and can be found inside of solid clusters. If atoms or molecules are picked up in region B, they stick to the surface of solid clusters. If a (super-)liquid cluster picks up a dopant, it may move within the droplet. Since the traversing cluster is much larger and heavier than a colliding monomer the trajectory is not affected significantly. Already pressures of $p_{b2} = 10^{-11}$ bars over a pickup length of a few centimeters can dope the cluster in significant form. At these low pressures, picking up atoms or molecules in region B requires less gas load on the system but is also less efficient than picking up in region B. To increase the pickup levels in region B, a gas cell can be used as much higher pressures can be achieved within the gas cell without putting too much gas-load on the overall system.

The collision with the cluster and a dopant does add energy to the cluster just as the cluster growth process itself. This is why the initial cluster will loose particles through evaporation upon pick up of a dopant [72]. The loss of particles through evaporative cooling is dependent on the ratio of dissociation energies of the two materials and can be written down as

$$N_{\text{Evaporated from cluster}} \approx \frac{\epsilon_{\text{cluster}}}{\epsilon_{\text{dopant}}}, \quad (2.24)$$

with the dissociation energy of the cluster $\epsilon_{\text{cluster}}$ and of the dopant ϵ_{dopant} . In the case, where a helium droplet is doped with xenon atoms, we may use the dissociation energies of helium $\epsilon_{He} = 0.6 \cdot 10^{-3}$ eV and xenon $\epsilon_{Xe} = 0.6 \cdot 10^{-3}$ eV [11, 72], such that approximately 250 helium atoms evaporate by picking up 1 xenon atom.

We can extend this idea to estimate the amount of picked-up atoms, if we were to know the amount of atoms in the cluster before and after the pickup area. An estimate of the initial cluster size $\langle N_{\text{cluster}} \rangle$ can be reached through the scaling laws¹³ as discussed in section 2.2.1. A measure to estimate the cluster size after the pickup can be established through measuring the partial pressure of the cluster material p_{cluster} of helium¹⁴, when the particle jet hits a wall and evaporates (see figure 2.9). The partial pressure p_{cluster} then scales linearly with the initial cluster size $\langle N_{\text{cluster}} \rangle$, such that

$$\langle N_{\text{dopant}} \rangle \approx \frac{\epsilon_{\text{cluster}}}{\epsilon_{\text{dopant}}} \cdot \frac{\Delta p_{\text{cluster}} \langle N_{\text{cluster}} \rangle}{p_{\text{cluster}}}, \quad (2.25)$$

¹³As already established the actual cluster size produced with a supersonic jet will vary, hence the average cluster size $\langle N_{\text{cluster}} \rangle$.

¹⁴For example with a residual gas analyzer.

2. Fundamental Concepts

where $\Delta p_{\text{cluster}}$ denotes the partial pressure difference with pickup and without.

2.3. Soft X-rays in matter

A full description of light-matter interaction is mathematically challenging and not the purpose of this thesis. In the following subsections, we will break down the light-matter interaction into its components. The components of the interaction of photons with matter can be split into five categories, 1) coherent-elastic scattering (see sub-section 2.3.1), 2) inelastic processes (absorption, see sub-section 2.3.2), 3) incoherent scattering (Compton effect) and high-energy physics effects of 4) pair production and 5) absorption effects with the nucleus. As it already shines through, the effects are dependent on the wavelength and the cross-sections for 3-5 can be neglected in the soft X-ray regime. We will therefore concentrate the discussion on points 1-2 and restrict ourselves to the for the experiment necessary theory.

2.3.1. Small angle X-ray scattering

We can describe a linear polarized, electric field of a continuous electromagnetic wave via the following expression [23]

$$\vec{E}(\vec{r}, t) = \vec{\epsilon} E_0 e^{i\vec{k}\cdot\vec{r}}, \quad (2.26)$$

with $\vec{E}(\vec{r}, t)$ being the electromagnetic field of the wave, the wave vector \vec{k} , the Cartesian coordinate vector \vec{r} , the complex amplitude if the electric field is then $E_0 \exp^{i\vec{k}\cdot\vec{r}}$ and because of the polarization we use $\vec{\epsilon}$ such that $\vec{\epsilon} \cdot \vec{k} = \vec{k} \cdot \vec{E} = \vec{k} \cdot \vec{H} = 0$. Through a relative comparison, of the incoming intensity I_0 and the scattered intensity I_{sc} , we can phenomenologically establish the differential cross-section over a certain solid angle $\Delta\Omega$ as

$$\left(\frac{d\sigma}{d\Omega} \right) = \frac{(\text{Number of X-rays scattered per second into } \Delta\Omega)}{(\text{Incident flux}) (\Delta\Omega)} = \frac{I_{\text{sc}}}{(I_0/A_0) \Delta\Omega}, \quad (2.27)$$

with A_0 being the covered area of the incident beam. If an electro-magnetic wave encounters an electron, we can describe the scattering semi-classical by imagining how an electron starts to oscillate once it sees an incoming electric wave. The electron then functions as a dipole antenna eventually radiating the wave into a certain solid angle $\Delta\Omega$. Depending on the polarization of the incident beam we can reduce equation 2.27 to

[23]

$$\left(\frac{d\sigma}{d\Omega} \right) = r_0^2 P, \quad (2.28)$$

with the classical electron radius $r_0 = 2.82 \cdot 10^{-5} \text{ Å}$ and the polarization factor P

$$P = \begin{cases} 1 & \text{vertical scattering plane,} \\ \cos^2(\Psi) & \text{horizontal scattering plane,} \\ \frac{1}{2}(1 + \cos^2(\Psi)) & \text{unpolarized source.} \end{cases} \quad (2.29)$$

We can now move on and use this knowledge for atoms, where we have Z electrons. To describe electrons in an atom, let us proceed by introducing the electron density $\rho_e(\vec{r})$ that describes the probability density of electrons in an atom. Figure 2.10 illustrates the scattering process in one atom. An incident beam with wave number \vec{k} is elastically scattered at a point \vec{r} into a wave with \vec{k}' such that $|\vec{k}| = |\vec{k}'|$. In this wave picture, the scattering process must be seen as a superposition of waves and it is particularly illustrated how the wave scattered at the origin of the atom is scattered as well. As both waves are scattered at different points, they have an optical path difference 2δ . This difference in path length results in a phase difference to each other and eventually leads to interference between the waves. So, we can describe the phase difference $\Delta\Phi(\vec{r})$ of the waves scattered at \vec{r} and the origin by

$$\Delta\Phi(\vec{r}) = (\vec{k} - \vec{k}') \cdot \vec{r} = \vec{Q} \cdot \vec{r}, \quad (2.30)$$

with \vec{Q} being denoted as the *wave vector transfer*. Through trigonometry, we can establish the more common denotation of the wave-vector \vec{Q}

$$\vec{Q} = 2|\vec{k}| \sin\left(\frac{\Theta}{2}\right) = \frac{4\pi}{\lambda} \sin\left(\frac{\Theta}{2}\right), \quad (2.31)$$

with the wavelength of the light λ and the scattering angle Θ .

A volume element $d\vec{r}$ at \vec{r} will now scatter depending on its electron density, namely by $-r_0\rho(\vec{r}) d\vec{r}$. At scattering angle $\Theta = 0$, i.e. $\vec{Q} = 0$ the atomic scattering factor f^0 is

$$f^0(\vec{Q} \rightarrow 0) = Z, \quad (2.32)$$

because all scatterer are in phase. As we increase the scattering angle Θ , the phase difference $\Delta\Phi(\vec{r})$ leads to interference, which we can describe by multiplying a phase factor $e^{i\vec{Q} \cdot \vec{r}}$ to the electron density $-r_0\rho(\vec{r}) d\vec{r}$. In the limit of $\vec{Q} \rightarrow \infty$, the atomic

2. Fundamental Concepts

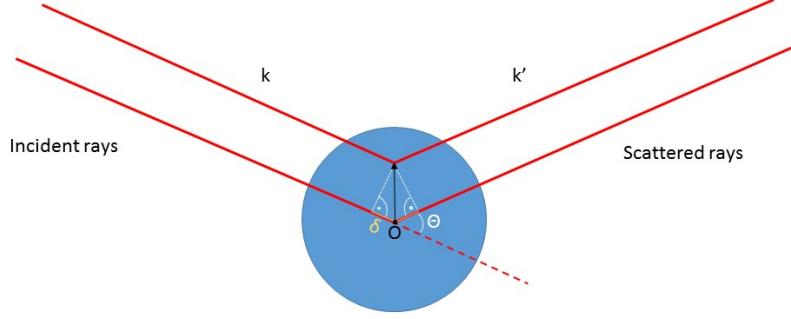


Figure 2.10.: Principle of scattering rays of an atom. After [23, 73].

scattering factor then is $f^0(\vec{Q} \rightarrow \infty) = 0$. We can integrate over the total scattering length, and write down

$$-r_0 f^0(\vec{Q}) = -r_0 \int \rho_e(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}. \quad (2.33)$$

This important result is called the atomic scattering factor in units of $-r_0$ and it can be understood as a Fourier transform of the electron density of an atom. We can also remember from optics the light scatter of an object can be inverse Fourier transformed and projects an image of the object again.

Let us continue with the scattering of a molecule or cluster that consist of multiple atoms. We can label the atoms in such an object by

$$F^{object}(\vec{Q}) = \sum_j f_j^O(\vec{Q}) e^{i\vec{Q} \cdot \vec{r}}, \quad (2.34)$$

with the atomic scattering factors $f_j^0(\vec{Q})$ for the j 'th atom and call $-r_0 F^{object}$ the scattering length of the object. Strictly speaking and as defined in (2.34), $F^{object}(\vec{Q})$ and $f_j^Q(\vec{Q})$ is \vec{Q} depended. As this is inconvenient, let us consider the following evidence in order to neglect this dependency. In the angular range of \vec{Q} , where $F^{Object}(\vec{Q})$ is

2.3. Soft X-rays in matter

not 0, f_j^Q can be considered constant [see 73, p. 6-7]. In human hemoglobin, the range in which the molecule scattering length $F^{Object}(\vec{Q})$ is not 0, the carbon atomic form factors change less than 0.4%. Neglecting this \vec{Q} dependency in f_j^Q allows us to describe the scattering length of extended objects $F^{Object}(\vec{Q})$ via one continuous electron density $\rho_e(\vec{r})$, where certain volume elements $d\vec{r}$ scatter proportional to their electron density $\rho_e(\vec{r})$. Let us write down the more convinient expression for the scattering length of an object

$$-r_0 F^O = -r_0 \int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}, \quad (2.35)$$

and we can see that it is mostly the phase factor that yields information about the structure of the object as it is the phase factor that constitutes the diffraction pattern. The total scattered intensity $I(\vec{Q})$ in a diffraction pattern can expressed through

$$I(\vec{Q}) = |A|^2 = I_0 \left| F^0(\vec{Q}) \right|^2, \quad (2.36)$$

where an incident beam with intensity I_0 with a complex amplitude A performs an operation that can be interpreted as a Fourier transform of the objects electron density. The process of measuring the scattered light, for example through a detector, merely measures the modulo of an amplitude $|A|^2$, which eliminates the phase factor $e^{i\Delta\Phi(\vec{r})} \cdot e^{-i\Delta\Phi(\vec{r})} = 1$. In order to reconstruct the object that scattered in realspace, e.g. to understand its shape or to study its function, we need to recover the for the structure most important phase information. We will discuss iterative algorithms that can recover phase information in section 4.3.

Let us briefly address the scattering of a rare-gas cluster, as the cluster can be considered as a spherical symmetric object. That allows to express the electron density of a cluster with radius R as

$$\rho(\vec{r}) = \begin{cases} 1 & \text{for } R \geq \vec{r} \geq 0, \\ 0 & \text{for } \vec{r} > R. \end{cases} \quad (2.37)$$

2. Fundamental Concepts

Using equation (2.37), we can solve the integral in equation (2.35) by transforming into spherical coordinates

$$F_{\text{Sphere}}^O(\vec{Q}) = \int_0^\pi \int_0^{2\pi} \int_0^R r^2 \sin(\Theta) e^{i\vec{Q} \cdot \vec{r} \cos(\Theta)} dr d\Theta d\Phi \quad (2.38)$$

$$= \frac{\sin(\vec{Q}R) - \vec{Q}R \cos(\vec{Q}R)}{\vec{Q}^3 R^3} = \frac{J_1(\vec{Q}R)}{\vec{Q}R}, \quad (2.39)$$

with J_1 being the Bessel function of first kind. Formula (2.39) can be easily abused to determine the size of a spherical particle using local minima in the diffraction pattern¹⁵ or through a numerical fit of the resulting curve.

2.3.2. Ionization of matter

Let us quickly remember the atomic scattering factor $f^0(\vec{Q})$ that were introduced in the last section by neglecting a variety of (wavelength depended) effects through Fourier transforming the electron density of an atom. As we established, we can compare the photon-electron interaction to the analogue of the forced harmonic oscillator, where an electric field drives a (bound) electron. However, it is not only the light field that drives the electron, also the electron has an effect to the light field. As the wave propagates through a medium, the phase velocity of light v_{phase} is slower than the speed of light in vacuum c due to interacting with electrons. We can describe this effect via the refractive index $n \equiv c/v_{\text{phase}}$. Another aspect to consider is a reduction of the amplitude of the incoming electro-magnetic wave (absorption), when the energy of the photons is higher than the binding energies of electrons [23, 74]. These two effects are connected to the atomic scattering factors $f^0(\vec{Q})$ and are called dispersion corrections. Let us include these corrections to the atomic scattering factor and define the atomic form factor

$$f(\vec{Q}, \hbar\omega) = f^0(Q) + f'(\hbar\omega) + i f''(\hbar\omega), \quad (2.40)$$

where $f'(\hbar\omega)$ corrects for the phase velocity and the wave amplitude correction/absorption $f''(\hbar\omega)$. In the limit of high photon energies $\hbar\omega$, bound electrons can be largely seen as free, as the binding energies become a little factor, therefore $f'(\hbar\omega) \rightarrow 0$ and $f''(\hbar\omega) \rightarrow 0$. As the photon energies $\hbar\omega$ are closer to the atomic level, which is the case at soft X-rays for many materials, $f'(\hbar\omega)$ and $f''(\hbar\omega)$ can become large factors.

We shall not derive this topic in its full extend as it can be found in [see 74, p. 55ff],

¹⁵Equation (2.39) can be solved numerically for the distance between the first two minima $\Delta\vec{Q}R = 3.24$, such that $R = \frac{3.24}{\vec{Q}_{\min n+1} - \vec{Q}_{\min n}}$

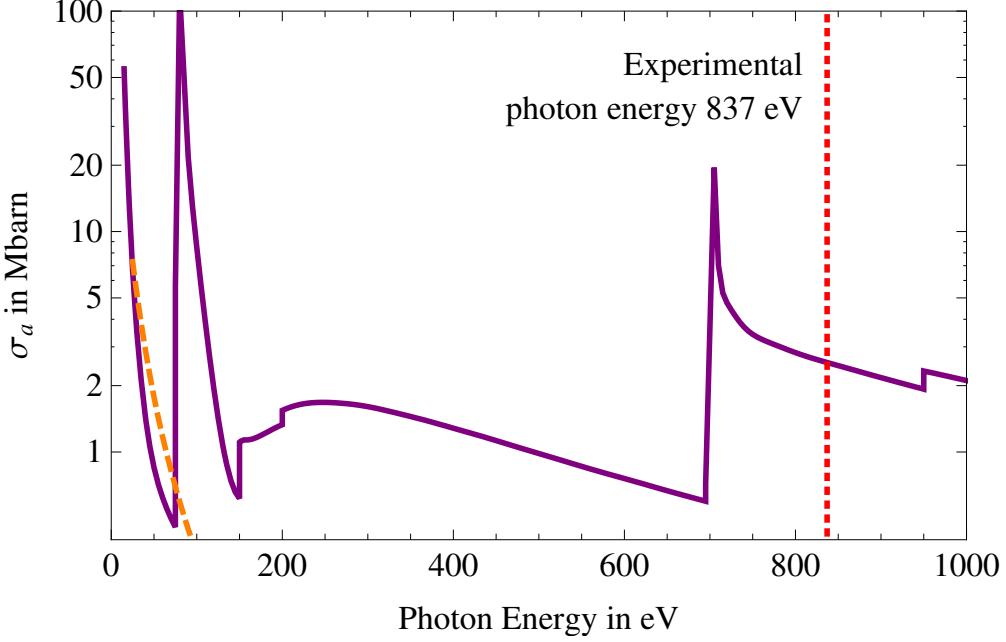


Figure 2.11.: Total absorption crosssections σ_a in megabarn for xenon and helium. The purple curve represents the total cross-section of xenon. The orange dashed curve represents the total cross-section of helium. The red dashed line represents the photon energy used at the experiment described in the present work. Data points from [75–77]

but we shall qualitatively compare the equation for the complex refractive index $n(\omega)$ to forced harmonic oscillator. For simplicity, we reduce the following considerations to the case of forward scattering, where $\vec{Q} = \Theta = 0$.

Let us start by imagining a electromagnetic wave propagating in a medium. The wave propagating in a medium along the axis z can be written as

$$e^{inkz} = \underbrace{e^{i(1-\delta)kz}}_{\text{phase shift absorption}} \underbrace{e^{-\beta z}}_{\text{absorption}} , \quad (2.41)$$

where n is the complex refractive index, δ the real dispersion correction resulting in a phase shift of the wave and β being the imaginary dispersion correction resulting in a decline in amplitude of the wave¹⁶. The relation between the complex refractive index

¹⁶We jump between wave and particle picture as it pleases us. Here, a decline in amplitude in the wave picture can be read as absorption in the particle picture.

2. Fundamental Concepts

n , β and δ is explicitly given by

$$n \equiv \frac{c}{v_{\text{phase}}} = 1 - \delta + i\beta. \quad (2.42)$$

We can compare this equation (2.42) to equation (2.40) and realize that we are allowed to define this dispersion relation through the atomic form factor as [see 23, p. 76]

$$n \equiv 1 - \frac{2\pi\rho_{\text{atom}}r_0}{k^2} \left(f^0(\vec{Q}=0) + f'(\hbar\omega) + if''(\hbar\omega) \right), \quad (2.43)$$

with the atomic number density ρ_{atom} and we identify

$$\delta = \frac{2\pi\rho_{\text{atom}}r_0}{k^2} \left(f^0(\vec{Q}=0) + f'(\hbar\omega) \right), \quad \text{and} \quad (2.44)$$

$$\beta = - \left(\frac{2\pi\rho_{\text{atom}}r_0}{k^2} \right) f''(\hbar\omega). \quad (2.45)$$

We have already established in equation (2.41) that β reduces the amplitude of the incoming wave through absorption. Using this insight about absorption, we can rewrite equation (2.45) and define $f''(\hbar\omega)$ in terms of being proportional to an absorption cross section σ_a , which reads

$$f''(\hbar\omega) = - \left(\frac{k}{4\pi r_0} \right) \sigma_a. \quad (2.46)$$

Figure 2.11 shows the total absorption cross-sections σ_a for xenon, helium at which a bound electron absorbs a photon and excited into the continuum, thus the atom is ionized. To get a better understanding of the fundamental absorption related details about xenon and helium, table 2.2 and 2.3 show the differential photo-absorption cross sections and ionization potentials for various energy levels and ionization configurations at the photon energy 837 eV. The calculations were performed with the Los Alamos Atomic Physics code based on [78]. It appears that certain energy levels, or here subshells if one disregards the hyperfine structure¹⁷, tend to have a higher absorption cross-section than others. This brings us back to the picture of the forced harmonic oscillator, where an electron is driven by a light field. If the frequency of the light field is close to the eigenfrequency of the bound electron, in other words, if the energy of a photon is close to the energy level of a bound electron, the system is in resonance and absorption is highly likely. As the photon energy and electron level energy differ, the system is off resonance and it is less likely to absorb a photon. As energy levels in atoms are discrete, electrons can only be excited from one energy level to another or need a certain (minimal) ionization energy to

¹⁷A shift in energy levels due to interaction of electrons with the nucleus [see 79, p 166 ff.].

2.3. Soft X-rays in matter

| Shell | Subshell | Cross-section in Mb | subshell ionization potential in eV |
|-------|----------|------------------------|--|
| K | 1s | - | 34630.0 |
| L | 2s | - | 5466.4 |
| | 2p | - | 4899.1 |
| M | 3s | - | 1153.3 |
| | 3p | - | 965.4 |
| | 3d | 2.2505 | 682.7 |
| N | 4s | 0.0305 | 223.7 |
| | 4p | 0.1247 | 161.8 |
| | 4d | 0.2587 | 68.2 |
| O | 5s | 0.0040 | 27.3 |
| | 5p | 0.0120 | 12.5 |

Table 2.2.: Differential absorption cross-sections and ionization potentials for certain electronic configurations of xenon at 837eV. Calculations based on [78].

| El. Configuration, and ionized subshell | Ionization of subshell | Cross-section σ_a in Mbarn | subshell ionization potential in eV |
|--|---------------------------|--------------------------------------|--|
| He ⁺⁰ , 1s2 | 1s2 | 0.0007 | 24.4 |
| He ⁺¹ , 1s1 | 1s1 | 0.0005 | 54.4 |
| Xe ⁺⁰ , 5p6 | 3d10 | 2.2505 | 682.7 |
| Xe ⁺¹ , 3d9 | 3d9 | 2.1487 | 733.6 |
| Xe ⁺¹ , 5p5 | 3d10 | 2.2443 | 693.7 |
| Xe ⁺² , 5p4 | 3d10 | 2.2390 | 705.9 |

Table 2.3.: Absorption cross-sections σ_a and ionization potentials for certain electronic configurations, including certain ionization profiles. Calculations based on [78].

ionize an atom and excite an electron into the continuum. Therefore, the likelihood of a core-electron that is strongly bound being ionized is by far the most probable using X-rays. When a core electron gets ionized, the electronic structure changes and particular ionization energies and (absorption) cross-sections change. To discuss the parameters that are most applicable to this thesis, a comparison of the most probable transition at the photon energy 837eV is given for helium and xenon in table 2.3. The ionization energies change drastically, whether a core electron or a less tight bound electron is ionized. As per absorption cross-sections, helium can be considered transparent and xenon atoms have a much larger absorption cross-section. The amount of ionization configurations can become rather complex and the table shall give the reader merely a broad understanding of some likely configurations.

2. Fundamental Concepts

| El. Configuration, and ionized subshell | Scattering factor f^0 in barn |
|--|------------------------------------|
| He^{+0} , 1s2 | 2.5539 |
| He^{+1} , 1s1 | 0.649465 |
| Xe^{+0} , 5p6 | 1874.36 |
| Xe^{+1} , 3d9 | 1813.56 |
| Xe^{+1} , 5p5 | 1814.68 |
| Xe^{+2} , 5p4 | 1754.08 |

Table 2.4.: Atomic scattering factor f^0 for certain electron configurations. Calculations based on equation (2.33). From [80]

The total atomic scattering factors f^0 for neutral and ionized, helium and xenon can be found in table 2.4. It is interesting to see that although a xenon atom has only 27 times more electrons than a helium atom the scattering factor f^0 of neutral xenon is over 900 times stronger than helium. Upon ionization, the absolute changes in f^0 of helium are therefore smaller compared to xenon. The relative change in helium of f^0 after one electron is ionized is 75%, thus (ionized) helium barely scatters. As xenon has multiple occupied subshells, the scattering factors of different ionized subshells are shown in table 2.4. As discussed, it is most likely to ionize the xenon 3d subshell, however, within a few femtoseconds subsequent relaxation processes¹⁸ lead to different ionization configurations, for example a double ionized 5p subshell. For the scattering factor, there is little change whether the 3d or 5p subshell becomes ionized and the change in f^0 is only 0.05%. As xenon has 54 electrons, the relative change upon ionization of one electron in f^0 is only 3%. Xenon is therefore a much stronger scatterer than helium and xenon still scatters well upon ionization of inner or outer shell electrons. In the experiment described in the following chapters, the photon energy is explicitly chosen to have a comparably high absorption cross-section for xenon but is off absorption resonance, a comparably low absorption cross-section for helium and a wavelength short enough to receive high resolution images through coherent diffraction imaging. In such a setting xenon is most likely to absorb X-rays and helium can be considered as transparent. Furthermore, xenon acts as the strong scatterer and we are most interested in how the scattering changes when xenon and helium cluster are in a combined environment.

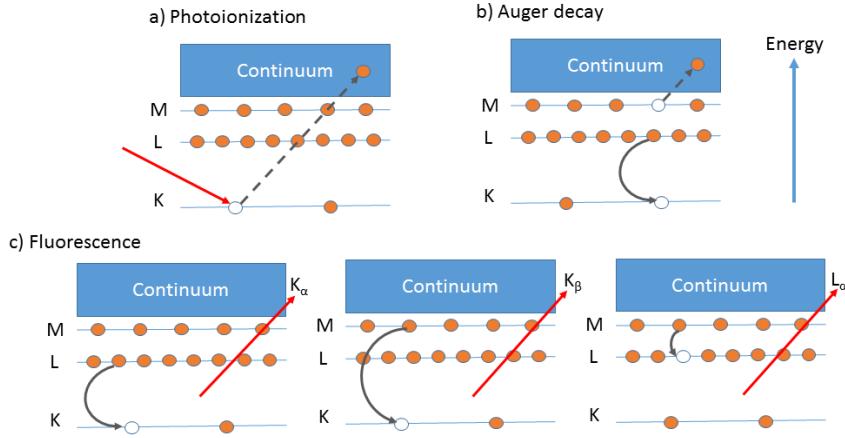


Figure 2.12.: Schematic illustration of common charge transfer processes. a) describes a direct emission of an K-shell electron after absorbing a X-ray photon. Process b) shows a secondary relaxation process called Auger decay, where a K-shell hole is filled with an electron from the L-shell and the remaining energy is released through emission of an electron in an outer shell, here M-shell, into the continuum. Process c) illustrates fluorescence, where an electron hole is filled with an electron from an outer shell and the remaining energy is released through photons. Process a) has a distinct spectra depending on the ionized element and the wavelength of the absorbed photon, the released particles in b-c) show an element specific spectra. After [23, p. 19]

2. Fundamental Concepts

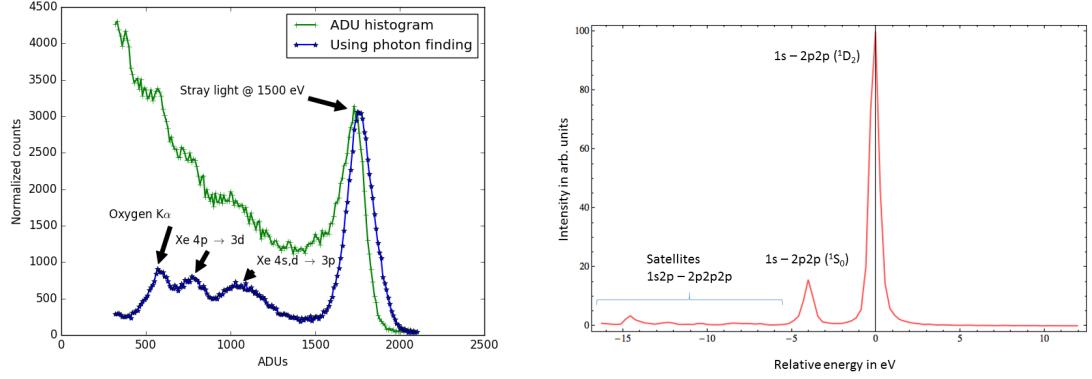


Figure 2.13.: Left spectra shows fluorescence peaks from xenon and oxygen illuminated with 1.5keV photons from the LCLS and detected with pnCCD detectors [81, 82]. The green curve is a ADU histogram of the pnCCD detector and the blue curve uses a coalescent photon finder as described in section 4.2. Right, selection of the K-LL Auger spectrum with rel. energy 0 corresponding to 804.5eV. The ionization starts in the K shell, i.e. a 1s hole, and the Auger relaxation process ends up with two holes, e.g. in the L-shell denoted as LL or 2p2p. As electrons energy levels arrange due to their quantum numbers, multiple peaks appear for similar hole configurations, e.g. 2p2p [37, 83].

