

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 increasing 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-clusters using an ultrafast, XFEL accelerator-based X-ray pump–X-ray probe technique. A first X-ray pulse triggers 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 $\sim 10^{18} \text{ W cm}^{-2}$. The delay Δt is varied from 0 fs to a 800 fs delay. The probe creates a diffraction image of the ~ 30 to ~ 1000 nanometer-sized objects and coincidentally ions are captured via time-of-flight (TOF) spectroscopy. He- and Xe-clusters are generated through a supersonic gas expansion into a vacuum. Mixed HeXe-clusters are created when He-droplets pick up Xe-atoms in a doping unit.

The study reveals single-shot snapshots of Xe-, He- and HeXe-clusters that undergo the nanoplasma phase transition. The reconstruction of a $\sim 25 \text{ nm}$ radius Xe-cluster with $\sim 6 \text{ nm}$ is shown. A large-scale structural analysis of the size and number of scatterers in Xe-clusters 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 dependent ionization pattern in Xe-atoms and HeXe-clusters, while pristine He-droplets do not exhibit this dependency. The structural analysis of few hundred nanometer radius HeXe-clusters show that the doped Xe-atoms arrange in small clusters of a plum-pudding type. The He-droplet acts thereby as a shell and the Xe-clusters as a sample. The X-ray pump–X-ray probe study on HeXe-clusters shows structural damage in the He-droplet, while Xe-clusters 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-clusters.

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1. Introduction

Following the discovery of X-radiation at the end of the 19th century by Röntgen, X-rays have been used to understand and investigate matter in unprecedented ways. Soon after this discovery, X-rays were used to take the first medical image. Later, X-rays lead to the understanding of fundamental aspects of atoms [1] and crystals [2, 3]. Today, the success story continues in various fields of science. A large and active scientific field is structural biology. Here, 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 into large crystals making the molecular shape determination challenging. The advent of new lightsources, namely the X-ray free electron laser (XFEL) [4], enable new methods to study bio-molecules and other particles with intense and short-pulse X-rays [5, 6]. However, all matter irradiated by intense X-ray radiation disintegrates into its atomic components on ultrafast timescales¹ [7]. This process is a form of *radiation damage* and is a major challenge for imaging methods with XFEL [8].

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 [9] and non-biological particles, such as rare-gas clusters [10]. It has been a rapidly developing field that has recently succeeded in visualizing 3D images of nano-objects [11, 12].

A key driver of this success is the development of new lightsources with more and more spectral brightness. The first hard XFEL was built at Stanford University and is called the Linac Coherent Light Source (LCLS) [13]. It is a ~ 4.1 km long machine² that produces X-rays with wavelengths from 4.6 nm to 0.1 nm, has a highly intense beam of up to $10^{18} \frac{\text{W s}}{\text{cm}^2}$, and ultra-short pulses ranging from 1 – 500 fs. LCLS is a user facility and

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

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 in operation and is a focal point for experiments ranging from biological imaging to basic science [14].

Let us now imagine that we expose a nanoparticle to the highly intense X-rays from LCLS. Within the first moment of light-nanoparticle interaction, photons elastically scatter in an angular distribution distinctive to the shape of the particle that we are able measure in 2D. However, the particle will also absorb the rays from the first moment on, which leads to inner atomic-shell vacancies [15]. Subsequent processes, such as the Auger-decay, occur only a few femtoseconds later and eventually the nanoparticle is transformed into a nanplasma. The nanplasma is very hot, comparable to the conditions of the surface of the sun. Several forces will expand the plasma on a femtosecond timescale [16]. Finally, the nanplasma 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 of “outrunning” 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 [17] and novel methods from AMO physics, such as molecule alignment [18] and sacrificial tamper layers [19, 20] may inhibit it.

This thesis describes the nanplasma phase transition in detail. A novel X-ray pump – X-ray probe method was employed to study the nanplasma evolution in the testbed nanoparticles superfluid 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” at a later time. Coincident diffraction imaging and time-of-flight mass spectroscopy data is taken to answer the following questions:

- How does X-ray induced damage compare to optical light induced damage?
- On what timescales do absorption cross-sections change due to X-ray irradiation?
- How do mixed HeXe-clusters self-organize as nanoparticles?
- Does He compare to sacrificial tamper layers in mixed HeXe-clusters?

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

2. Fundamental Concepts

This chapter condenses the theoretical concepts that will reoccur throughout this 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 lasers?

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 they are commonly created in synchrotron facilities for scientific purposes. In a synchrotron facility, electrons are produced in bursts by an *electron gun* and formed to a collimated *electron bunch*. Then, these electrons are accelerated near the speed of light, with kinetic energies, γ , of $\gamma >$ MeV, and injected into a storage ring. The electrons are deflected by 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 storage ring can store many electron bunches allowing a high repetition rate of light pulses on the order of megahertz. The X-ray pulses are characterized through a parameter that is called spectral brightness [21] or sometimes brilliance. We can define the spectral brightness as [22]

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

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

2.1. Why X-ray free electron lasers?



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 ~ 4.1 km long machine. The accelerator and buildings are stretched far because of the light generation process. From [23]

modern synchrotron light sources is hence often measured and compared to previously achieved brightness values. The motivation to improve the spectral brightness is manifold and follows the recipe to let a sample interact with as many photons possible, in the shortest time possible, and with the best energy resolution possible. In other words, more brilliant light sources enable imaging of even smaller particles, or investigate dynamics that are even faster.

To get a numerical understanding, 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 $\sigma = 1$ megabarn (Mb) [24]. Typical X-ray focii² are $A = 1 \mu\text{m}^2$ such that the number of photons, n_{in} , needed to absorb just one photon per atom, n_{abs} , is

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

We can compare this to a modern synchrotron source, e.g., NSLS-II. This synchrotron produces 1.710^4 photons per pulse in the Si(111) bandwidth at pulse durations of a few tens of picoseconds [25]. That is far out of reach for investigating non-linear, or multi-photon, processes. While this back of 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 entirely new aspects of nature. As it is not possible to use conventional optical methods to increase the number

¹Soft X-rays have wavelengths of 10 nm to ~ 0.2 nm.

²The focus size at the AMO instrument of LCLS is $1 \mu\text{m}^2$.

2. Fundamental Concepts

of X-ray photons there were drastic ideas. 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 anti-(space)missile defense [26]. In a similar time, it was also proposed to build free electron laser [27, 28] to increase the spectral brightness.

Free electron lasers, amplify the light along a straight line to create optical laser-like radiation. Construction of the first hard XFEL finished in 2009 and it is called the Linac Coherent Light Source. LCLS can be seen from a birds-eye view in Figure 2.1. XFEL are able to create 10^{12} photons per pulse and achieve pulse lengths of a few femtoseconds. The beam parameters of the XFEL increased the spectral brightness of user facilities by many orders of magnitude³. This allows the study of, for example, the ultrafast movement of electrons in chemical reactions [29, 30], the imaging of nanoparticles [6, 9] and the discussed nonlinear dynamics of atoms, molecules and clusters [15, 31–33].

Only a few XFEL exist today. The LCLS at SLAC National Accelerator Laboratory (SLAC) in the United States and the SACLAC at Rikagaku Kenkyūsho (RIKEN) in Japan are the two currently operating XFEL user-facilities. Due to their success, more XFEL are being built around the world, for example, the European XFEL near Deutsches Elektron Synchrotron (DESY) in Germany, the SwissFEL at Paul Scherrer Institut (PSI) in Switzerland, and the PAL-XFEL at Pohang Accelerator Laboratory (PAL) in South Korea.

2.1.1. From bending magnets to undulators

In the beginning of X-ray lightsources, the radiation was generated using *bending magnets*. A bunch of electrons was accelerated near the speed of light and traversed a bending magnet. The acceleration from the magnet resulted in the emission of electro-magnetic radiation. The first improvement to creating X-rays over bending magnet sources was through a *wiggler*. Wigglers consist of magnets arranged in an alternating order. An electron bunch traveling through a wiggler is “wiggled” along its path due to 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 , [35]

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

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

2.1. Why X-ray free electron lasers?

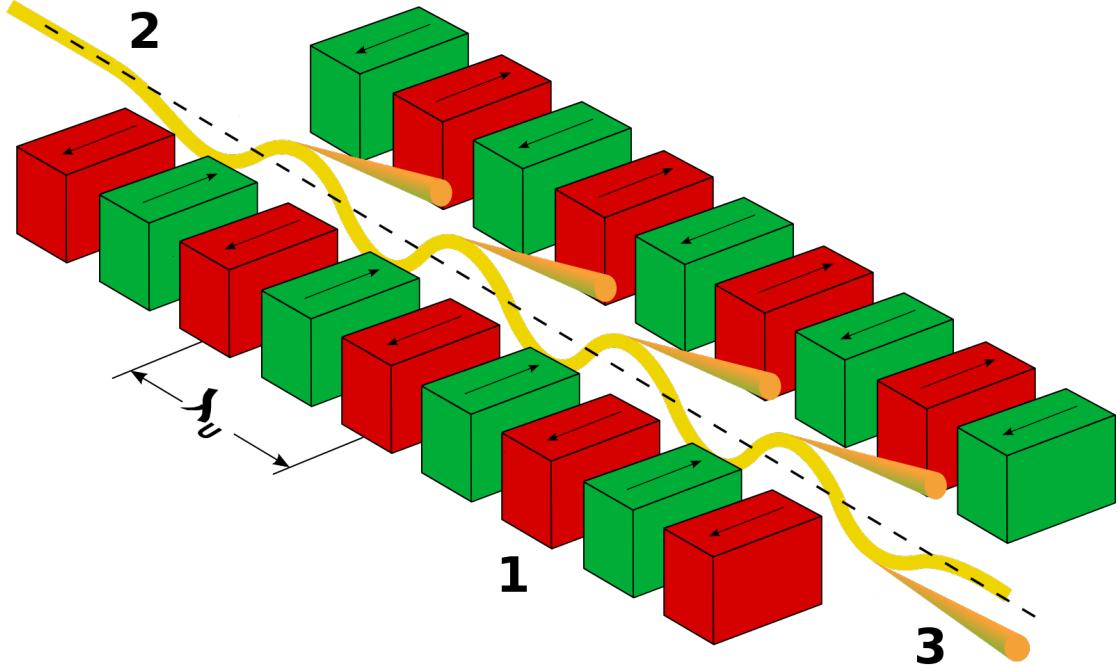


Figure 2.2.: Schematic setup of an undulator with a period of λ_U . (1) Magnets in alternating polarity; the arrows indicate the direction of the magnetic field. (2) Incoming electron bunch near the speed of light. (3) Emitted light in beam direction due to sinusodial movement of the electron bunch. From [34].

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 were used at the Stanford Synchrotron Radiation Lightsource (SSRL) in 1979 to generate X-rays. Independently from wigglers, undulators were developed [36]. A schematic setup of an undulator can be seen in Figure 2.2. Wigglers and undulators create radiation on 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 specific and named undulator period, λ_U . The undulator period and magnetic fields are chosen such that their emitted radiation per period constructively interfere with each other. Thus the emitted power, P_W , now scales as [37]

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

The X-rays emitted by undulators have typically a narrower spectrum and a higher flux than wigglers. We can further characterize undulators (and wigglers) by the strength

2. Fundamental Concepts

parameter, K , which is given by, [38]

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

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

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

Undulators 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 centimeters. The electrons emit radiation in the nanometer wavelength regime because electrons near the speed of light have to be considered relativistic. In the frame 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 [38]

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

with the kinetic energy γ of the electron bunch in the undulator and the electron observation angle Ψ .

2.1.2. Self-amplification by spontaneous emission

If an electron bunch travels through just one undulator, the emitted power scales linearly with the number of electrons, N_e , which is due to the finite size and randomly distributed density of an electron bunch. If the electrons emit light from the same point or separated by $n \lambda_r$, with $n = (1, 2, 3, \dots)$, the emitted photons would constructively interfere. XFELs use this idea to generate their light pulses. XFELs have a straight and long undulator section⁴, where multiple undulators are connected in series. As the electron bunch travels through the XFEL 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. This slight velocity difference means that the co-propagating photons and electrons have a phase difference and interact with each other. Depending on the phase, an electron will either gain or lose velocity. Over each undulator period, we can

⁴LCLS has a 112 m long undulator section.

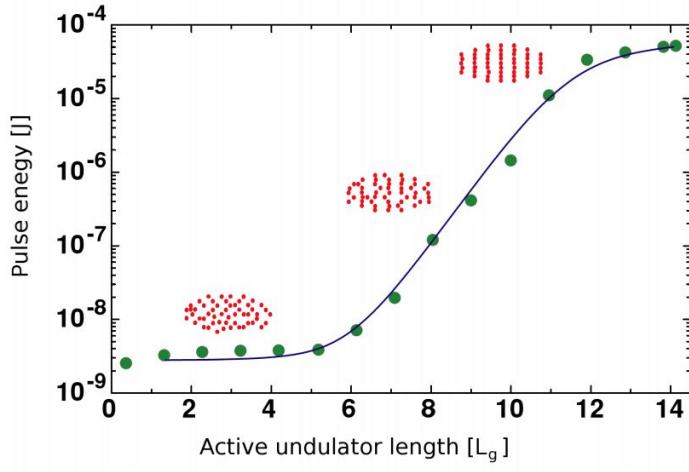


Figure 2.3.: Undulator gain curve correlated to microbunching. The X-ray pulse energy is plotted logarithmically over the undulator length L_g (blue curve, green dots) and shows an exponential growth until saturation. The electron bunch (red dots) starts with a random density distribution. As the bunch travels through the undulator, its density is modulated periodically such that the electrons microbunch. Upon optimal *microbunching*, the X-ray lasing process saturates. From [39, 40]

2. Fundamental Concepts

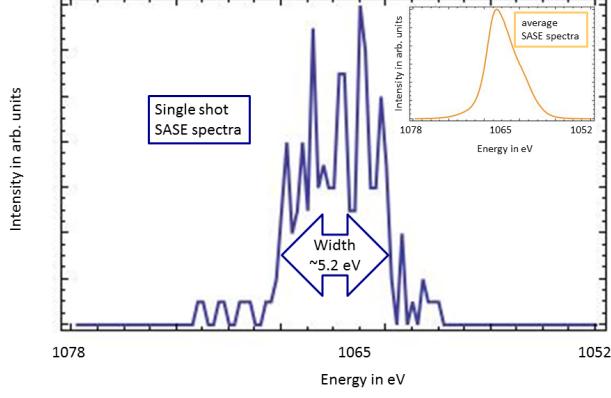


Figure 2.4.: The large blue spectra is a SASE spectra from a single LCLS shot measured with a photoelectron [see 41]. Note the spiky peak structure on a background pedestal. Within the narrow bandwidth of an XFEL pulse some energies are more strongly amplified due to the microbunching. The yellow graph in the inset is an average spectrum of several hundred single-shots and shows a low energy tail, which is due to XFEL-jitter.

describe this *slippage* with $\lambda_r(\Psi = 0)$. As a result, the initial uniform electron density is periodically modulated as it travels through the undulators of a FEL. The modulated electron bunch structure is called *microbunching*. The increasingly structured electron beam amplifies a narrower 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. This process is illustrated in Figure 2.3. The microbunching is defined by the initially emitted photons of pseudo-random wavelength, since the bunch amplifies these specific wavelengths as it travels through the undulators through subsequent spontaneous emission. Hence, this type of radiation (or XFEL operation mode) is called *Self-Amplification by Spontaneous Emission* (SASE). SASE achieves laser-like amplification of the radiation power P_{SASE} scales as [see 22, 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 photon-field because of the narrow spatial and kinetic energy distributions that define the so-called *emittance* of an electron bunch.

2.1. Why X-ray free electron lasers?

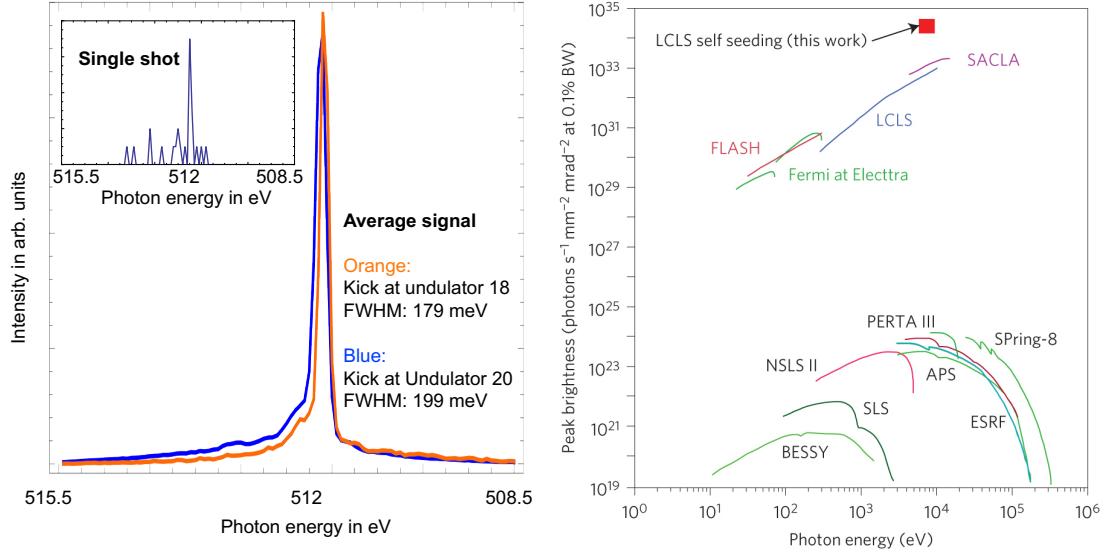


Figure 2.5.: Left, normalized average spectra of soft X-ray self-seeding (SX RSS) operations using the AMO instrument at LCLS [see 41]. The self-seeding spectra is characterized by a sharp spectral peak around a desired energy accompanied by a SASE-radiation-type spectral pedestal. The often undesired SASE pedestal is suppressed, when the electron bunch travel through undulators is shortened. The right image shows the peak spectral brightness of various light sources over a wide photon energy range. SX RSS operations have a spectral brightness that exceeds current SASE FEL sources. From [43].