2.3.3. Charge migration

After an atom has been (core-)ionized due to absorption of a photon as depicted in figure 2.12a, the atom is not in its most energetically favorable state. In order to emit energy and transition into its new ground state, the atom can emit particles according to the schematics in figure 2.12b-c. In a fluorescence decay (2.12c), the electron hole in the (K-)shell is filled by an electron in an energetically higher shell, here L or M shell, and thereby emits a photon of the discrete energy difference between the transitioning levels. If one spectrally resolves the discrete peaks are element specific and modern photoemission spectroscopy can yield insight into for example element identification, excitation dynamics or chemical bonds. Figure 2.13 left shows measured fluorescence lines of oxygen and xenon. In this measurement, xenon atoms and residual oxygen atoms have been illuminated with 1500 eV photons from the Linac Coherent Light Source and the fluorescence photons have been measured with the LAMP pnCCD detectors that are described in section 3.3. The green curve is a ADU histogram of the pixel-detector using the detector calibrations described in section 4.2. The blue curve additionally uses a

¹⁸See the following section 2.3.3.

2.4. Ionization of clusters in intense X-ray pulses

photon-finding algorithm as the signal from just one fluorescence photon splits up into multiple pixel. The coalescent-photon finding algorithm looks for pixel above a certain threshold and includes neighboring pixel above a certain threshold, thus correcting the measured signal to yield a proper ADU count per photon.

The Auger decay is another possibility for the atom to emit absorbed energy is through a 2-step process. First, an outer shell electron is emitted into the continuum, the so called Auger-electron¹⁹. Secondly, simultaneously to the first process another electron fills the electron-hole. An Auger decay occurs typically on the few femtosecond timescale [83]. Emitted Auger-electrons have discrete energies depending on the combination of electrons involved in the process. Similar to Fluorescence spectroscopy, one can use this attribute to, for example, identify elements or calibrate energies. Figure 2.13 right shows a partial K-LL²⁰ Auger spectrum from neon illuminated by 1050 eV photons from the LCLS and measured with a hemispherical analyzer as described in [37]. In this example, neon is ionized in the K-shell and an electron-hole in 1s is created. An electron from the L-shell fill the 1s hole and another electron from the L-shell, the Auger electron, is emitted into the continuum. As there is a variety of electronic configurations that can be involved in this process multiple peaks appear for similar occupation configurations, e.g. 1s - 2p2p. More complex structures, called satellites, appear when the atom is initially ionized, for example an additional hole in the L-shell and then an absorption that creates a hole in the K-shell will lead to KL-LLL satellites.

Similar to the Auger decay, where electrons from an outer shell are involved in the relaxation process, the transition can also be of the same shell and is then called a Coster-Kronig transition. Relevant transitions are for example the N-NN Coster-Kronig transitions in xenon [84].

So far we have looked at X-ray induced processes from atoms. Extended objects, whether a bio-molecule or a cluster, will respond differently than just the atoms they consist of. Nanometer-sized objects will develop a distinct character due to their electronic bond with other particles. This includes rare-gas clusters that are weakly bound Van der Waals forces. We shall explore this behavior in the next section 2.4.

2.4. Ionization of clusters in intense X-ray pulses

Cluster have a long history as a testbed sample to investigate light-matter interaction. The response of a cluster upon irradiation with light often differs from just the atomic

¹⁹Named after the french physicist Pierre Auger.

²⁰This nomenclature means a single hole in the K-shell is followed by a two holes in the L shell after the Auger decay.

2. Fundamental Concepts

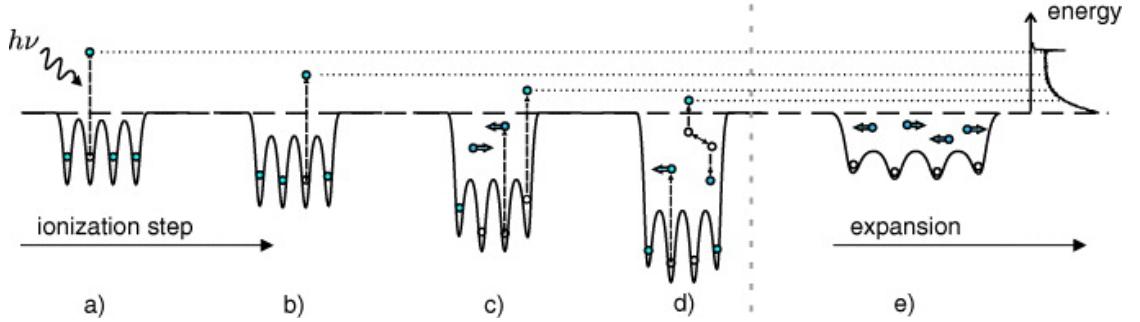


Figure 2.14.: Schematic of the nanoplasma creation and expansion. In step a) X-ray photons ionize electrons from a cluster. b) subsequent *multistep ionization* try to relax the electronically excited system, deepening the Coulomb potential of the cluster. Step c) shows a deepened Coulomb potential of the cluster, due to which the multistep ionization becomes (partially) frustrated and electrons are trapped in the potential. In step d) trapped electrons collide and start to thermalize. Collisions can lead to emission of trapped electrons. e) The superheated nanoplasma starts to expand. From [86,]

response. Collective effects change the microscopic (sample) environment and it is now the collective of atoms that generate a response to the interacting light. Clusters provide therefore a testbed environment to study collective effects ranging from atomic, to molecular and to bulk material attributes. While we went over some benefits of using clusters in section 2.2, it shall also be said that they provide an ideal testbed sample to control light-driven many-particle processes [85]. In this section, we study how rare-gas cluster respond to femtosecond long, high intense X-ray pulses, which is particularly interesting as it allows us to study radiation damage processes, which are similar to the the sample damage bio-molecules exhibit upon interaction with (intense) X-ray radiation.

2.4.1. Formation and expansion of a nanoplasma

Let us begin by recapture the elastic, coherent scattering part of the response that has been discussed in sub-section 2.3.1. Equation (2.34) indicates how the scattering length of a cluster can be calculated and, even though we neglect inelastic processes, this response is close to actual measured scattering patterns. If, however, we consider the inelastic effects discussed in section 2.3.2, it should be clear that the elastic scattering length $-r_0 F^{Object}$ is reduced due to the (atomic) dispersion corrections $f'(\omega)$ and $f''(\omega)$ that reduce the scattering length $-r_0 f^0(\vec{Q})$ of a single atom. On the one hand, the dominating change in scattering length is driven by the absorption process that we introduced via the imaginary dispersion correction $if''(\omega)$ but we know from table 2.4

2.4. Ionization of clusters in intense X-ray pulses

that the changes in scattering cross-section are relatively small, on the other hand, there are X-ray induced effects that change the scattering behavior of clusters. We know from previous experiments that these changes are related to the nanoplasma expansion. Let us follow figure 2.14 and [86, 87] in the next five steps. Step a) of the nanoplasma transition, the cluster gets ionized due to intense radiation²¹. Step b), further ionization through emission of photo electrons and Auger electrons lead to a so called *multistep ionization* that steepens the Coulomb potential [88–90]. Step c), the multistep ionization is suppressed (or frustrated) because the Coulomb potential depth is larger than the atomic excess energy of photo- and Auger electrons. The emitted electrons are now trapped in the cluster potential and are *quasi-free*. Upon increasing *inner ionization*, the nanometer sized object undergoes a phase transition to a nanoplasma²². Step d), the temperature of the nanoplasma is initially defined by the atomic excess energies (a rather discrete spectrum) but collisions with other particles lead a (kinetic) energy distribution of the electrons that is similar to thermal distributions and can be measured via the spectra of evaporated electrons [91, 92]. Step e) Hydrodynamic and Coulomb forces drive an expansion of the cluster and the cluster will ultimately disintegrate. The hydrodynamic portion of the force is due to the increasing hot plasma and the resulting increase outward pressure, whereas the Coulomb portion comes from the repelling force of same charges. Both these forces reasonably describe the expansion process, are not mutually exclusive and depend mostly on sample size and irradiation technique.

Regarding the sample size, large clusters efficiently trap electrons in their Coulomb potentials such that the quasi-free electrons thermalize and subsequently heat the nucleus. The hot nanoplasma system then tries to expand due to the increase in internal pressure. Electrons thermalize on the attosecond timescale and simulations show that the energy transfer to the ions can be as fast as 50 fs [93]. Small clusters trap photo and Auger electrons less efficiently and electrons are free such that the heating process is suppressed. In the case of small clusters, the ions see the repelling force due to Coulomb interaction of same charges with each other [94].

The nanoplasma expansion is also wavelength dependent. At optical to UV wavelengths strong field ionization can lead to ionization of clusters and a subsequent nanoplasma expansion [95]. At VUV, XUV and soft X-rays, direct photoionization becomes the main driver of the nanoplasma expansion and depending on the wavelength, certain multistep ionization cascades are enabled [86]. It remains to discuss the radiation intensity, which

²¹The wavelength of radiation must be above the ionization threshold of at least one subshell, however, it must not be X-rays with a wavelength on the nanometer length scale.

²²Plasma is another state of matter, similar to solid, liquid and gaseous, where molecular bonds dissociate and positive and negative particles are present in increasing numbers.

2. Fundamental Concepts

affects the ultimately achieved charge-state combination. The more intense the radiation is, the more energy is absorbed by the cluster. For the nanoplasma expansion, this determines the speed of the nanoplasma phase-transition and the expansion.

2.4.2. Imaging of transient states

The nanoplasma transition is so interesting is because every matter irradiated by a free-electron laser will undergo a nanoplasma transition and finally disintegrate. This is a challenge for structural biology and called radiation damage or sample damage[8]. Sample damage changes the structure of a biomolecule and it is particularly the structure many scientists want to investigate. In order to prevent falsified measurements, one needs to understand the nanoplasma transition as it occurs while the pulse is propagating through the sample. First attempts to perform a combined spectroscopic and imaging technique revealed correlations between the complex refractive index [96] and the diffraction patterns but also correlations of the ion spectroscopic data and the diffraction patterns intensity [97]. More recently, simulations on diffraction patterns could show the expanding electron density [17] as it is also shown in figure 2.15. In this particular study, an infra-red laser was used start (pump) a nanoplasma transition in a xenon cluster and subsequently image (probe) this state with a XFEL pulse. As the time delay between pump and probe pulse is varied, the resulting diffraction patterns of the 15-20 nm Xe-cluster show declining intensities at larger scattering angles with increasing time delay $\Delta t > 100\text{fs}$. The loss in signal could be explained through an expanding electron density [98, 99]. The electron density thereby expands increasingly over time due to the Coulomb and Hydrodynamic forces and, first the outer layers expand and at larger time delay also the inner atomic layers. In this study, an electron temperature of 200eV could be measured by comparing plasma simulations to the ion spectroscopy signal. The possible spatial resolution out of the diffraction patterns has been estimated to be 8 nm but through assuming a shape the electron density model is sensitive below this resolution.

In another study with shorter time delays of $\Delta t < 100\text{fs}$, xenon cluster compress in size [50]. Since clusters form as a crystal²³, one can determine their structure through crystallographic approaches as it is explained in full detail in [23, chapter 5]²⁴. Figure 2.16a is showing Bragg peaks under certain conditions over the scattering vector \vec{Q} . The

²³See section 2.2.1.

²⁴In short, crystals scatter light and create Bragg spots at large \vec{Q} -values. These Bragg spots occur when the so called Bragg-law is fulfilled. Bragg's law reads $m\lambda = 2d \sin(\frac{\Theta}{2})$, with m being an integer, λ being the wavelength of the scattered light, d the distance between crystalline layers and Θ the scattering angle. When Bragg's condition is fulfilled, the rays interfere constructively and the location of the Bragg peaks gives insight to the crystalline structure.

2.4. Ionization of clusters in intense X-ray pulses

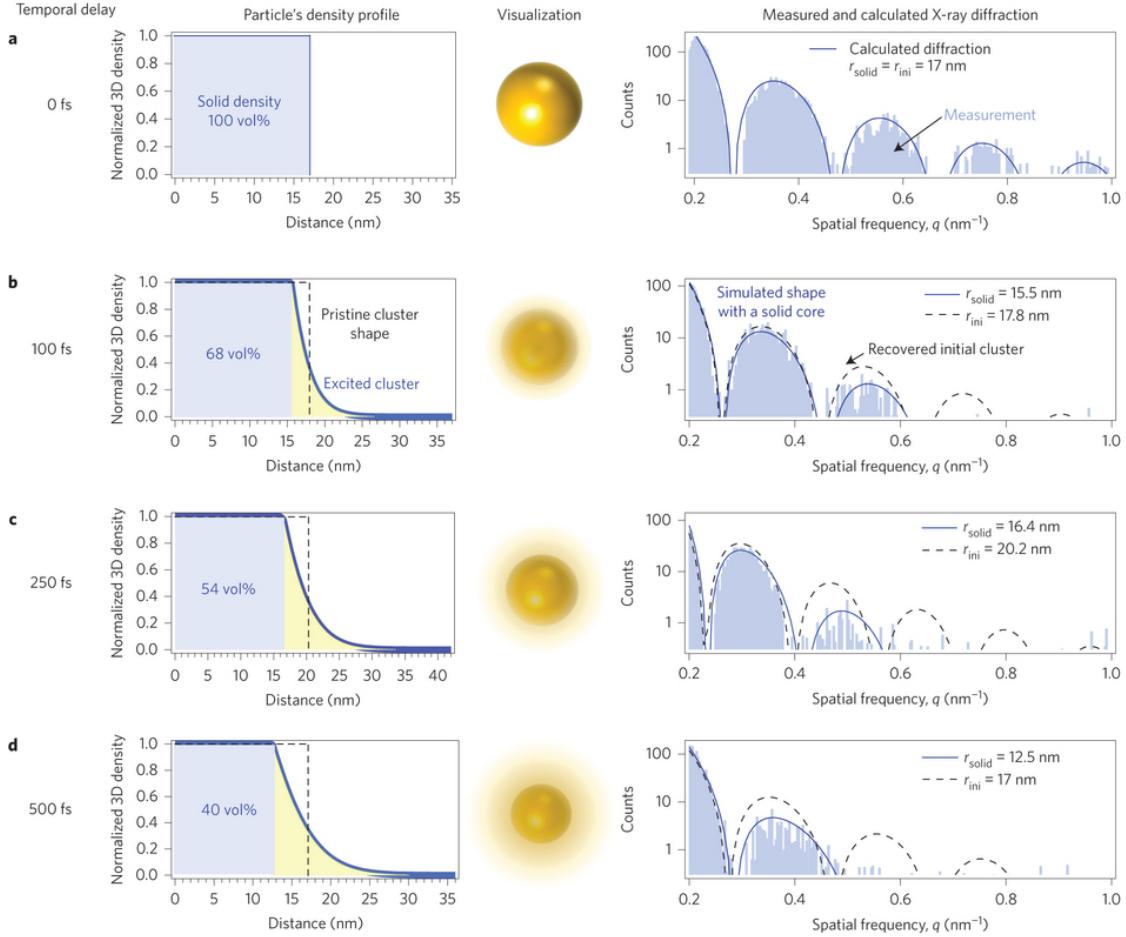


Figure 2.15.: Left series, simulation of of diffraction patterns. Right series, measured diffraction patterns of (spherical) xenon clusters pumped with an NIR laser pulse and probed a certain time delay with an LCLS pulse. The diffraction pattern show a decrease in intensity at larger q values, which can be explained through an expanding electron densities, i.e. a nanoplasma expansion. Electron density simulations are performed in 1D and the densities Fourier transform is fitted to the measurement for a solid sphere (dashed line) and an expanding sphere (solid line). From [17]. Reprinted with permission from Nature Publishing Group.

2. Fundamental Concepts

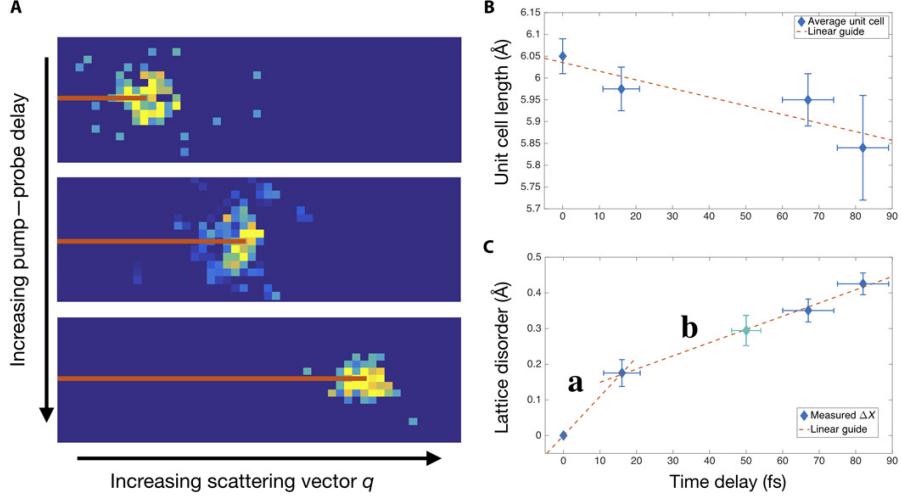


Figure 2.16.: X-ray pump – X-ray probe scattering experiment on Xe-cluster that shows an early evolution of the nanoplasma transition. A, single-shot Bragg peaks at varying time delays. The scattering vector q increases over time delay. B, unit cell length over time delay. The unit cell length decreases, therefore the cluster shrinks in size. C, Lattice disorder over time delay. The measured fcc lattice is becoming disordered after being pumped with a X-ray pulse. From [50]. Reprinted with permission from AAAS.

signal moves to larger scattering vectors \vec{Q} and, as $\vec{Q} = \frac{2\pi}{a}$, the unit cell length a is shrinking over the time delay $\Delta t = \{0, \dots, 100\}$. This unintuitive and contradictory result is attributed to the changes in electronic configuration upon ionization. Electrons that are trapped in the cluster Coulomb potential have an increased mobility and are able to contribute comparable to valence electrons and therefore change the chemical bonding character of the Van der Waals cluster. As a result, the unit cell changes on the Ångstrom length scale and the lattice becomes increasingly disordered (see figure 2.16c).

These two studies allow us to conclude that the nanoplasma transition is a multistep process. First, the initial ionization occurs, followed by an increased Coulomb potential that traps electrons, which then change the structure of the nanosample, e.g. compression of a lattice. Eventually, the system becomes strongly ionized and hot such that Coulomb and hydrodynamic forces start an expansion of the system until eventually the forces disintegrate the sample into its atomic components.

2.4.3. Tampered layers to inhibit the nanoplasma expansion

To overcome radiation damage, the most common method is to *outrun* radiation damage processes using very short pulses [8]. Pulses from the XFEL must be shorter than the

2.4. Ionization of clusters in intense X-ray pulses

lifetime of Auger processes, thus on few femtosecond long, to fully outrun the multistep ionization. However, by limiting the XFEL pulse duration, one inevitably limits the pulse energy as current pulse compression methods typically generate much less fluence. This means that currently, many coherent diffractive imaging experiments are performed with pulse widths of 40fs or more to generate enough scattered intensity. But even if these technical limitations can be overcome, outrunning radiation damage does not circumvent photoionization and it is therefore expected that also few femtosecond long pulses only reach a certain spatial resolution [9]. To be more precise, it is an open question, whether electron densities and here particular bonding configuration are obtainable by solely outrunning radiation damage. As radiation damage is unavoidable it can be mitigated in several ways. As the underlying processes are well understood, one way to mitigate for the radiation damage would be to simulate the effects, however, this can only be done for small particles. Another way to fundamentally increase resolution in single particle imaging is due to prior alignment of particles such that their orientation is known while the image is taken. Molecule alignment has seen some success for small molecules [19] but it is currently unknown, whether this works for larger molecules as the strong light fields, which are needed to align the molecules, may change their structure. Here it should be noted that recent advances with CDI algorithms made it possible to computationally determine the orientation of a particle at the time of imaging [12, 100] without prior knowledge if at least a few hundred diffraction images are provided. Anyway. In this thesis, we shall discuss a method to reduce effects of radiation damage through artificial tampered layers. Artificial shells around a sample supply it with electrons and function as sacrificial layer that protects the sample [21]. For aerosol particles, this method has also only been investigated through ion spectroscopy [101, 102]. In the study shown in figure 2.17 a core-shell system of argon and xenon was constructed and here xenon compares to the sample and argon compares to the sacrificial layer around the particle (see figure). The heterogeneous cluster were irradiated with 93eV photons from *FLASH*²⁵ at which mostly xenon atoms are ionized. As described in the nanoplasma creation process (see section 2.4.1), the increasing ionized cluster creates a steep Coulomb potential trapping electrons. Trapped electrons are available for recombination with the ionized atoms. In the small core-shell system of Ar-Xe with 400 particles (figure 2.17 top-panel), the time of flight mass spectroscopy data shows Xe and Ar ions meaning that the charge recombination is suppressed and the cluster disintegrates upon irradiation. In the large Ar-Xe cluster system with 4000 particles (bottom-panel), mostly Ar ions are in the

²⁵Short for **F**ree electron **L**ASer in **H**amburg. An extreme ultra violet (XUV) free electron laser in Hamburg, Germany.

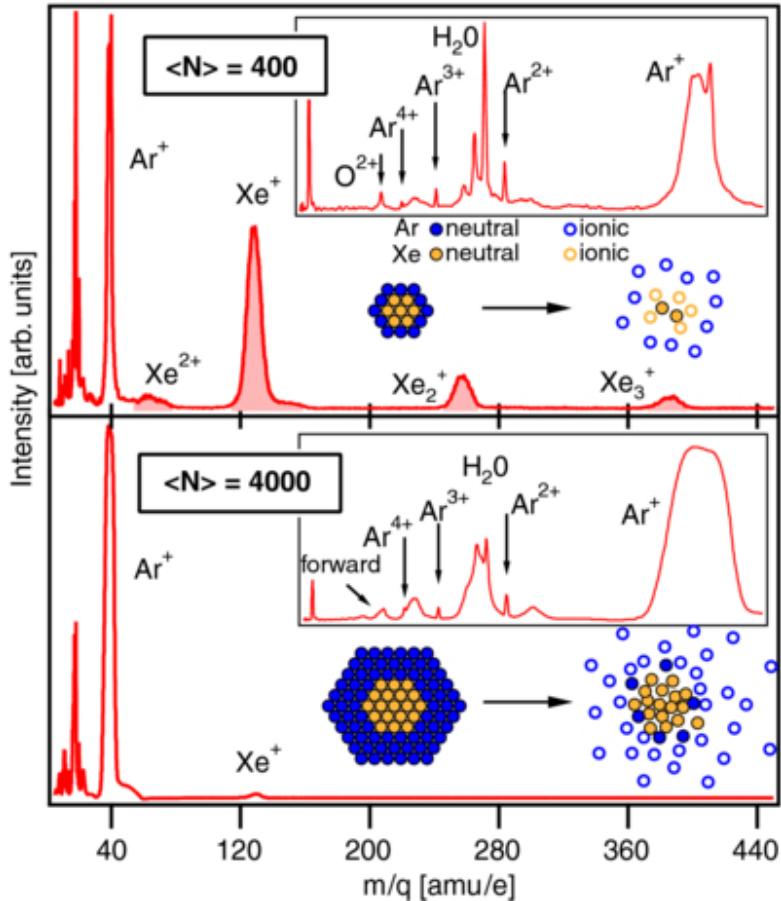


Figure 2.17.: Time of flight (TOF) traces of argon and xenon core shell systems irradiated with 93eV X-ray pulses from FLASH. At this energy, mostly Xe is ionized and the ionized atoms create a steep Coulomb potential that traps electrons towards the center of the cluster. The top panel shows smaller clusters with 400 particles, in which the trapping is inefficient, few electron-ion recombinations occur, thus Xe and Ar ions are detected in the TOF detector. The bottom panel shows large clusters with 4000 particles and a thicker argon shell. Here, Xe-ions recombine in the center and the TOF shows mostly Ar ions as the neutral Xe remains undetected. From [101,].

2.4. Ionization of clusters in intense X-ray pulses

TOF data meaning the Xe ions in the center of the cluster recombine with the electrons that were attracted to the center by the steep Coulomb potential of the large cluster. The neutral Xe is not detected by the TOF detector. The Ar ions in the outer layers contributed electrons to the center of the cluster due to the attractive potential but were shed off the cluster. It is also evident that the argon atoms in the large cluster case release more kinetic energy than in the small cluster case, which is likely an effect that cools the intact cluster core.

3. Experimental Setup

The experiment described in the present thesis has been performed using the LAMP end-station in the Atomic, Optical and Molecular Physics instrument of the Linac Coherent Light Source, which is located at SLAC National Accelerator Laboratory. SLAC National Accelerator Laboratory (SLAC) is funded by the Department of Energy (DOE) and operated by Stanford University. SLAC was founded in 1962 as Stanford Linear Accelerator Center. The accelerator was mainly used for high-energy physics experiments and resulted in three Nobel Prizes in Physics [103–105] and many other accomplishments [14, 106]. SLAC’s research topics broadened in the 70’s and with the Stanford Synchrotron Radiation Project, SLAC has become a X-ray user facility in 1974. The synchrotron source was modernized and is now known as the Stanford Synchrotron Radiation Lightsource (SSRL). The linear accelerator has been repurposed to function as the world’s first hard X-ray free electron laser (XFEL) and it is now known as the Linac Coherent Light Source (LCLS). LCLS began operations in April 2009 [14] and the AMO instrument started user October 2009 [107]. AMO started up using the HFP and then the CAMP end-station, however, the LAMP end-station was commissioned in September 2013 and has been in use ever since. This thesis experiment was performed in January 2014¹ in the LAMP end-station of the AMO instrument..

This chapter is organized as follows, section 3.1 goes over the details of the AMO instrument. Section 3.2 focuses on the specifics of the LAMP end-station. Section 3.4, which centers around relevant sample delivery. The chapter ends with section 3.3 and 3.5 that describe important detectors, namely the pnCCD and time-of-flight (TOF) detectors, for the LAMP end-station.

3.1. The atomic, molecular and optical physics instrument and front end enclosure at the LCLS

The atomic, molecular and optical physics (AMO) instrument is located closest to the undulators of the LCLS at hutch 1. The AMO instrument is designed for soft X-ray

¹Experimental identifier at SLAC: AMOA1214

3.1. The AMO instrument and FEE at the LCLS

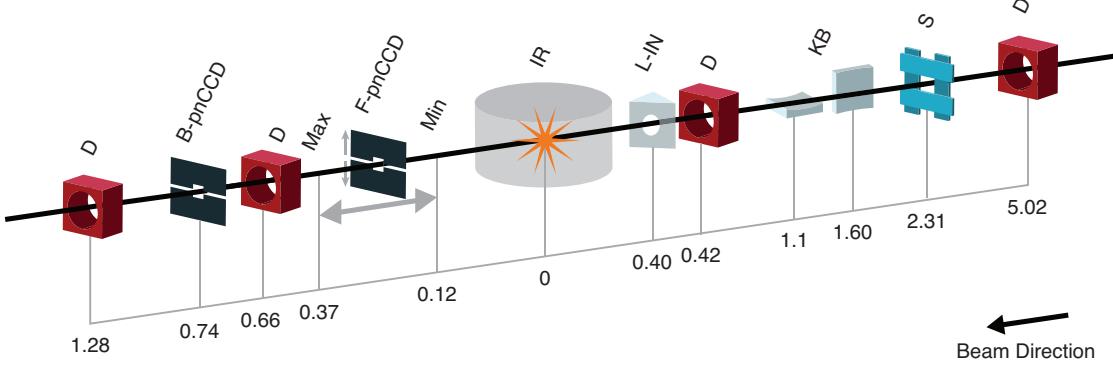


Figure 3.1.: Schematic overview of the AMO beamline instrumentation in the LAMP configuration. The indicated distances below the schematic items are in meters from the interaction region. As the X-ray beam enters the instrument, it can be visualized on a YAG crystal diagnostics (D). A set of 2 slits (S) cuts the beam in the vertical and horizontal to reduce straylight from the Kirkpatrick-Baez (KB) optics. The differential pumping section of the LAMP end-station houses another YAG crystal diagnostics (D) and an option couple in an optical laser (L-IN) on-axis with the X-rays. The front and back pnCCD (F/B-pnCCD) are located downstream of the IR with further beam viewing options (D). From [108].

photons in the energy range from 280 eV - 2000 eV [108, 109], where the beam divergence is a limiting factor for lower energies and the B4C-coating on some mirrors leads to absorption above 2000 eV. After the X-ray pulse generation in the undulators of the LCLS the beam is transported to the Front End Enclosure (FEE) [110], where the electron beam is deflected using magnets and subsequently dumped in a beam stop such that only X-rays continue. Optionally, the XTCAV [111] can be used to give insight into the kinetic energy and pulse duration of the electron beam. In the FEE, the X-rays can be attenuated with either a gas or a solid attenuation scheme. A X-ray pulse energy monitor, often referred to as gas detector, measures the pulse energy of a single shot before and after the attenuation [112]. Eventually, the X-ray beam is deflected through a mirror system into the desired hutch. To direct the beam to the AMO hutch, the soft X-ray offset mirrors (SOMS) are being used. SOMS are a set of three mirrors, where the first two are shared to steer the beam into hutch 2 or the Soft X-ray (SXR) instrument [113–115]. The AMO instrument is very versatile in its configuration and can use three different end-stations. From the time of first commissioning, end-station 1) is the High-Field Physics (HFP) end-station [107, 109], 2) the CFEL-ASG Multi-Purpose (CAMP) end-station [116] and 3) the LAMP instrument [81, 108]. As the experiment described in

3. Experimental Setup

the present work has been performed with the LAMP end-station, we shall focus on that configuration from here on. A schematic overview of the AMO beamline instrumentation in the LAMP configuration can be found in figure 3.1. As the X-ray beam travels from the FEE to the AMO beamline, it can be projected onto a YAG crystal diagnostics (D). Here the shape and position of the beam can be well determined as it is several meters downstream of the SOMS such that a difference the SOMS angle and position can be determined with sub-millimeter precision. The projection also reveals the alignment of the beam to several differential pumping apertures that are located in the FEE and the beam should be centered to those apertures [117]. In the described experiment, the X-ray beam became unstable and the pointing of the electron beam was jumping. The most upstream YAG crystal of the AMO instrument was able to detect this jitter. A beamline alignment laser (typical HeNe-laser with low beam divergence) can be coupled into the beamline shortly downstream of the YAG screen² such that it co-propagates with the X-rays. Beamline alignment laser are invaluable tools to pre-align a system before X-rays are taken. For the described experiment, it was necessary to align the particle jet of the pristine Xe-cluster and the particle jet of the HeXe-cluster to be perpendicular to the X-ray beam (see 3.8). In order to perform this alignment, a beamline alignment laser that co-propagates with the X-rays is useful if not required.

The X-ray beam then travels through a set of 4 blades (S) that can be moved independently to cut into the beam to reduce effects of straylight on the detectors, especially straylight originating from the Kirkpatrick-Baez (KB) optics [118]. In collaboration with the Single-Particle Initiative, it was investigated how the 4-blades reduce unwanted scattering from and it was found that the blades should not cut into the main intensity profile of the beam, but rather conservatively cut into the halo of the beam [119]. This still sufficiently reduces straylight but does not reduce the peak intensity of the X-ray pulse (compare green and blue curve in figure 3.2). The KB optics focus the X-ray beam into the interaction region. The optics consist of two 400 mm long silicon (Si) substrates that are coated with boron carbide (B4C). They reflect the X-rays in grazing incidence at 13.85 mrad and are sometimes called KB mirrors. One mirror reflects the beam in the horizontal and the other reflects the beam in the vertical. As the mirrors are located at different positions, the mirrors are designed to have a focal length of 1600 mm in the horizontal and 1100 mm in the vertical. Additionally, the mirrors are bent to change their focusing position along the Z-axis³ and through 1) the study of time-of-flight (TOF) mass-spectroscopy [81] or 2) imprint analysis [120, 121] the focus can be characterized. A

²Not shown in figure 3.1

³The LCLS uses a right-handed coordinate system, where the index finger (Y-axis) points up and the middle finger (Z-axis) points parallel to the X-ray beam.

3.1. The AMO instrument and FEE at the LCLS

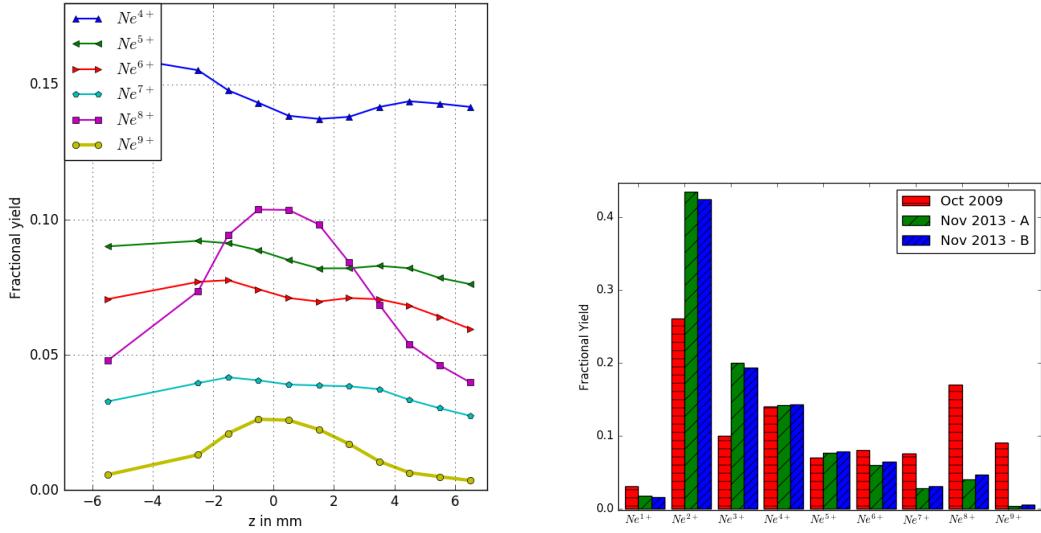


Figure 3.2.: Left graph: Atomic neon charge state yield from time-of-flight mass spectroscopy as a function of Z , relative to optimal focus position $Z = 0$. $Z = 0 \pm 1$ is a favorable length for sample injection. Right diagram: Comparison of atomic neon charge state yield from time-of-flight mass spectroscopy for different cases. Red: Experimental data from October 2009 with 4 blades (S) opened. Green: Experimental data from November 2013 with (S) closed. Blue: Experimental data from November 2013 with (S) opened.

3. Experimental Setup

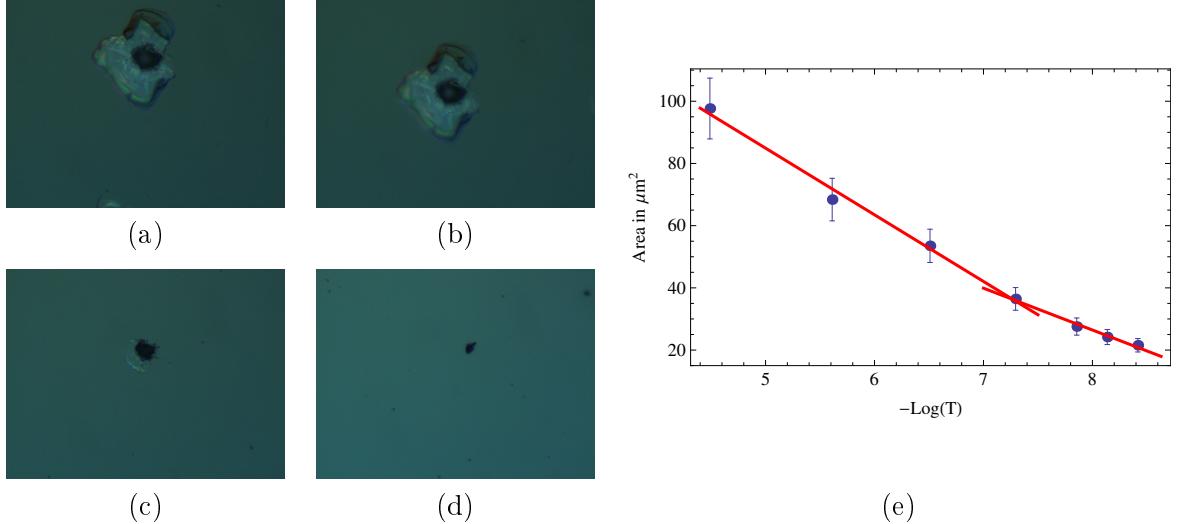


Figure 3.3.: a)-d), ex-situ microscope imprint study of a lead tungstate (PbWO_4) sample that was irradiated with single LCLS pulses at 1600 eV at different gas attenuation using the LCLS gas attenuator. e) non-linearity in Liu plot due to LCLS's super-gaussian beam profile. The approximate FWHM can be determined from the slope of the linear fits, see more in text.

study and manipulation of the X-ray focus is necessary to achieve small X-ray focii that increase the fluence of the sample interaction region, which is desired in coherent diffractive imaging as thus more photons scatter from the sample and, ideally, to understand the coherent wavefront that creates an image of the particle better.

3.1.1. Focus characterization using a TOF spectrometer

Figure 3.2 left shows a focus characterization along the Z-axis using a TOF spectrometer. The fractional neon ion yield per charge state is summed and plotted as a function of Z-position. An area of 2 mm around $Z = 0$ mm could be determined as useful operating condition. Figure 3.2 right, compares fractional neon ion yield at optimal focus position from November 2013 [81] to October 2009 [122]. The comparison reveals that high charge states of neon, for example Ne^{8+} and Ne^{9+} , are less frequent due to deteriorated beamline optics.

3.2. The LAMP end-station at AMO

3.1.2. Focus characterization via imprint study

Figure 3.3 left shows images from a microscope of how a LCLS X-ray pulse at 1600eV interacts with a lead tungstate (PbWO_4) sample at different transmission values T . We can describe the energy fluence $E(r)$ as

$$E(r) = E_0 e^{\frac{-r^2}{2\sigma^2}} \quad (3.1)$$

with the radial coordinate r , the spatial radius σ and the peak fluence E_0 . So, while σ stays a constant beam parameter, at different pulse energies $E_p \propto E_0$ change the crater area in the sample. We can further approximate the craters using a circle such that the area is πr_0^2 , with the crater radius r_0 . As shown in [123], $r_0^2 = 2\sigma^2 \log(\frac{E_0^2}{E_0^1})$, with $E_0^{1/2}$ being the peak fluence at different attenuation level. We can express the peak fluence more conveniently in terms of the pressure p in the attenuator

$$\log(E_0) = \log(E_{in}) + \log(T) = -p \cdot c + \text{const.}, \quad (3.2)$$

with the peak fluence into the gas attenuator E_{in} and the transmission T . In the gas attenuator, the transmission is $T = e^{-p \cdot c}$ and a constant c . The constant c can be derived from [124] and for the LCLS attenuator filled with N2 gas over 410cm at 1600 eV photon energy, $c \approx 0.5611415 \text{ Torr}^{-1}$. Finally, the full width at half maximum (FWHM) is $\text{FWHM} = 2\sqrt{2\ln(2)}\sigma$. Figure 3.3 right shows the crater area as a function of $-\log(T) = p \cdot c$ (Liu's plot) and is linearly fitted. The data indicates non-linearities that come from a super-gaussian beam profile. Therefore, at different attenuation level, different σ^2 are measured due to the damage threshold of the PbWO_4 sample [125, 126]. In this data set, using the slope of the linear fit at smaller transmissions a $\text{FWHM} \approx 3.4 \mu\text{m}$ is determined. However, for the described experiment in this thesis, the X-ray beam focal size in FWHM was determined to be $\text{FWHM} \approx 1.5 \mu\text{m}$, with an effective area a $5 \mu\text{m}^2$ [81]. The LCLS beam parameter are summarized in table 3.1. The pulse duration was determined due to analysis of the electron beam and the delay Δt precision is estimated from geometric considerations of the delay chicane.

3.2. The LAMP end-station at AMO

Still following the beamline layout in figure 3.1, the X-ray beam enters the LAMP end-station after the KB mirrors (see also the overview in figure 3.4). LAMP begins with a differential pumping (DP) section that separates the interaction (C1) and detector

3. Experimental Setup

| | pump beam | probe beam |
|----------------------------|----------------|-----------------|
| wavelength | | 1.5 nm |
| mean pulse energy | 80-100 μ J | 0.8- 1 mJ |
| X-ray beam FWHM | | $\sim 1.5\mu$ m |
| pulse duration | | ~ 25 fs |
| delay Δt precision | | ~ 25 fs |

Table 3.1.: Summary of LCLS beam parameter

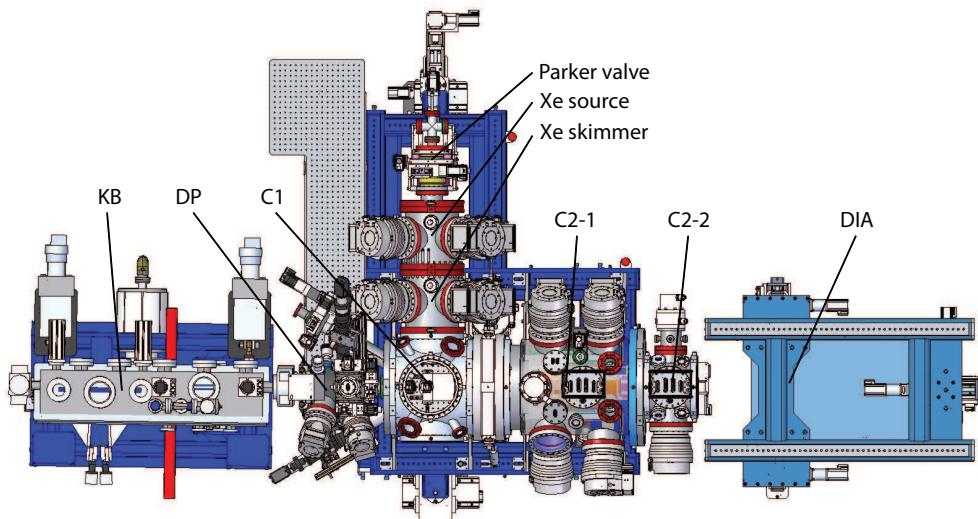


Figure 3.4.: Overview of the AMO instrument in the LAMP end-station configuration. From left to right, the beam propagates through the Kirkpatrick-Baez (KB) optics, the differential pumping (DP) section, the interaction chamber (C1), the front pnCCD chamber (C2-1), the rear pnCCD chamber (C2-2) and finally the diagnostics stand (DIA). The xenon jet is installed including the manipulator that holds the Parker valve, the Xe source chamber and the Xe skimmer chamber. The helium jet is not included in this drawing but mounted perpendicular to the Xe jet and the vacuum pumps have not been installed as shown here. For scale, the large, open conflat flanges on the C1 chamber are 12 inch.

3.2. The LAMP end-station at AMO

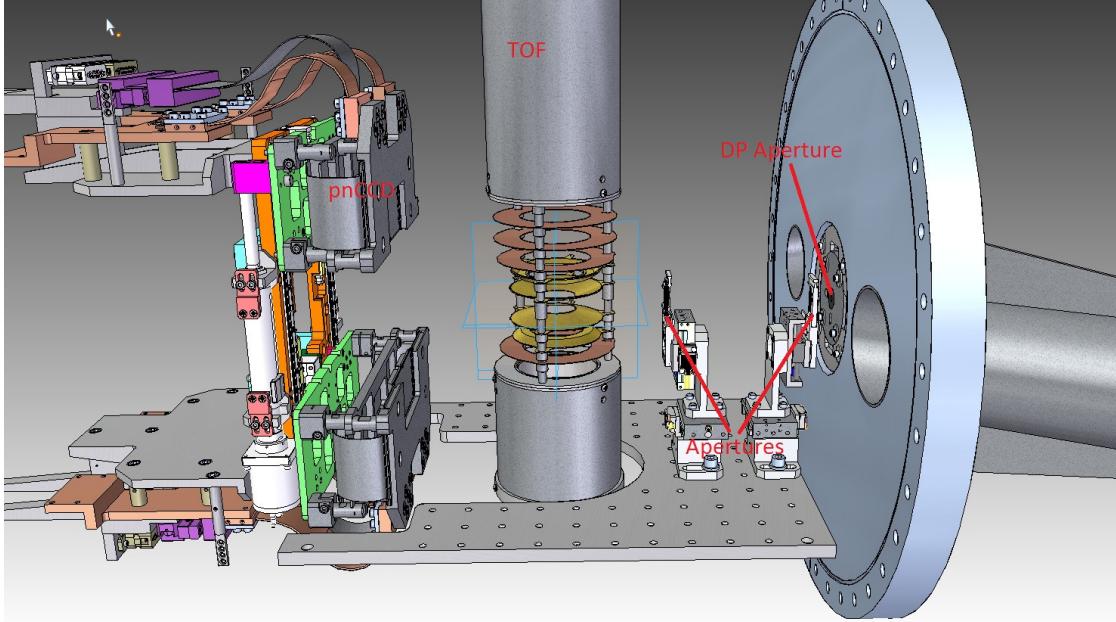


Figure 3.5.: Inside view of the C1 chamber showcasing the interaction region.

chambers (C2-1, C2-2) from the KB optics and other upstream beamline instrumentation. The differential pumping section consists of two small chambers that are pumped via turbo-molecular pumps and are interconnected to the LAMP chamber system via 5 mm, 8 mm, or 10 mm diameter differential pumping apertures (indicated in figure 3.5). The differential pumping stage is able to maintain up to 4 orders of magnitude pressure difference, for example $1e^{-10}$ bar in the KB-optics vacuum tank and $1e^{-6}$ bar in the interaction region. The first differential pumping stage holds a YAG crystal to examine the X-ray beam after the KB optics. The second stage holds optionally a laser in-coupling mirror to overlap X-rays with an optical laser or a straylight aperture to prevent scattering from the differential pumping apertures and upstream elements.

The beam then travels into the C1 chamber that encloses the interaction region. Before reaching the sample interaction region, the beam is cut by apertures, further reducing straylight (see figure 3.5). The apertures are mounted on encoded piezo stages with sub-micron movement precision. The used aperture material is silicon nitride (Si_3N_4) with tapered edge windows to allow the X-rays to traverse. The windows can be either fit to the size of the X-ray beam diameter, which can be estimated using geometric optics, or by using one corner of the window on the first aperture stage and the opposite corner on the second stage. As straylight is a concern in CDI type experiments, an improved aperture system was designed using blades with tapered edges. This allows full control

3. Experimental Setup

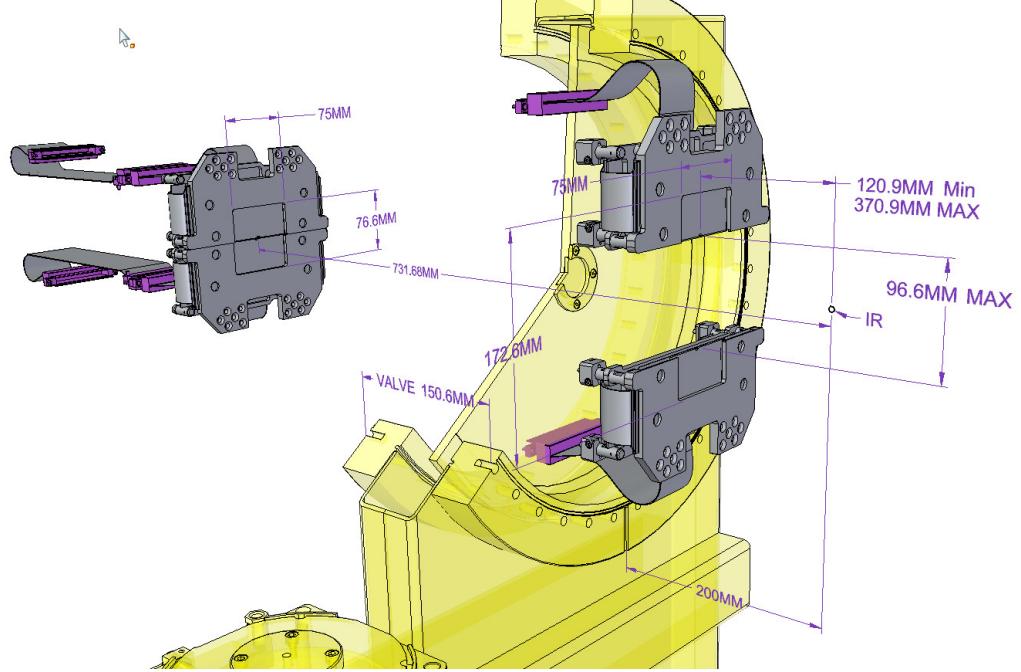


Figure 3.6.: Side view of the rear and front pnCCD detector in C1, C2-1 and C2-2. The interaction region (IR) is in the center of C1. The beam propagates along the Z-axis where the rear (top) pnCCD is placed 728.53 mm away from the IR (original engineering distances). The half detector height is 38.3 mm and results in a scattering angle of $\Theta = 4.26^\circ$. With the gate-valve installed, the front pnCCDs are able to travel along the Z-axis from 370.9 mm to 120.9 mm downstream of the IR. The front pnCCDs position along the Y-axis is adjustable and they can detect photons up to 48.3 mm from the beam axis. At maximum extension, the pnCCDs are able to detect photons up to a scattering angle of $\Theta = 38.11^\circ$.

over the aperture from each direction and was commissioned in collaboration with the Single Particle Imaging initiative [119].

In the center of C1, where sample and X-rays interact, a time-of-flight spectrometer is located (see figure 3.5) that we will describe in the section 3.5. The beam then passes the front pnCCD, which is mounted on a moveable stage. Another in-vacuum manifold allows the use of another YAG crystal (D), an optical filter and a B4C beam stop just before the rear pnCCD. Figure 3.6 shows relevant engineering design distances of the pnCCD detectors inside the LAMP instrument. In the following, we consider the instrument to have the gate valve mounted and that the FEL focus position is in the center of the C-1 chamber. The distance from the focus to the bottom rear pnCCD detector module is 731.68 mm and the top, rear pnCCD module is 3.15 mm closer to the C-1

3.3. The large area pn-CCD detectors

chamber⁴. As mentioned, the front pnCCD module can be moved along the Z-axis. The distance from the front-bottom pnCCD module to the focus can be set between 117.75 mm - 367.75 mm. The front-top pnCCD module is again 3.15 mm closer to the center of C-1. The front detectors can also be moved along the Y-axis and the maximum extent is 48.3 mm from the beam to the onset of the detector. The manufacturing size of the gate-valve along the z-axis is 150.6 mm. In the experiment, the front pnCCD have been in the most rear position.

3.3. The large area pn-CCD detectors

Diffraction patterns are recorded with pnCCD detectors in LAMP's C2-1 and C2-2 chambers. A pnCCD is a versatile device and has found usage in astronomy and material science. pnCCDs have been used previously at LCLS, namely in the CAMP instrument. At LCLS, detectors are mostly used for coherent diffractive imaging applications but have also spectroscopically capabilities, which were demonstrated in the left figure 2.13. The pnCCDs are attractive photon area detectors because of the following 4 reasons. First, their high quantum efficiency (QE) and good signal to noise ratio. Second, their read-out rate is very high (up to 200hz) and enables us to use the full repetition rate of LCLS (120hz). Third, their large, consecutive active areas cover wide scattering angles, and lastly, the detectors are almost defect free after applying the usual image corrections. These points are explained in detail in the following [81].

Let us begin describing their chip geometry. Each pnCCD detector (front or rear) is made out of two modules. Figure 3.7 shows the layout of a single pnCCD module. The chip consists of 512×1024 pixel. Each pixel has a size of $75 \times 75\mu\text{m}^2$, so the area that the detector covers is $38.4 \times 76.8\text{mm}^2$. To allow the FEL beam to travel through the instrument, each module has a rectangular region cut out. On a single module this area is $4.5 \times 1.65\text{mm}^2$ and for the whole detector this 'hole' has the dimensions $4.5 \times 4.5\text{mm}^2$. The size of this hole has been chosen to slightly oversize the diverging FEL beam at the rear pnCCD position (assuming a focus in the C1 chamber). The borders of each module are insensitive to photons and are $1.10 - 1.15$ mm thick. To minimize the overall detector area that is insensitive to photons, the two pnCCD modules are mounted such that the not sensitive areas overlap. As a result from that, each top module is 3.15 mm closer to the interaction region than each bottom module. The effective gap that is seen in the

⁴These design distances are offset by +5mm along the Z-axis due to customization during the initial setup.

3. Experimental Setup

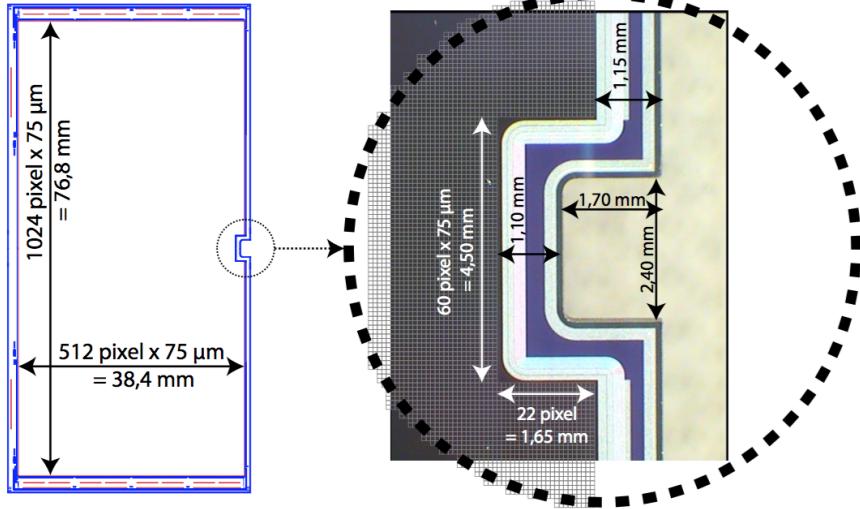


Figure 3.7.: Geometry of a single pnCCD module with a detailed view of the beam conveying hole. A single module consists of 1024×512 pixel. Each pixel is $75\mu\text{m}$ which results in an active area of $76.8 \times 38.4\text{mm}^2$. The chip is surrounded by a non-active edges, which are 1.15mm wide on beam facing edges. The hole reduces the active area on one module by 60×22 pixel, or $4.5 \times 1.65\text{ mm}$ and allows the beam to propagate through a $2.4 \times 1.7\text{mm}^2$ hole.

laboratory frame images between each top and bottom module measures 16 pixel, i.e. $\sim 1.2\text{ mm}$.

The pnCCD chip is read out with a specifically for the pnCCDs designed CMOS multi-channel Analog MultiplEXer (CAMEX). The CAMEX pre-amplifies the charges through a set of gain amplifiers and enables a parallel read-out of 128 pixel rows simultaneously. Each CAMEX converts the signal to an analog output, enabling to read out all pnCCD rows at once, thus allowing the high read-out speed of up to 200hz. The analog signal is converted to a digital signal and the image information is stored by the LCLS Data Acquisition (DAQ) in the LCLS psana network, where it is accessible for analysis.

The pnCCD can be operated in different gain modes to be more sensitive to photons (high gains) or to have more dynamic range (lower gains) as shown in table 3.2. The different gain amplifications are applied through the CAMEX. Gain $\frac{1}{1}$ is the highest gain and $\frac{1}{256}$ is the lowest gain. As you step from highest to lower relative gains (e.g. from 1 to $\frac{1}{64}$), the ADU value creation per photon goes as well with that fraction. Hence, going to lower gains reduces the signal-to-noise ratio but increases the dynamic range. Note, that the table shows typical operating values using 1 keV photons and that the ADU value creation is dispersive. The thin and unstructured radiation entrance win-

| Key | relative gain | approx. ADU/keV | max. photons per pixel |
|-----|---------------|-----------------|------------------------|
| 1 | 1/256 | 5 | 1100 |
| 2 | 1/128 | 10 | 640 |
| 3 | 1/64 | 20 | 320 |
| 4 | 1/16 | 79 | 80 |
| 5 | 1/4 | 316 | 20 |
| 6 | 1 | 1250 | 5 |

Table 3.2.: Typical generated ADU values and dynamic range using 1k eV photons at all pnCCD gain settings. It is a valid approximation to linearly extrapolate to other photon energies.

dows, have a high quantum-efficiency from the infra-red (IR) to soft X-ray regime and in order to avoid unwanted scattering, the photon entrance windows (located at the back of the detector) are coated with 50 nm aluminum to reduce their sensitivity from infra-red and optical light. This aluminum coating does attenuate the soft x-rays at AMO only slightly but the detectors maintain a QE of 90%. At AMO it is thus possible and handy to linearly extrapolate the generated ADU values to other photon energies, for example a 1.5k eV photon will generate approximately 1750 ADU in highest gain (compare figure 2.13). There is also an optical aluminum filter mounted from the front of the chip to drastically reduce wrongly directed scattering and straylight.