Only the linear accelerator components of an 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, XFELs use one (compressed) electron bunch⁵ 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 [42], which leads to higher repetition rates and more narrow spectrum but fewer photons per pulse.

2.1.3. Soft X-ray self-seeding

Another free electron laser (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,

⁵the European XFEL uses a so-called *bunch train*, where multiple electron bunches are accelerated in series.

2. Fundamental Concepts

mostly this wavelength is amplified as the bunch travels through the undulator alongside the seed. The initial photon seed 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 case of the infra-red (IR) to extreme ultra-violet (XUV) wavelength range, conventional lasers can be used to produce the initial photon seed. However, due to the lack of lasers available at X-ray wavelengths, the idea of *self-seeding* gained traction. In self-seeding, an electron bunch is first sent 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 sent 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 panel of 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 LCLS SASE operations. However, in their main peak, self-seeded beams have a higher spectral brightness when compared to a SASE beam. Using Equation (2.1), the increase in spectral brightness compared to SASE is understandable and it is illustrated in the right panel of Figure 2.5. Self-seeded beam operations have recently been demonstrated at LCLS. For hard X-rays, the Hard X-Ray Self-Seeding (HXRSS) instrument uses a diamond crystal to select a wavelength slice [44]. At soft X-rays, the Soft X-ray Self Seeding (SX RSS) instrument uses a grating in a dispersive monochromator [45]. A seeded beam using an external laser to generate photons as an initial seed has been demonstrated at the XUV-FEL FERMI at Ellettra-Sincrotrone (ELETTRA) in Italy [46]. The peak intensity in a narrow spectral band makes seeded beams interesting for a variety of applications, particularly in spectroscopy, where it is instrumental to excite materials with narrow bandwidth photons. There are also applications in atomic and molecular physics, ranging from linear absorption spectroscopy [47], to ultrafast photoemission spectroscopy on molecules [41], to non-linear stimulated Raman spectroscopy [48], to ultra-fast photoemission studies. Particularly interesting for this work is the magnetic chicane from the SX RSS instrument when used as described in the next chapter.

2.1.4. Novel X-ray pump–X-ray probe techniques

In order to study X-ray induced phenomena using X-ray imaging and spectroscopy techniques, as it is discussed in this thesis, 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. 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 to verify time zero, or to probe the system before any dynamics have occurred. It is often desirable to have a pump- and probe-pulse of different wavelength. XFEL can produce two X-ray pulses of different wavelength and such types of operation are called “two-color” pump–probe schemes, which we will discuss in the following.

Creating two X-ray flashes to conduct a pump–probe experiment is a technical challenge, again, due to the lack of efficient X-ray optics. In order to overcome this challenge, two methods have been proposed. Method one is a mirror based beam-split and delay system [49, 50] that split one pulse into a pump- and probe-beam and allow the delay of the latter. These systems are typically limited to short time 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 [51, 52] 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 been useful complementing the more widely available optical laser pump–X-ray probe methods, particularly in the chemical sciences [30, 53, 54].

For two-color X-ray pump–X-ray probe experiments, current methods are limited to the parameters of Equation (2.7). The equation indicates possibly three schemes. 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 scheme 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 [55]. As the accelerator based X-ray pump–X-ray probe method has been used in the present work, let us describe these schemes in greater detail.

2. Fundamental Concepts

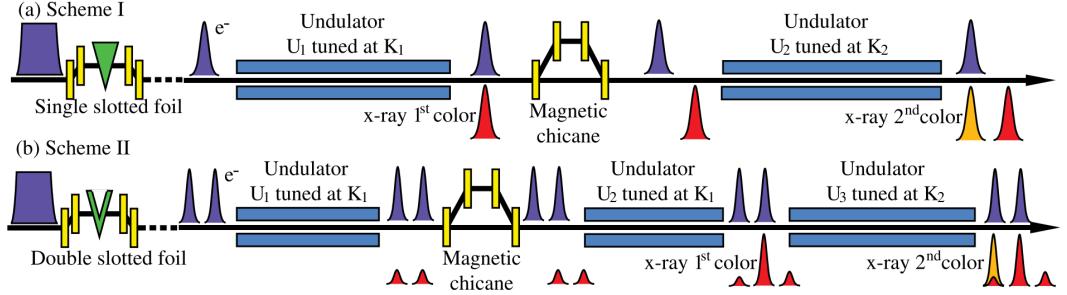


Figure 2.6.: Schematic setup of undulator parameter K_i based pump–probe schemes at LCLS. Scheme I) creates one electron bunch using a single slotted foil and scheme II) creates two electron bunches using a double slotted foil. The electron bunches emit radiation with a wavelength depending on K_i . A time delay Δt between pulses is introduced using a magnetic chicane. From [51]. Reprinted with permission from APS.

Undulator parameter- K based pump–probe schemes

The first developed accelerator based X-ray pump–X-ray probe technique at LCLS [51] uses a difference in undulator parameters, $K_{1,2}$, to create two pulses of different wavelength. The time delay is introduced through a magnetic chicane.

A schematic setup is shown in Figure 2.6. Following the figure to the top panel (a) Scheme I, one electron bunch is created through a single slotted foil⁶. The use of the slotted foil enables control over the pulse duration. The electron bunch then travels through the 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 the 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 between the two pulses is introduced by a magnetic chicane that extends the pathway of the electrons and leaves photons unaffected. At LCLS, a dedicated chi-

⁶A single slotted foil or emittance-spoiling foil works similarly 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 [56].

2.1. Why X-ray free electron lasers?

cane, for example, from the soft X-ray self-seeding instrument, can reach delays up to a maximum of 800 fs. In this scheme, several factors prevent a minimal time delay, Δt_{\min} , of zero. The minimal time delay opposed by the magnetic chicane, τ_{\min} , is dictated by the electron drift velocity mismatch to the speed of light. We can express that as,

$$\tau_{\min} = \frac{l}{v_{\text{drift}}} - \frac{l}{c} \approx 50 \text{ as}, \quad (2.9)$$

with $l \approx 4 \text{ m}$ being the length between undulator sections U_1 and U_2 , c being the speed of light, and v_{drift} being the drift velocity of the electron bunch. As the electron bunch drifts undeflected through the chicane close to the speed of light τ_{\min} is typically on the tens of attoseconds timescale. There is also a timing jitter between the two light pulses that is introduced by 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 imposed by the chicane. So, 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 as they travel through a undulator section. This mismatch can be estimated by

$$\Delta t_{\min} - \tau_{\min} = \frac{N_u \lambda_r}{c}, \quad (2.10)$$

with N_u being the undulator periods. Given the parameters in study [51], $\Delta t_{\min} = 3 \text{ fs}$, such that a partial overlap between the electron bunch and light pulse could be achieved after the magnetic chicane. It should be noted that this scheme has been used in the described experiment.

(b) Scheme II uses a double slotted foil⁷ to create two electron beams. The two beams have a longitudinal separation that translates into the time delay. 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 scheme, two saturated, lasing pulses can be generated; however, temporal overlap cannot be achieved.

⁷A double slotted foil works as a single slotted foil but it leaves two parts of the electron beam unspoiled through the two slots.

2. Fundamental Concepts

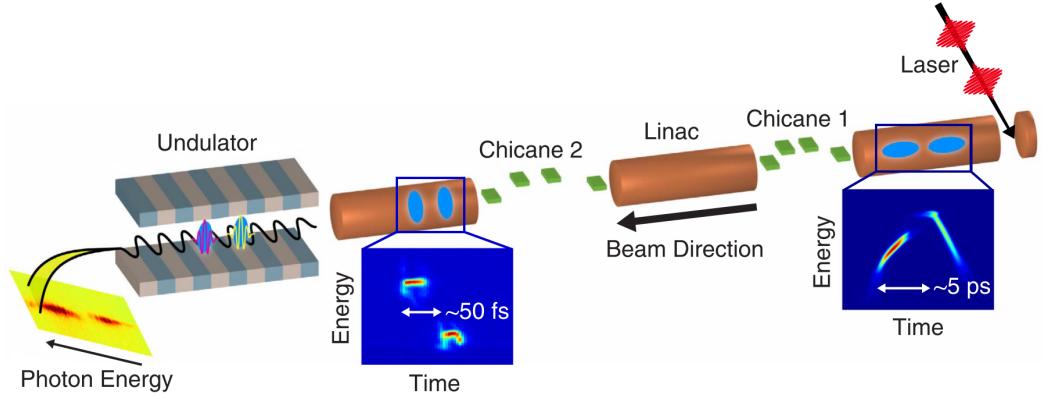


Figure 2.7.: Schematic setup of the two bunch, two color pump–probe setup at LCLS.

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 is on the ten femtosecond timescale. 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 [52, CC-BY].

The Twin bunch or Lorentz factor based pump–probe scheme

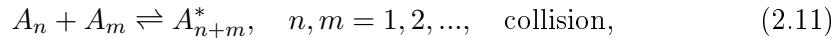
The second developed accelerator-based X-ray pump-X-ray probe technique at LCLS [52] uses two electron bunches of different energy. A schematic setup of this beam operation can be found in Figure 2.7. The electron bunches are created through a double laser pulse that impinges on a photocathode. Initially, these two bunches are delayed by 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 $\Delta t_{max} = 100fs$. For 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 with soft X-rays. In soft X-rays, the slotted spoiler foil can be used. This enables further control over the electron bunches and allows crossing time zero with both pulses.

2.2. Rare-gas clusters

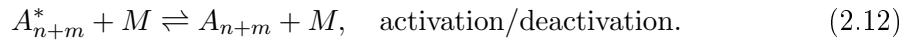
Clusters have a long history as samples to study the light-matter interaction for a few reasons. Their characteristics are well known, they can form interesting states, and they often have practical purposes [57]. Generally speaking, clusters are an aggregation of atoms or molecules and vary in size. 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 relatively 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 clusters typically form in an icosahedral⁸ shape when they are sufficiently small (up to nanometer sized) [58] and have mostly a fcc-crystal⁹ structure but exhibit also hcp-crystal¹⁰ structures [59, 60]. In the present work, superfluid helium clusters (or droplets), solid xenon clusters 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. Generation of homogenous clusters

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 [61]. In other words, clusters grow through collisions with monomer, dimer and other clusters. We can express a collision sequence 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 forms a metastable state A_{n+m}^* that will dissociate if no subsequent collision deactivates it



⁸An icosahedron is a polyhedron with 20 faces, i.e., a dice with 20 faces.

⁹fcc is an acronym for face-centered cubic. A very common crystal structure.

¹⁰hcp stands for hexagonal close-packed and is also a crystal structure.

2. Fundamental Concepts

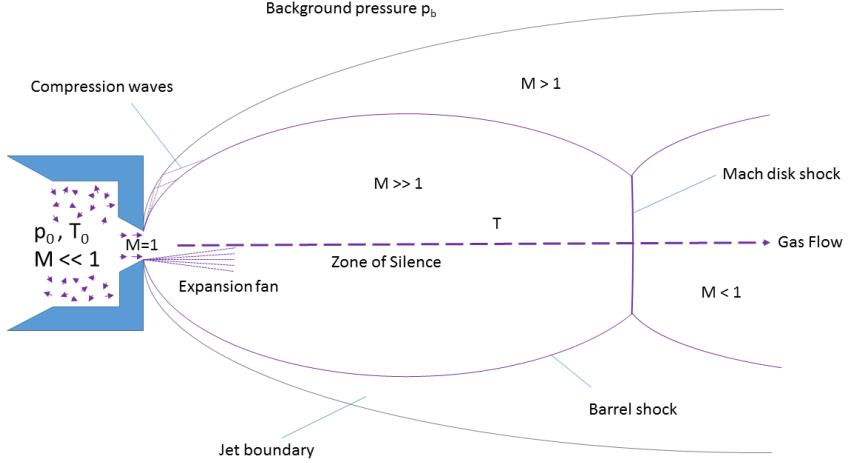


Figure 2.8.: Schematic of a supersonic gas expansion into the vacuum. Gas is stored in a reservoir at pressure p_0 , temperature t_0 and speed of the gas is thermally distributed ($M \ll 1$). As the gas enters the nozzle area, it is accelerated to the speed of sound ($M = 1$) and as the gas expands, the temperature T drops altering the speed of sound such that the gas now travels supersonically ($M \gg 1$). In this expansion, clusters are generated in the nozzle region, where $M = 1$ (see text for details). After [64].

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.

While the early stage of the cluster growth is driven by the monomer addition, cluster-cluster coagulation starts to dominate the later growth processes [62, 63]. This is due to the quantitative increase in small clusters in the generation process that then start to collide, similar to the above kinetic model. From empirical evidence, we know that clusters solely generated through monomer addition have a size distribution of an exponential decay with a rather large decay constant, whereas larger clusters that grew through coagulation follow a log-normal distribution. In other words, the density of smaller clusters including monomers and dimers decreases as larger clusters are formed of these particles through coagulation. 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 ¹¹. This is why many collisions occur during the expansion in the nozzle and the above described kinetic theory explains the cluster formation. However, this does not hold true in the supersonic molecular flow region, where no further cluster growth happens. To understand the expansion process in detail, we assume an ideal gas. To describe the gas expansion itself, we further assume that no clusters are formed and that turbulence and the effects of heat conduction are unimportant [57, 65].

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 by

$$H_0 = C_P T_0, \quad (2.13)$$

with the specific heat at constant pressure, C_P , for atoms

$$C_P = \frac{5}{2} k_B, \quad (2.14)$$

where k_B is the Boltzman constant. The expansion of the gas through the nozzle is driven by the pressure difference p_b/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 remaining enthalpy, H . So, in the expansion process, we can use the conservation of energy and Equation (2.14) to write down

$$H_0 = H + \frac{1}{2}m_{gas}v^2 = C_P T + \frac{1}{2}m_{gas}v^2, \quad (2.15)$$

with T being the local temperature along the gas flow and m_{gas} the atomic mass of the gas. To simplify, let us define the Mach number, M , as the ratio of the stream velocity, v , and the local speed of sound, c_s . We can express the local speed of sound as

$$c_s = \sqrt{\frac{\gamma k_B T}{m_{gas}}}, \quad (2.16)$$

with the ratio of specific heats $\gamma = \frac{C_P}{C_V}$ at constant pressure and volume. γ can be regarded as independent of temperature for atomic gases and we can rearrange Equation

¹¹A schematic drawing of the nozzle can be found in Figure 3.9. See also Equation (2.21) for non-pinhole nozzle openings.

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(2.15) to

$$T = T_0 \left(1 + \frac{1}{2} (\gamma - 1) M^2 \right)^{-1}. \quad (2.17)$$

Here the interplay between the Mach number and the local temperature give insight into the directed mass flow versus the remaining thermal energy in the system. As indicated in the Figure 2.8, M increases dramatically along the expansion axis and that is due to decrease in c_s , which is proportional to \sqrt{T} as indicated in Equation (2.16). The gas quickly reaches the terminal velocity while the speed of sound is decreasing. We may write the terminal velocity as

$$v_\infty = \sqrt{\frac{2R}{m_{gas}} \left(\frac{\gamma}{\gamma - 1} \right) T_0}, \quad (2.18)$$

with R being the universal gas constant. The expansion speed of the gas gives the name to such types of gas sources, namely supersonic jets. This equation is also useful to calculate gas or cluster flight times – $t_{\text{flight}} = \frac{D}{v_\infty}$ – if the distance D from nozzle to interaction point is known (see Section 3.4.1).

Let us describe the appearance of the jet stream (see Figure 2.8) next [64]. Upon exiting the nozzle, the Mach number increases by a wide margin ($M \gg 1$). This 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 or boundary conditions. As the supersonic flow exits the nozzle, it has to turn around the edge of the nozzle to further expand and it does so 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 shock* 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.

Helium	Neon	Argon	Krypton	Xenon
3.85	185	1646	2980	5554

Table 2.1.: Parameter K_{gas} values for rare-gases [68].

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 lose 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 [66]. Typically, the jet reaches temperatures of a few Kelvin and the cluster temperature is heavily dependent on their material, particularly the dissociation energy. Relevant for this study are the temperature of Xenon cluster, which is $\sim 75K^{12}$, and the fact that xenon clusters are solid as their melting temperature is higher [67]. 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 be apparent that the average cluster size is very much dependent on the gas type, stagnation temperature T_0 , stagnation pressure p_0 and the nozzle diameter. Indeed, an empirically found scaling law, named after Hagena [69–71], can be written down as

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

with the gas-specific parameter K_{gas} that can be found in Table 2.1 for some rare-gases, the gas specific parameter x 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} becomes [68]

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

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.,

¹²To put this temperature in perspective, krypton clusters are 50K and argon clusters 40K [66, 67].

Note that in this study the cluster size was $\bar{N} > 800$, hence above the minimum value to be size independent. For the evaporative cooling process to settle at a given temperature, a certain flight distance (in the cited study 6.5 cm) should also be taken into account.

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amount of accumulated particles per cluster $\langle N \rangle$, as follows

- $\Gamma^* < 350$, no cluster formation is 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 $\langle N \rangle$ is

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

Supersonic jets generally create clusters of different sizes. This size distribution is centered 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 [66, 72] has been used to determine the mean cluster size, mean temperature and mean geometry. Today, free electron lasers 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 [73].

2.2.2. Creation of heterogeneous clusters: The pickup principle

A possibility to create heterogeneous clusters is through the principle of picking-up atoms or molecules [57, 74]. 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

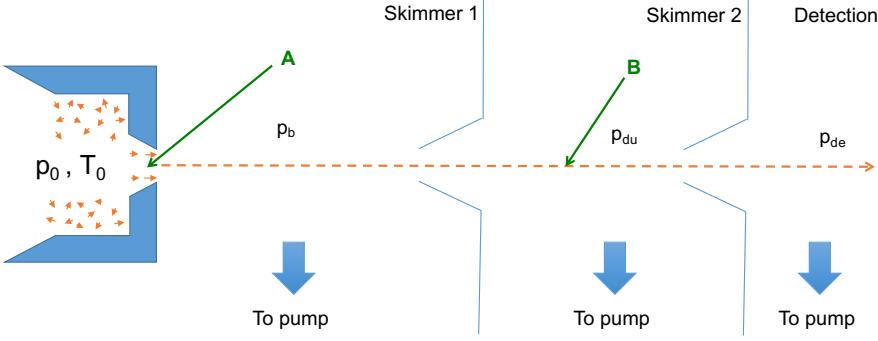


Figure 2.9.: Schematic setup to generate heterogeneous clusters through pickup. Thereby is a cluster generated via supersonic gas expansion, which is doped at regions marked A or B. In region A, the dopant gas is mixed in the nozzle such that it becomes part of the nucleus. In region B, the cluster condenses atoms on its surface from the background gas of pressure p_{du} . The cluster can be detected upon evaporation, e.g., due to contact with the chamber, through the pressure p_{de} . After [57, 74].

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 $p_{b2} = 10^{-11}$ bar over a pickup length of a few centimeters can dope the cluster significantly. 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. In this work, gaseous xenon was picked up by superfluid helium droplets in region B. To understand doping levels, the following considerations are helpful.

The collision with the cluster and a dopant does add energy to the cluster, as does the cluster growth process itself. This is why the initial cluster will lose particles through evaporation upon pick up of a dopant [75]. The loss of particles through evaporative cooling is dependent on the ratio of dissociation energies of the two materials and can be expressed 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

2. Fundamental Concepts

of helium, $\epsilon_{He} \approx 0.6 \cdot 10^{-3}$ eV, and xenon, $\epsilon_{Xe} \approx 0.15$ eV [10, 75], to conclude that approximately 250 helium atoms evaporate by picking up 1 xenon atom.

Now we can extend this idea to estimate the number of picked-up atoms, if we were to know the number 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. An estimate of the cluster size after the pickup can be established through measuring the partial pressure of the cluster material without the pickup, p_{de} , for example, in the detection chamber when the particle jet hits a wall and evaporates¹⁴ (see Figure 2.9), and the partial pressure with pickup, Δp_{de} . The relative difference $\frac{\Delta p_{de}}{p_{de}}$ then scales with

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

and the amount of picked up atoms, $\langle N_{\text{dopant}} \rangle$, can be estimated on average.

2.3. Soft X-rays in matter

When light interacts with a nanoparticle it either scatters or is absorbed. Although XFEL are intense lightsources, we can reduce the considerations in this section to the elastic and coherent scattering as well as relevant resonant effects. The Section 2.3.1 discusses the scattering of an electron and extends this concept to the scattering and imaging of a nanoparticle. The Section 2.3.2 discusses several effects due to absorption and the Section 2.3.3 discusses effects that occur after the absorption of a photon. This way, we follow the discussion in [22] and avoid effects that have negligible cross-sections such as the Compton effect, the pair-production, and the scattering from the nucleus.

2.3.1. Diffractive imaging

When light interacts with nanoobjects the fundamental scatterers are electrons. Let us first consider the scattering of an electron as a result of being accelerated in an electromagnetic field, i.e., a light wave. Then, we proceed to the scattering of an atom followed by the scattering of an extended object with a continuous electron density.

Let us introduce the electric field of an incident wave $E_{in} = E_0 e^{-i\omega t}$ that will irradiate an electron. The electron is accelerated in this electric field and will thus start to emit

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.

2.3. Soft X-rays in matter

radiation similarly to a small dipole antenna. We can write this radiated electric field as [22]

$$E_{rad}(R, t) = - \underbrace{\left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right)}_{r_0} E_{in} \frac{e^{ikR}}{R} \cos(\psi), \quad (2.26)$$

with k being the usual wave-number, R being the distance from the source of radiation, ψ being the observation angle, and r_0 being the *Thomson scattering length*, or the *classical electron radius*. r_0 can be written in practical units as

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \cdot 10^{-5} \text{ Å}, \quad (2.27)$$

where $-e$ is the charge of the radiating electron, m is the mass of the electron, c is the speed of light, and ϵ_0 is the permittivity of free space.

Now we would like to understand the cross-section of this scattering process better. We can establish a *differential cross-section*, $(d\sigma/d\Omega)$, which follows the same concept of the already discussed example in Equation (2.2). The only difference is that we now consider a scattered intensity, I_{sc} , of an incident flux, (I_0/A_0) , into a solid angle, $\Delta\Omega$. We may express this as

$$\left(\frac{d\sigma}{d\Omega} \right) = \frac{I_{sc}}{(I_0/A_0) \Delta\Omega} = \frac{|E_{rad}|^2 R^2}{|E_{in}|^2} = r_0^2 \cos^2(\psi). \quad (2.28)$$

By integrating over the full angular space, the total cross-section of the scattering of an electron, σ_T , results in

$$\sigma_T = \left(\frac{8\pi}{3} \right) r_0^2 = 0.665 \text{ b} \quad (2.29)$$

We can now move on and use this knowledge for atoms, where we have Z electrons. To describe electrons in an atom, let us introduce an electron density $\rho_e(\vec{r})$ that describes the probability density of electrons in an atom. Figure 2.10 illustrates the scattering process by one atom. An incident beam, with wave vector \vec{k} , is elastically scattered at a point \vec{r} into a wave with \vec{k}' such that $|\vec{k}| = |\vec{k}'|$. As the illustrated waves are scattered at different points, they have an optical path difference of 2δ . This difference in path length results in a phase difference in the wavefront, which leads to interference. We can

2. Fundamental Concepts

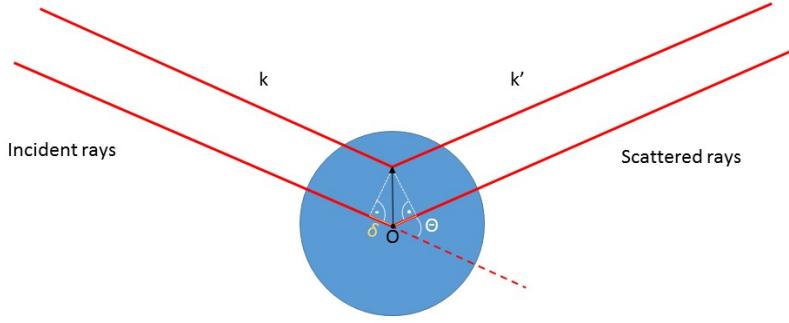


Figure 2.10.: Principle of scattering rays of an atom. After [22, 76].

describe this 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 $d\vec{r}$ of the atom at \vec{r} will now scatter proportional to 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 scatterers are in phase. As we increase the angle Θ , the phase difference, $\Delta\Phi(\vec{r})$, leads to interference. We can describe this by multiplying a phase factor $e^{i\vec{Q}\cdot\vec{r}}$ to the contribution of the scattered field, $-r_0\rho(\vec{r})d\vec{r}$. In the limit of $\vec{Q} \rightarrow \infty$, the atomic scattering factor then is $f^0(\vec{Q} \rightarrow \infty) = 0$. We can integrate to obtain the total

scattering volume, and note

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

This important result is called the atomic scattering factor in units of $-r_0$. It can be understood as a Fourier transformation of the electron density of an atom.

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

$$F^0(\vec{Q}) = \sum_{\vec{r}_j} f_j^0(\vec{Q}) e^{i\vec{Q}\cdot\vec{r}_j}, \quad (2.34)$$

with the atomic scattering factors $f_j^0(\vec{Q})$ for the j 'th atom and call F^0 the single particle *structure factor*. However, it is well known that for coherent and monochromatic radiation the scattered amplitude, $A(q)$, of a nanoparticle can be written in the kinematical approximaton¹⁵ as follows [77]

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

where $\rho(\vec{r})$ is the electron density of the scattering nanoparticle. The scattered intensity in a diffraction pattern can be expressed by

$$I_{sc}(\vec{Q}) = I_0 |A(\vec{Q})|^2 \quad (2.36)$$

where an incident beam with intensity I_0 ¹⁶ and complex amplitude A performs an operation that can be interpreted as a Fourier transformation of the object's electron density. The process of measuring the scattered light, for example through a detector, merely measures the scattered intensity and thus only 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 an image of the nanoparticle that scattered, for example to understand its shape or to study its function, we need to recover the phase information. We will discuss iterative algorithms that can recover the phase factor in Section 4.3.

Let us now make use of above's theory and address the scattering of a rare-gas cluster, as

¹⁵Sometimes called the weak-scattering limit, where multiple scattering effects are neglected.

¹⁶Here, we make use of the Born approximation and the intensity of the incident beam becomes constant, which holds true in the kinematical approximation

2. Fundamental Concepts

they will reoccur throughout this thesis. We may thus express an electron density of the desired object and Fourier transform it into reciprocal space to understand diffraction patterns better. Due to current resolution limitations¹⁷, we may approximate the shape of a few nanometer-sized cluster with a sphere. The density, ρ , of a hard sphere with radius, r , can be expressed by

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

Using Equation (2.37), we can solve the integral in Equation (2.35) by making use of spherical coordinates,

$$A_{\text{sphere}}(\vec{Q}) = \int_0^\pi \int_0^{2\pi} \int_0^r \bar{R}^2 \sin(\Theta) e^{i\vec{Q}\bar{R}\cos(\Theta)} d\bar{R} d\Theta d\Phi \quad (2.38)$$

$$= \rho \left(\frac{4}{3\pi} r^3 \right) \frac{\sin(\vec{Q}r) - \vec{Q}r \cos(\vec{Q}r)}{\vec{Q}^3 r^3}. \quad (2.39)$$

Formula (2.39) can be exploited to determine the size of a spherical particle, i.e., a cluster, using local minima in the diffraction pattern¹⁸ or through a numerical fit of the resulting curve.

2.3.2. Ionization of matter

Last section, we established that an electron was accelerated by a light field and radiated as a result. But it is not only the light field that drives the electron, also the electron has an effect on the light field. As the wave propagates through a medium, for example from air through glass, it interacts with it and changes direction according to Snell's law [22]. Here, a medium is attributed a refractive index,

$$n \equiv \frac{c}{v_{\text{phase}}}, \quad (2.40)$$

where v_{phase} is the phase velocity, to account for this interaction. n is wavelength dependent and for visible wavelengths it ranges between 1.2 and 2. X-rays have usually higher energies than the transition energies of most atoms and the refractive index turns out to $n < 1$. As a result one usually speaks of a *phase advance* as an X-ray field traverses

¹⁷Considering experimental details from Chapter 3

¹⁸Equation (2.39) can be solved numerically for the distance between the first two minima, \vec{Q}_{\min^n} and $\vec{Q}_{\min^{n+1}}$, such that $r = \frac{3.24}{\vec{Q}_{\min^{n+1}} - \vec{Q}_{\min^n}}$.

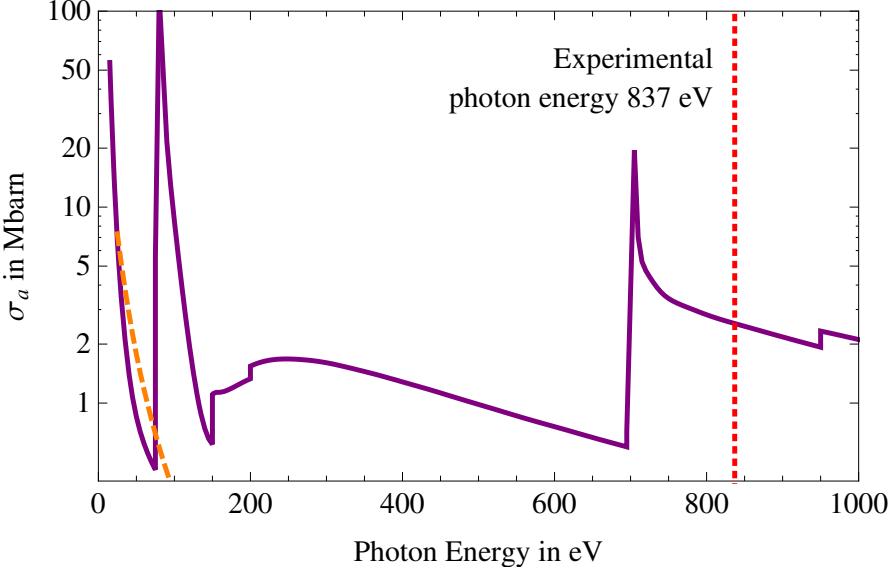


Figure 2.11.: Total absorption cross-sections σ_a in megabarn for xenon (purple line) and helium (orange dashed). The photon energy of the described experiment is ~ 837 eV (red dashed). Data points from [79–81].

an object. Intuitively there must be another aspect to consider when the light wave is traveling through a medium. This is a reduction of the amplitude of the incoming light wave. Particularly, when the energy of the photons is higher than the binding energies of electrons there must be absorption. We shall not derive this topic to its full extent as it can be found in [78, p. 55 ff], but we shall qualitatively compare the equation for the complex refractive index $n(\omega)$ to the atomic scattering factor, $f^0(\text{vec}Q)$, which was introduced in the last section. For simplicity, we reduce the following considerations to the case of forward scattering, where $\vec{Q} = \Theta = 0$.

Imagine an electro-magnetic wave propagating in a medium with the above considerations. The wave travels along the z -axis and can be written as [22, 78]

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

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 wave¹⁹. The relation between the complex refractive index

¹⁹We jump between the 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

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

Let us now consider the atomic scattering factor. One would imagine that the acceleration of a bound electron in an atom is affected. Electrons that are tightly bound, e.g., in the K-shell, are less “free” than those with little binding energy. Overall, the atomic scattering factor must be reduced by a wavelength dependent amount, which we denote as f' . The other wavelength dependent effect is absorption, which we can introduce as f'' . These two effects are called dispersion corrections to the atomic scattering factor, f^0 . Let us include these corrections to the atomic scattering factor and note

$$f(\vec{Q} = 0, \hbar\omega) = f^0(Q = 0) + f'(\hbar\omega) + if''(\hbar\omega). \quad (2.43)$$

In the limit of high photon energies $\hbar\omega$, bound electrons can be largely seen as free, as the binding energies become a minor 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 can compare Equation (2.42) to Equation (2.43) and realize that we are allowed to define the dispersion relation through the atomic form factor as [see 22, p. 76]

$$n = 1 - \frac{2\pi\rho_{\text{atom}}r_0}{k^2} \left(f^0(\vec{Q} = 0) + f'(\hbar\omega) + if''(\hbar\omega) \right), \quad (2.44)$$

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

$$\delta = \frac{2\pi\rho_{\text{atom}}r_0}{k^2} \left(f^0(\vec{Q} = 0) + f'(\hbar\omega) \right), \quad \text{and} \quad (2.45)$$

$$\beta = - \left(\frac{2\pi\rho_{\text{atom}}r_0}{k^2} \right) f''(\hbar\omega). \quad (2.46)$$

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 (2.46) and define $f''(\hbar\omega)$ in terms of being proportional to an absorption cross section, σ_a , which reads

$$f''(\hbar\omega) = - \left(\frac{k}{4\pi r_0} \right) \sigma_a. \quad (2.47)$$

Figure 2.11 shows the total absorption cross-sections σ_a for xenon and helium at various photon energies. The photon energy of the experiment was 837 eV. For helium, the

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 [82].

photon energy is much greater than the binding energy and thus the absorption cross-section is low. For the tightly bound electrons in xenon, the absorption cross-section is relevant as the photon energy is near the atomic levels. The absorption cross-section shows a resonant-type behavior, when the photon energy would be directly on an atomic level. To get a better understanding of the absorption cross-section with regard to atomic levels, 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 experimental photon energy 837 eV for xenon and helium. The calculations were performed with the Los Alamos Atomic Physics code based on [82]. It appears that certain energy levels, or here subshells if one disregards the hyperfine structure²⁰, 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 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 struc-

²⁰A shift in energy levels due to interaction of electrons with the nucleus [see 83, p 166 ff.].

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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 [82].

ture 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 tightly 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 number of ionization configurations can become rather complex and the table shall give the reader merely a broad understanding of some likely configurations.

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 $\sim 75\%$, 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 processes²¹ 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 $\sim 0.05\%$. 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

²¹See the following Section 2.3.3.

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 [84].

comparably high absorption cross-section for xenon – but is off the 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 transparent.

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 usually 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 signal, the discrete peaks are element-specific and modern photoemission spectroscopy can yield insight into, for example, element identification, excitation dynamics or chemical bonding. The left panel of Figure 2.13 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 photon-finding algorithm as the signal from just one fluorescence photon splits into multiple pixels. The coalescent-photon finding algorithm looks for pixels above a certain threshold and includes neighboring pixels above a certain, lower threshold, thus correcting the measured signal to yield a proper ADU count per photon.