3.4. Sample delivery

Two gas sources are used in order to create single rare-gas clusters. Single xenon and helium cluster are produced using the principle of the supersonic gas expansion into a vacuum that is described in section 2.2.1. Helium cluster doped with xenon are produced through the pickup principle as described in section 2.2.2. Given the time constraint of performing experiments at the LCLS, both sources are installed in one setup and operate independently, allowing a quick sample change. A schematic setup can be found in figure 3.8 and a list of used vacuum pumps can be found in table 3.3.

The AMO cluster source, that produces single xenon cluster, consists of a Parker-Hannifin Series 99⁵ - pulsed valve using a solenoid with a custom manufactured conical copper nozzle, two vacuum chambers to mount two skimmers, a third adjustable piezo-slit skimmer and several vacuum pumps. It is a well characterized source that has been used extensively in the past [17, 50, 70, 97, 108]. The pulsed solenoid valve (see figure 3.9)

⁵Series 99 is at the time of writing not produced/advertised as a straight, in-line pulsed valve anymore.

3. Experimental Setup

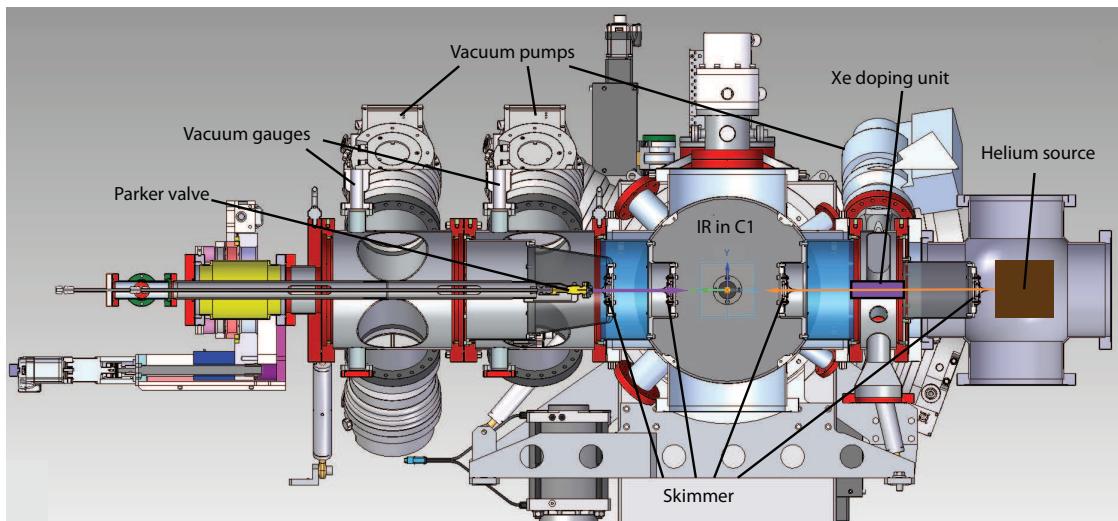


Figure 3.8.: Downward view of a slice through the interaction region in C1 of the experimental setup. The purple arrow indicates the xenon gas flow, the orange arrow indicates the helium gas flow.

| Chamber | Turbomolecular pump mod. | Roughing pump mod. |
|----------------|---------------------------------|--------------------|
| Xenon source | 4x Leybold Turbovac TMP 361 | |
| Xenon skimmer | 2x Leybold Turbovac Mag W 300 P | |
| Helium source | 2x Leybold PK-S 1300 | adixen ACG600 |
| Helium skimmer | 2x Pfeiffer HiPace 300 | |
| LAMP C1 | 1x Pfeiffer HiPace 700 | |
| LAMP C2-1 | 4x Pfeiffer TC 400 | adixen ACP 120G |

Table 3.3.: Installed vacuum pumps per chamber in the experiment.

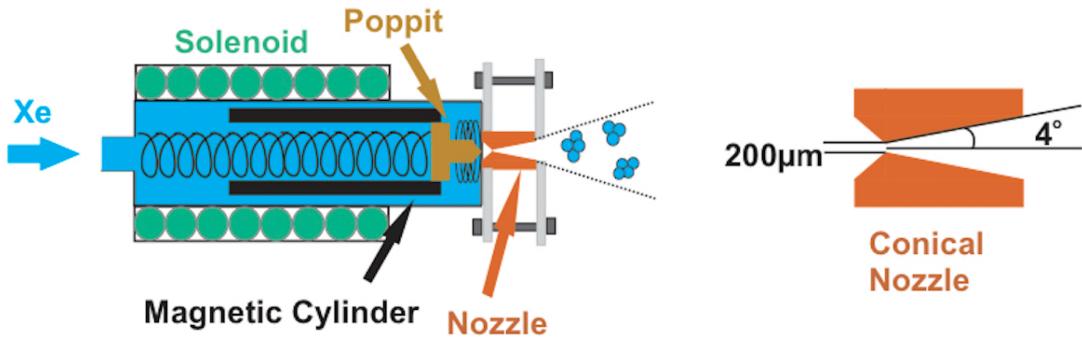


Figure 3.9.: Schematic of the Parker-Hannifin Series 99 pulsed in-line valve and custom copper nozzle. The nozzle is clamped to the pulsed valve using an indium gasket to seal. The vespel poppet is attached to the magnetic cylinder and opens or closes the valve. If a current is run through the solenoid, the magnetic cylinder and thus the valve actuated. From [127]

is controlled and operated by a Parker-Hannifin Iota One pulsed valve driver. The valve driver applies a current to the solenoid, a magnetic cylinder actuates and the attached poppet opens and closes again after a set TTL signal from driver. The valve's opening time is set to 1 ms and repetition rates of up to 30 hz can be set at a xenon reservoir pressure of $p_0 = 1\text{--}20$ bar. The pulsed valve heats up substantially during operations and due to material deterioration, the vespel poppet is replaced every 60h of operating time, or as needed, to prevent a leaking gas source. The nozzle has a $200\text{ }\mu\text{m}$ diameter opening and an opening half angle of 4° . It is clamped to the Parker valve using an indium gasket to seal. Two skimmer with an opening of 1mm diameter and an adjustable piezo-skimmer have been installed to define the gas jet. The piezo skimmer allows fine control over the slit opening formed by two razor blades. The blades can be closed by applying a voltage $U = \{0, \dots, 12V\}$. At $U = 8V$, the cluster source operates in the single cluster regime. The background pressure $p_{\text{source}}, p_{\text{skimmer}}$ is handled through the pumps installed on the source and skimmer vacuum chambers, see table 3.3. Ultimately, the skimmer stages lowers the gas pressure in the interaction region $p_{\text{IR}} \leq 10^{-5}$.

Helium droplets were produced in a free gas expansion using an electron microscope diaphragm as nozzle (Plano A0200P) that has a $5\text{ }\mu\text{m}$ orifice and a orifice channel length of $2\mu\text{m}$ [72]. The nozzle is cooled to cryogenic temperatures $T = 5.8$ K using a Sumitomo cold-head. The particle beam is defined by a first 0.5mm and a second 1mm diameter skimmer. As explained above, a third piezo-skimmer allows to define the gas jet to single helium droplets. A doping unit is installed in the skimmer chamber of the helium source.

3. Experimental Setup

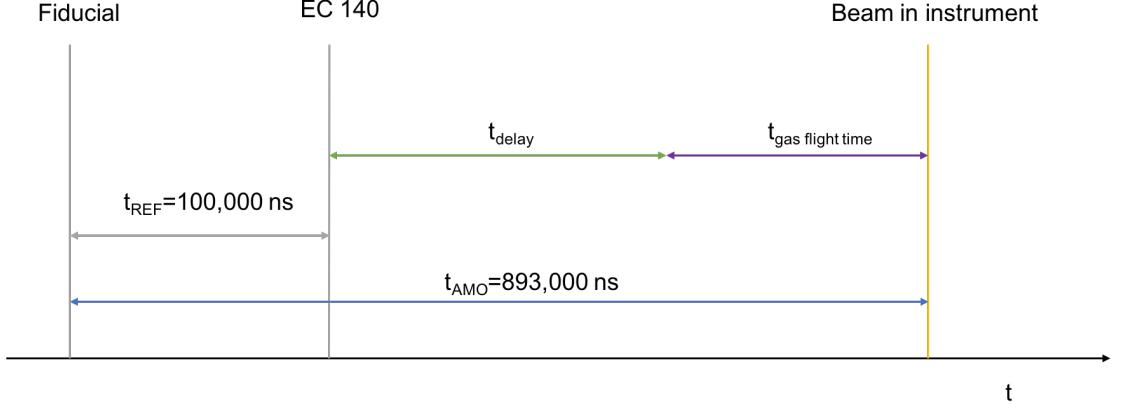


Figure 3.10.: Schematic of LCLS EVR timing system.

The doping unit is a separate smaller chamber in the skimmer chamber, where He-cluster can traverse through. The gas cell allows locally increasing the background pressure of the cell with xenon to $p_{du} \leq 2.3 \cdot 10^{-3}$ Torr. The pressure is manually controlled using a leak valve. Since the gas load is confined in the doping unit, the vacuum system is not overloaded. As shown in figure 2.9, the partial helium pressure is determined with a residual gas analyzer (RGA) in the source chamber of the AMO cluster source, which can then be used to determine the depletion of the helium cluster through the pickup of xenon atoms. A thorough alignment of the sources is necessary to overlap the particle beams such they traverse through all skimmers.

3.4.1. Sample jet timing at LCLS

Pulsed gas jets such as the Parker solenoid valve require an electric trigger to open the valve. To not get into too much detail of the LCLS timing system we shall merely say that an event generator sends a fiducial, i.e. a clock signal with 360 hz, and several event codes, e.g. at 120 hz, to an event receiver (EVR) over a fiber network [128] with a 10 ps precision. The EVR processes these signals and then sends custom electric trigger signals to systems in need. The triggers coming from the EVR can be based on a specific event code (EC), for example EC 40 operates at 120 hz or EC 41 operates at 60 hz, and may be delayed with respect to the EC. Figure 3.10 schematically illustrates the timing system. The process starts with the fiducial, the EC is delayed by time of event code x (TECx) and after a certain time of the fiducial the LCLS beam arrives. At the AMO instrument this time is $t_{AMO} \approx 893000$ ns⁶. The LCLS control system automatically

⁶Times are in nanoseconds (ns) and a format to comply with the LCLS interface.

3.4. Sample delivery

corrects for different TECx by internally correcting the delay to a reference time t_{REF} that corresponds to EC 140 (120 hz & beam). The reference time is set to $t_{\text{REF}} = 100000$ ns and thus we can write down the following equation for sample jets.

$$t_{\text{delay}} = t_{\text{AMO}} - t_{\text{REF}} - t_{\text{gas flight time}}, \quad (3.3)$$

with t_{delay} being the delay value for the LCLS EVR control system and $t_{\text{gas flight time}}$ the flight time of the sample from the gas source to the interaction region (IR). As described in [61], the terminal velocity v_∞ of a sample from a supersonic jet is

$$v_\infty \approx \sqrt{\frac{2RT_0}{m} \left(\frac{\gamma}{\gamma - 1} \right)}, \quad (3.4)$$

with the universal gas constant R, the temperature in the stagnation chamber T_0 and the ratio of specific heats $\gamma = \frac{c_P}{c_V}$, which is $\gamma = \frac{5}{3}$ for monoatomic gases such as rare gases. The flight time of a certain gas can then be calculated by measuring the distance d between the source and the interaction region (IR), thus $t_{\text{gas flight time}} = \frac{d}{v_\infty}$. The approach may be extended to approximate flight times of molecules, e.g. using the mass of CO $m = 28$ amu, and also to gas mixtures, for example the mass of a 2% xenon-131 and 98% helium-4 gas mixture can be estimated using a weighted average according to their relative contributions, thus $m = 6.54$ amu.

Figure 3.11 shows measured and calculated flight times using an Even-Lavie supersonic gas source (Serial no: EL 5 HRR NO 114) instead of the described Parker valve. The Evan-Lavie source has a very defined opening time of 22 μs and thus a defined gas jet, which can be time consuming to trigger properly without knowing t_{delay} . The data show very good overlap of the calculated delay times t_{delay} and ion yield maximum of the particle beam. The calculated flight times include an error margin, which can also be read as a recommended scan range. While the electric triggering and actual valve opening times may add errors on the microsecond time scale, uncertainties in temperature and distance from nozzle to IR change delay times drastically. For completeness, the (here used) terminal velocity of argon is $v_{\infty, \text{argon}} = 512 \frac{\text{m}}{\text{s}}$ and of xenon is $v_{\infty, \text{xenon}} = 305 \frac{\text{m}}{\text{s}}$ at room temperature.

Very long flight times can occur when heavy gases such as xenon are used or long distances d are necessary. If the flight times $t_{\text{gas flight time}} > t_{\text{AMO}} - t_{\text{TREF}}$ the system has to be delayed onto the next event as negative delays are not possible in the LCLS timimng

3. Experimental Setup

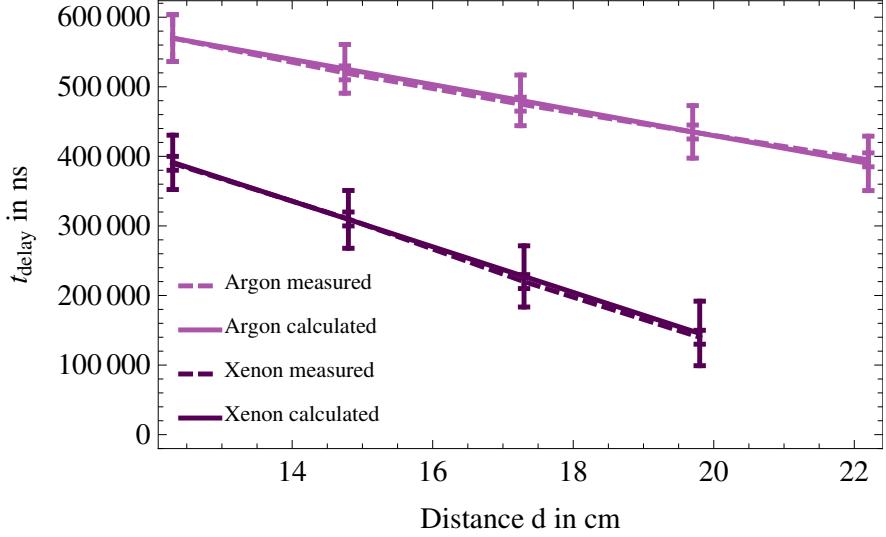


Figure 3.11.: t_{delay} as a function of the gas source distance to the interaction region. Xenon and argon has been used as sample gas in an Even-Lavie pulsed valve. The calculated delay values (solid lines) agree well with the measured delay times (dashed lines) to overlap the onset of the pulsed jet with the laser.

scheme and equation (3.3) can be rewritten to

$$t_{\text{delay}} = \frac{1}{f_{\text{rr}}} + t_{\text{AMO}} - t_{\text{REF}} - t_{\text{gas flight time}}, \quad (3.5)$$

with f_{rr} originating from the repetition rate of the event code.

3.5. Time of flight mass-spectrometer

An ion time of flight spectrometer was used in the interaction region to detect xenon and helium ions. A time of flight spectrometer uses electric fields to accelerate ions from the interaction region (IR) towards a detector. The detector unit often consists of a micro-channel plate (MCP) that allows a position sensitive detection of the particle signal. In the first stage, the ions are accelerated from the IR towards the detector. Here, the

3.5. Time of flight mass-spectrometer

electric potential energy is converted into kinetic energy

$$qU = \frac{1}{2}m \left(\frac{d_1}{t_1} \right)^2, \quad (3.6)$$

$$t_1 = \sqrt{\frac{m}{2qU}} \cdot d_1, \quad (3.7)$$

with q being the elementary charge of the ion, U the Voltage difference- and d_1 the distance between the IR and spectrometer, m is the mass of the ion and t_1 is the time of flight in the acceleration stage. The ions then travel through a drift tube of length d_2 that is fieldless. As the velocity remains constant, we can write down

$$t_2 = \sqrt{\frac{m}{2qU}} \cdot d_2, \quad (3.8)$$

with t_2 being the time of flight in the drift tube. The total flight time can then be written as

$$t_{\text{time of flight}} = t_1 + t_2 = \sqrt{\frac{m}{2qU}} (d_1 + d_2), \quad (3.9)$$

$$t_{\text{time of flight}} \propto \sqrt{\frac{m}{q}}. \quad (3.10)$$

Typically, in an experiment all other constants can be considered constant. As the spectrometer is a cylindrical system, the time of flight denotes the final position on the detector and vice versa. Therefore the position sensitive MCP yields insight into the $t_{\text{time of flight}} \propto \sqrt{\frac{m}{q}}$ of the ensemble of ions in the IR upon interaction with an X-ray pulse. Usually, ions start with a kinetic energy $E_{\text{kin}} \neq 0$ such that the flight times are altered. This results in a distribution of the ion signal instead of a strict peak structure. Atomic ion time of flight data typically exhibits a distinct peak structure while signal from clusters is strongly broadened due to kinetic energy from the nanoplasma expansion. Using this information, element specific data up to insights in the ionization cascades can be gained [129].

The in the experiment used time of flight spectrometer is depicted in figure 3.12. It consists of an electron and a longer ion side. With ± 5 keV power supplies, ions can be detected up to kinetic energies of 50eV with a time of flight resolution of 100 ps [108]. If only the ion side is used, ions with kinetic energies of up to 100 eV can be detected. The use of ± 10 keV power supplies allows a detection of kinetic energies up to 150 eV. Electrons can be measured up to kinetic energies of 150 eV using ± 5 keV power supplies, 300 eV if only the electron side is used and 400 eV using ± 10 keV power supplies. Ions

3. Experimental Setup

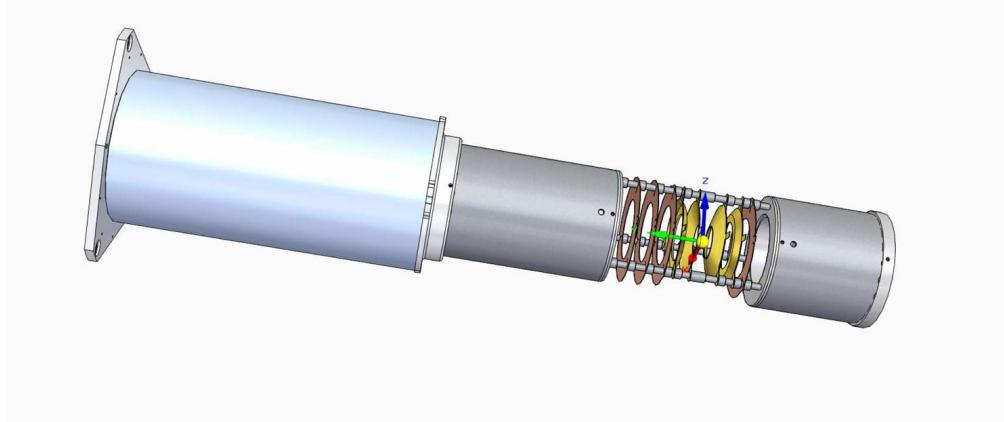


Figure 3.12.: Drawing of the time of flight spectrometer.

| Ion-side Connection | Voltage in V | El. Side Connection | Voltage in V |
|----------------------------|---------------------|----------------------------|---------------------|
| MCP Front | -2600 | MCP Front | 200 |
| MCP Back | 5 | MCP Back | 2200 |
| Holder | 200 | Phosphor | 3000 |
| Conical lens 70deg | -923 | Holder | 6000 |
| Conical lens 53deg | -1393 | Conical lens 70 deg | 500 |
| Flat lens #1 | -1490 | Conical lens 53 deg | 1370 |
| Flat lens #2 | -1564 | Flat lens | 1940 |
| Flat lens #3 | -1639 | Flight tube | 2736 |
| Flight tube | -1714 | - | - |

Table 3.4.: Applied voltages to the time of flight spectrometer. Ion side use only.

and electrons can be detected whether they are emitted in direction, in other words the spectrometer has a 4π solid angle collection [130]. A side view of the spectrometer can be found in figure 3.13. Ion, electron and photon trajectories upon interaction with a LCLS pulse have been simulated using SIMION by [130]. An conical lens stack avoids casting a shadow on the pnCCD detectors (top of image). The applied voltages in the experiment can be found in table 3.4. Here, the electron side is powered to have unperturbed electric fields across the interaction region.

3.5. Time of flight mass-spectrometer

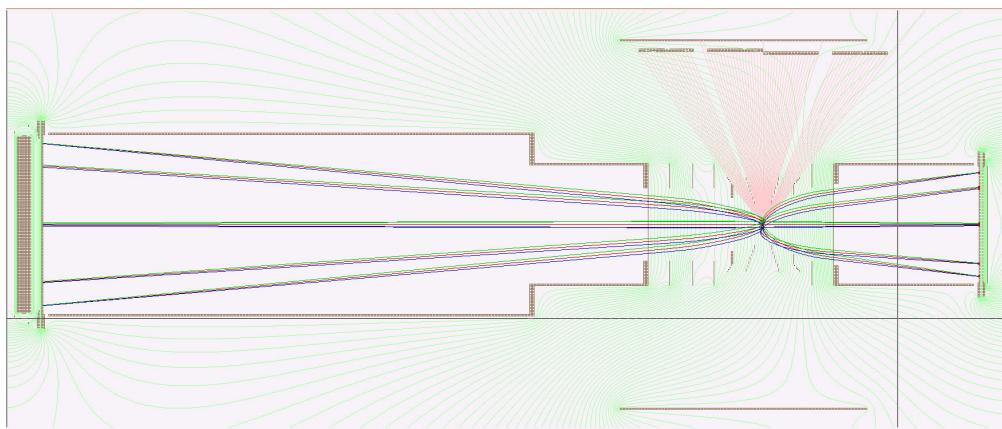


Figure 3.13.: Sideview of the spectrometer showing ion, electron and photon trajectories upon interaction with LCLS. The image was created with SIMION. From [130]

4. Methods

Let us conservatively estimating how much data is produced when using the LAMP end-station with both pnCCD detectors in use at a 120hz. Each pnCCD produces 120 images per second, each image is in a 32 bit per pixel format such that an image is vaguely 4 megabyte in size. So, every minute the front & rear pnCCD produce approximately 60 gigabyte of data. To analyze these vasts amount of data an extensive set of methods and optimized algorithms is required. This chapter is devoted to illuminate the analysis methods used in the present thesis.

The chapter is organized as follows, section 4.1 describes the general LCLS computing environment to establish an overview of the hard- and software capabilities. Section 4.2 discusses corrections that are applied to the raw pnCCD images. In section 4.6, several hitfinding methods are being evaluated. Section 4.3 goes over used phase-retrieval algorithms. Finally, section 4.4 discusses simulations of 2D projections of spheres and corresponding diffraction patterns.

4.1. The computing environment at LCLS

As estimated above, the vast amounts of data generated by many detectors are unhandy to handle by a single group of scientists that perform experiments at LCLS. For this reason the LCLS data acquisition (DAQ) group has incorporated many detectors, for example the the pnCCD and Aqciris digitizer, into their framework. All data taken at LCLS is stored in the LCLS computing environment, where the data can also be analyzed. As indicated in figure 4.1, DAQ readout nodes send the data traffic via Ethernet to a short-term cache and fast feedback (FFB) layer. While the data is being transferred, online monitoring nodes are able to 'see' a fraction of the live (online) data and run analysis. With a delay of a few ten seconds, the FFB nodes can be used to run analysis on the full data stream using parallelization, thereby having 'online' and 'offline' data access. Eventually the data is being moved to the 'offline' layer, where the data is managed by an integrated Rule-Oriented Data System (iRODS). The data is stored in .XTC file containers and it can also be accessed from outside SLAC (Router & ESNET).

4.1. The computing environment at LCLS

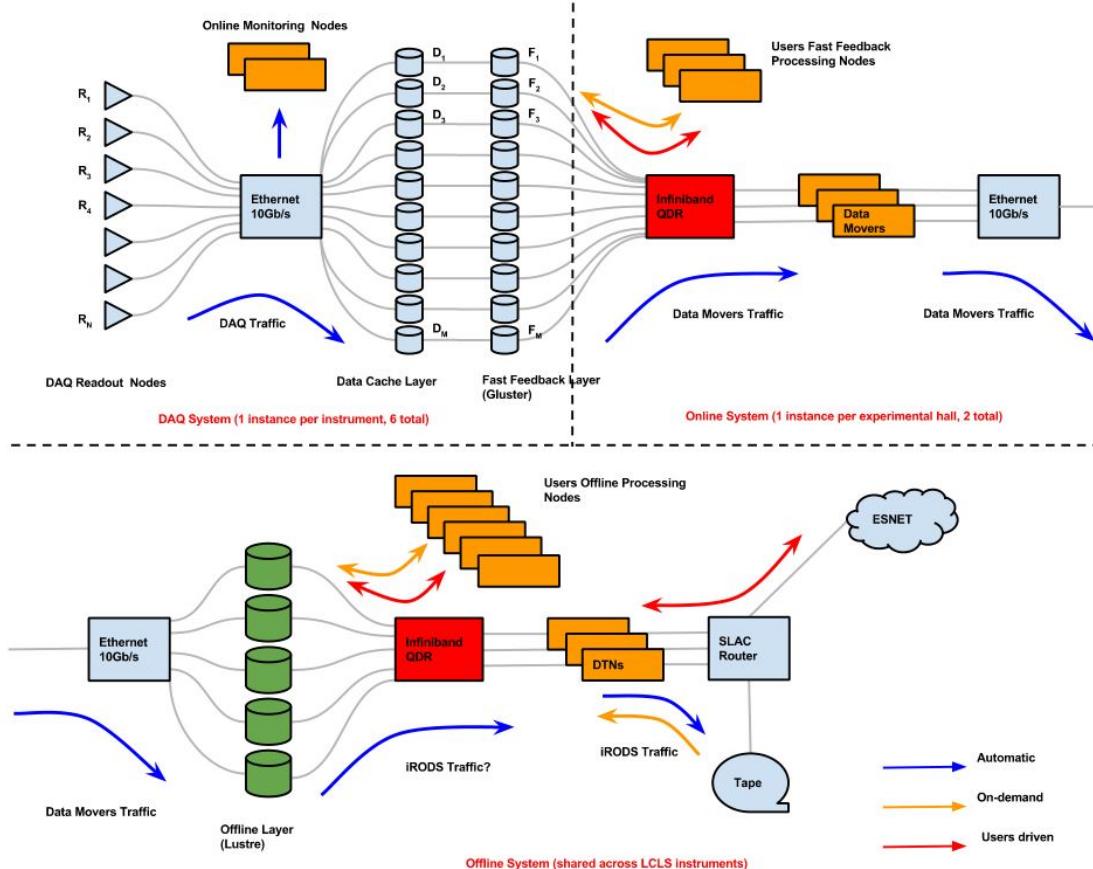


Figure 4.1.: Diagram of the computing environment at LCLS and DAQ traffic. The recorded data is exchanged through Ethernet and after digitization, is stored on a cache and FFB cluster, where psana computer have access to the online environment during the experiment. Eventually, the data is moved to the more permanent offline environment, where data can be analyzed on psana computers or through a load sharing facility. See more in text. From [131]

4. Methods

The stored data has certain storage quotas and times. In brief, there is a 6 months short-term storage without quota limitations and a two-year medium-term storage with a storage quota of 10000 Giga-Byte. After that, the data is automatically stored for at least 10 years on magnetic tape (long-term storage) and can be restored upon request. A web interface is provided by the DAQ group to simplify and automate the data-handling and logging process. The short- and medium term storage solutions can also be used to analyze the data using the psana-framework to access data and to perform computations on the psana computer cluster with over 1000 CPU cores. A load sharing facility (LSF) allows the scheduling of (parallelized) batch jobs. The psana-framework can be interacted with python 2.7. The interacting python script calls functions within the psana-framework that are programmed in C(++)¹, for example detector calibrations. Psana allows parallelization via MPI and it is therefore possible to analyze many events (LCLS pulses) simultaneously. Also complex analysis is able process at the rate of the incoming data using MPI, when the FFB is used. Python scripts can be written for 'online' or 'offline' analysis and are of similar syntax.