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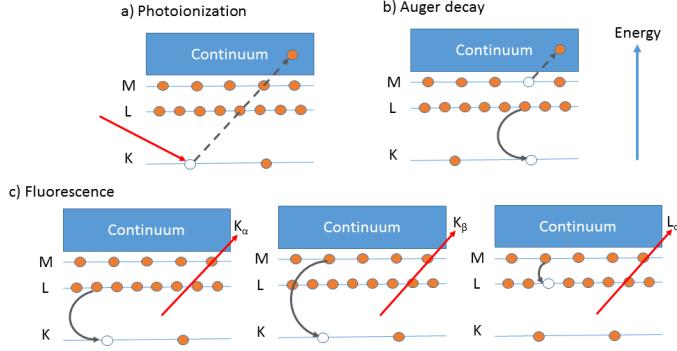


Figure 2.12.: Schematic illustration of common charge transfer processes. a) Photoionization: Describes a direct emission of a K-shell electron after absorbing an X-ray photon. b) Auger decay: A relaxation process, where a K-shell hole is filled with an electron from the L-shell and the remaining energy is released through emission of an electron in an outer shell. c) Fluorescence: An electron hole is filled with an electron from an outer shell and the remaining energy is released through photons. After [22, p. 19].

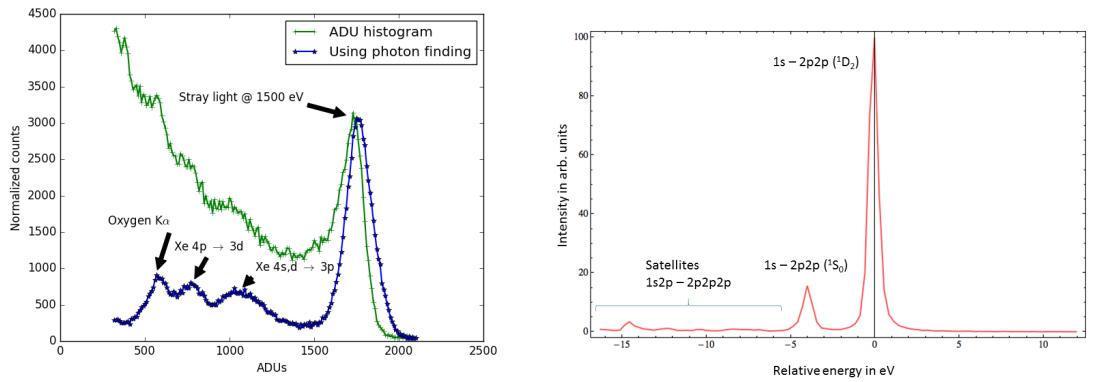


Figure 2.13.: Left spectra shows fluorescence peaks from xenon and oxygen illuminated with 1.5keV photons from the LCLS; detected with pnCCD detectors [85, 86]. The green curve is an ADU histogram of the pnCCD detector and the blue curve uses a coalescent photon finder. Right, partial K-LL Auger spectrum with rel. energy 0 corresponding to 804.5 eV. Spectrum measured with photoelectron spectrometer [41], peaks identified as in [87].

2.4. Ionization of clusters in intense X-ray pulses

The Auger decay is another possibility for the atom to emit energy through a two-step process. One, an outer shell electron is emitted into the continuum, the so-called *Auger-electron*²². Two, another electron in the atom simultaneously fills the electron-hole. An *Auger decay* occurs typically on the few femtosecond timescale after ionization [87]. 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-LL²³ Auger spectrum from neon illuminated by 1050 eV photons from the LCLS and measured with a hemispherical analyzer as described in [41]. In this example, neon is ionized in the K-shell and an electron-hole in the 1s shell is created. An electron from the L-shell fills 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 already ionized, for example, the atom has a hole in the L-shell and then an absorption that creates another hole in the K-shell. This 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 [88].

2.4. Ionization of clusters in intense X-ray pulses

The response of a cluster upon irradiation with light often differs from just the atomic 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 [89]. In this section, we study how rare-gas clusters respond to femtosecond long, high intense X-ray pulses and reflect on recent experiments.

²²Named after the French physicist Pierre Auger.

²³This nomenclature means a single hole in the K-shell is followed by a two holes in the L shell after the Auger decay.

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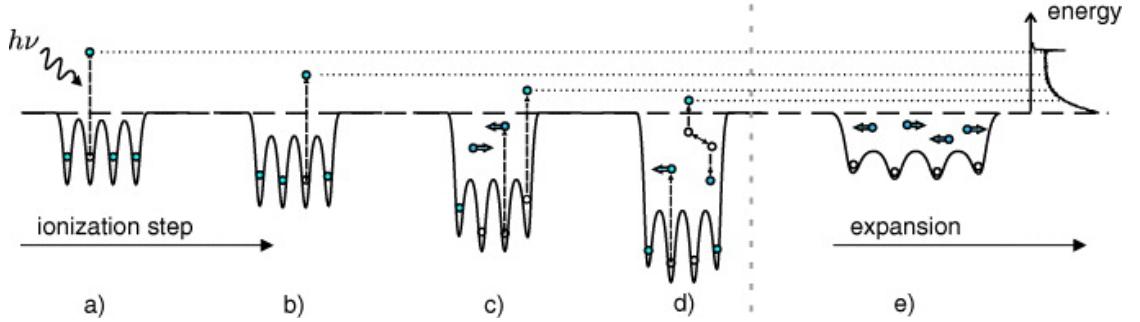


Figure 2.14.: Schematic of the nanoplasma creation and expansion. In step a) X-ray photons ionize electrons from a cluster. b) Subsequent *multistep ionizations* try to relax the electronically excited system, deepening the Coulomb potential of the cluster. Step c) shows a deepened Coulomb potential 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 [90,].

2.4.1. Formation and expansion of a nanoplasma

Let us recapture the scattering and absorption effects discussed in last section Section 2.3. Equation (2.35) indicates how the diffracted amplitude of a nanoparticle can be calculated. Although we disregard inelastic or incoherent processes, the modulo of the amplitude is close to actual measured scattering patterns. However, if we consider the resonant effects discussed in Section 2.3.2, it should be clear that the structure factor of a nanoparticle is affected by the dispersion corrections $f'(\omega)$ and $f''(\omega)$ that reduce the atomic scattering length, $-r_0 f^0(\vec{Q})$. On the one hand, a dominating change in the atomic scattering length is driven by the absorption process that we introduced via the imaginary dispersion correction $if''(\omega)$. Upon ionization, the atomic scattering factors, $f^0(\vec{Q})$, change as the absorption cross-sections start to vary. These small changes are indicated in Table 2.3 and such processes are expected to occur on the few femtoseconds timescale, on which the ionization dynamics occur. Additionally, due to photoionized electrons in the atom, the atomic scattering factors change on the few femtoseconds timescale. Such small changes are indicated in Table 2.4. On the other hand, there are X-ray induced effects that change the scattering behavior of the collective of atoms, i.e., the cluster. We know from previous experiments [16] that these changes are related to the nanoplasma expansion and can significantly affect diffraction patterns.

Let us follow Figure 2.14 and [90, 91] in the next five steps to get a better understanding

2.4. Ionization of clusters in intense X-ray pulses

of the nanoplasma phase-transition. Step a) of the nanoplasma transition, the cluster gets ionized due to intense radiation²⁴. Step b), further ionization through emission of photo electrons and Auger electrons lead to a so-called *multistep ionization* that steepens the Coulomb potential [92–94]. 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 nanoplasma²⁵. 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 to a (kinetic) energy distribution of the electrons that is similar to thermal distributions and can be measured via the spectra of evaporated electrons [95, 96]. 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 developing hot plasma and the resulting increase in outward pressure, whereas the Coulomb portion comes from the repelling force of like charges. Both 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 [97]. 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 like charges with each other [98].

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 [99]. 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 [90]. It remains to discuss the radiation intensity, which affects the ultimately achieved charge-state combination. The more intense the radiation

²⁴The 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.

²⁵Plasma 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.

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is, the more energy is absorbed by the cluster. For the nanoplasma this determines the electron temperature and possibly the expansion speed.

2.4.2. Imaging of transient states

To study the nanoplasma transition, a coincident imaging and spectroscopy technique has proven successful [100]. First experiments aimed to reveal correlations between the diffraction patterns and the ion spectroscopic data [33, 101]. The advent of pump–probe techniques has been combined with the coincident measuring technique and recently, snapshots were taken of the expanding electron density [16]. The snapshots are shown in Figure 2.15. In this particular study, an infra-red laser (pump) was used to cause a nanoplasma transition in a xenon cluster and subsequently image this state with an XFEL pulse (probe). 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, $\Delta t > 100$ fs. The loss in signal could be explained through an expanding electron density [102, 103]. The electron density expands increasingly over time due to the Coulomb and Hydrodynamic forces. First, the outer layers expand, and second, for larger time delay also the inner atomic layers start to expand. In that study, an electron temperature of ~ 200 eV could be measured by comparing plasma simulations to the ion spectroscopy signal. The spatial resolution of the diffraction patterns has been estimated to be 8 nm, but by assuming a spherical shape of the clusters, the electron density model is sensitive below this resolution.

In another study with shorter time delays of $\Delta t < 100$ fs, xenon clusters compress in size [53]. Since clusters form as a crystal²⁶, one can determine their structure through crystallographic approaches as it is explained in full detail in [22, chapter 5]²⁷. Figure 2.16a shows Bragg peaks, which occur under certain conditions over the scattering vector, \vec{Q}_{peak} . In the figure, the signal moves to larger scattering vectors and, as $\vec{Q}_{\text{peak}} = \frac{2\pi}{a}$, the unit cell length a shrinks over the time delay $\Delta t = (0 \text{ to } 100)$ fs. This unintuitive and contradictory result is attributed to the changes in electronic configuration upon ionization. Electrons that are trapped in the cluster’s Coulomb potential have an increased mobility and are able to contribute comparably to valence electrons and, therefore, change

²⁶See Section 2.2.1.

²⁷In short, crystals scatter light and create Bragg spots at large \vec{Q} -values. These Bragg spots occur when Bragg’s law is fulfilled. Bragg’s law reads $m\lambda = 2d\sin\left(\frac{\Theta}{2}\right)$, 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

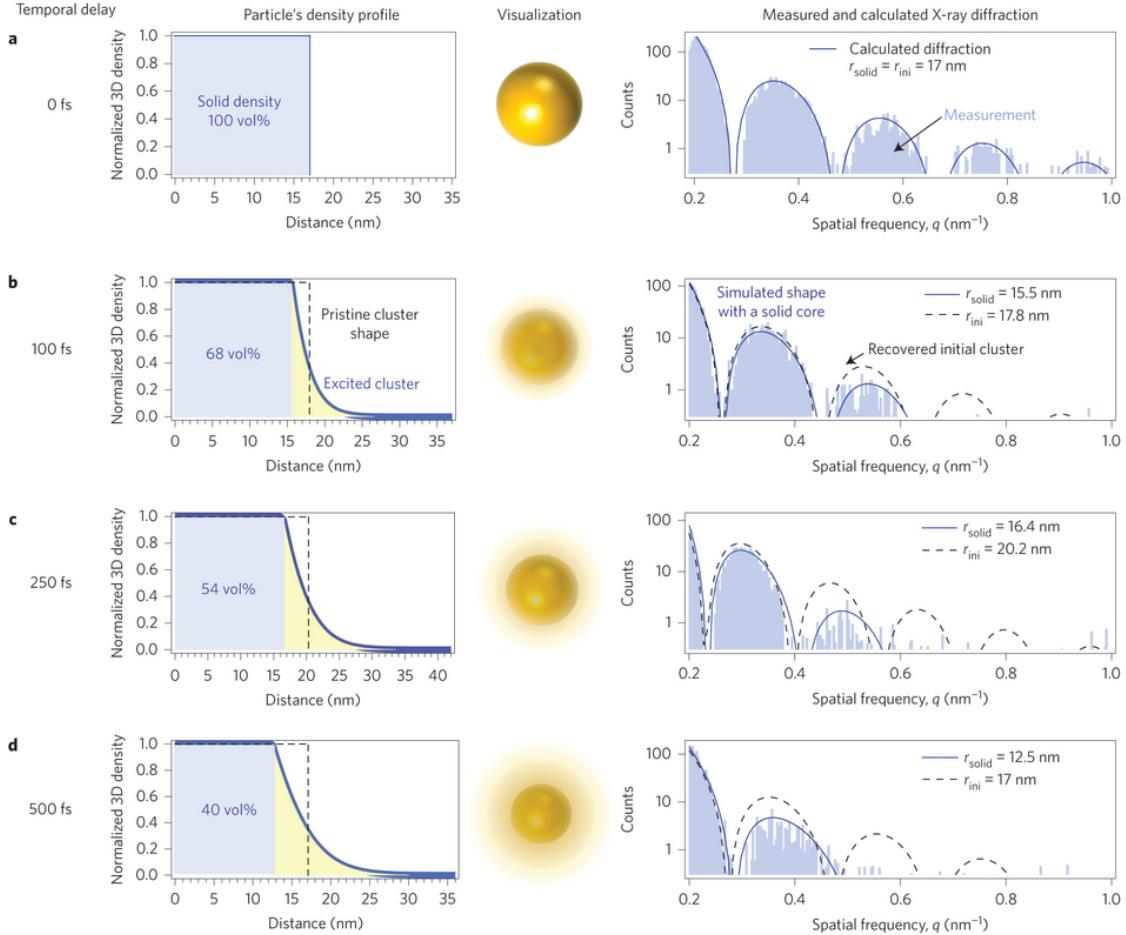


Figure 2.15.: Xe-clusters after being pumped with a NIR laser pulse and probed at a certain time delay (indicated left) with a LCLS pulse. Left series, simulation of electron densities. Right series, measured diffraction patterns. The diffraction patterns show a decrease in intensity at larger q values, when the delay is increased. This can be explained through expanding electron densities, i.e., a nanoplasma expansion. Fourier transformation of electron densities are fitted to the measurement for a solid sphere (dashed line) and an expanding sphere (solid line). From [16]. Reprinted with permission from Nature Publishing Group.

2. Fundamental Concepts

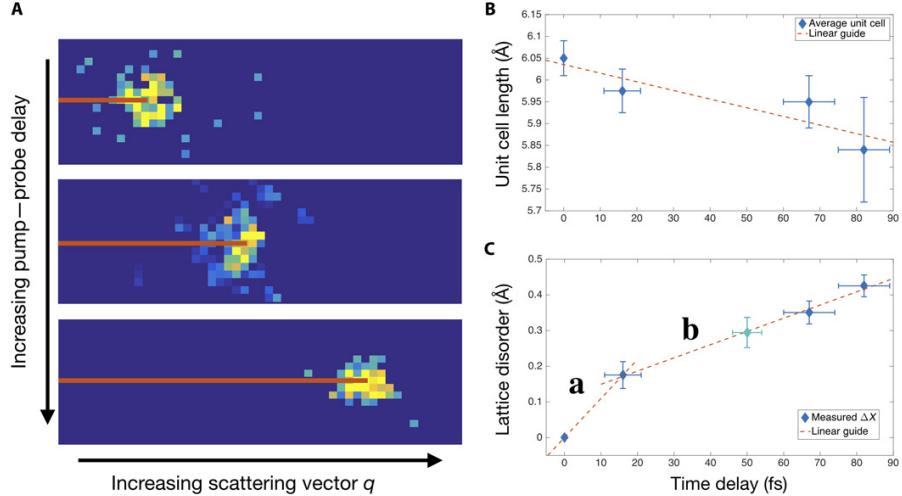


Figure 2.16.: X-ray pump–X-ray probe scattering experiment on an Xe-cluster that shows an early evolution of the nanoplasma transition. A, single-shot Bragg peaks at varying time delays. The scattering vector q increases over time delay. B, unit cell length over time delay. The unit cell length decreases, therefore the cluster shrinks in size. C, Lattice disorder over time delay. The measured fcc lattice is becoming disordered after being pumped with an X-ray pulse. From [53]. Reprinted with permission from AAAS.

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 the sample disintegrates into its atomic components.

2.4.3. Tampered layers to inhibit the nanoplasma expansion

As we have discussed, the nanoplasma phase-transition occurs on the femtosecond timescale and affects diffraction patterns. To *outrun* this radiation damage, pulses from the XFEL must be shorter than the lifetime of Auger processes, thus a few femtoseconds long. And by limiting the XFEL pulse duration, one limits the pulse energy as current bunch compression methods typically generate much less fluence. Often, this fluence is not enough

2.4. Ionization of clusters in intense X-ray pulses

and means that many coherent diffractive imaging experiments are currently performed with pulse widths of 40 fs 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 few-femtoseconds long pulses have spatial resolution limitations [8]. To be more precise, it is an open question, whether electron densities and particular bonding configuration are obtainable by solely outrunning radiation damage. Although radiation damage is unavoidable it can be mitigated in several ways. One way to mitigate radiation damage is to simulate the effects, however, this can only be done for small particles. Another way is to fundamentally increase resolution in single particle imaging 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 [18], but it is currently unknown, whether this is applicable for larger molecules. The strong light fields that are needed to align the molecules, may change their structure. Here, it should be noted that recent advances with diffractive imaging algorithms made it possible to computationally determine the orientation of a particle at the time of imaging [11, 104]. The orientation can be automatically determined – without prior knowledge – when at least a few hundred diffraction images are provided. However, in this thesis, we shall discuss a method to reduce the effects of radiation damage through artificial tamper layers. Artificial shells around a sample supply it with electrons and function as a sacrificial layer that protects the sample [20]. For aerosol particles, this method has only been investigated through ion spectroscopy [105, 106].

In the study shown in Figure 2.17, a core-shell system of argon and xenon was constructed and here xenon is to the sample and argon corresponds to the sacrificial layer around the particle (see figure). The heterogeneous clusters were irradiated with 93 eV photons from *FLASH*²⁸. At this photon energy, mostly xenon atoms are ionized. As described in the nanoplasma creation process (see Section 2.4.1), the increasingly 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 ArXe with 400 particles (Figure 2.17 top-panel), the time of flight mass spectroscopy data show Xe and Ar ions. These ions mean that the charge recombination is suppressed and the cluster disintegrates upon irradiation. In the large ArXe-cluster system with 4000 particles (bottom-panel), mostly Ar ions are in the TOF data. These ions mean that the Xe-ions in the center of the cluster recombine with the electrons that were attracted to

²⁸Short for **F**ree electron **L**ASer in **H**amburg. An extreme ultra violet (XUV) free electron laser in Hamburg, Germany.

2. Fundamental Concepts

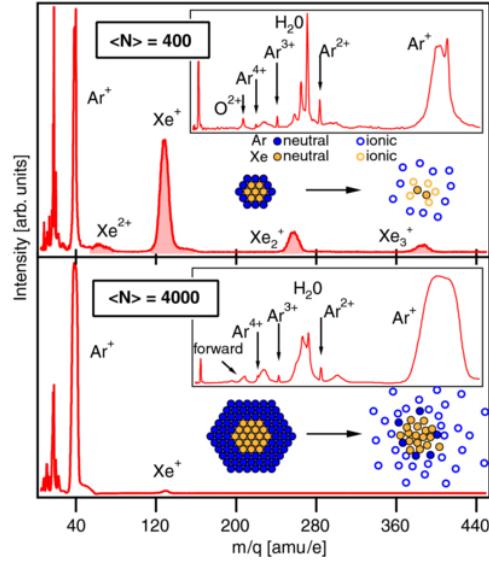


Figure 2.17.: Time of flight (TOF) traces of argon and xenon core shell systems irradiated with 93eV X-ray pulses from FLASH. At this energy, mostly Xe is ionized and the ionized atoms create a steep Coulomb potential that traps electrons towards the center of the cluster. The top panel shows smaller 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 xenon remains undetected. From [105, CC BY].

2.4. Ionization of clusters in intense X-ray pulses

the center of the core-shell system due to the steep Coulomb potential of the large cluster. Neutrally charged xenon is not detected by the TOF detector. The Ar-ions in the outer layers contributed electrons to the center of the cluster but were shed off the mixed ArXe-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 a size-dependent effect that shows an energy transfer process from the initially ionized Xe-core to the Ar-shell.

3. Experimental Setup

The experiment described in the present thesis has been performed using the LAMP end-station in the Atomic, Molecular and Optical (AMO) Physics instrument of the Linac Coherent Light Source, which is located at 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 [107–109] and many other accomplishments [13, 110]. SLAC’s research topics broadened in the 70’s and with the Stanford Synchrotron Radiation Project, SLAC became an 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 and it is now known as the LCLS. The LCLS began operations in April 2009 [13] and the AMO instrument started user operations in October 2009 [111]. AMO began operations using the High-Field Physics (HFP) and CFEL¹-ASG² Multi Purpose (CAMP) end-station, however, the so-called “LAMP” end-station was commissioned in September 2013 and has been in use at AMO since then. The experiment described in this thesis was performed in January 2014³ in the LAMP end-station of the AMO instrument.

This chapter is organized as follows; Section 3.1 discusses the the details of the AMO instrument; Section 3.2 focuses on the specifics of the LAMP end-station; Section 3.3 goes over the pnCCD detector and its geometry; and Section 3.4 centers around relevant aspects of the sample delivery. The chapter ends with Section 3.5 that describes the time-of-flight (TOF) detector for the LAMP end-station.

¹Acronym for the Center for Free Electron Laser Science on the DESY campus in Hamburg, Germany.

²Short for the Advanced Study Group of the Max Planck Society in Hamburg, Germany.

³Experimental identifier at SLAC: AMOA1214

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

The AMO instrument is located closest to the undulators of the LCLS at hutch 1. It is designed for soft X-ray photons in the energy range from 280 eV - 2000 eV [112, 113], 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 through vacuum to the Front End Enclosure (FEE) [114], where the electron beam is deflected using magnets and subsequently dumped in a beam stop such that only X-rays continue. Optionally, the XTCAV [115] 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. An X-ray pulse energy monitor, often referred to as a gas detector, measures the pulse energy of a single shot before and after the attenuation [116]. 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 used. SOMS are a set of three mirrors, where the first two are shared with hutch 2, which is named the Soft X-ray (SXR) instrument [117–119] and the third one is dedicated to the AMO instrument. The AMO instrument is versatile in its configuration and three different end-stations have been used so far. In historic order, one, the HFP end-station [111, 113], two, CAMP end-station [120], and three, the LAMP end-station [85, 112]. As the experiment described in the present work has been performed with the LAMP end-station, we shall focus on that AMO-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 diagnostic viewer (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 of the SOMS angle and position can be determined with sub-millimeter precision. The projection also reveals the alignment of the beam with respect to several differential pumping apertures that are located in the FEE and the beam should be centered to those apertures [121]. In the described experiment, the X-ray beam became unstable and the beam’s pointing became erratic. The most upstream YAG crystal of the AMO instrument was able to detect this jitter such that the accelerator could be tuned to correct the erratic pointing. However, a beamline alignment laser (typical HeNe-laser with low beam divergence) can be coupled into the

3. Experimental Setup

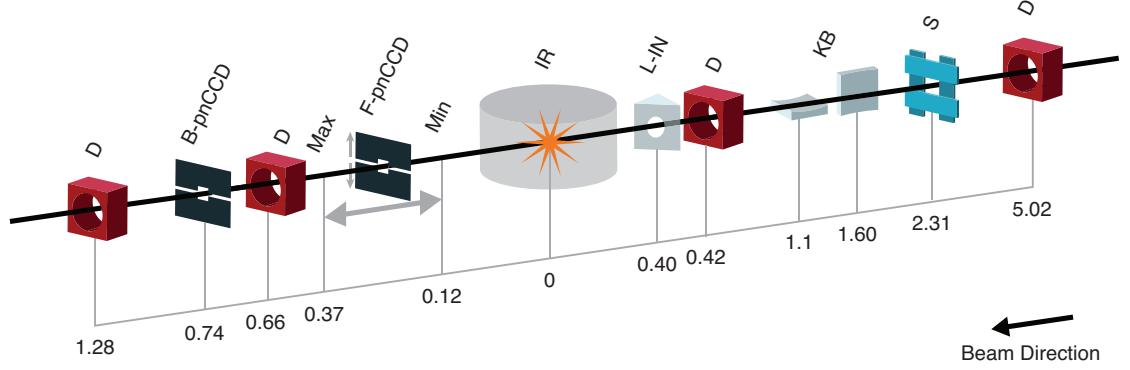


Figure 3.1.: Schematic overview of the AMO beamline instrumentation in the LAMP configuration. The indicated distances below the schematic items are in meters from the interaction region. As the X-ray beam enters the instrument, it can be visualized on a YAG crystal diagnostics (D). A set of 2 slits (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 [112].

beamline shortly downstream of the YAG screen⁴ such that it co-propagates with the X-rays. Beamline alignment lasers are invaluable tools to pre-align a system before X-rays are employed. 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 was useful, if not required. The X-ray beam then travels through a set of four blades (S) that can be moved independently to cut into the beam to reduce noise effects on the detectors, especially originating from the the Kirkpatrick-Baez (KB-)optics [122]. In collaboration with the Single-Particle Initiative [8], it was investigated how the blades reduce unwanted scattering. 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 [123]. This sufficiently reduced straylight but did 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.

⁴Not shown in Figure 3.1

3.1. The AMO instrument and FEE at the LCLS

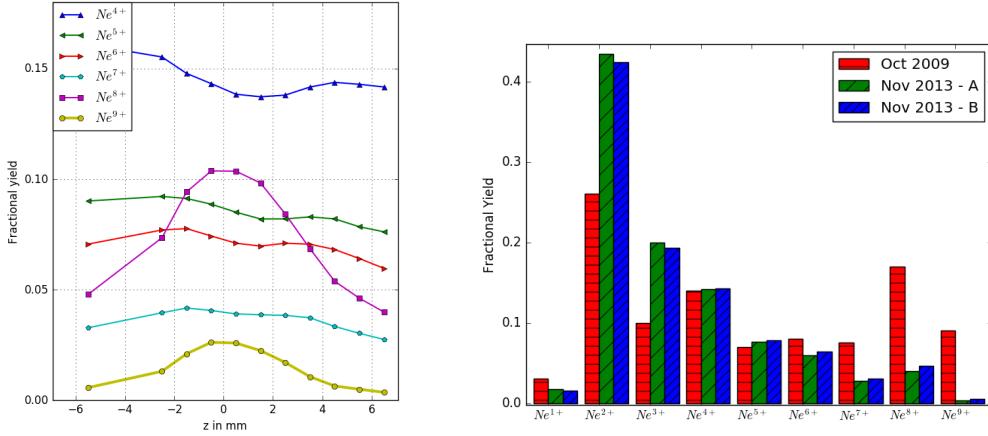


Figure 3.2.: Left graph: Atomic neon charge state yield from TOF as a function of Z-position, relative to optimal focus position $Z = 0$. $Z = 0 \pm 1$ mm is a favorable length for sample injection. Right diagram: Comparison of atomic neon charge state yield from TOF for different cases. Red: Experimental 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.

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 in the horizontal and vertical, they are designed to have a focal length of 1600 mm in the horizontal and 1100 mm in the vertical. Additionally, the mirrors can be bent to change their focusing position along the Z-axis⁵ and the optimal focus can be found and characterized through 1) the study of time-of-flight (TOF) mass-spectroscopy [85] and 2) imprint analysis [124, 125]. A study of the X-ray focus is necessary to achieve the smallest focus, thus increasing the fluence at the sample interaction region.

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. A 2 mm region centering around the focal plane at $Z = 0$ mm was located, where the beam was suitable for the experiment. The right panel of Figure 3.2 compares the fractional neon ion yield at the optimal focus position from November 2013 [85] to

⁵The 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. Experimental Setup

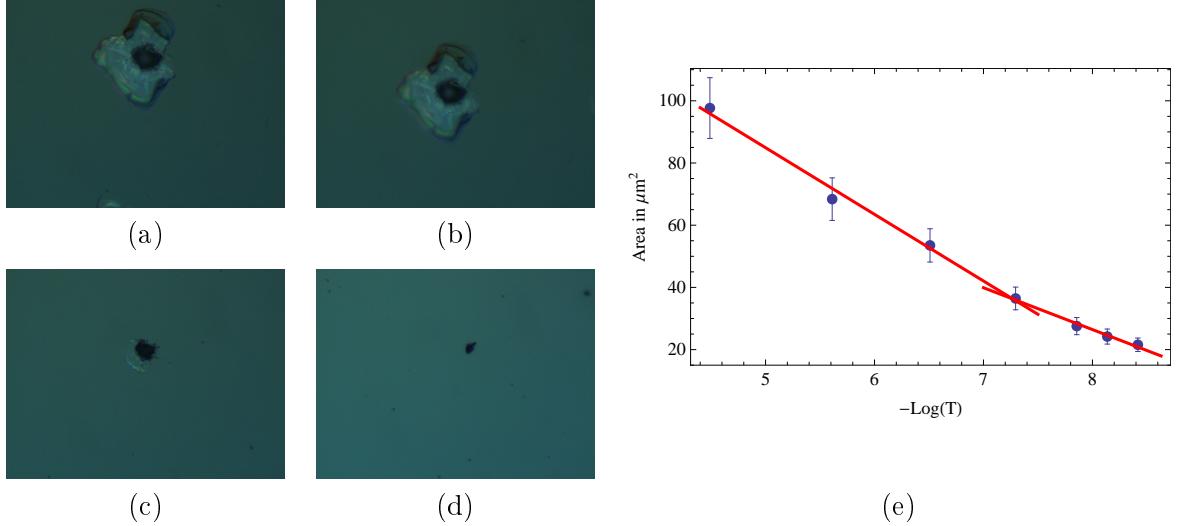


Figure 3.3.: a)-d) Ex-situ microscope imprint study of a lead tungstate (PbWO_4) sample that was irradiated with single, 1600 eV LCLS pulses at different gas attenuation. e) Non-linearity in Liu plot due to LCLS's super-gaussian beam profile. The approximate $\text{FWHM} \approx 3.4 \mu\text{m}$ is determined from the slope of the linear fits, see more in text.

October 2009 [126]. The comparison reveals that high-charge states of neon, for example, Ne^{8+} and Ne^{9+} are less frequent. We attribute this to deteriorated beamline optics.

3.1.2. Focus characterization via imprint study

Figure 3.3 left shows images from an optical microscope of the result of a LCLS X-ray pulse at 1600eV interacting 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 , a characteristic radius σ and the peak fluence E_0 . Typically, σ stays a constant beam parameter, but different peak fluences change the crater area in the sample, e.g., more peak fluence usually increases the crater area as more of the PbWO_4 surface is irradiated with powers above the damage threshold. We can measure the peak fluence, E_0 , proportional to the pulse energy, E_p , which is measured with the gas detector. Let us explicitly note $E_p \propto E_0$. Now, we can express the peak fluence

3.2. The LAMP end-station at AMO

	pump beam	probe beam
wavelength		1.5 nm
mean pulse energy	80-100 μJ	0.8- 1 mJ
X-ray beam FWHM		$\sim 1.5\mu\text{m}$
pulse duration		$\sim 25\text{ fs}$
delay Δt precision		$\sim 25\text{ fs}$

Table 3.1.: Summary of LCLS beam parameters during experiment.

more conveniently in terms of the pressure, p , in the gas attenuator

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

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 [127]. For the LCLS attenuator filled with nitrogen gas (N2) over its 410 cm length at 1600 eV photon energy, $c \approx 0.5611415 \text{ Torr}^{-1}$. We can further approximate the crater surface area using a circle. The area then is πr_0^2 , with the crater radius r_0 . As shown in [128], $r_0^2 = 2\sigma^2 \log(\frac{E_0^{1/2}}{E_0^1})$, with $E_0^{1/2}$ being the peak fluence at two different attenuation levels. Thus, the slope of a linear fit between the two points $E_0^{1/2}$ is $2\pi\sigma^2$. 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 fitted with two linear fits. The data indicates non-linearities that come from a super-gaussian beam profile [129, 130]. 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 was determined to be $\text{FWHM} \approx 1.5\mu\text{m}$, with an effective area of $5\mu\text{m}^2$ [85]. The LCLS beam parameters are summarized in Table 3.1. The pulse duration was determined through analysis of the electron beam and the delay, Δt , precision is estimated from geometric considerations of the delay chicane (see also Section 2.1.4).