For LCLS-II [131], the analysis and data-access scheme is designed to be similar to figure 4.1 with the exception of the online monitoring nodes. It is therefore recommended to build analysis schemes that are based on psana and use the FFB for online analysis, which can then be adapted easily for offline analysis as well. A quick introduction on how to use psana can be found at <https://confluence.slac.stanford.edu/display/PSDM/LCLS+Data+Analysis> (from Dezember 2016).

4.2. pnCCD photon detectors

Before the pnCCD detectors can be used to take data, it is good practice to apply corrections to the raw detector image in order to cope with electronic noise. Since these corrections are used often, the LCLS detector and DAQ group has implemented a calibration manager tool¹ that provides the necessary algorithms and helps with the procedure of applying image corrections and more. We discuss the two most often used corrections next. One, corrects for the electronic noise pedestals (levels) of each pixel, and two, accounts for common modes, e.g. artifacts from the read-out electronics that appear for the pnCCD in columns.

The effects of applying these corrections are illustrated in figure 4.2 through a set of histograms. The histogram bins are showing ADU values from dark pnCCD images in

¹The calibration manager tool 'calibman' can be found in the 'psana' software package. More information under <https://confluence.slac.stanford.edu/display/PSDM/Calibration+Management+Tool> (Oct 2016)

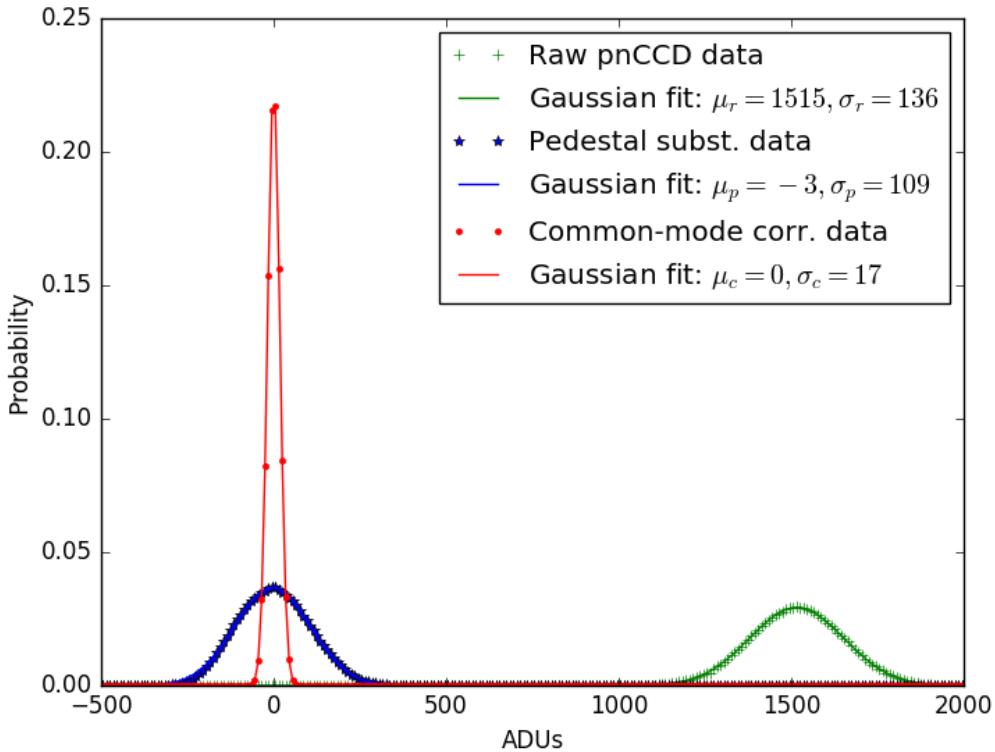


Figure 4.2.: ADU histograms from electronic noise of not illuminated pnCCDs in highest gain mode. The green, plus symbols reflect a histogram of ADU values from raw electronic noise of pnCCD pixel. One can see that the noise is set off zero at $\mu_r = 1515$ ADU and has a standard deviation $\sigma_r = 136$. The same data shifts to the blue stars are after applying the pedestal subtraction. The noise is centered around $\mu_p = -3$ and it's standard deviation is reduced to $\sigma_p = 109$. For the red data points, the common-mode corrections have additionally been applied. Now, the noise is well-centered at $\mu_c = 0$ ADU and σ_c is significantly reduced to 17. Note again, that this is an ADU histogram of purely electronic noise in highest-gain imaging mode.

4. Methods

highest gain. The green curve shows the ADU values of a raw detector image where no corrections have been applied, i.e. the electronic noise response from the chip has a standard deviation of $\sigma_r = 136$. Note, that there is also a significant offset of the distribution from 0 to $\mu_r = 1515$ ADU. The blue curve shows the same data but is using the pedestal corrections found in 'calibman'. The pedestal corrections reduce the noise slightly to $\sigma_p = 109$ ADU, and as expected, the pedestal corrections drastically move the normal distribution to be centered around $\mu_p = -3$. Finally, the red curve is also the same data than the green curve but includes pedestal and common-mode corrections. The corrected read-out modes drastically improve the standard deviation to $\sigma_c = 17$ and slightly move the mean to $\mu_c = 0$.

As a guideline, the pedestal corrections should be always used to account for the mean offset. The common-mode calibration, however, should be tested before applying. The algorithm that determines common-modes needs to find a baseline and therefore needs pixel with no signal in each row and column. In single-particle imaging the detector is illuminated in (almost) every pixel. Then the common-mode correction algorithm may treat real signal as noise and fail to find a common baseline.

In the present thesis, pedestal and common-mode correction has always been applied on the front detectors, as these pixel hold mostly signal from single photons. The rear pnCCD uses the pedestal correction but corrects common-modes only above a certain, conservative threshold. See figure 4.3 for the visible effect on front detector (large, top/bottom arrays) and rear detector (small, centered array).

4.2.1. Combining multiple pnCCD detectors

In order to maximize resolution, it is most useful to combine multiple pnCCD detector modules into one image. While this is a simple task on itself, it becomes more complex, when the combined images need to undergo a phase-retrieval process that use fast Fourier transformations (FFTs). In fact, it has not yet been shown in single-particle imaging that it is possible to retrieve a real space image from multiple detectors in different planes. The reason for this is that thus far there was little incentive of merging multiple detectors. Until recently, typical samples were on the order of several hundred nanometers in diameter such that little signal could be detected at large scattering angles. With the intensities provided by LCLS and the single-particle imaging capabilities of the LAMP end-station objects that are smaller than a hundred nanometer in diameter can be studied. Besides the ability to cover larger scattering angles, multiple detectors can be operated in different gains and still be combined efficiently. For the pnCCD, this

4.2. pnCCD photon detectors

allows not only an increase in dynamic range but improves the signal-to-noise.

Let us now describe the process of combining diffraction images, while simultaneously preparing them for the inverse problem of phase-retrieval. The discussion now follows the code shown in appendix 7.2. The input for the following procedure are two pnCCD images. The images should be pedestal corrected and if possible common-mode corrected. Analysis of the electronic noise determines an cutoff or offset between signal-to-noise for each image (see left figure 2.13 and 4.2). At this step it is also convenient to account for different detector gain settings using the table 3.2 and normalize detector distances using, e.g., the following equation to correct the signal to the front pnCCD plane

$$\text{image}_{\text{normalized}} = \text{image} \cdot \frac{\text{gain}_{\text{front}}}{\text{gain}_{\text{rear}}} \cdot \frac{\text{distance}_{\text{rear}}^2}{\text{distance}_{\text{front}}^2} \quad (4.1)$$

The pnCCD front top and bottom module are placed in an enlarged array to reflect the real geometry in the plane of the front pnCCD. We can now translate this with pixel constructed geometry to use the more general scattering angle Θ

$$\Theta = \arctan \left(\frac{\sqrt{\text{pixel}_x^2 + \text{pixel}_y^2} \times a}{d} \right), \quad (4.2)$$

with pixel_x and pixel_y being the length of the pixel array from the beam along the X- and Y-axis, respectively. We can use this information to further generalize the matter and attribute a scattering vector \vec{Q} to each pixel

$$\vec{Q} = 4\pi \frac{\sin(\frac{\Theta}{2})}{\lambda}, \quad (4.3)$$

with λ being the wavelength of the scattered photons. We can now add the signal from the rear pnCCD to the enlarged array, while using the generalized coordinates \vec{Q} . In this generalized downsampling process, the mean pixel is used, which is why a normalization factor needs to be carried. The downsampling into the enlarged array also preserves the pixel size of the front pnCCD (enlarged) array and allows Fast Fourier Transformation (FFT) algorithms to use the array. The usage of FFT algorithms is of great interest to reduce computing times in iterative phase-retrieval algorithms.

Figure 4.3a shows a diffraction pattern from a spherical xenon cluster of ~ 50 nm in radius. The front pnCCD detector was set to slightly overlap with the rear pnCCD detector along the Y-axis but the front detector was set ~ 365 mm closer to the interaction region along the Z-axis. All four of LAMP's pnCCD modules have been combined in one

4. Methods

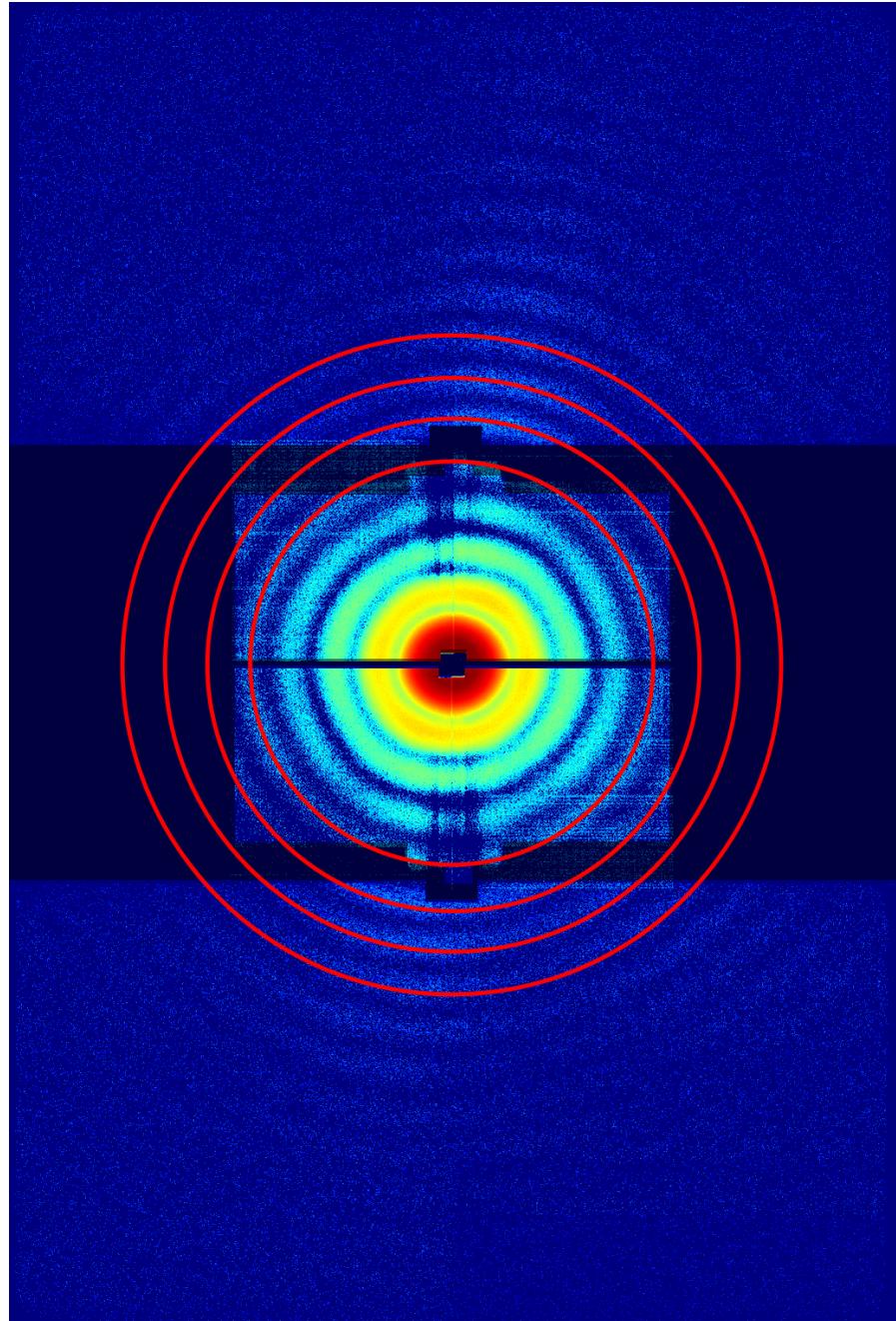


Figure 4.3.: A combined pnCCD image using the full image of the front pnCCD and a down-sampled image of the rear pnCCD. The red circles in the image are drawn in to visualize the alignment of the detectors. As described in the text, the intensities in the image are normalized and corrected for different electronic gains and distance to specific detectors. The shaded areas are not covered by the pnCCDs and are therefore masked out.

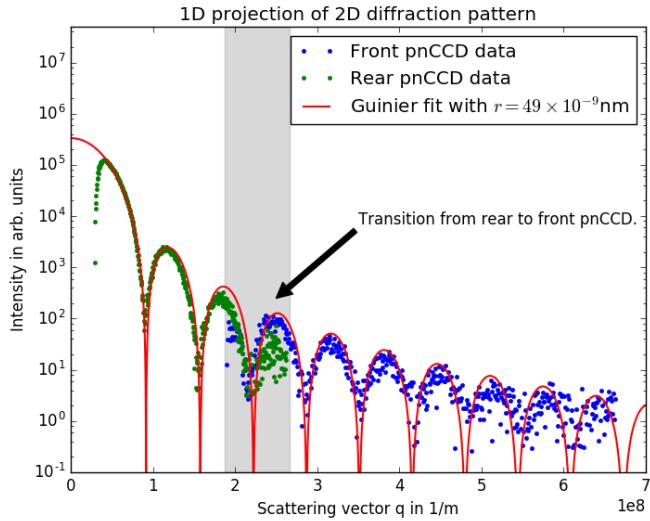


Figure 4.4.: In this graph a 2D diffraction image was projected onto 1D assuming a spherical symmetry of the diffraction pattern. The green data points are gathered from the rear pnCCD and the front pnCCD data points are reflected by the blue data points. The red curve is a simulated scattering curve from an ideal sphere (see equation (2.39)). The amplitude of the red curve has been fitted to the data points and it agrees well with the data over 8 diffraction rings. The gray shaded area shows the transition area from rear to front detector.

image, and since the rear pnCCD is farther away from the interaction region it appears smaller on the combined image. The red circles are a help for the eye to align the modules and show how the diffraction pattern overlaps. In this case, the front pnCCD was operated in highest gain $\frac{1}{1}$ and the rear pnCCD was operated in lowest gain $\frac{1}{256}$.

The radial intensity profile yields valuable information about the geometric alignment and intensity normalization. Figure 4.4 shows the radial intensity profile of the spherical symmetric diffraction image over 5 orders of magnitude above the noise level. The red curve illustrates the expected scattering intensity of a spherical object using equation (2.36) and (2.39). An automated fitting routine determined the radius r of the cluster, here $r = 49$ nm and the incident beam intensity I_0 , which was determined based on zero order scattering. The curve showcases the validity of the detected signal up to the edges of the front pnCCD, where little signal is present. There are also some discrepancies from the red curve on the transition from the rear to front pnCCD, which are due to the shade projected from the front onto the rear pnCCD and the resulting lack of signal.

4. Methods

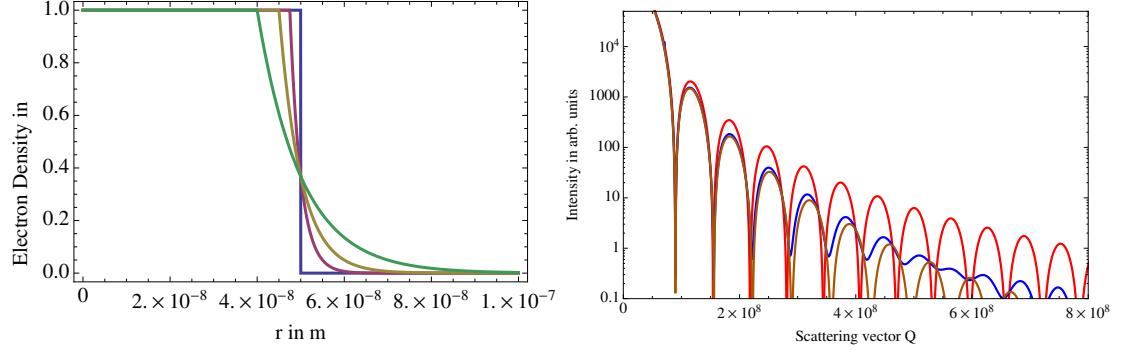


Figure 4.5.: Left: electron density of an expanding spherical symmetric nanoplasma. Right: red line, scattering of an intact sphere. Brown, scattering of an expanding sphere with $k = 5\text{nm}$. Blue, combined scattering of an intact and expanding sphere that has been pumped with 10% and probed with 90% of the overall pulse energy. See more information in text.

4.2.2. Impact of X-ray pump – X-ray probe on diffraction pattern

In a coherent diffractive imaging X-ray pump – X-ray probe experiment, both pulses contribute to the scattering image. The pump pulse will project an image of the solid and intact cluster, while the probe pulse will propagate an image of the expanding, damaged cluster. In the present experiment, the pump pulse was set at $\sim 10\%$ of the overall pulse energy, while the probe pulse was set to $\sim 90\%$ of the overall pulse energy. In order to simulate the effects of the X-ray pump– X-ray probe setup, a 1D simulation is conducted using electron densities $\rho(r)$ of spheres. Although rare-gas cluster exhibit an icosahedral structure, at present resolution cluster can be well simulated using spheres. The spheres are allowed to expand after the model

$$\rho(r, k) = \begin{cases} 1 & \text{for } R - k \geq r \geq 0, \\ e^{\frac{(R-k)-r}{k}} & \text{for } R > r - k, \end{cases} \quad (4.4)$$

with R being the cluster radius and k an expansion coefficient such that

$$\int_0^\infty \rho(r, k) dr = R, \quad \text{if } 0 < k < R \quad (4.5)$$

4.3. Phase retrieval from a single diffraction pattern

The electron density can then be Fourier transformed into reciprocal space using the transformation [73]

$$I(\vec{Q}) = I_0 F^2(Q) = I_0 \left(\int_0^\infty \rho(r, k) \frac{\sin(Qr)}{Qr} 4\pi r^2 dr \right)^2, \quad (4.6)$$

with I_0 being an intensity scaling factor. The electron densities for $R = 50$ nm and $k = \{0, 2.5, 5, 10\}$ nm are shown in figure 4.5 left. Figure 4.5 right showcases several cases of (expanding) spheres in reciprocal space. The red line is the scattering of a solid sphere F_{intact}^2 , with A being used to scale the intensity to typical experimental data. The brown curve is the scattering of an expanding sphere $F_{\text{expanding}}^2$ with $R = 50$ nm and $k = 5$ nm. Lastly, the blue curve corresponds to the case, where $A \cdot F^2 \rightarrow A \cdot 10\%F_{\text{intact}}^2 + A \cdot 90\%F_{\text{expanding}}^2$. Although the pump pulse influences the diffraction pattern visibly at high-Q values, the added signal remains in the noise level of $F^2(Q) < 1$ (compare figure 4.4).

4.3. Phase retrieval from a single diffraction pattern

As deducted in section 2.3.1, coherent diffractive imaging merely measures the intensity in reciprocal space and the phase information, i.e. complex fields, are lost. Iterative algorithms can retrieve this lost information because there are only limited sets of phases that uniquely reproduce the diffraction image [132, 133]. To fully recover the original function, i.e. real and complex values of the diffraction pattern, the diffraction image must be oversampled [134]. Here, the Nyquist-Shannon sampling theorem says that a Fourier transformed object of size X can be fully recovered if its sampling rate is at the Nyquist rate of $\frac{1}{2X}$. The Nyquist rate can be translated into a minimum (pnCCD) pixelsize in realspace using the following relation between a discrete Fourier transform and pixel length Δ_r [135]

$$\Delta_r = \frac{\lambda L}{2X}, \quad (4.7)$$

with the wavelength λ , the length to the detector L and the object length along one dimension X . For typical experimental values, the sampling pixel size must be $\Delta_r \geq 2.7$ mm to fully recover the particle's (projected) electron density. In the present experiment, the pnCCD pixel size of $75 \times 75 \mu\text{m}^2$ samples the object sufficiently enough.

4. Methods



Figure 4.6.: Principle of a phase retrieval algorithm. The real space object $g_k(x)$ is Fourier transformed to $G_k(q)$. The function $G_k(q)$ is altered to fit the constraints set in Fourier space, hence $G'_k(q)$. $G'_k(q)$ is inverse Fourier transformed to $g'_k(x)$. After fulfilling the real space constraints the iterative starts again using $g_{k+1}(x)$. After [136].

4.3.1. Principle of phase retrieval

To recover the phase from an oversampled diffraction pattern and thus reconstruct an image of the object, iterative algorithms have been developed [136]. Figure 4.6 illustrates such an iterative algorithm, where the image of an object $g_k(x)$ is Fourier transformed to reciprocal space $G_k(q)$ and then back again resulting in $g_{k+1}(x)$, while sufficing certain constraints.

The constraints are rather strict defined in the reciprocal space as they have to reproduce the actual measurement $I = A \cdot A^*$, which is sometimes called the modulo constraint. The criteria that need to be met in real space can be chosen more freely. Generally, the recovered object should be physical, i.e. should be of a certain (known) size. One can introduce a support structure S that meets the physical constraints and can therefore be used to, for example, zero outlying values. Throughout the iterations, the functions $g_k(x)$ evolve and eventually converge into a solution. If one uses the above criterion, one can show that the error between the reconstructions and the actual measurement continuously reduces, which is why it is commonly referred to as error-reduction algorithm [137].

4.3.2. 2D reconstructions and image resolution

Hawk program for 2D image phase retrieval

For all image reconstructions in 2D, the Hawk software package [138] has been used. Hawk is available under the GNU General Public License² and can be downloaded with

²Hawk copyright: <https://github.com/FKIhub/hawk/blob/master/Copyright>

4.3. Phase retrieval from a single diffraction pattern

| Parameter | Setting |
|---------------------------|-----------------|
| Starting Guess | random phases |
| Autocorrelation Selection | threshold |
| Autocorrelaton Threshold | 0.04 |
| Phasing method beta | 0.9 |
| Beta range | 0 - ∞ |
| Enforce positivity | false |
| Enforce real | false |
| Perturb weak reflections | false |
| Phasing algorithm | raar |
| Blur | 12 - 0.7 |
| Blur range | 0 - 12000 |
| Center image | false |
| Object area | 0.0022 - 0.0019 |
| Object area range | 0-8000 |
| Support update algorithm | area |

Table 4.1.: Typical parameter used in the Hawk software package. The object area depends strongly on the actual particle size and thus varies.

installation instructions from <https://github.com/FXIhub/hawk>. In previous efforts to retrieve a real-space image from FEL based coherent diffractive imaging, Hawk has been used successfully in several reconstructions, ranging from viruses [10, 12] to other objects [139]. The usage of the program is straight forward in three steps. First, the diffraction images are transformed into the '.cxi' format [140]. Second, diffraction images are prepared in *Hawk's editor*, where particular effort has to be made to create a proper mask. The mask allows to forgo saturated, shadowed or otherwise faulty pixel. The software suite automatically interpolates between masked pixel. The successful edited '.cxi' file is then saved in Hawk's '.h5' format. Third, *Hawk's phaser* can be used to iteratively retrieve the phase from the '.h5' intensity file. Typical parameter for the phaser can be found in table 4.1. Here the *RAAR algorithm* [141] in combination with initially strong *blurs*, extension of the *phasing beta range* and a proper determination of the *object area* (support structur) resulted in useful reconstructions. Note, that the *object area* size differs from particle to particle, or intensity file to intensity file. After 10^5 to $1.5 \cdot 10^5$ iterations, the real space object typically converges.

Resolution enhancement through combination of rear and front pnCCD

While there is no consensus on how to define resolution in a coherent diffractive imaging pattern and the resulting reconstruction, there are various good estimates. A simple

4. Methods

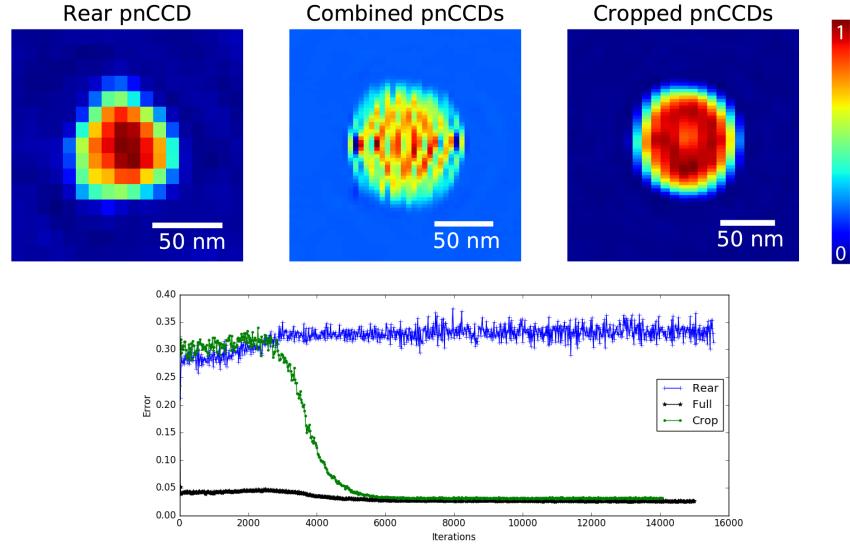


Figure 4.7.: A set of reconstructions of Xe-cluster yielded from the diffraction pattern in figure 4.3 and the corresponding real-space error over number of iterations. The real space image gathered from the rear pnCCD uses no data from the front pnCCD. This reconstruction shows a not spherical object although the density distribution appears to be reasonable for a nano-particle. The real space image reconstructed from the full front and rear pnCCD data set appears to be a spherical object but the missing areas disturb the diffraction pattern and it has become unphysical. The Xe-cluster reconstructed without the dead areas has the expected spherical shape and the density distribution appears to be physical.

4.3. Phase retrieval from a single diffraction pattern

and conservative method to define resolution in a diffraction pattern is Abbe's criterion, which comes from microscopy and calculates the minimal resolvable feature size in a diffraction pattern. The fundamental limit that the minimal resolvable feature size is depended on the wavelength has also given us the inspiration to build short-wavelength machines such as the free electron laser and synchrotron light sources.

First, we can verify that we are in the far field by fulfilling the following requirement [135]

$$\frac{d^2}{\lambda L} \ll 1 \quad (4.8)$$

with the wavelength of the X-rays λ , the distance to the detector L and the object size d .

In the far field, Abbe's criterion can be written down as

$$d = \frac{\lambda}{2n \sin(\frac{\Theta}{2})}, \quad (4.9)$$

with the minimal resolvable feature size d , the refractive index n and the half scattering angle $\frac{\Theta}{2}$. The scattering angle is restricted by either the active detector area, which goes back to the typical understanding of a numerical aperture, or the signal intensity up to certain angles. The latter is in interplay with the photon wavelength and object cross-sections. This interplay leads to the current assessment that very high energy photons, e.g. 8 keV photons that are commonly used for crystallographic purposes, scatter too little signal. Additionally, low- \vec{Q} scattering is often unresolvable due to straylight. As current results indicate, using 0.5 – 5 keV photons ultimately leads to higher resolution images than using 8 keV photons [9].