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 cham-

3. Experimental Setup

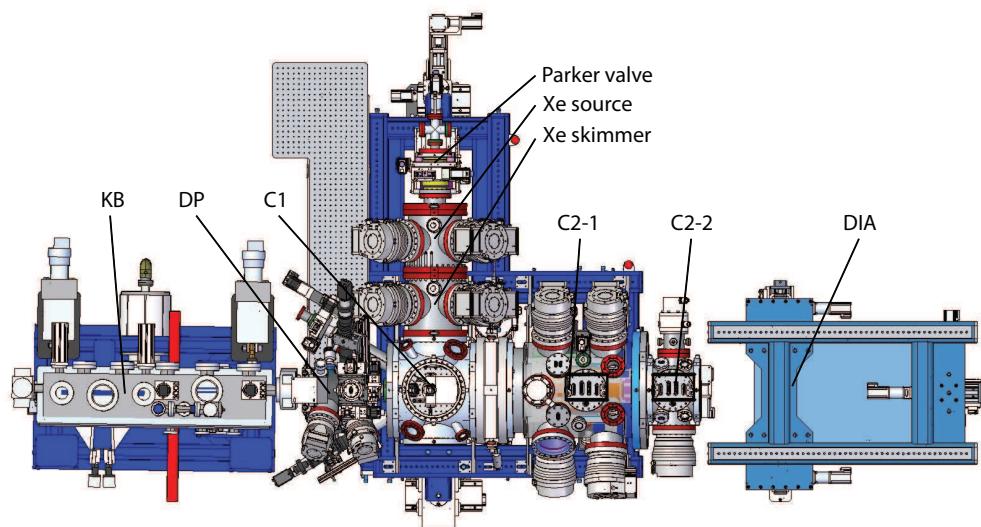


Figure 3.4.: Overview of the AMO instrument in the LAMP end-station configuration. From left to right, the beam propagates through the Kirkpatrick-Baez (KB) optics, the differential pumping (DP) section, the interaction chamber (C1), the front pnCCD chamber (C2-1), the rear pnCCD chamber (C2-2) and finally 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

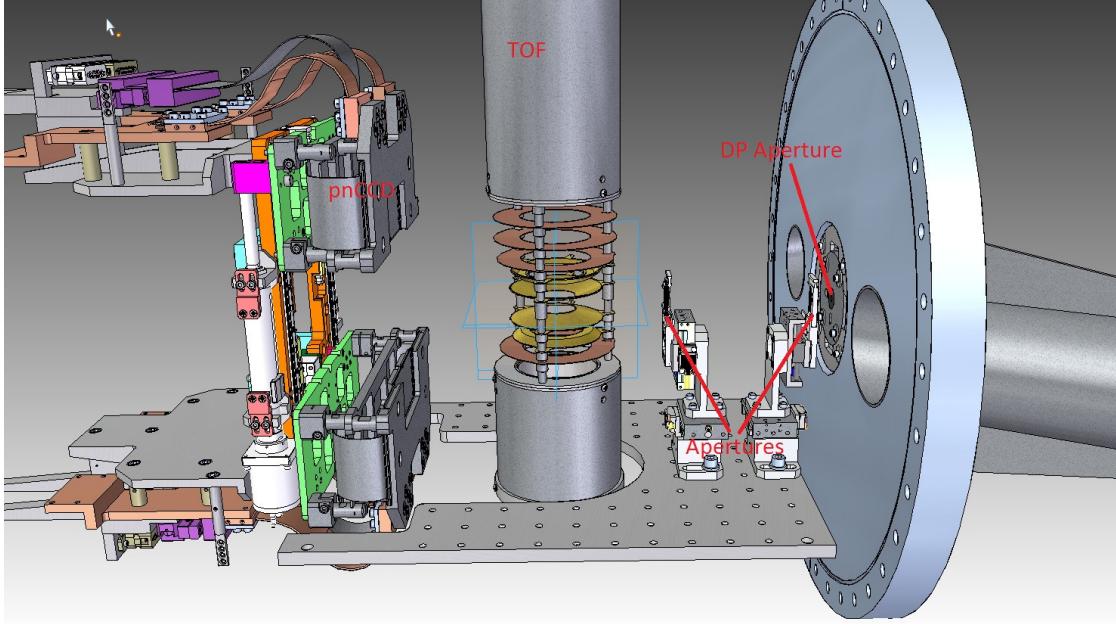


Figure 3.5.: Inside view of the C1 chamber showcasing the interaction region.

bers (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 connected 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, the pressure in the C1 vacuum chamber, p_{C1} , may rise to $p_{C1} = 10^{-6}$ bar as the sample injection starts and the pressure in the KB-optics vacuum tank, p_{KB} , is maintained at $p_{KB} = 10^{-10}$ bar due to the differential pumping section. The first differential pumping stage holds a YAG crystal to examine the X-ray beam after the KB optics. The second stage holds a removable laser in-coupling mirror to overlap X-rays with an optical laser or an 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 (see Figure 3.5). The apertures are mounted on encoded stages that are driven by piezoelectric actuators with absolute sub-micron movement precision. The aperture material is silicon nitride (Si_3N_4) with tapered-edge windows to allow the X-rays to traverse. The window-size can be either fit to the size of the X-ray beam diameter, which can be estimated using

3. Experimental Setup

geometric optics, or by using one corner of the window on the first aperture stage and the opposite corner on the second stage. As part of this thesis work, an improved aperture system was designed using four aperture blades with tapered edges. These allow full control over the aperture from four directions, thus allowing short aperture alignment times and a more controlled reduction of unwanted effects. For soft X-rays, it is important to note that the flat surface of the tapered aperture is facing the beam such that the tapered-edge is facing downstream. Otherwise unwanted reflections may occur. This aperture system was commissioned in 2015 for diffractive imaging experiments at the AMO instrument.

In the center of C1, where sample and X-rays interact, a time-of-flight spectrometer is located (see Figure 3.5), which we will describe in the Section 3.5. The beam then passes between the modules of 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. These distances are relevant for the digital combination of pnCCD-images in different planes, which we will discuss in Section 4.2.1. 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 C1 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 chamber⁶. As mentioned, the front pnCCD 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 and 367.75 mm. The front-top pnCCD module is again 3.15 mm closer to the center of C1. 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 described experiment, the front pnCCD modules were 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

⁶These design distances are offset by $\sim +5$ mm along the Z-axis due to customization during the initial set up.

3.3. The large area pn-CCD detectors

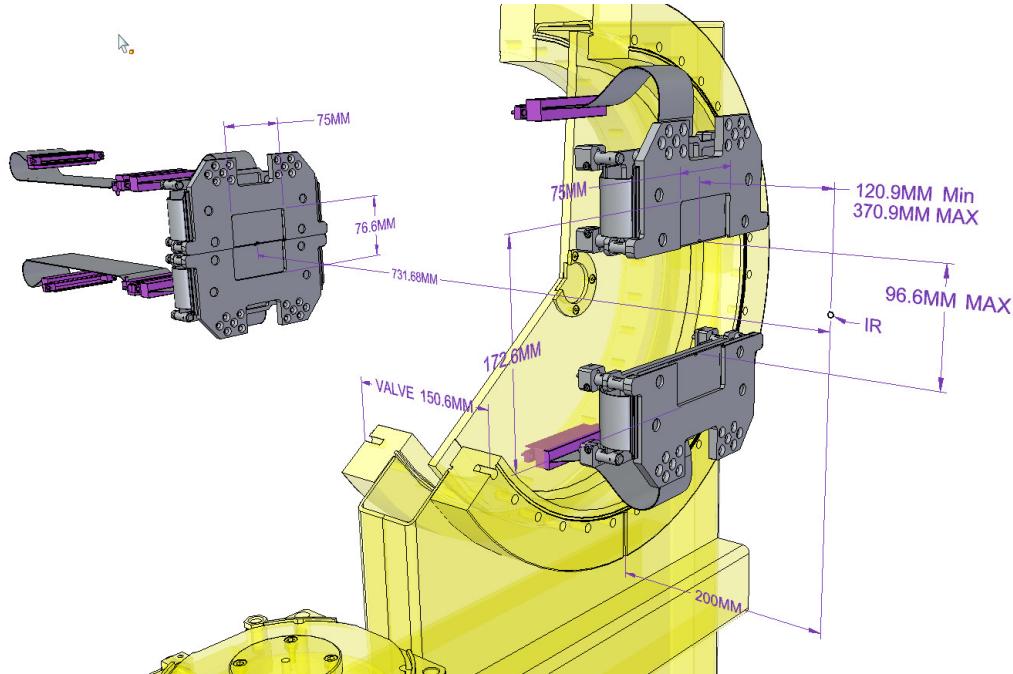


Figure 3.6.: Side view of the rear and front pnCCD detector in C1, C2-1 and C2-2. The interaction region (IR) is in the center of C1. The beam propagates along the Z-axis where the rear (top) pnCCD is placed 728.53 mm away from the IR (original engineering distances). The half detector height is 38.3 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 $\Theta = 38.11^\circ$.

3. Experimental Setup

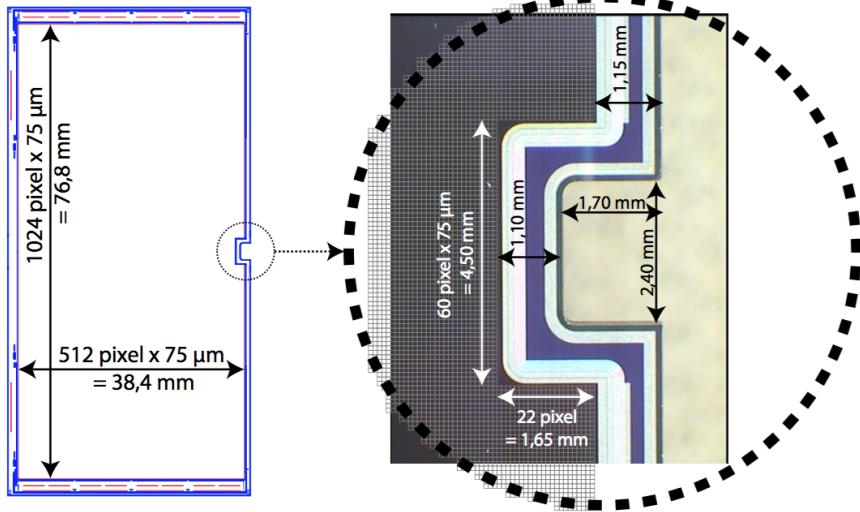


Figure 3.7.: Geometry of a single pnCCD module with a detailed view of the beam conveying hole. A single module consists of 1024×512 pixel. Each pixel is $75 \mu\text{m}$, which results in an active area of $76.8 \times 38.4 \text{ mm}^2$. The chip is surrounded by non-active edges, which are 1.15 mm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

science. pnCCDs have been used previously at LCLS, namely in the CAMP instrument. At LCLS, these detectors are mostly used for coherent diffractive imaging applications, but have also spectroscopic capabilities. These are demonstrated in the left panel of Figure 2.13. The pnCCDs are attractive photon area detectors because of the following four reasons. Reason one, their high quantum efficiency (QE) and good signal to noise ratio. Two, their read-out rate is very high – up to 200 Hz – and enables us to use the full repetition rate of LCLS, which is 120 Hz. Three, their large, consecutive active areas cover wide scattering angles, and last, the detectors are almost defect free after applying widely-used pixel detector image corrections. These points are explained in detail in the following [85].

Let us begin by describing the chip geometry. Each front or rear pnCCD detector is made out of two modules. Figure 3.7 shows the layout of a single pnCCD module. The chip consists of 512×1024 pixels. 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 $4.5 \times \sim 4.5 \text{ mm}^2$.

3.3. The large area pn-CCD detectors

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.

The size of this hole has been chosen to slightly oversize the diverging FEL beam at the rear pnCCD position, when the focus is in the middle of the C1 chamber. The borders of each module are insensitive to photons and are 1.10 to 1.15 mm thick. To minimize the overall detector area that is insensitive to photons, the two pnCCD modules are mounted such that the non sensitive areas overlap. As a result of 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 laboratory frame images between each top and bottom module measures 16 pixels or ~ 1.2 mm.

The pnCCD chip is read out with a custom CMOS multichannel 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 the read out of all pnCCD rows at once, thus allowing the high read-out speed of up to 200 Hz. 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 in high gains or to have more dynamic range in lower gains. Table 3.2 shows data of gain setting and signal generation in arbitrary detector units (ADU). The following considerations are necessary when combining detectors of different gain settings or ADU generation. 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 one steps from highest to lower gains, e.g., from 1 to $\frac{1}{64}$, the ADU value creation per photon goes with that fraction in good approximation. Hence, going to lower gains reduces the signal-to-noise ratio but

3. Experimental Setup

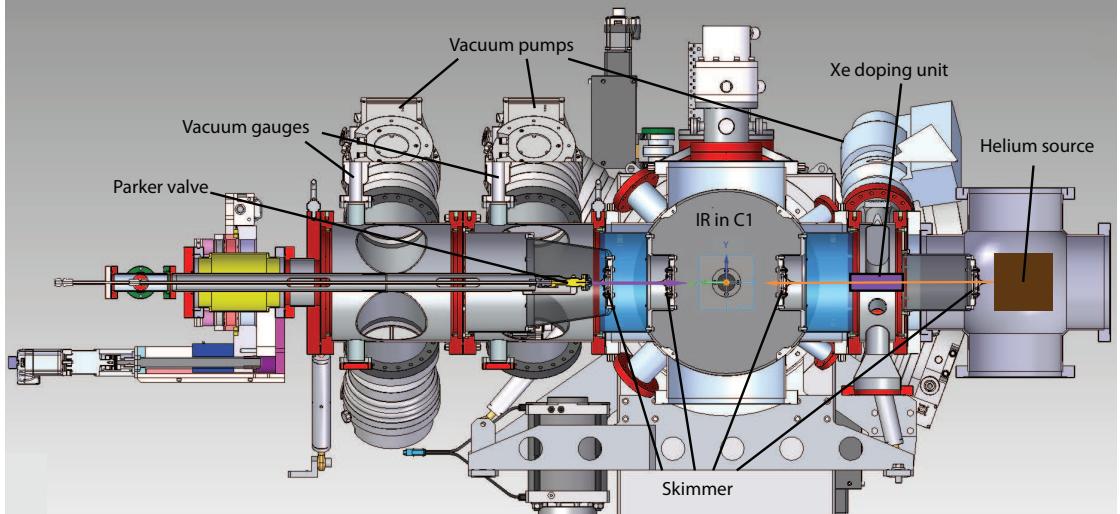


Figure 3.8.: Downward view of a slice through the interaction region in C1 of the experimental setup. The purple arrow indicates the xenon gas flow, the orange arrow indicates the helium gas flow.

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 windows have a high quantum-efficiency from the infra-red (IR) to soft X-ray wavelength range. In order to avoid unwanted scattering, the photon entrance windows are located at the back of the detector, thus facing upstream of LCLS, and 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 slightly but the detectors maintain a QE of $\sim 90\%$. At AMO, it is thus possible 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). The in this thesis used 837 eV photons will approximately generate ~ 1087 eV. There is also an optical aluminum filter mounted from the front of the chip, thus facing downstream of LCLS, to drastically reduce wrongly directed scattering.

3.4. Sample delivery

Two gas sources are used in order to create single rare-gas clusters. Single xenon and helium clusters are produced using the principle of the supersonic gas expansion into a vacuum that is described in Section 2.2.1. Helium clusters that are doped with xenon are produced through the pickup principle as described in Section 2.2.2. Given the time con-

3.4. Sample delivery

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.

straint of performing experiments at the LCLS, both sources are installed in one setup and operate independently, allowing quick sample changes. A schematic setup of the sample environment 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, which produces a single xenon cluster, consists of a Parker-Hannifin Series 99⁷ - 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 was used extensively in the past [16, 33, 53, 73, 112]. The pulsed solenoid valve (see Figure 3.9) 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 the 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 range of (1 to 20) bar. The pulsed valve heats up substantially during operations and due to material deterioration and the vespel poppet is replaced every ~ 60 h of operating time, or as needed to prevent a leakage from the gas source. The nozzle has a 200 μm opening diameter and an opening half angle of 4°. It is clamped to the Parker valve using an indium gasket to seal. Two skimmers with an opening of 1 mm 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 , from (0 to 8) V. At $U = 8$ V, the cluster source operates in the single cluster regime. The background pressures in the respective source and skimmer chambers is handled through turbo-molecular pumps that are connected to roughing pumps (see Table 3.3). Ultimately, these chambers lower the gas pressure in the interaction region, p_{IR} , or C1 chamber to $p_{\text{IR}} \leq 10^{-5}$ bar.

⁷Series 99 is at the time of writing not produced/advertised as a straight, in-line pulsed valve anymore.

3. Experimental Setup

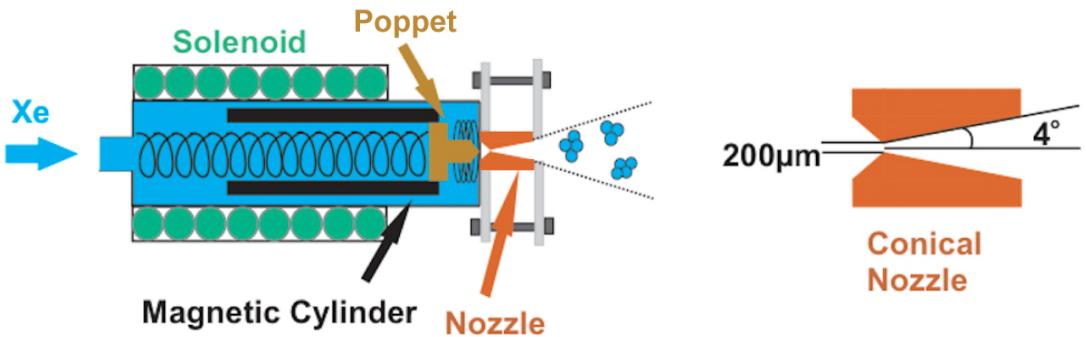


Figure 3.9.: Schematic of the Parker-Hannifin Series 99 pulsed in-line valve and custom copper nozzle. The nozzle is clamped to the pulsed valve using an indium gasket to seal. The vespel poppet is attached to the magnetic cylinder and closes the valve. If a current is run through the solenoid, the valve actuates and opens. Adapted from [131,].