In the far field, we can use the following equation to investigate the pixel size [135]

$$\Delta_s = \frac{\lambda L}{N \Delta_d}, \quad (4.10)$$

with L being the length from the interaction region to the detector, Δ_i being the linear pixel size that is linked to each other through the discrete Fourier transformation and N being the side length of the discrete detector array.

Figure 4.7 top shows several reconstructions of xenon cluster at $\lambda = 1.0$ nm using different snippets of the diffraction pattern in figure 4.3. If just the rear pnCCD is used for reconstructions, a maximum scattering angle of $\Theta \approx 4.2^\circ$ is recorded, which results in a minimal resolvable feature size of $d \approx 14$ nm. However, in the present data a shadow is cast on the CCD reducing the maximum scattering angle in the image '**Rear pnCCD**' to $\Theta \approx 3.8^\circ$ and thus the resolution to $d \approx 15$ nm. The pixel size is $\sim 10\text{nm} \times \sim 12\text{nm}$.

4. Methods

The image '**Combined pnCCDs**' uses the whole data including the empty areas next to the rear pnCCD. The image shows an unphysical electron density distribution, which originates from the empty areas next to the rear pnCCD data. In these areas, the interpolation along the Y-axis/ extrapolation along the X-axis fails. The next image '**Cropped pnCCDs**' uses data in full extend along the Y-axis but crops the image along the X-axis such that the blank areas are excluded. The reconstruction converges into an object that appears physical. The maximum scattering angle here is $\Theta \approx 9.2^\circ$ and the resolution thus $d \approx 6$ nm. The pixel size here is $\sim 10\text{nm} \times \sim 3\text{nm}$.

This is a factor ~ 5 improvement over common cited studies in single particle imaging [10] and still a factor ~ 3 better than [142], where measured diffraction patterns have been 'computationally purified'. The resolution enhancement due to the combination of detectors can be abused further using EMC algorithms [100], where multiple images can be arranged due to their rotation and averaged, hence filling the missing areas next to the rear pnCCDs and allowing 3D reconstructions with (few³) nanometer resolution.

4.3.3. 1D projections and phase reconstructions

To display many effects in diffraction pattern, they have sometimes been reduced from two dimensions to merely one. A 1D representation of the data allows easy to interpret comparison to analytical models. To reduce the 2D diffraction data to 1D the program shown in appendix 7.1 has been employed. It is based on Matlab to efficiently iterate through pixel arrays. The input for this program are pedestal calibrated diffraction images that have unwanted areas masked out and a true image center defined. Key elements of the algorithm are to iterate through every pixel, filtering signal from noise, determining the \vec{Q} -value of every pixel and sum signal over \vec{Q} , while normalizing the data over pixel. Additionally, an algorithm has been designed to perform phase retrieval on the 1D data. The algorithm follows the fundamental scheme described in sub-section 4.3.1. Thereby, the realspace data of the object is forced to be real and positive, which is also the error criterion in real space. The difference to the measured data yields the error criterion in Fourier space. The algorithm allows monitoring of the Fourier- and realspace error, the phase and the actual Fourier and realspace images. The iterative algorithm is aborted based on the error criterion.

4.4. 2D electron density and diffraction image simulations

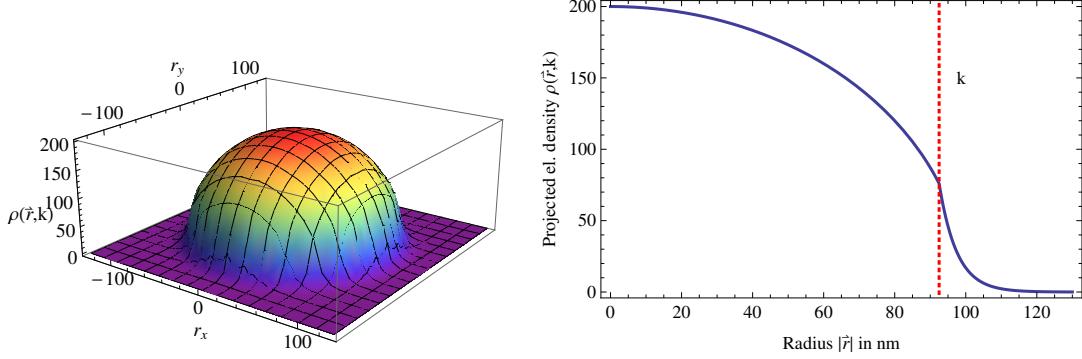


Figure 4.8.: Left: Electron density of a $R \approx 100\text{nm}$ expanding sphere with $k = 5 \text{ nm}$, projected onto a 2D plane. Right: Blue curve, spherical projection of the 2D projection to 1D. Red dashed line, point of expanding density at $k = 5 \text{ nm}$.

4.4. 2D electron density and diffraction image simulations

The interpretation of the helium cluster doped with xenon data requires a more thorough investigation than with 1D fits possible. Therefore two dimensional studies were performed to simulate electron densities of (doped) clusters. The electron density is then Fourier transformed to yield 2D diffraction images, which can be compared to the experimental data. The 2D simulations can then optionally be reduced to 1D using a spherical integration (see subsection 4.3.3) to be easily compared to the experimental data and other analytical models. The clusters are approximated using spheres, which is at the current resolution an acceptable estimation of the icosahedral cluster structure. In the simulated cluster, i.e. core-shell system, the shell consists of one large cluster with low electron density (helium) and the core comprises smaller dense spheres (xenon) at different locations within the shell. Furthermore, the spheres can expand to simulate the effect of a nanoplasma expansion. We can express such spheres using the formalism

$$\rho_i(\vec{r}, k) = \begin{cases} 2\sqrt{R^2 - |\vec{r}|^2} \cdot \rho_0 & \text{for } R - \frac{3k}{2} \geq |\vec{r}| \geq 0, \\ 2\sqrt{R^2 - |\vec{r}|^2} \cdot \rho_0 e^{\frac{(R - \frac{3k}{2}) - |\vec{r}|}{k}} & \text{for } R > |\vec{r}| - \frac{3k}{2}, \end{cases} \quad (4.11)$$

with ρ_0 being the density, R being the cluster radius and k an expansion coefficient such that

$$\int_0^\infty \rho(|\vec{r}|, k) d|\vec{r}| = R, \quad \text{if } 0 < k < R \quad (4.12)$$

³Depending on the position of the front pnCCD.

4. Methods

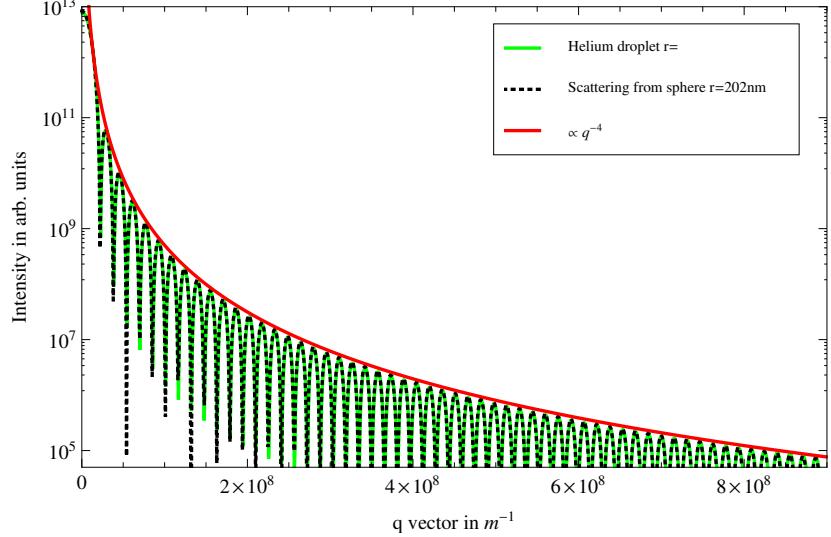


Figure 4.9.: Comparison of analytical scattering from a sphere of radius $R = 202$ nm (black curve), equation 2.39, and scattering of a sphere of radius $R = 202$ nm from 2D simulations projected onto 1D (green, dashed curve). Envelope of scattering intensity, called Porod's law, which is $\propto q^{-4}$ (red curve). The analytical scattering and developed simulations agree well with each other.

Multiple spheres $\rho_i(\vec{r})$, with $i = 1, 2, 3, \dots$, can be positioned using $\vec{r} \rightarrow \vec{r} - \vec{r}_0$, with \vec{r}_0 being the center of mass of the sphere ρ_i . The density ρ_0 was set to $\rho_{0,\text{helium}} = 1$ for liquid helium and $\rho_{0,\text{xenon}} = \frac{3.640}{0.1412} \approx 25.8$ for xenon. The numerator of the fraction for $\rho_{0,\text{xenon}}$ is the density of bulk xenon in g/cm³ and the denominator is the density for liquid helium in g/cm³. Using equation (4.11), a large array of $\sim 1500 \times 1500$ is generated that is comparable to the combined pnCCD image array size. The array is then Fourier transformed using Matlab's `fft2` and the output is subsequently rearranged using `fftshift`.

Figure 4.9 shows a comparison of the analytical derived scattering of a sphere (see equation 2.39) with a radius of $r = 202\text{nm}$ (black, dashed line) and the scattering of the 2D simulations reduced to 1D (green, solid line). The red curve is the envelope of the functions, called Porod's law that scales with $\propto q^{-4}$. The developed simulation agrees well with the analytical scattering.

4.5. Acqiris data sampling considerations

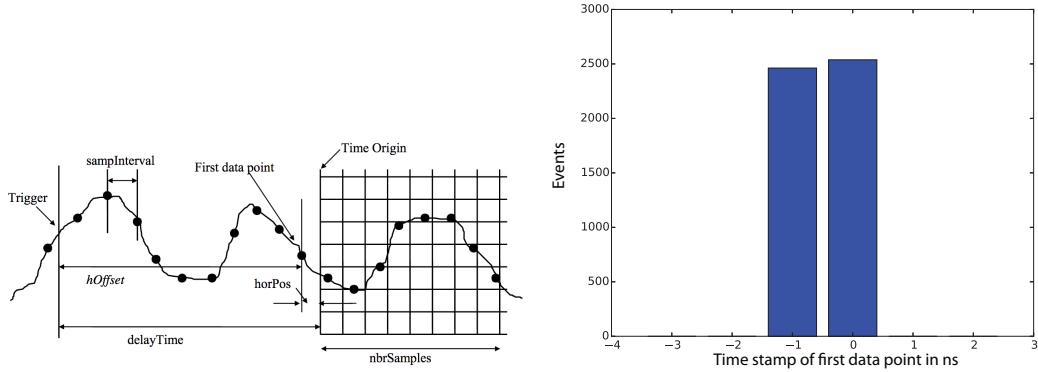


Figure 4.10.: Left image from [143], it shows the schematics of the timing system in the Acqiris after receiving a trigger. Due to the finite sampling of the trace, the first data point can be before time zero. Right image is an histogram of the the timestamp from the first data point.

4.5. Acqiris data sampling considerations

An Acqiris digitizer (now called: Agilent U1065A) has been used to read out the waveform signal from the time-of-flight spectrometer discussed in section 3.5. For technical reasons, the Acqiris sampling and the electronic trigger to start the readout process is generally not in sync. The electronic trigger can occur between sample {1, 2, .., 10}. In other words, the Acqiris reads out 40,000 samples but the trigger for the clock comes between sample 0 and 10. As it is illustrated in figure 4.10 left, the time difference between the first data point and the time origin is within the sampling interval, thus {-1ns, 0ns}, at the sampling rate at 40,000, which is 1 ns per channel [143]. Figure 4.10 right is an histogram of the First data point timestamp showing the evenly distributed discrepancy. As each read out sample would be different length {39991, 39992, ..., 40000}, the LCLS DAQ group adds zeros to the end of each array to simplify the analysis of handling arrays of different lengths.

However, in an LCLS experiment, the origin of time is best defined by the light peak. The time of flight spectrometer will detect photons scattered off the sample as the pulse is traversing through the system. Figure 4.11 bottom shows an analysis of the light peak channel position. The lightpeak occurs within a ~ 10 ns window and is evenly distributed around channel 1514 due to the Acqiris sampling. Figure 4.11 top shows a merely averaged TOF trace (blue curve) and a TOF trace that has been corrected for the light peak occurring at different position (red curve). The LCLS DAQ changes the output of the Acqiris to start with time 0 or -1 and gives out a 40,000 channel long trace

4. Methods

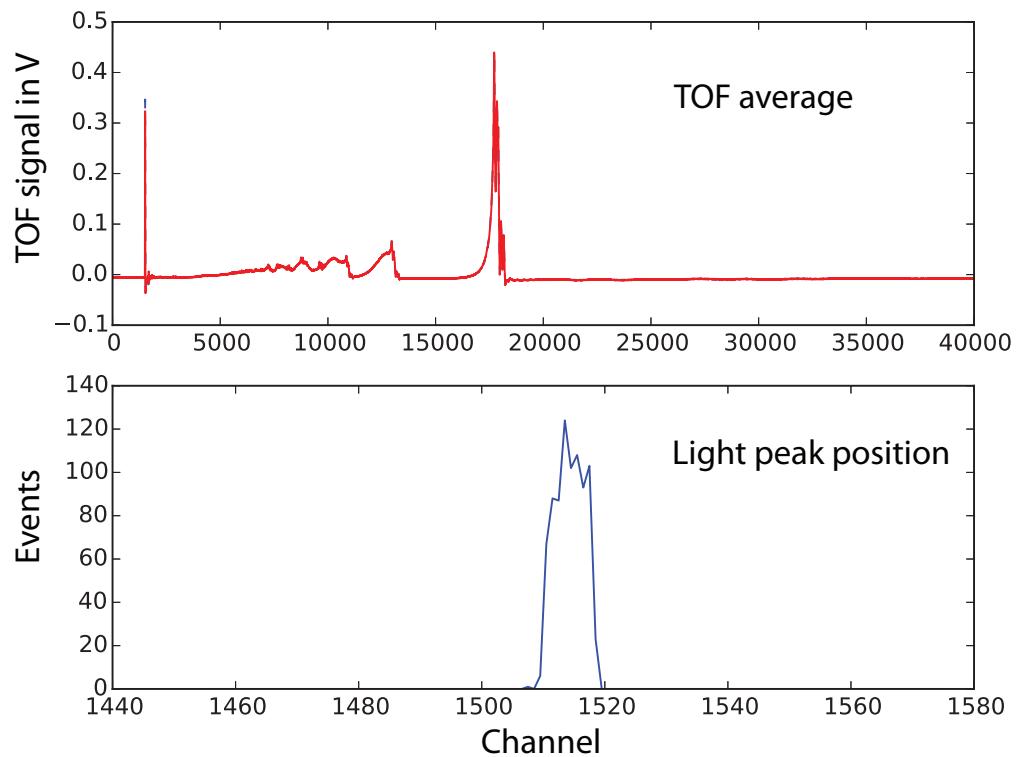


Figure 4.11.: Top plot, average TOF trace of xenon cluster. Red curve, corrected run average to account for shifted light peak due to Acqiris sampling. Blue curve, uncorrected average. Bottom image, histogram of light peak channel position ranging between $\sim \pm 5$ of channel 1514.

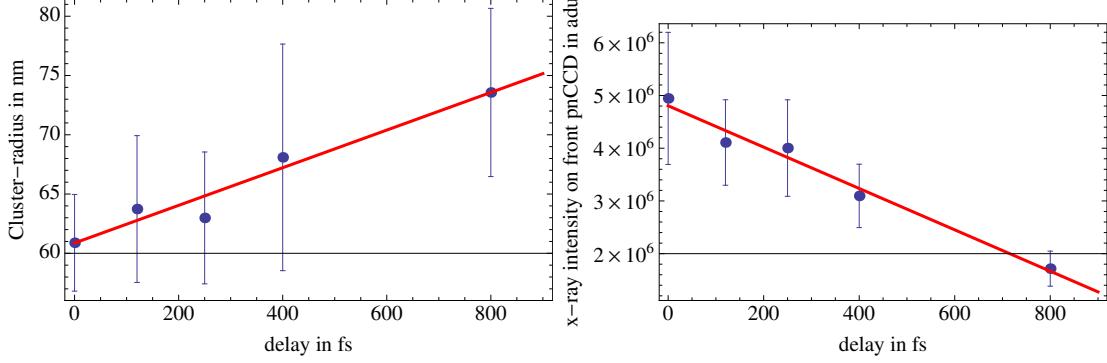


Figure 4.12.: Left: Average Xenon cluster size of intense hits as a function of pump–probe delay Δt . Right: Average intensity on the front pnCCD of intense hits as a function of the pump–probe delay Δt .

by adding zeros for every unsampled channel due to the trigger arrival.

The time-of-flight analysis in this thesis accounts for both of these effects and additionally corrects for a common baseline.

4.6. Data filtering

As described in the above sections, LCLS produces large amounts of data. This data has to be filtered to a point, where it can be used for phase retrieval. The coincident detection of diffraction image and time of flight spectroscopy allow great freedom to filter on useful events. For the present work, a useful event is the interaction of X-ray pump – X-ray probe with a single cluster system. On the one hand, cluster produce the most intense signal on pnCCD and TOF detectors when they are in the center of the intensity profile of the LCLS beam [97]. On the other hand, as the time delay Δt of the X-ray pump – X-ray probe is increased, the nanoplasma expansion leads to a decrease in signal on the pnCCD (see figure 4.12). This can be extrapolated to an extreme, where cluster would not produce any signal on the front pnCCD. In order to filter on the full bandwidth of interesting hits, a series of filters have been applied. Filtering on ion time of flight high charge states states has been successful in overall gathering images resolving pump–probe dynamics. In figure 4.12 left, the xenon pump–probe data has been automatically pre-filtered on xenon ion high-charge states, leaving several thousand events that were then semi-automatically reduced to over 350 single-hit diffraction images. In this semi-automatic process it was determined, whether it was a single hit and the size of a cluster. The size determinations have been performed using the first maxima as described (see section 2.3.1). The remaining events indicate a linear

4. Methods

average cluster radius increase of $\sim 15\%$ over the course of the first 800 fs at a given pump pulse energy. However, to perform phase retrieval and to solve the inverse problem, bright hits containing many photons are required. Therefore, an additional hitfinder on a snippet of the rear pnCCD detector has been implemented. This hitfinder determines the scattering intensity in single hits and brightest hits that show pump-probe dynamics have been selected undergo a phase retrieval to reveal their electron density. Events show dynamics, when the 1d reduction of the intensity profile differs from the scattering of an intact sphere, i.e. $F_{\text{intact}}^2/I \gg 1$.

5. Results and discussion

This chapter discusses the experimental data. First, the nanoplasma transition in pristine Xe-cluster is discussed in section 5.1. The section 5.2 discusses the time depended response in ion TOF of Xe-atoms to X-ray pump– X-ray probe beams. Ion TOF spectroscopy is continued on superfluid He- and mixed HeXe-cluster in section 5.3. The arrangement and of Xe-atoms in HeXe-cluster is discussed in section 5.4 using 2D-simulations. Sample damage scenarios of HeXe-cluster are compared in section 5.5. Finally, section 5.6 compares structural damage from the nanoplasma expansion for the different samples He-, Xe- and HeXe-cluster to each other.

5.1. Structural damage in Xe-cluster induced by intense X-rays

A large scale analysis of size, shape and other parameter has been performed on single-shot diffraction patterns of xenon cluster to investigate the nanoplasma transition. Thereby a X-ray pump pulse starts X-ray induced effects, i.e. the nanoplasma transition and a X-ray probe pulse at a later time Δt enables us to take a snapshot of the system.

The analysis starts by selecting hits from non-hits using the methods described in section 4.6. Using these filters, a typical run length per delay time is 20 mins, i.e. $\sim 144,000$ images. These events are automated reduced to ~ 1000 events and then semi-automated reduced to a subset of 30 - 60 single-shot diffraction patterns per delay setting. This breakdown further allows the estimation that 0.02% – 0.04% of all imaged xenon cluster had good parameter for analysis. This figure is likely understating the amount of analyzable hits, however, this selection includes the events that show a nanoplasma transition but are still suitable for phase-retrieval (compare figure 4.12).

Figure 5.1 shows a distribution of sizes at the pump–probe delays $\Delta t = \{0, 800\}$ fs. Here, equation (2.39) has be abused to semi-automate the size determination process to enable the high-throughput size evaluation. The size distribution of Xe-cluster follows a log-normal distribution [144] and at $\Delta t = 0$ fs the mean cluster radius is 61 nm. When the delay is increased to $\Delta t = 800$ fs, the mean cluster radius increases to 74 nm. Addi-

5. Results and discussion

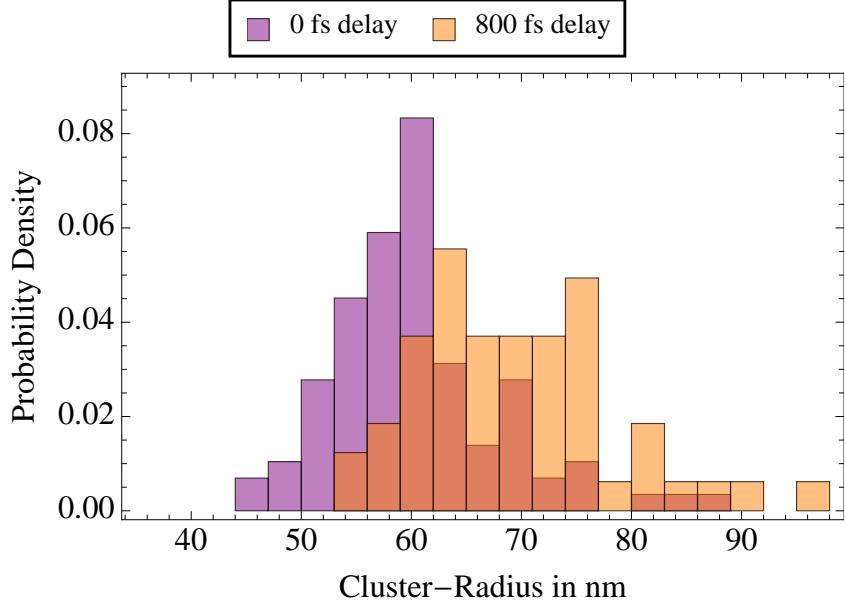


Figure 5.1.: Size evaluation of ~ 30 single Xe-cluster hits per time delay Δt step. At $\Delta t = 0$ fs, the size distribution follows an expected log-normal distribution, while at $\Delta t = 800$ fs the distribution broadens and shifts towards larger radii due to the nanoplasma transition.

tionally, the distribution becomes more broad, which is due to the varying pump-pulse strength. Over the course of 800 fs, the nanoplasma transition drives an expansion of the cluster that is on average $\sim 20\%$. Figure 4.12 left shows that the expansion speed is constant and summarizes the mean cluster radii over the pump-probe delay steps $\Delta t = \{0, 120, 250, 400, 800\}$. From here, we can estimate the electron temperature of the nanoplasma. It is assumed that electrons thermalize with the nucleus within a few femtoseconds such that the mean velocity of the hot electron gas follows a Maxwell-Boltzmann distribution. If we use the average expansion speed ~ 15250 m/s as mean velocity of a Maxwell-Boltzmann distribution the electron temperature is determined to be ~ 125 eV. We can compare the electron temperature to a similar IR pump – X-ray probe study [17], where electron temperatures of ~ 200 eV have been estimated. This also explains the fast expansion speed in this optical pump–probe study. For the sake of completeness, the IR pump laser had power densities of only $\sim 10^{15}$ W cm $^{-2}$ compared to the $\sim 10^{17}$ W cm $^{-2}$ of the X-ray pump laser in this study but the smaller X-ray absorption cross-sections explain the difference in total absorbed energy from the pump pulse.

The total number of scatterers, i.e. electrons that interact with LCLS, was deducted

5.1. Structural damage in Xe-cluster induced by intense X-rays

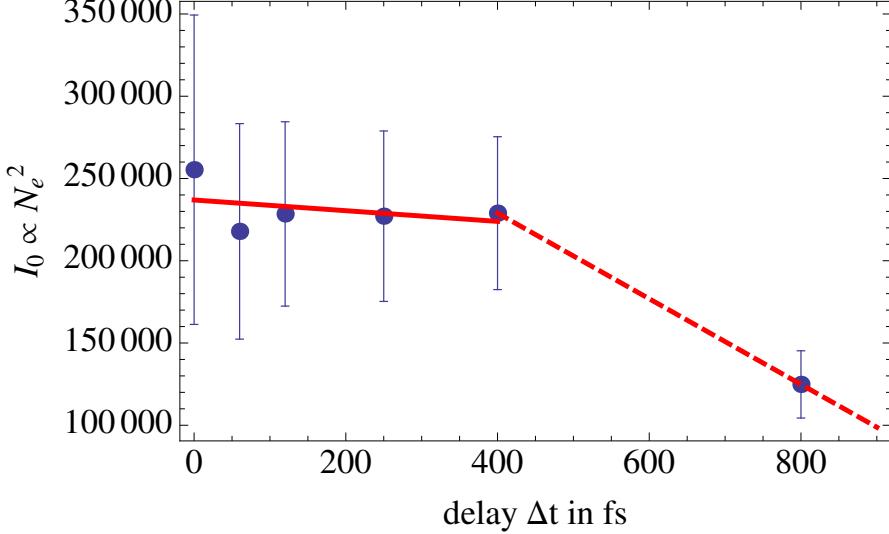


Figure 5.2.: Intensity I in arb. units at $\vec{Q} \rightarrow 0$, which is proportional to the total amount of scatterer squared N_e^2 , here electrons. The data show that the expanding cluster Coulomb traps electrons steadily in the initial stages of the nanoplasma expansion but as the trapping potential decreases due to the multistep ionization a sudden decrease of $\sim 65\%$ electrons is observed.

from the diffraction patterns as well. As described in the theory section 2.3.1, when

$$I(\vec{Q} \rightarrow 0) \propto N_e^2, \quad (5.1)$$

with the scattered intensity I as a function of the scattering vector \vec{Q} and number of electrons that contribute to the scattering process N_e . Figure 5.2 shows the average fitting parameter I_0 , from equation (2.36) and (2.39), as a function of the time delay Δt (blue dots). Two linear fits (red lines) have been added to the graph to visualize the effect. The averages were obtained in the analysis of $\sim 15 - 30$ single xenon cluster diffraction pattern per delay step. The data show that up to a delay of $\Delta t = 400$ fs the amount of electrons N_e in the cluster remains rather constant. However, at a time delay of $\Delta t = 800$ fs, the amount of scattering electrons decreased on average by $\sim 26\%$. This confirms that Coulomb trapping efficiently traps electrons from the ionization process in the initial stages of the nanoplasma expansion, here up to 400 fs after the pump pulse, but eventually the electrons overcome the trapping potential dissipate the interaction region such that they do not contribute to the diffraction image anymore. The key drivers that lower the trapping potential, thus releasing the electrons, is the expansion of the cluster and the progressing multistep ionization. The concept of radiation damage

5. Results and discussion

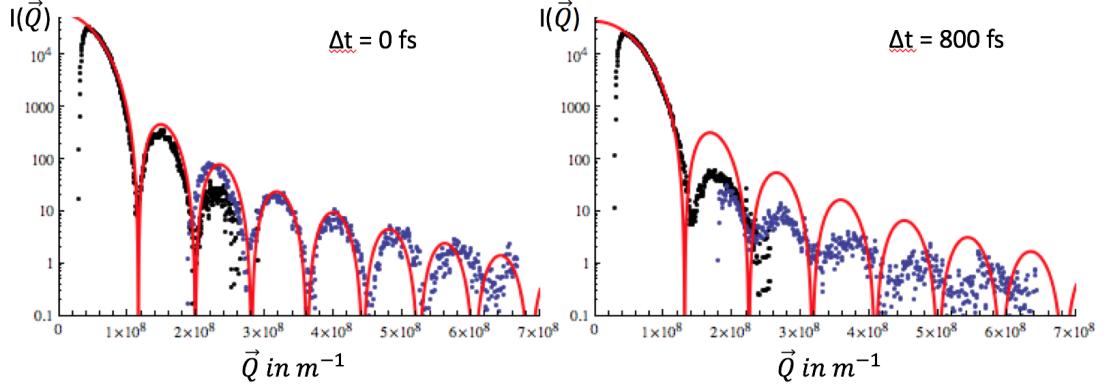


Figure 5.3.: Single shot diffraction pattern at certain pump–probe delays Δt . The red curve simulates the scattering of a sphere, the black data points are from the rear pnCCD detector and the blue data points are from the front pnCCD. The nanoplasma expansion manifests in the scattering intensity I at large spatial frequencies \vec{Q} , where I decreases as described in [17].

including trapped electrons has been simulated in [20], where trapped electrons dominate the damage process due to secondary collisional ionization. Let us now perform a thought-experiment in which a CDI is performed using long X-ray pulses of 100 fs (or so). In such an experiment, electrons would get ionized and trapped efficiently by the Coulomb potential, as the cluster has not yet expanded significantly. During the X-ray pulse duration, multistep ionization increases the ionization level significantly and thus the amount of quasi-free electrons. Now, the trapped electrons in the nanoplasma can be treated non-relativistic, thus they do contribute (coherently) to the scattering pattern. But their contributions blur the effective shape of the imaged object and one has to keep in mind that this comes on top of the actual sample damage, for example broken bonds or further shape changes. A similar electronic damage of a sample is described in [18] and that computational methods may compensate for such damage.

Single-shot diffraction pattern 1D projections can be found in figure 5.3. The figure shows a red line, which is the scattering from a sphere as per equation (2.36) and (2.39) fitted onto the low- \vec{Q} signal of the zeroth diffraction scattering order using the radius variable and the incident beam intensity. The black data points are projected from the rear pnCCD, the blue data points are projected from the front pnCCD using the projection method described in 4.2.1. At $\Delta t = 0$ fs, the scattering of the Xe-cluster can be well approximated with the scattering of a sphere and the fit (red line) agrees well with the data points up to scattering angles of $\Theta \approx 9^\circ$. As the time delay Δt increases, the large- \vec{Q} scattering signal decreases and the scattering of a plain sphere does not well

5.1. Structural damage in Xe-cluster induced by intense X-rays

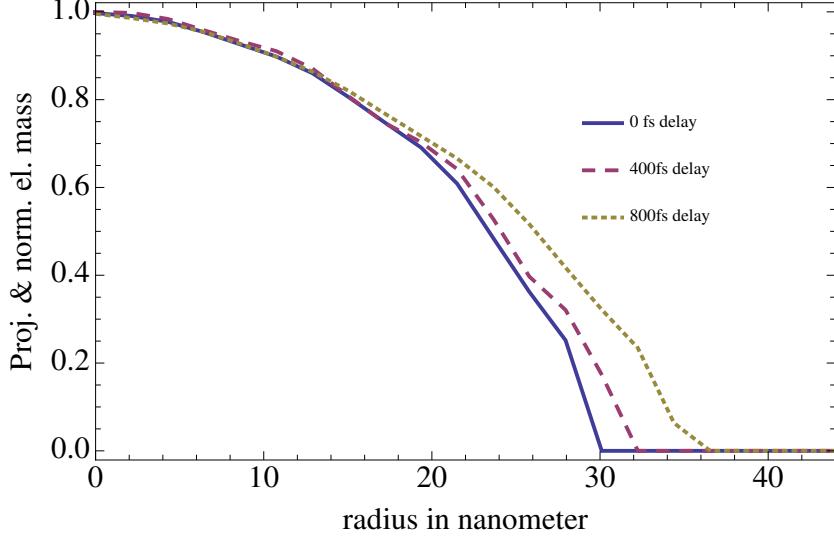


Figure 5.4.: Single shot 1D reconstruction of Xe-cluster at various time delays Δt . The figure shows the projected and normalized cluster-mass as a function of the radius, i.e. the electron density. The reconstructions reveal that the cluster is expanding at an accelerated rate with the outer layers being the most affected.

fit the scattering here. A similar effect is also observed in the previously mentioned IR pump–probe study [17]. Due to the nanoplasma transitions the Xe-cluster is expanding with the outer layers expanding faster than the core as it is described in, e.g. [20]. A similar damage model has been introduced in section 4.4 and generally fits the data well. This is shown in great detail in [17, 145]. Note that the pump–probe considerations from section 4.2.2 would minimize the effect of a decreased scattering at large scattering angles.

To move on with a description of the Xe-cluster electron density, the real-space image of the cluster has been recovered in 1D (see methods section 4.3.3). Figure 5.4 shows 1D reconstructions of the normalized and projected electron density from single xenon cluster at time delays $\Delta t = \{0, 400, 800\}$ fs. The density curves are normalized and clearly indicate an expansion of the middle and outer atomic layers of the Xe-cluster. This selection of hits further visualizes the nanoplasma expansion, whereby here the cluster radius expands over $\sim 20\%$ over a time delay of $\Delta t = 800\text{fs}$ and that this results in a substantial structural change. These hits have comparable initial sizes as they are selected from the lower end of the size distribution.

For the sake of completeness, the recovered modulo of the amplitude $|A|$ and the recovered phase factor are shown in figure 5.5 for the data points at $\Delta t = 800$ fs. The

5. Results and discussion

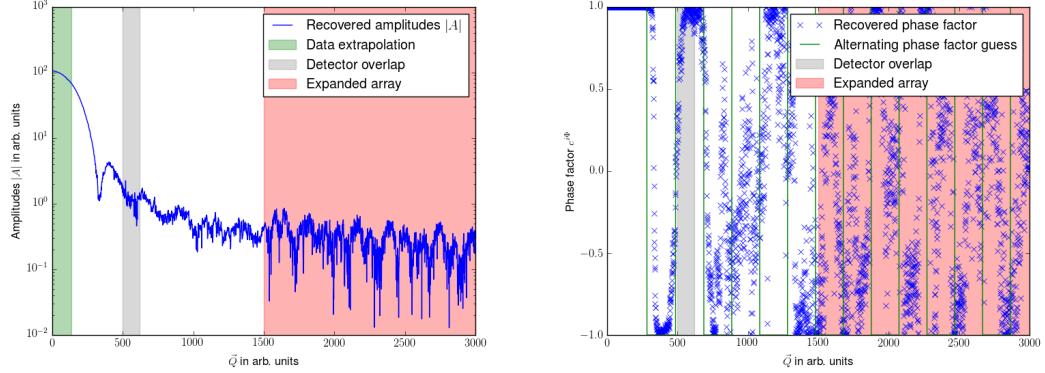


Figure 5.5.: Recovered amplitudes $|A|$ and phase factor of the 1D phase retrieval (see section 4.3.3). The green and red background indicates the space where initial data points were extrapolated. The gray area discloses the detector overlap.

measured amplitudes $|A|$ have been replaced in the space with white background. The initial data in with the green background was interpolated using the anticipated scattering of a sphere. The grayed area is from the pnCCD detector overlap and the red background are extrapolated data points from the scattering of a sphere. The red area therefore increases the resolution. The data points of the k -times iterated Fourier-space function $G'_k(\vec{Q})$ in the white area were replaced with the original data set while $G_k(\vec{Q})$ was allowed to evolve freely in the remaining area. The phase factor retrieval starts with an initial guess of alternating signs per diffraction ring of the sphere and then evolves freely. One can see how the recovered phase factor is alternating as one would expect from the scattering of a sphere.

Figure 5.6 shows 2D reconstructions of single Xe-cluster at $\Delta t = 0$ fs (left) and $\Delta t = 800$ fs (right). The cluster appear generally spherical, however an icosahedral shape is imaginable. Both cluster have a radius of $r \approx 50$ nm. The reconstructions constitute one of the smallest objects recovered with CDI at the time of writing. The minimal resolvable feature size in these images is $\sim 14 \times \sim 6$ nm along the $X \times Y$ -axis (see section 4.3.2). The reconstruction at $\Delta t = 800$ fs shows a ringing around the actual cluster, which is likely an artifact of the spherical support structure. This ringing becomes visible due to the lower signal-to-noise ratio compared to the reconstruction at $\Delta t = 0$ fs. The lower signal is due to the in figure 5.2 described loss of electrons.

5.2. Time-depended response of Xe-atoms due to a X-ray pump–probe beam

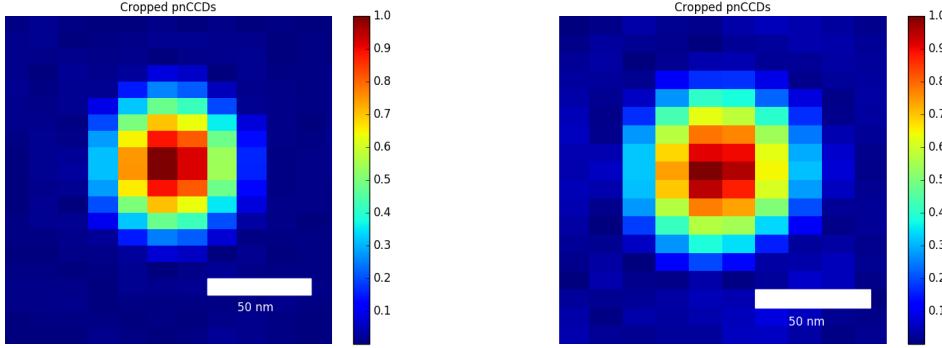


Figure 5.6.: Single-shot 2D reconstructions of diffraction pattern from single Xe-cluster. The left image shows a ~ 50 nm radius Xe-cluster at a pump–probe delay $\Delta t = 0$ fs. The cluster has a spherical or arguably icosahedron electron distribution that is distinct compared to the background. The right image shows a ~ 50 nm radius Xe-cluster at a time delay $\Delta t = 800$ fs that shows a similar symmetry but due to the loss of scatterer (see fig 5.2), the signal to noise ratio decreases and a ringing that is likely from the support structure in the phase-retrieval process is surrounding the cluster.

5.2. Time-depended response of Xe-atoms due to a X-ray pump–probe beam

Ion time of flight traces of atomic xenon at different time delays $\Delta t = \{0, 120, 250, 400, 800\}$ fs and X-ray pump only data is shown in figure 5.7. The time of flight data show a resonance type of behavior of the atomic xenon high charge states with a peak of high-charge state yield at $\Delta t = 250$ fs. The initial increase of high xenon charge states can be explained with intensity-induced X-ray transparency [16]. In the present study, the xenon 3d-subshell is efficiently ionized by the X-ray pump pulse. These electron-holes are typically repopulated on the few femtosecond timescale due to the Auger decay, however, the increasingly ionized atom has longer electron-hole lifetimes. It has been measured that Ne^{8+} has core-hole lifetimes of 230 fs. But why does the charge state distribution then not level out for later delays $\Delta t > 250$ fs? When the strongly pumped atom does not absorb energy near saturation, slower relaxation processes, for example fluorescence, occur that effectively dissipate energy from the nanosample, thereby reducing the average ionization level.

5. Results and discussion

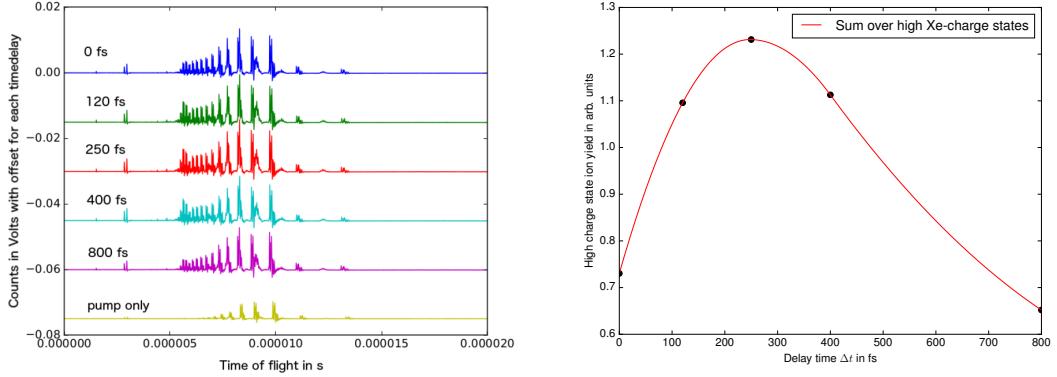


Figure 5.7.: Atomic xenon ion time-of-flight data shows resonant type behavior. As the X-ray pump-pulse traverses through the xenon ions, the 3d-subshell becomes highly ionized and thus the atom increasingly transparent for the probe-pulse ($\Delta t \approx 0 - 120$ fs). The electron-holes have a longer lifetime due to the highly ionized subshell. After the Auger decay populates the 3d-subshell, the atom becomes less transparent and the X-ray pump-pulse efficiently ionizes the atoms ($\Delta t \approx 250$ fs). Eventually other relaxation processes, e.g. fluorescence, dissipate energy from the pump-pulse away from the nanosample leading to a lower high charge states.

5.3. Time-resolved response of highly ionized He-cluster and with xenon doped He-cluster

The response of clusters in highly intense X-ray radiation is more complex than the atomic signal. Size dependent effects [146, 147] and recombination effects in the nanoplasma [148] alter the sample's ionization pathways. Figure 5.8 shows ion time of flight data of pristine He-cluster charge fragments at pump–probe delays $\Delta t = \{0, 250, 800\}$ fs. The pristine He-droplets have a radius of $r_{\text{He}} \approx 810$ nm or $\langle N_{\text{He}} \rangle \approx 5 \cdot 10^{10}$ on average using the relation [72]

$$r_{\text{He}} = 0.22(N_{\text{He}})^{\frac{1}{3}} \text{ [nm].} \quad (5.2)$$

The data show overall a similar behavior regardless of the delay Δt , although minor changes in the charge fragmentation distribution can be made out. More importantly for the reference purposes, the traces indicate no contribution of doubly charged helium atoms. The lack of double charged helium can be explained to the comparably low absorption cross-sections of helium (see table 2.3) [80].

Strongly with xenon doped helium cluster time of flight traces are shown in figure 5.9. Here the He-droplets have a radius of $r \approx 600$ nm or $\langle N_{\text{He}} \rangle \approx 2 \cdot 10^{10}$ particles with a

5.3. Time-resolved response of highly ionized He- and HeXe-cluster

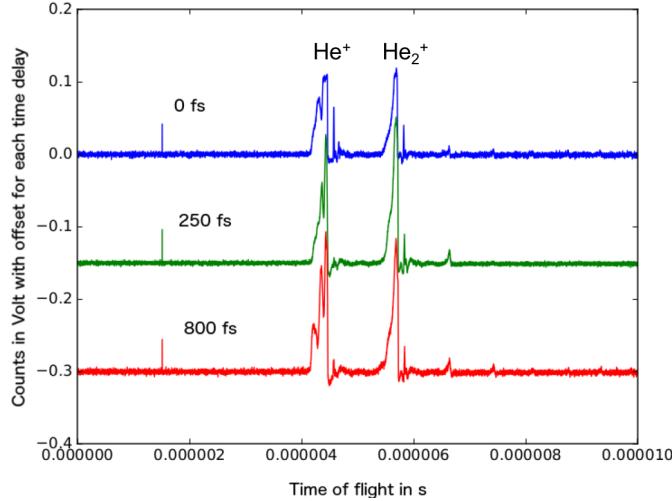


Figure 5.8.: Ion time of flight traces of He-cluster with a radius of $r_{\text{He}} \approx 810$ nm. Although minor changes in the charge fragmentation are observed, we shall note that there are no He^{2+} ions in this data. The absorption cross-section of helium are too low to lead to doubly charged states [80].

$\sim 0.6\%$ doping level of xenon. So here, the helium depletion is $\sim 62\%$ (see section 2.2.2). Most notably on the one hand is the presence of He^{2+} ions and a strongly increased signal from He^+ ions. And on the other hand, only few xenon charge fragments are observed. This is counter intuitive as the absorption cross-section from xenon is vastly higher than from helium (see table 2.3). We can therefore synthesize that, one, there must be an efficient, ultrafast energy transfer process from the xenon particles to the He-droplet, and two, that the helium atoms function as electron reservoir as the initially photoionized xenon atoms are hardly detected. As the time delay Δt is varied, we observe that the He-ion signal shows a resonant type behavior. At $\Delta t = 200$ fs, the signal from He^{2+} and He^+ peaks, however, the helium signal is less intense at the delay times $\Delta t = 0$ and 800 fs. We can make use of the earlier discussion from figure 5.8 and 5.7 and conclude that this behavior does not originate from the absorption and ionization dynamics of the He-cluster but rather of the xenon atoms that the He-droplet has been doped with.

Figure 5.10 shows ion time-of-flight data of with $r \approx 775$ nm radius He-droplets and a 0.06% level doping at pump-probe delays $\Delta t = \{0, 800\}$ fs. So here, the helium depletion is measured to be $\sim 13\%$. We note, again, the presence of He^{2+} ions and more signal from He^+ ions. However, the compared to the stronger doped data these peaks are less intense. Qualitatively this can be explained with the less strong doping, because the X-

5. Results and discussion

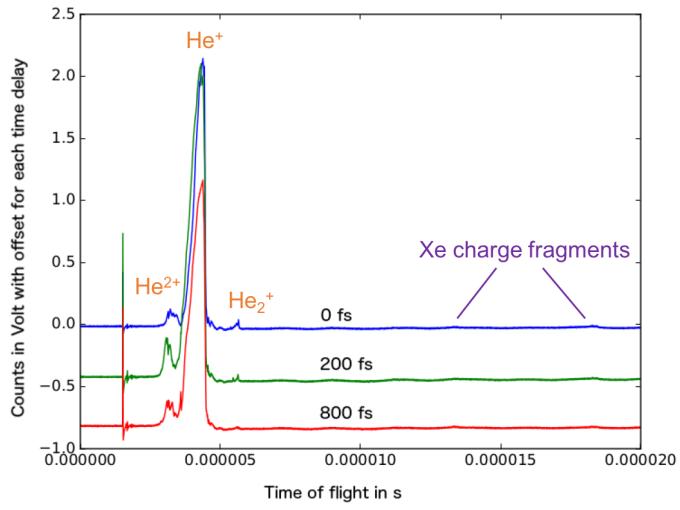


Figure 5.9.: Ion time of flight spectra of He-cluster with $\langle N_{\text{He}} \rangle \approx 2 \cdot 10^{10}$ particles and $\sim 0.6\%$ as many xenon particles. The Xe-atoms absorb X-rays efficiently and transfer the absorbed energy to the He-atoms. The Xe-ions recombine and only few xenon charge fragments are observed. Due to the energy transfer, doubly charged He-ions are detected and the KER is increased as well. As the delay time $\Delta t = \{0, 200, 800\}$ is varied, the system undergoes a resonant type behavior that is attributed to the ionization dynamics of Xe-atoms. More in text.

5.3. Time-resolved response of highly ionized He- and HeXe-cluster

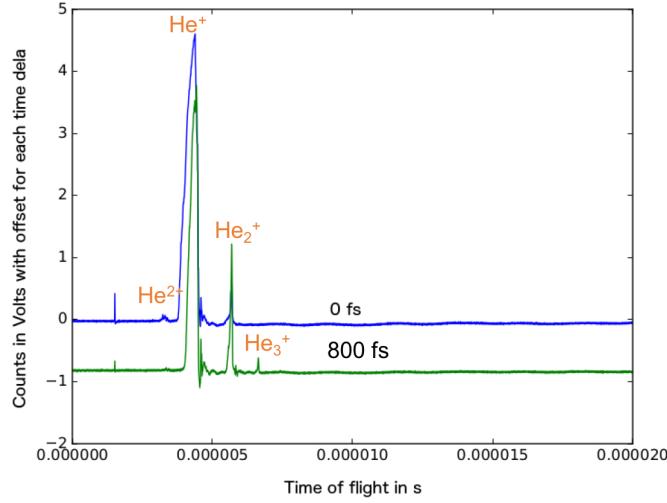


Figure 5.10.: Ion time of flight spectra of He-cluster with $\langle N_{\text{He}} \rangle \approx 4.4 \cdot 10^{10}$ particles and $\sim 0.06\%$ as many xenon particles. These lesser doped He-cluster show a lower He-ion count due to the reduced absorption of the Xe-atoms. As the delay time $\Delta t = \{0, 800\}$ is varied, the system shows dynamics in the population of the ion-states and it is likely that these dynamics are also to be attributed to the atomic xenon ionization dynamics. More in text.

ray absorption from the xenon atoms and subsequent energy transfer to the helium atoms dominate the helium ion characteristics. Less doping results in fewer photon absorption processes and thus less energetic helium ion characteristics. At different time delays Δt , the height of each peak shifts. The He^{2+} and He^+ states become less frequent but a stark increase in He_2^+ and He_3^+ ion peaks is observed. It is likely that the ionization dynamics undergo a resonant type behavior, however, there are too few data points to investigate this in detail.

Summarizing, pristine He-droplets show little dynamics as the time delay Δt is varied and only singly charged He^+ ions are measured. If the He-droplets are doped with xenon, a doubly charged He^{2+} ions are detected, the kinetic energy release (KER) is stronger and the time-of-flight data reveals dynamics that are comparable to atomic xenon, when the delay Δt is varied. As the xenon doping is increased, the presence of He^+ and He^{2+} ions after the pump-probe is more frequent. This data suggests an ultrafast and efficient energy transfer from the xenon atoms to the helium atoms, for example through collisions. The helium particles furthermore act as an electron reservoir such initially photoionized xenon atoms recombine and only few xenon charge fragments are detected by the time of flight spectrometer. The underlying idea that a low-Z material acts as a

5. Results and discussion

electron supplier for the high-Z material has also been studied similarly in [101].

5.4. Condensation of xenon in helium cluster: Plum-pudding type cluster

It is not well known how heterogeneous helium-xenon cluster form a core-shell system. As described in section 2.2.2, the liquid helium cluster picks up xenon atoms as it traverses the doping unit. The xenon atoms move unhindered in the superfluid helium and eventually the xenon atoms condense to energetically favorable cluster structures. [11] reports that at a doping level of 0.02%, i.e. 5000 more helium atoms than xenon atoms, multiple smaller clusters form and locate at vortexes of the rotating helium droplet. However, it is unknown how xenon atoms arrange in non-rotating droplets and also at higher doping levels. The two competing hypotheses are, one, xenon atoms condense to one large cluster within a helium droplet, two, multiple smaller Xe-cluster form within a droplet. Let us call hypothesis two a plum-pudding core-shell system *plum pudding core-shell system*¹ that we can further divide into a few (larger) and many (smaller) scatterer scenario.

The core-shell arrangements are shown in figure 5.11 along with their Fourier-space representations. The shown He-droplet has a radius of $r \approx 125$ nm and a constant xenon doping level of $\sim 20\%$, i.e. the figure shows an artistic representation of the simulated real-space core shell systems. These 2D-simulations are described in more detail in section 4.4. In the illustration, it becomes obvious that the formation of the xenon atoms within the He-droplet dominates the scattering pattern, which is due to the Xe-cluster density being ~ 25.8 times larger than the density of liquid He-droplets. In simplified terms, the one scatterer case shows a large modulation in the diffraction image, which comes from the Xe-core and a small, more intense modulation that comes from the He-shell (similar to orange, dashed line). At low spatial frequencies \vec{Q} , the He-droplet dominates the signal on the diffraction image and at large spatial frequencies \vec{Q} , the Xe-cluster influence is more concise. Ultimately, this is related to the size of each cluster and the mentioned modulations in Fourier-space. In the few scatterer case with $N_{sc} = 8$ scattering centers, the diffraction pattern at low spatial frequencies \vec{Q} is still dominated from the He-shell and at large spatial frequencies \vec{Q} from the Xe-cores. However, the diffraction image appears more complex structured at large \vec{Q} -values due to intense decentered scatterers. Also, the average scattering intensity is well above the scattering of a sphere (red line) that has been fitted onto the zeroth diffraction order. The location of the few scatter

¹The name plum-pudding model comes from J.J. Thomson's model of the atom in 1904 and has here been reused to describe the arrangement of atoms in heterogeneous (rare-gas) clusters.

5.4. Condensation of xenon in helium cluster: Plum-pudding type cluster

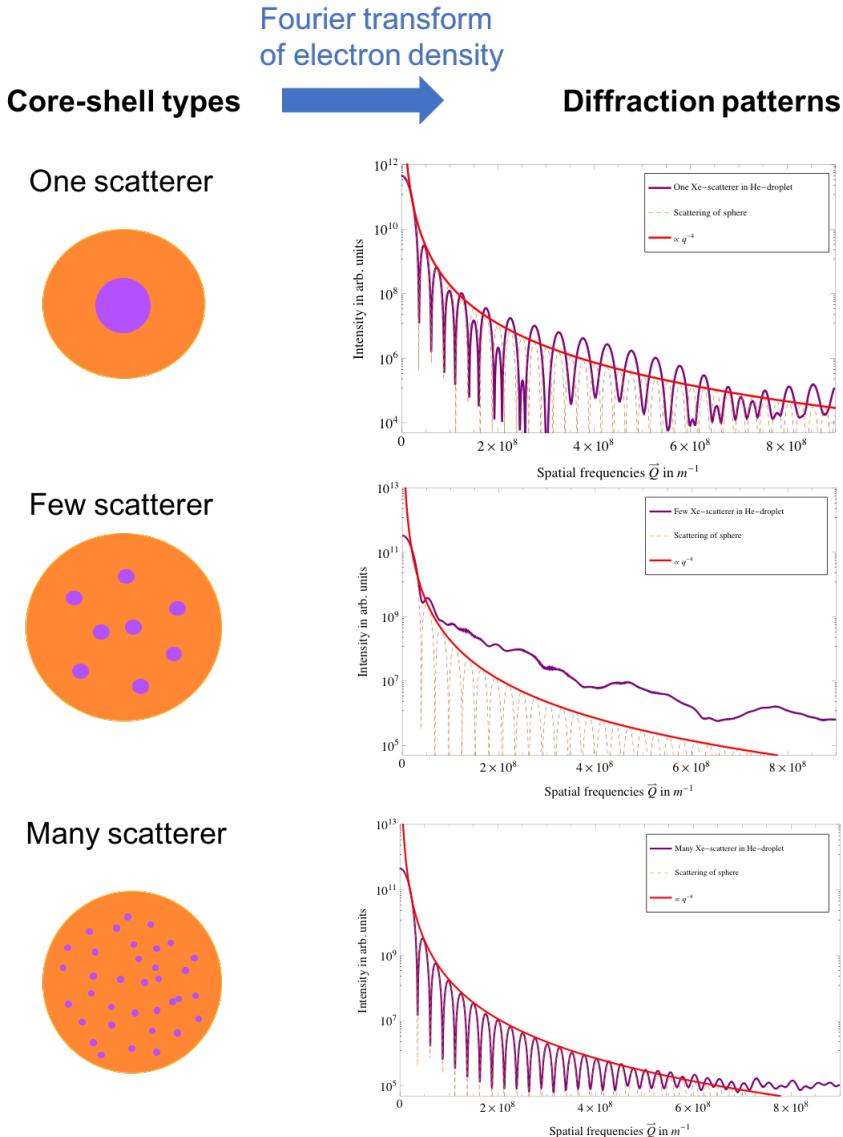


Figure 5.11.: Potential arrangement of xenon atoms in a liquid helium cluster and corresponding 1D diffraction patterns. The He-droplet has a radius of ~ 125 nm and the Xe-doping level is at $\sim 20\%$. The extreme cases, i.e. one xenon scattering center $N_{sc} = 1$, few scatterer $N_{sc} = 8$ and many scatterer $N_{sc} = 100$ are shown to illustrate their impact on diffraction pattern. In short, the scattering pattern is dominated by the signal from the He-droplet at low \vec{Q} -values and at large \vec{Q} -values the signal is dominate by the *Xe-clusters*. This is mostly due to the size of the Xe-clusters and smaller scattering centers are resolved at larger scattering angles. More in text.

5. Results and discussion

plays a lesser role in the 1D projection of the 2D diffraction image, as long as the scattering centers are distributed throughout the He-droplet, i.e. do not reproduce the case of one scatterer. Finally, the many scatterer case with $N_{sc} = 100$. The 100 within the He-droplet randomly distributed scatterer are significantly reduced in size to match the constant xenon doping level of $\sim 20\%$. For the outer shape, the small clusters appear similar to constant electron density increase, which is visible at low to mid \vec{Q} -values thus the scattering is practically identical to the scattering of a similar sized sphere (orange, dashed line). Only at large \vec{Q} -values that reveal small structures, the Xe-scatterer start to dominate the signal, i.e. signal is above the envelope function of the scattering of the sphere.