Helium droplets are produced in a continuous free gas expansion using an electron microscope diaphragm as nozzle (Plano A0200P) that has a $5\text{ }\mu\text{m}$ orifice and an orifice channel length of $\sim 2\text{ }\mu\text{m}$ [75]. The nozzle is cooled to cryogenic temperatures $T = 5.8\text{ K}$ using a Sumitomo cold-head. The particle beam is defined by a first 0.5 mm and a second 1 mm diameter skimmer. As explained above, a third piezo-skimmer allows the definition of the gas jet to single helium droplets. A doping unit is installed in the skimmer chamber of the helium source. The doping unit is a separate, smaller chamber in the skimmer chamber, where He-clusters can traverse through. The gas cell allows locally increasing the pressure of the cell with gaseous xenon to $\leq 3 \cdot 10^{-6}\text{ bar}$. 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 one using the Parker solenoid valve require an electric trigger to open the valve. At LCLS, 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 with a 10 ps precision [132]. The EVR processes these signals and systems in

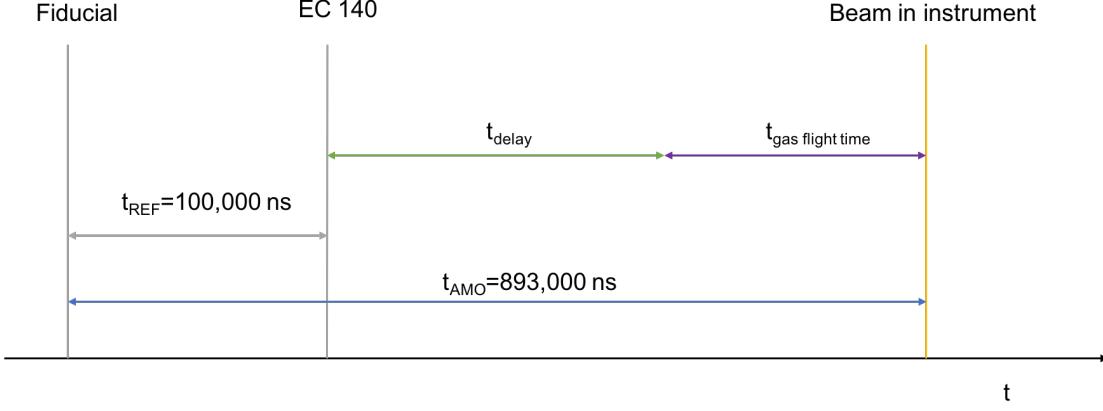


Figure 3.10.: Schematic of LCLS EVR timing system.

need of an electric trigger can be connected to the EVR to receive a specific one. The triggers coming from the EVR are based on specific event codes (ECs), for example, EC 40 operates at 120 Hz and may be delayed with respect to the EC. Figure 3.10 schematically illustrates the timing system. Following the figure, the process starts with a fiducial, an EC is delayed by time of event code x (TECx) and after a certain time of the fiducial a LCLS pulse arrives. At the AMO instrument, this time is $t_{AMO} \approx 893000$ ns⁸. The LCLS control system automatically corrects for different TECx by internally correcting the delay to a reference time t_{REF} that corresponds to EC 140, which occurs on 120 Hz, when the beam is present. The reference time is set to $t_{REF} = 100000$ ns and thus we can write down the following equation for the delay time of the trigger for a sample jet at LCLS to coincide with the beam.

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

with t_{delay} being the delay value for the LCLS EVR control system and $t_{gas\ flight\ time}$ the flight time of the sample from the gas source to the interaction region (IR). As described in [64], 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.

⁸Times are in nanoseconds (ns) and in a format to comply with the LCLS interface.

3. Experimental Setup

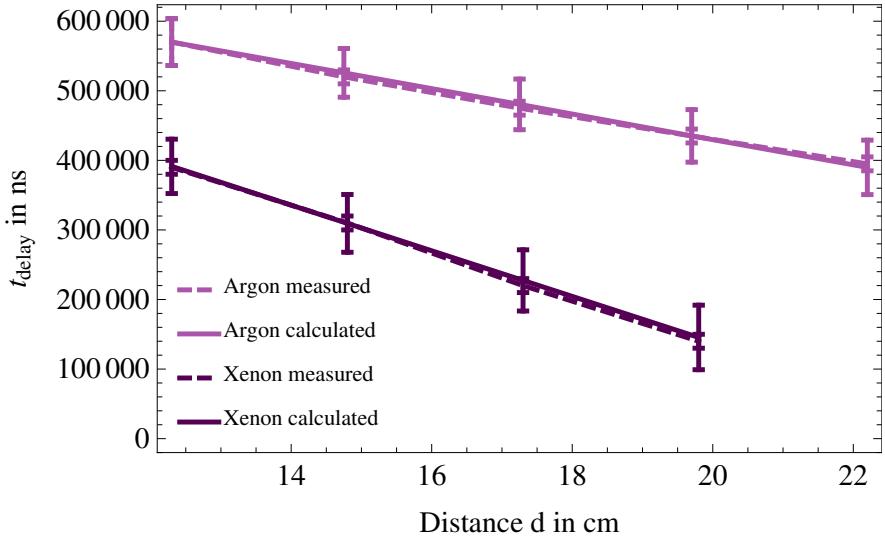


Figure 3.11.: t_{delay} as a function of the gas source distance to the interaction region. Xenon and argon has been used as sample gas in an Even-Lavie pulsed valve. The calculated delay values (solid lines) agree well with the measured delay times (dashed lines) to overlap the onset of the pulsed jet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

The flight time of a certain gas can then be calculated by measuring the distance, D , between the source and the interaction region, 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, $m_{\text{CO}} = 28$ 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 $m_{\text{HeXe}} = 6.54$ amu.

Figure 3.11 shows measured and calculated flight times using an Even-Lavie (EL) supersonic gas source⁹ instead of the earlier described Parker valve. The Evan-Lavie source has a very well-defined opening time of 22 μs and thus a well-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 terminal velocity of

⁹The EL-valve has the serial no.: EL 5 HRR NO 114.

3.5. Time of flight mass-spectrometer

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 timing scheme and Equation (3.3) can be rewritten to

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

with f_{rr} being 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 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 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, 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 field free. As the velocity remains constant, we can write down

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

3. Experimental Setup

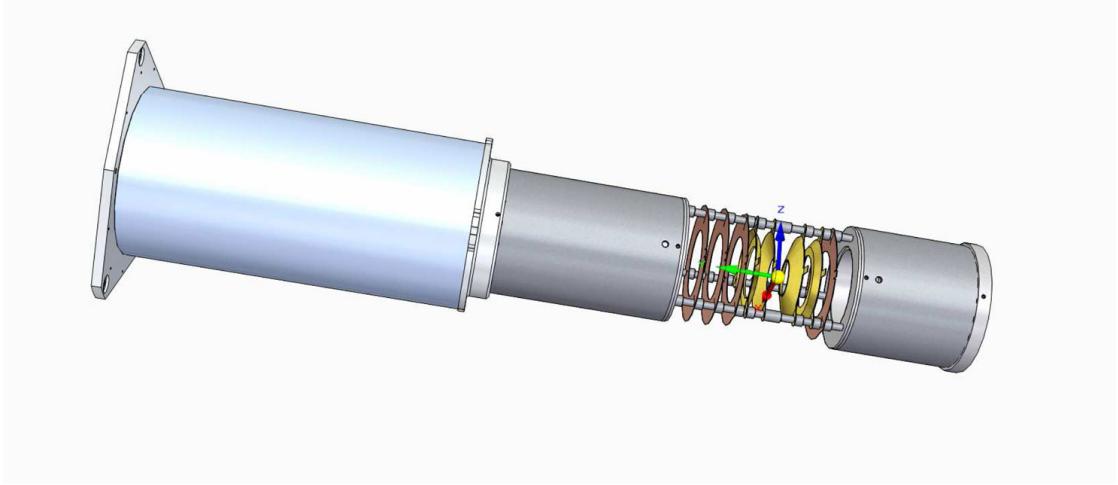


Figure 3.12.: Drawing of the time-of-flight spectrometer.

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

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

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

Typical for an experiment, all values aside from m and q 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 $E_{kin} \neq 0$, 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 the signal from clusters is strongly broadened due to kinetic energy release from collective effects. Using this information, element specific data including insight in the ionization cascades can be gained [133].

The configuration of the here 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 50 eV with a time of flight resolution of 100 ps [112]. If only the ion side is used, ions with kinetic energies of up to 100 eV can be

3.5. Time of flight mass-spectrometer

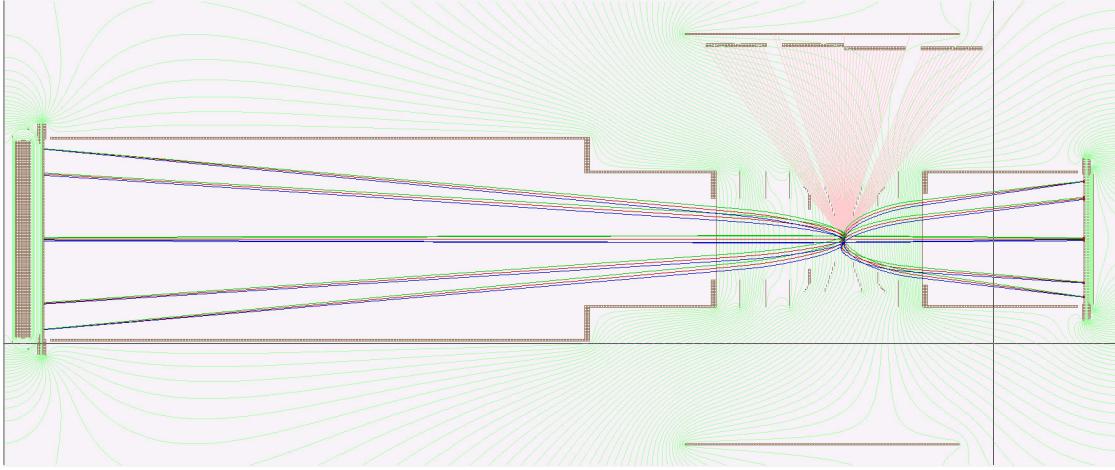


Figure 3.13.: Sideview of the spectrometer showing ion, electron and photon trajectories upon interaction with LCLS. The image was created with SIMION. From [134].

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).

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 when using ± 10 keV power supplies. Ions and electrons can be detected whether they are emitted in any direction, in other words the spectrometer has a 4π solid angle collection [134]. 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. A 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.

4. Methods

Let us conservatively estimate how much data is produced when using the LAMP end-station with both pnCCD detectors at a 120 Hz. Each pnCCD produces 120 images per second, each image is in a 32 bit-per-pixel format such that an image is approximately 4 megabyte in size. So, every minute the front & rear pnCCD produce approximately 60 gigabytes of data or 700 gigabytes per 12h shift. 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 and it 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. Section 4.3 goes over used phase-retrieval algorithms and Section 4.4 discusses simulations of 2D projections of spheres and corresponding diffraction patterns. The Section 4.5, discusses the Acqiris data acquisition and sampling, while Section 4.6 evaluates several hitfinding methods.

4.1. The computing environment at LCLS

As estimated above, the vast amounts of data generated by many detectors are unwieldy 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 pnCCD and Acqiris 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 tens of 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 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). The

4.1. The computing environment at LCLS

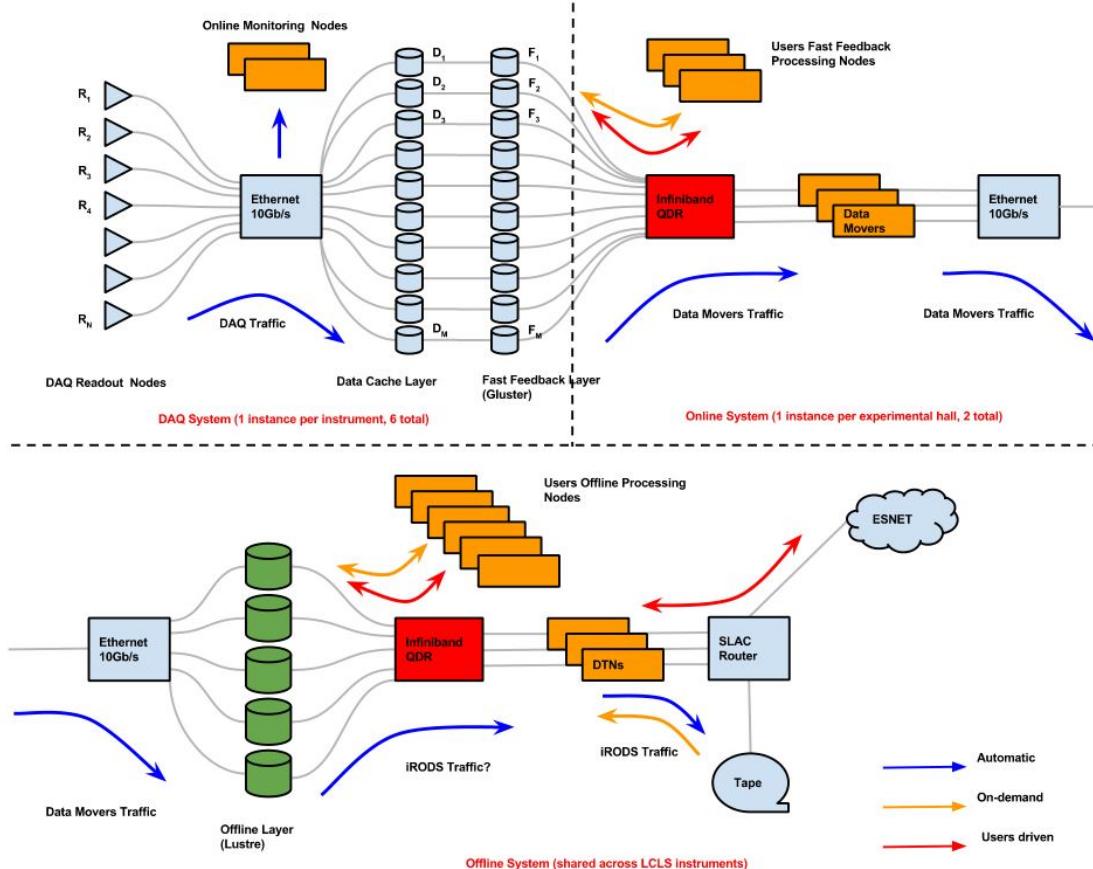


Figure 4.1.: Diagram of the computing environment at LCLS and DAQ traffic. The recorded data is exchanged through Ethernet and after digitization, is stored on a cache and FFB cluster, where psana computer have access to the online environment during the experiment. Eventually, the data is moved to the more permanent offline environment, where data can be analyzed on psana computers or through a load sharing facility. See more in text. From [135].

4. Methods

stored data has certain storage quotas and times. In brief, there is a six month short-term storage without quota limitations and a two-year medium-term storage with a storage quota of ten thousand gigabytes. After that, the data is automatically stored for at least ten 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 one thousand CPU cores. A load sharing facility (LSF) allows the scheduling of (parallelized) batch jobs. The psana-framework can be interacted with via python 2.7. The interacting python script calls functions within the psana-framework that are programmed in C(++), 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 to be processed at the rate of the incoming data using MPI, when the fast feedback buffer (FFB) is used. Python scripts can be written for 'online' or 'offline' analysis and are of similar syntax.

For LCLS-II [135], 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. The first, corrects for the electronic noise pedestals (levels) of each pixel, and, the second, accounts for common modes, e.g., artifacts from the read-out electronics that appear, for the pnCCD, in columns.

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)

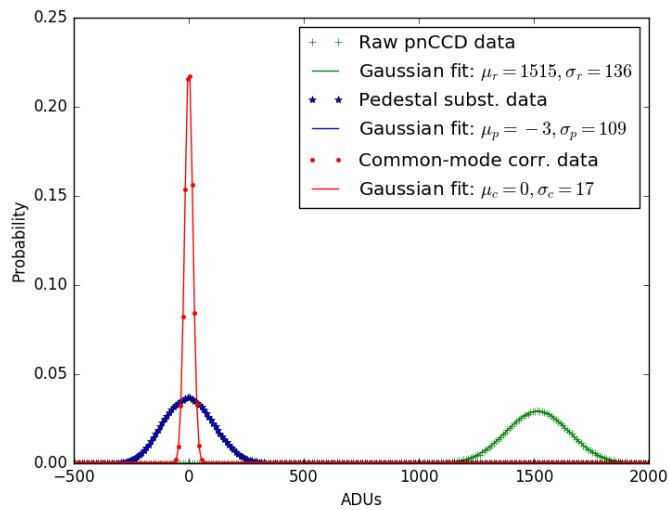


Figure 4.2.: ADU histograms from electronic noise of not illuminated pnCCDs in highest gain mode. The green plus symbols reflect a histogram of ADU values from raw electronic noise of pnCCD pixel. The noise is set off zero at $\mu_r = 1515$ ADU and has a standard deviation $\sigma_r = 136$. The same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

4. Methods

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 highest gain. The green curve shows the ADU values of a raw detector image where no corrections have been applied and 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 a pixel with no signal in each row and column [136]. In single-particle imaging, the detector is illuminated in (almost) every pixel. In this case, 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 image from a single-shot into one larger image. While this is a simple task in 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, so far, there was little incentive for 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

4.2. pnCCD photon detectors

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

Let us now describe the process of combining multiple detector images from a single-shot, 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 applicable, common-mode corrected. Analysis of the electronic noise determines a cutoff or offset between signal-to-noise for each image (see the left panel of Figure 2.13 and 4.2). At this step it is also convenient to account for different detector gain settings using 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 a 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 arithmetic mean of the downsampled pixel is used, which is why a normalization factor needs to be carried. The downsampling

4. Methods

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 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 spherically 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 shadow projected from the front onto the rear pnCCD and the resulting lack of signal.