To quantify the effect of the Xe-cluster size using a crude estimate. For that we can make use of Abbe's criterion (4.9) and the wave vector definition (2.31) to write down the minimal resolvable feature size d as follows

$$d = \frac{2\pi}{|\vec{Q}_r|}, \quad (5.3)$$

with $|\vec{Q}_r|$ being the point in reciprocal space, where the signal starts to be dominated by the smaller structures, here the Xe-clusters. To move ahead, we can relate the resolvable feature size d to the radius r of the smaller spherical structures via $d \approx 2r$. This relation works well for the one-scatterer case $r \approx 15$ nm. However, as the structures become more complex one has more spatial frequency contributions from not only the smaller structures, i.e. the Xe-cluster, but also the space in between smaller structures and the space from the smaller structures to the boundary of the system, i.e. the He-droplet. Multiple smaller structures thus form a *superstructure* that appears larger than its individual components when estimated via equation (5.3). For the plum-pudding cases the Xe-cluster form superstructures with the He-droplet. This superstructure is ~ 3 times larger in the few scatterer case and ~ 10 times larger in the many scatterer case than its individual, simulated Xe-cluster components.

Coherent diffractive imaging is a direct structural measurement technique and allows us to investigate the actual arrangement within a HeXe-cluster. Figure 5.12 shows a reconstruction of a HeXe-cluster that has a radius of $r \approx 210$ nm and a Xe-doping level of $\sim 0.5\%$. The reconstruction indicates a plum-pudding arrangement, where a few Xe-cluster (intense, dark red spots) are randomly distributed within the He-droplet (less intense, green to orange area). The normalized intensity map from the reconstruction may be offset to guide the eye to dense centers. To move on, we may move the gained information from the reconstructions to reverse engineer the electron density and subse-

5.5. Understanding structural damage in plum-pudding type cluster

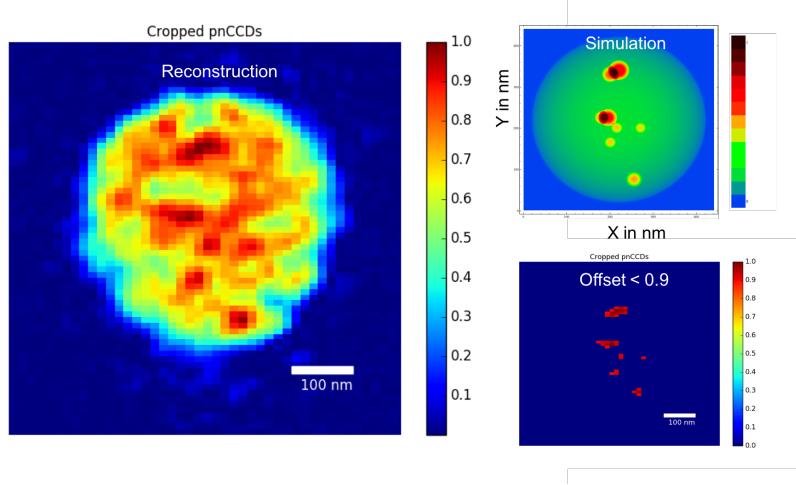


Figure 5.12.: Real-space reconstruction of a HeXe-cluster that has a radius of $r \approx 210$ nm and a Xe-doping level of $\sim 0.5\%$ and corresponding simulation. The electron density indicates a Xe-cluster arrangement of the plum-pudding few scatterer case discussed in figure 5.11. The largest Xe-cluster appear to be ~ 50 nm in diameter and should therefore be well resolved. The normalized intensity map can then be offset and mimicked by 2D electron density projections.

quently study the diffraction image in more detail. This is discussed in the next section and also a focus on the influence of radiation damage onto the diffraction pattern is set.

5.5. Understanding structural damage in plum-pudding type cluster

Figure 5.13 shows a diffraction pattern from the simulated plum-pudding type electron density shown in figure 5.12 that illustrate radiation damage. As described in section 4.4, the radiation damage is simulated via an expansion of the outer layers of a sphere. The He-droplet has a radius $r_{\text{He}} = 210$ nm and a strong Xe-doping of $\sim 20\%$ to illustrate the effect. The blue, solid curve describes the scenario, where all spheres, i.e. clusters, are intact and no X-ray induced dynamics are present. The purple, dashed curve shows the case, where the last 15% in units of the He-droplet radius r expand but leaving the Xe-cluster intact. Conversely, the green, dashed curve shows the effect, where the last $r \cdot 15\%$ of the Xe-clusters expand but leaving the He-shell intact. Lastly, all spheres are expanding at $r \cdot 15\%$. It can be clearly seen, that the expansion of each cluster type effects either low spatial frequencies when the He-droplet is expanding or high spatial

5. Results and discussion

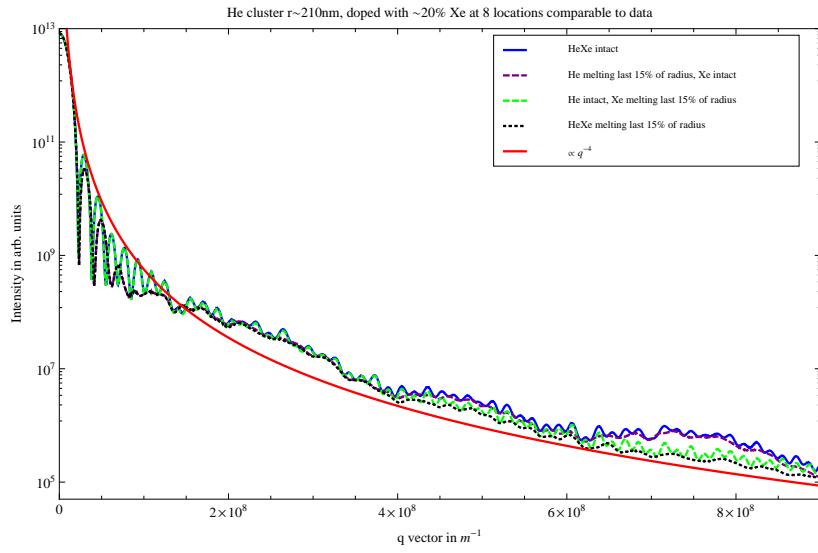


Figure 5.13.: Diffraction images from 2D electron density simulations that illustrate structural damage in HeXe-cluster. Electron densities as per figure 5.12. In reciprocal space: The blue curve shows the helium droplet as well as Xe-clusters intact. The purple, dashed curve shows an expanding He-droplet, leaving the Xe-clusters intact. The green, dashed curve leaves the He-droplet intact but shows expanding He-clusters. The black, dashed curve shows both cluster types expanding. The red curve is the envelope of the scattering of a sphere fitted to the zeroth order. More in text.

5.5. Understanding structural damage in plum-pudding type cluster

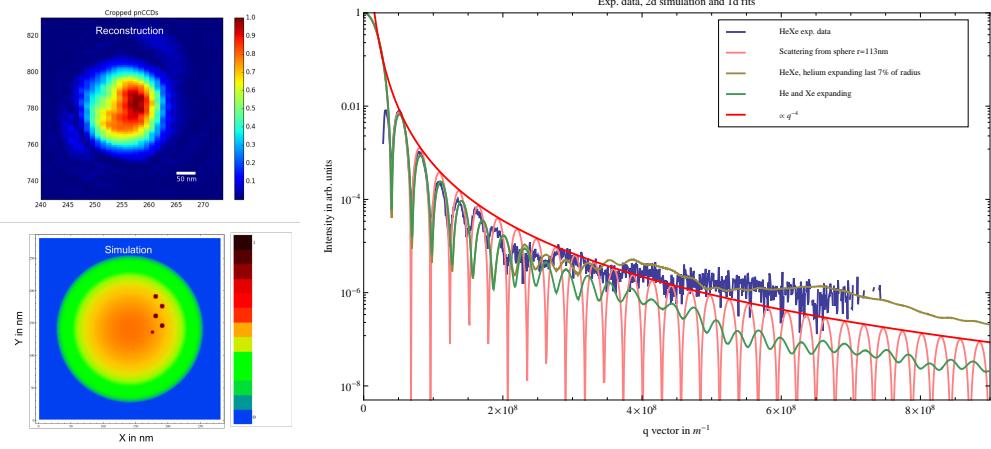


Figure 5.14.: 2D simulations adapted to real-space and Fourier-space data. Left: Electron densities of HeXe-cluster from reconstruction (left, top) and simulation (left, bottom). The diffraction pattern (right) shows the experimental data (blue curve) from the same HeXe-cluster taken at $\Delta t = 800$ fs but also the Fourier-transformed el. densities, where the He-droplet is expanding with the Xe-cluster are intact (yellow curve) and the Xe-cluster expanding (green curve). Scattering of a sphere with radius $r = 113.5\text{ nm}$ and envelope function \tilde{Q}^{-4} fitted to experimental data. The simulations of an expanding He-droplet and intact Xe-cluster fit the experimental data well. More in text.

frequencies when the (much smaller) Xe-cluster are expanding. The vast size differences of the Xe-cluster $r_{\text{Xe}} = \{25, 22, 20, 1817, 14, 14, 13.5\}$ nm allow a strict separation between the He-droplet, e.g. the expanding shell and the Xe-clusters, e.g. the intact cores in the diffraction pattern analysis.

These insight can be used to compare the 2D-simulations to measured diffraction pattern. Figure 5.14 shows a HeXe-cluster reconstruction, a simulation and corresponding 1D diffraction pattern. This data has been taken at a time delay $\Delta t = 800$ fs. The HeXe-cluster has a radius $r_{\text{He}} \approx 113$ nm. The dense spots in the reconstruction have been simulated with nine Xe-cluster of radii $r_{\text{Xe}} = \{4, 4, 4, 4, 3, 0.5, 0.5, 0.5, 0.5\}$ nm, thus a $\sim 0.5\%$ Xe-doping. In the diffraction pattern, the scattering of a sphere with radius $r = 113$ nm (pink line) and its envelope (red line) are shown as a comparison. The yellow curve is a simulated diffraction pattern that shows an expanding He-droplet, where the last 7% of the shell is exponentially expanding, while the Xe-clusters stay intact. The green curve shows the simulated diffraction pattern, where the He-droplet is expanding at the last 7% of its radius and, to make the effect clear, 90% of the Xe-clusters outer radii are expanding. The simulations show a very good agreement with the expanding

5. Results and discussion

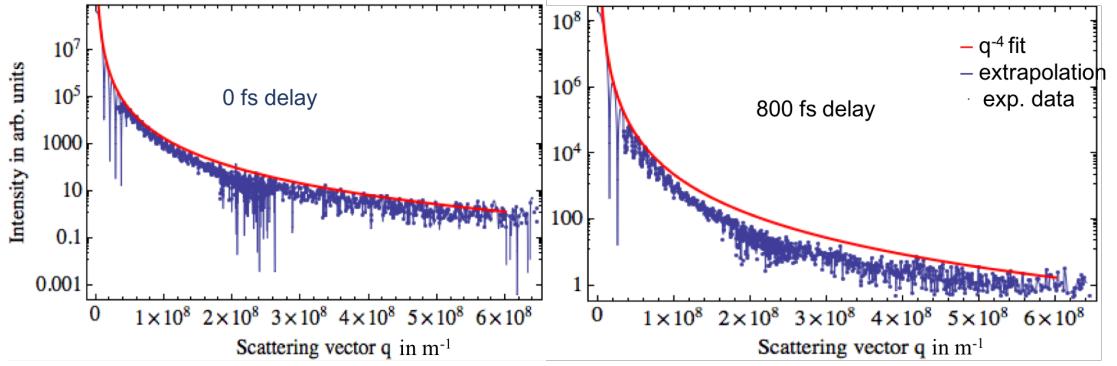


Figure 5.15.: Single shot diffraction images of pristine He-droplets.

He-droplet at low spatial frequencies \vec{Q} . At high frequencies, only the yellow curve that uses intact Xe-clusters in the simulation reproduces the scattering image well. It should be noted, however, that the structural damage in the Xe-cluster is still possible but may not be detectable due to current resolutions limitations.

5.6. Sacrificial layers: Comparison of structural damage in He- and HeXe-cluster

Single-shot diffraction images of He-droplets with radii $r_{\text{He}} \approx \{379, 302\}$ nm, at time delays $\Delta t = \{0, 800\}$ fs, respectively, are shown in figure 5.15. For clarity, only the experimental data (blue points), spherical extrapolation at low \vec{Q} -values (blue line) and the envelope of the spherical extrapolation function (red line) is shown. At $\Delta t = 0$ fs, the local maxima of the experimental data agree well with the envelope function. This indicates an intact He-droplet, as shown in more detail in section 5.1. As the time delay is varied to 800 fs, the diffraction pattern of the droplet shows that the local maxima between $\vec{Q} \approx \{1, \dots, 4\}10^8$ m⁻¹ are well below the envelope. As shown previously, this indicates structural damage.

Single-shot diffraction images of HeXe-cluster with radii $r_{\text{He}} \approx \{116, 113.5\}$ nm, at time delays $\Delta t = \{0, 800\}$ fs, respectively, are shown in figure 5.16. The experimental data at $\Delta t = 800$ fs is the same as in figure 5.14. The black dots are data points from the rear pnCCD and the blue dots are data points from the front pnCCD. The pink, dashed curve is the scattering from a sphere fitted to the first order of diffraction and the red curve is its envelope. Here, the differences in the diffraction images as the time delay Δt is varied from 0 fs to 800 fs shall yield as another indication that helium functions as a sacrificial

5.6. Sacrificial layers: Comparison of structural damage in He- and HeXe-cluster

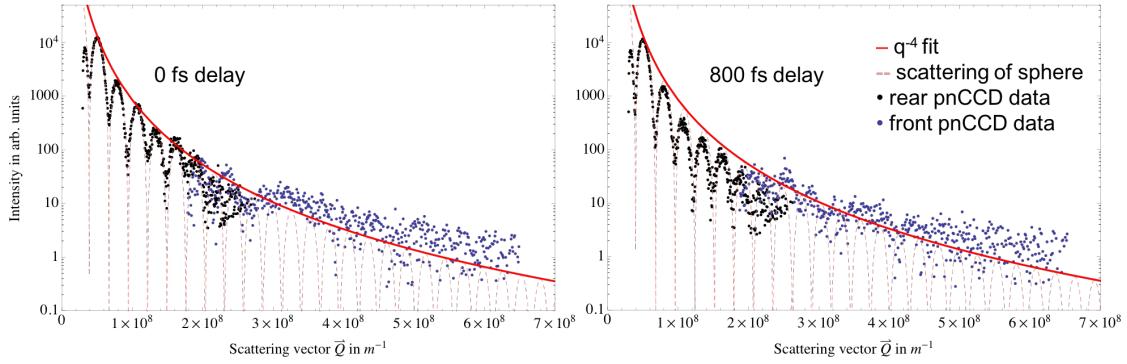


Figure 5.16.: Single-shot diffraction pattern of HeXe-cluster at time delays $\Delta t = \{0, 800\}$ fs. At $\Delta t = 0$ fs, the diffraction pattern follows the scattering pattern of a sphere at low spatial frequencies \vec{Q} but stays well above the envelope function \vec{Q}^{-4} at high spatial frequencies \vec{Q} . At $\Delta t = 800$ fs, the scattering curve deviates from the scattering pattern of a sphere at low \vec{Q} -values indicating damage to the He-shell structure. At large \vec{Q} -values, the signal changes little compared to the $\Delta t = 0$ fs data indicating intact Xe-cluster, i.e. cores. Thus, the He-droplet functions as sacrificial shell keeping the Xe-cluster sample intact. More in text.

Measured scattering / expected scattering

| For sample | At time delay Δt | |
|--------------|--------------------------|---------------------|
| | 0 fs | 800 fs |
| Xe-cluster | $0.91 \pm \sim 0.1$ | $0.26 \pm \sim 0.1$ |
| He-droplet | $0.89 \pm \sim 0.1$ | $0.65 \pm \sim 0.1$ |
| HeXe-cluster | 1 | $1.33 \pm \sim 0.3$ |

Table 5.1.: Relative comparison of measured scattering versus expected scattering for Xe-, He- and HeXe-cluster. More in text.

layer in HeXe-clusters. At $\Delta t = 0$ fs, the rear pnCCD data points agree well with the simulated scattering of a sphere, while the data points from the front detector lay well above the scattering envelop function of the sphere. As already discussed, at $\Delta t = 800$ fs the rear pnCCD data points do not agree well with the scattering of a sphere, meaning structural damage in the He-droplet, however, the blue data points appear to be similar as in the $\Delta t = 0$ fs event.

A more quantitative comparison provides a challenge as each single-shot event has a certain uniqueness attributed to it. However, an attempt to compare the measured scattering vs. expected scattering is made in the following and the results are summarized in table 5.1. The diffraction pattern of a pristine He- or Xe-cluster can be well compared

5. Results and discussion

to the scattering curve of a sphere $f(\vec{Q})$. Hence, we can introduce a function $g(\vec{Q})$ that interpolates and sums the data points of pristine He- and Xe-cluster and calculate the relative difference at a certain time delay $\frac{\sum g(\vec{Q})}{\sum f(\vec{Q})} |_{\Delta t}^{\text{sample}}$. Since the effect is most visible at large \vec{Q} -values, the functions g and f sum between $2.8 \cdot 10^8 \text{ m}^{-1}$ to $6.4 \cdot 10^8 \text{ m}^{-1}$. For Xe- and He-cluster, we find values close to the expected scattering of similar sized spheres, thus is the measured scattering / expected scattering $91\%|_{\Delta t=0\text{fs}}^{\text{Xe}}$ and $89\%|_{\Delta t=0\text{fs}}^{\text{He}}$. As already established, the actual scattering is reduced due to the nanoplasma expansion such that $26\%|_{\Delta t=800\text{fs}}^{\text{Xe}}$ and $65\%|_{\Delta t=800\text{fs}}^{\text{Xe}}$. The interpolating function seems to underestimate the actual scattering by $\sim 10\%$ from which we can deduct the error since other errors, such as electronic noise, make up for the underestimate of the interpolating function. HeXe-cluster can not be compared to the scattering of a sphere, however, we may compare similar single-shot events at different time delays. The two single-shot events shown in figure 5.16 have the same amplitude constant A in the $A\vec{Q}^{-4}$ fit and have a size difference of only $\sim 2\%$ at the same source and doping conditions. In other words, we may compare the interpolating functions $g(\vec{Q})|_{\Delta t=800\text{fs}}^{\text{HeXe}}/g(\vec{Q})|_{\Delta t=0\text{fs}}^{\text{HeXe}}$ at different time delays Δt , which yields a factor 1.33 more scattering from Xe-cluster despite the fact that damages in the He-droplet are visible at low spatial frequencies \vec{Q} . The estimation error in this method origins mainly from a varying pickup pattern of Xe-atoms as the underestimation due to the interpolating functions should nullify, however, the error must be at least $\sim 30\%$.

Synthesizing, we find a reduction in scattering intensity of $\sim 65\%$ in Xe-cluster and $\sim 24\%$ in He-droplets 800 fs after the beginning of the nanoplasma expansion. We attribute this change to structural change of the sample, thereby neglecting additional loss of scattering intensity from electronic damage (see figure 5.2). If Xe-cluster are embedded in a He-droplet, neither structural nor electronic damage is detected in Xe-cluster, although the He-droplet shows structural damage. The He-droplet thus functions as sacrificial tampered layer that provides the initially ionized Xe-cluster with electrons and transports kinetic energy away from the sample.

6. Summary and outlook

For the present study, a novel, accelerator based X-ray pump – X-ray probe technique was used for the first time at LCLS [47] and the new soft X-ray end-station LAMP was built and commissioned [108]. Using this new experimental setup, a coincident single particle imaging (SPI) and time-of-flight mass spectroscopy was employed. Diffraction images of single nanometer sized aerosol particles were measured with thus far unprecedented resolution. The successful combination of data from multiple detectors increases the numeric aperture and extends the dynamic range of the detector system. The developed coincident imaging and spectroscopy, X-ray pump – X-ray probe technique allows the study of X-ray induced dynamics on the few ten femtosecond timescale with a spatial resolution in SPI on the few nanometer lengthscale.

The present work experimentally investigates how tampered layers protect aerosol particles from X-ray radiation damage. Therefore, single, nanometer-sized, rare-gas cluster, namely superfluid He-, solid Xe- and mixed HeXe-cluster are pumped with X-rays to undergo the phase transition to a nanoplasma, i.e. experience radiation damage. This transition is probed at a later time delay $\Delta t = 0 - 800$ fs. The coincident imaging and spectroscopy measuring method reveals that pristine He- and Xe-cluster exhibit stark electronic and structural damage due to the nanoplasma transition. Xe-clusters, for example, exhibit a radial expansion, i.e. structural damage, that shows in the first delay step at $\Delta t = 60$ fs and over the course of 800 fs manifests in a $\sim 20\%$ increase of their average radius $r \approx 61$ nm. The hot Xe-nanoplasma is heated to electron temperatures of ~ 125 eV. This thesis then shows that mixed HeXe-cluster, generated through the pickup-principle at doping levels up to 0.5%¹, arrange in a *plum-pudding* type, meaning that multiple Xe-cluster are embedded in a greater He-droplet. Finally, when mixed HeXe-cluster are pumped with intense X-rays, Xe-atoms are the main absorbent of the radiation. Data show that the main absorbent, xenon, exhibits little electronic damage and, at current resolution, no structural damage. However, the weak absorbent, helium, experiences violent electronic and structural damage. This indicates that the He-droplet functions as sacrificial shell around the Xe-particles due to two processes. One, a kinetic

¹0.5% as many xenon atoms as helium atoms.

6. Summary and outlook

energy transport from the Xe-clusters to the He-droplet, and two, the He-droplet supplies electrons to the initially ionized Xe-particles, minimizing their electronic damage. These results are beneficial to a variety of fields. First, the insights gained from [17, 101] are extended and it is shown that tampered layer can be used to inhibit radiation damage. This is important for SPI, where it is foreseen that radiation damage will be a limiting factor in the ultimate achievable resolution [9]. Second, new and existing SPI data may make use of combining multiple detectors thereby increasing the resolution by a factor ~ 5 . Combined diffraction images unfold their full potential when combined with an EMC algorithm [100]. This allows an orientation and averaging of diffraction images thus enabling a high-resolution 3D reconstruction of the sample. Finally, the pioneered X-ray pump – X-ray probe technique can be and already has been extended to various other atomic and molecular physics experiments such as [44, 49, 50, 149, 150], allowing entire new insights in thus far unreachable regimes.

7. Appendix

7.1. Matlab code on spherical integrations

Excerpt of the Matlab code that has been used to reduce 2D diffraction images to 1D arrays with the intensity as a function of the scattering vector \vec{Q} .

```
%%% CENTER OF HIT
x_center=xLen/2; % Actually Y-center
y_center=yLen/2; % Actually X-center
for r=(1:1500)
    %looping over points
    for y=(1:yLen)
        for x=(1:xLen)
            %check if in circle
            if (x - x_center)^2 + (y - y_center)^2 < r^2
                %norm
                rnorm(r)=rnorm(r)+1;
                % testing for noise/photons
                if rearpnccd(x,y)>0
                    circleSum(r)=circleSum(r)+rearpnccd(x,y);
                end
            elseif (x - x_center)^2 + (y - y_center)^2 == r^2
                %norm
                rnorm(r)=rnorm(r)+(1/2);
                % testing for noise/photons
                if rearpnccd(x,y)>0
                    circleSum(r)=circleSum(r)+(rearpnccd(x,y)/2);
                end
            end
        end
    end
    if rnorm(r)==0
        rnorm(r)=1;
    end
    if r==1
        plotSum(r)=circleSum(r)/rnorm(r);
    elseif rnorm(r)-rnorm(r-1)>0
```

7. Appendix

```

        plotSum(r)=(circleSum(r)-circleSum(r-1))/(rnorm(r)-rnorm(r-1));
    else
        plotSum(r)=0;
    end
end

```

7.2. Python code on combining detectors

Python code that has been used to combine pnCCD detectors.

```

# Imported Packages
import numpy as np

### Gaps between front top and bottom pnCCD to middle of rear pnCCD
gapTop = 231                         # In pixel
gapBot = 252                          # In pixel

### offset between rear and front pnCCDs
xShift = -1                           # In pixel

##### Things to adjust per run/experiment
pixelSizePnccd=75*10**-6             # Size of a pixel in meter.

distanceOfRearPnccd=0.74              # Distance IR to front pnCCD in meter
distanceOfFrontPnccd=0.36             # Distance IR to front pnCCD in meter
gainRearPnccd=1./64.                 # Detector gain multiplier
gainFrontPnccd=1.                     # Detector gain multiplier

scatteredWaveLength=1.5*10**-9       # Wavelength of photons in meter

pathToHDF5=                            # Adapt to your needs

### Functions
# Phi - scattering angle
def PhiScatt(pixel, pixelSize, distanceToDetector):
    return np.arctan(pixel * pixelSize / distanceToDetector)

# Q-vector function
def qVector(pixel, pixelSize, distanceToDetector, waveLength):
    return 4.*np.pi*np.sin(PhiScatt(pixel, pixelSize,
                                    distanceToDetector)/2)/waveLength

```

7.2. Python code on combining detectors

```

### Reading intensity files ,
intFrontTop=    # Adapt to your needs
intRear=           # Adapt to your needs
intFrontBottom= # Adapt to your needs

### Intensity normalization and offset of electronic noise .
# Rear int. normalization
intRear=intRear*(1/gainRearPnccd)*(distanceOfRearPnccd**2)*
(1/distanceOfFrontPnccd**2)

# Offset
intRear[intRear<15*(1/gainRearPnccd)*(distanceOfRearPnccd**2)*
(1/distanceOfFrontPnccd**2)]=0.0
intFrontTop[intFrontTop<350]=0.0
intFrontBottom[intFrontBottom<350]=0.0

### Combining front detector
ztop=np.concatenate((intFrontTop,np.zeros
((gapTop+gapBot,1028)),intFrontBottom))

### Combining rear with front detector
# Creating pixel to Q-vector correlation vectors
yRear, xRear =np.ogrid[(-len(intRear))/2:(len(intRear))/2,
-(len(intRear[0]))/2:(len(intRear[0]))/2]

# To transform Q-values from rear pnCCD to front pnCCD pixel values
qDiv=qVector(1, pixelSize=pixelSizePnccd,
             distanceToDetector=distanceOfFrontPnccd,
             waveLength=scatteredWaveLength)

# Spanning Q-space
y_comb=len(ztop)/2
x_comb=len(ztop[0])/2

qyRear=np.round(qVector(yRear, pixelSize=pixelSizePnccd,
                        distanceToDetector=distanceOfRearPnccd,
                        waveLength=scatteredWaveLength)/qDiv).astype(int) + y_comb
qxRear=np.round(qVector(xRear, pixelSize=pixelSizePnccd,
                        distanceToDetector=distanceOfRearPnccd,
                        waveLength=scatteredWaveLength)/qDiv).astype(int) + x_comb + xShift

# Keep track of per pixel additions to create mean intensities
norm=np.zeros(ztop.shape)

```

7. Appendix

```
# Iterating over the array, slow but works
it=np.nditer(intRear, flags=['multi_index'])

while not it.finished:
    # read pixel transform coordinates
    y_idx = qyRear[it.multi_index[0],0]
    x_idx = qxRear[0,it.multi_index[1]]

    # add intensities and add to norm
    ztop[y_idx,x_idx] += it[0]
    norm[y_idx,x_idx] += 1

    it.iternext()

# Corrections to norm so not 1/0, seems inefficient but is fast enough.
norm -= 1
norm[norm<0]=0
norm += 1

### Combined mean intensities of front and rear detector.
ztop = ztop/norm
```

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A. Publications by the author

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B. Eidestattliche Versicherung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und eigenhändig, sowie ohne unerlaubte fremde Hilfe und ausschließlich unter Verwendung der aufgeführten Quellen und Hilfsmittel angefertigt habe.

Chicago, den 16. Dezember 2016

Maximilian Jakob Bucher

Ort, Datum

C. Acknowledgment

This has to be written.

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