4.2.2. Impact of the 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 pump-pulse to the diffraction image, a 1D simulation is conducted using electron densities of spheres, $\rho(R)$. Although rare-gas clusters exhibit an icosahedral structure, at our present resolution the cluster can be well-simulated using

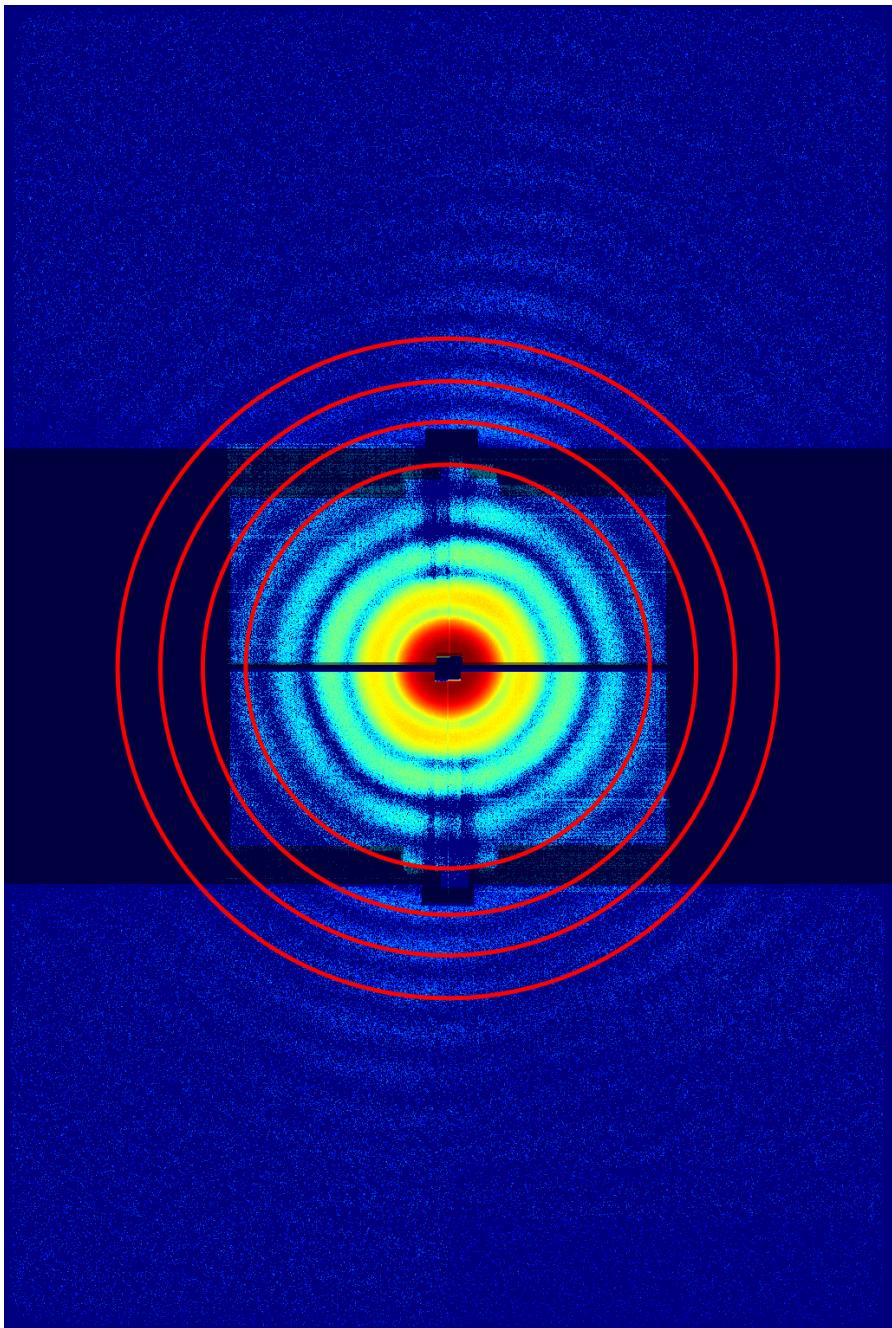


Figure 4.3.: A combined pnCCD image using the full image of the front pnCCD and a down-sampled image of the rear pnCCD. The red circles in the image are drawn to visualize the alignment of the detectors. As described in the text, the intensities in the image are normalized and corrected for different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

4. Methods

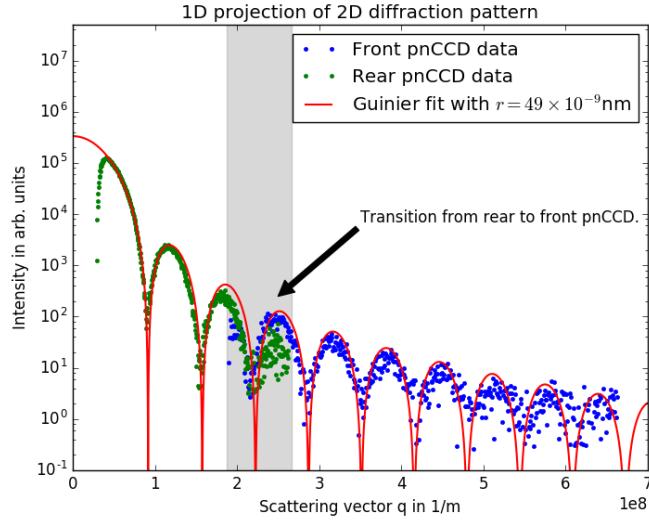


Figure 4.4.: Spherical projection of 2D diffraction image onto 1D. The data points are from the rear pnCCD (green points) and the front pnCCD (blue points) have been combined. The gray shaded area shows the transition area from rear to front detector. The red curve is a simulated scattering curve from 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.

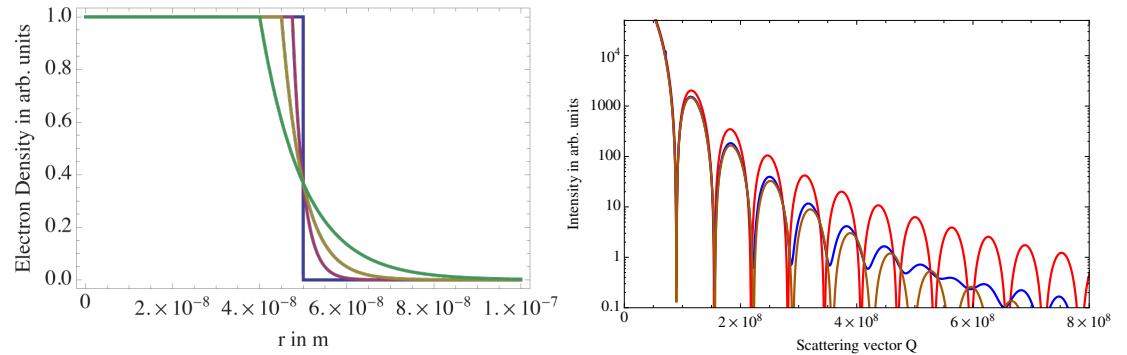


Figure 4.5.: Left: electron density of an expanding spherically symmetric nanoplasma. Right: red line, scattering of an intact sphere. Brown, scattering of an expanding sphere with $k = 5 \text{ nm}$. Blue, combined scattering of an intact and expanding sphere that has been pumped with 10% and probed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

4.3. Phase retrieval from a single diffraction pattern

spheres. The spheres are allowed to expand according to the model

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

where r is the cluster radius, R is the distance from the center of the cluster, and k an expansion coefficient such that

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

The electron density can then be Fourier transformed into reciprocal space using the transformation in 1D due to the symmetry [76]

$$I(Q) = I_0 F^2(Q) = I_0 \left(\int_0^\infty \rho(R, k) \frac{\sin(QR)}{QR} 4\pi R^2 dR \right)^2, \quad (4.6)$$

where an incident beam has the intensity I_0 . The electron densities for $R = 50$ nm and $k = (0, 2.5, 5, \text{ and } 10)$ nm are shown in the left panel of Figure 4.5. The right panel of Figure 4.5 showcases several cases of expanding spheres in reciprocal space. The red line is the scattering of a solid sphere, F_{intact}^2 . 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 $I_0 F^2 \rightarrow 10\% \cdot I_0 F_{\text{intact}}^2 + 90\% \cdot I_0 F_{\text{expanding}}^2$. Here the pump-pulse affects the diffraction pattern at high Q -values and decreases the fringe contrast. However, the added signal from the pump-pulse remains within the noise level of $I(Q) < 1$ ADU. For this assessment, the simulated incident beam intensities, I_0 , and cluster radius, r , have been fitted to match the experimental data of Figure 4.4.

4.3. Phase retrieval from a single diffraction pattern

As alluded to in Section 2.3.1, coherent diffractive imaging measures the continuous intensity distribution of an object 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 [137, 138]. To fully recover the original function, i.e., real and complex values of the imaged object, the diffraction image must be oversampled [139]. Here, the *Nyquist-Shannon sampling theorem* says that a Fourier transformed object, $A(\vec{Q})$, of size X can be fully recovered if its sampling rate is at the Nyquist rate of $\frac{1}{2X}$. However, we measure the

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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 and becomes $G'_k(q)$. $G'_k(q)$ is inverse Fourier transformed to $g'_k(x)$. After fulfilling the real space constraints the iterative starts again using $g'_{k+1}(x)$. After [141].

intensity distribution, $I(\vec{Q})$, which already has a period of $\frac{1}{2X}$. In this case, the Nyquist rate – with an “oversampling” of two – can be translated into a minimum pixel-size in real-space that samples $I(\vec{Q})$ using the following relation between a discrete Fourier transformation and pixel length along one dimension, Δ_r . We note [140]

$$\Delta_r \leq \frac{\lambda L}{4X}, \quad (4.7)$$

with the wavelength λ , the length from IR to the detector L , and the object length along one dimension X . This means that larger objects require a more frequent sampling of the scattered intensity distribution. If a large, micrometer-sized object is imaged under typical experimental parameters, where $\lambda = 1.5 \text{ nm}$, $L = 0.371 \text{ m}$, and $X = 100 \text{ nm}$, the detector pixel-size must be $\Delta_r \leq 1.39 \text{ mm}$ along each pixel dimension 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 also the largest measured objects sufficiently.

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 [141]. 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 strictly defined in the reciprocal space as they have to repro-

4.3. Phase retrieval from a single diffraction pattern

duce 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 [142].

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 [143] has been used. Hawk is available under the GNU General Public License² and can be downloaded with 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 [9, 11] to other few-hundred-nanometer-sized objects [144], but has not yet been used to recover the real space image from rare-gas cluster. The usage of the program is straight-forward in three steps. First, the diffraction images are transformed into the “.cxi” format, which uses HDF5 as base and adopts a variety of other rules to have a uniform format for SPI data-files [145]. Second, diffraction images are prepared in *Hawk’s editor*, where particular effort has to be made to create a pixel mask. The mask prevents shadowed or otherwise faulty pixels from introducing unphysical signals into the reconstruction algorithm. The software suite automatically interpolates between masked pixel regimes, which is acceptable over the length of a few pixels in one direction. Third, *Hawk’s phaser* can be used to iteratively retrieve the phase from the “.cxi” intensity file. Typical parameters for the program can be found in Table 4.1, which can be tedious to find. Therefore, it is worth emphasizing that particularly the *RAAR algorithm* [146] in combination with initially strong *blurs*, the extension of the *phasing beta range*, and a proper determination of the *object area* resulted in useful reconstructions using Hawk. Note, that the object area size differs from particle to particle and is a sensitive parameter. After 10^5 to $1.5 \cdot 10^5$ iterations, the real space object typically converges.

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

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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 parameters used in the Hawk software package. The object area depends strongly on the actual particle size and thus varies.

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 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 dependent on the wavelength has also given us the inspiration to build short-wavelength machines such as the free electron laser and new synchrotron light sources.

First, we must verify that we are in the far field by fulfilling the following requirement [140]

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

with the wavelength of the X-rays λ , the distance to the detector L and the object size X . In this work, the criterion is met.

4.3. Phase retrieval from a single diffraction pattern

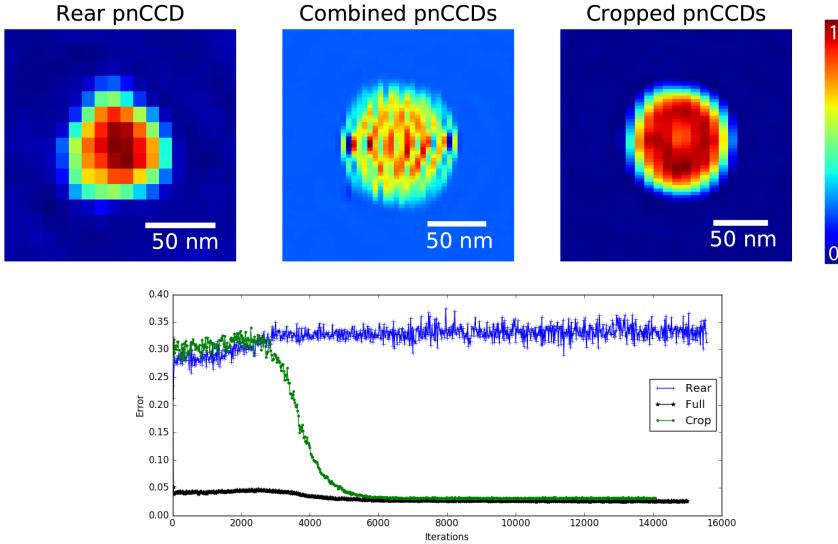


Figure 4.7.: Illustration of resolution enhancement due to detector combination. The diffraction pattern in Figure 4.3 of a Xe-cluster has been reconstructed to illustrate several cases. Top left: Rear pnCCD data only reconstruction yields a non-spherical object; error criterion shows no convergence (see graph). Top middle: Front & rear pnCCD data results in a spherical object but missing areas next to the rear pnCCD disturb the reconstruction process, such that the electron density becomes unphysical. Top right: A cropped diffraction image without the missing areas next to rear pnCCD enables a physical reconstruction.

4. Methods

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

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

with the minimal resolvable feature size d_r , 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 scattering cross-sections.

In the far field, we can use the following relation to determine the actual size of a pixel, Δ_s , in a recovered real space image of an object. We note [140]

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

with L being the length from the interaction region to the detector, Δ_i being the linear detector pixel size, and N being the side length of the discrete detector array.

Figure 4.7 top shows several reconstructions of a xenon cluster at $\lambda = 1$ nm using different portions 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 $d_r \approx 14$ nm. However, in the present data a shadow is cast on the CCD reducing the maximum scattering angle in the image **Rear pnCCD** in the top left panel of Figure 4.7 to $\Theta \approx 3.8^\circ$ and thus the resolution to $d_r \approx 15$ nm. The pixel size is $\sim 10\text{nm} \times \sim 12\text{nm}$. The image **Combined pnCCDs** of Figure 4.7 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, which have been masked out, the interpolation along the Y-axis and the extrapolation along the X-axis fails. The next image labeled **Cropped pnCCDs** in Figure 4.7 uses data in its full extent along the Y-axis, but is cropped 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 $d_r \approx 6$ 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 [9] and still a factor ~ 3 better than [147], where measured diffraction patterns have

4.4. 2D electron density and diffraction image simulations

been “computationally purified”. The resolution enhancement due to the combination of detectors can be exploited further using EMC algorithms [104]. EMC algorithms arrange multiple diffraction patterns according to their orientation and are thus able to compute averaged 3D diffraction patterns of a few hundred diffraction images of the same object. When conducting such an experiment, the missing areas next to the rear pnCCDs would fill with data due to random orientations, thus allowing 3D reconstructions of nanoparticles with nanometer resolution³.

4.3.3. 1D projections and phase reconstructions

The main goal of reconstructions in this thesis is to recover an image of the object while it undergoes the nanoplasma transition. The effects of the nanoplasma transition on the spherically symmetric cluster can be considered isotropic [16]. It is thus useful to display diffraction patterns and projected electron densities in one dimension to simplify the comparison of the transient states. A 1D representation of the data allows furthermore simplifies the 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 a true image center defined. Key elements of the algorithm are to iterate through every pixel, filtering signal from noise, disregarding missing areas, determining the scattering angle of every pixel, and sum signal over $|\vec{Q}|$, while normalizing the data over the pixel number. To recover the object in real space, 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 real space 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 real space error, the phase and the actual Fourier and real space images. The iterative algorithm is aborted when the error criterion meets a predetermined threshold.

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 is possible with 1D fits. Therefore, two dimensional studies were performed to simulate electron densities of pristine and doped clusters. The electron

³Depending on the position of the front pnCCD.

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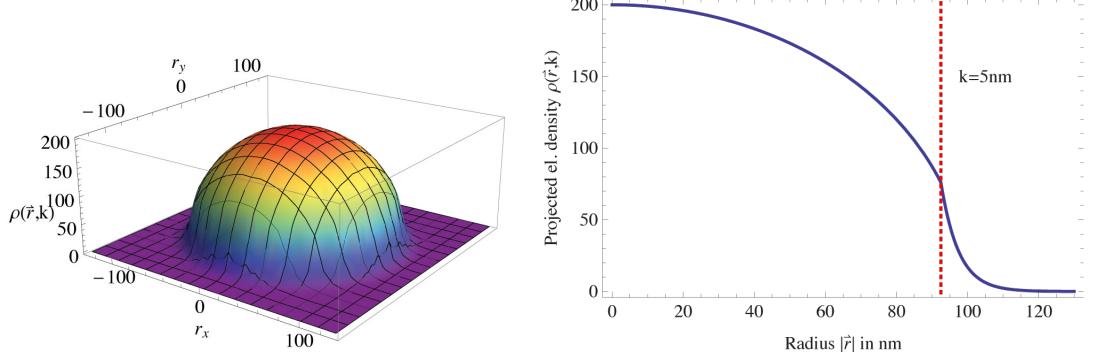


Figure 4.8.: Left: Electron density of a $R \approx 100\text{nm}$ expanding sphere with $k = 5\text{ nm}$, projected onto a 2D plane. Right: Blue curve, spherical projection of the 2D simulation to 1D. Red dashed line, point of expanding density at $k = 5\text{ nm}$.

density is then Fourier transformed and squared 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 Section 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, doped cluster, or more general the core-shell system, the shell consists of one large cluster with low electron density, which simulates a helium droplet, and the core comprises smaller dense spheres, which simulate the xenon doping. The spheres can be arranged at different locations within the shell. Furthermore, the simulated spheres can expand to simulate the effect of a nanoplasma expansion. We can express the electron density of a single sphere that has been projected onto a 2D plane using the formalism

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

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

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

This sphere can be positioned arbitrarily in a 2D array, which simulates the real space image, using $\vec{R} \rightarrow \vec{R} - \vec{R}_0$, with \vec{R}_0 being the center of mass of the sphere. From here,

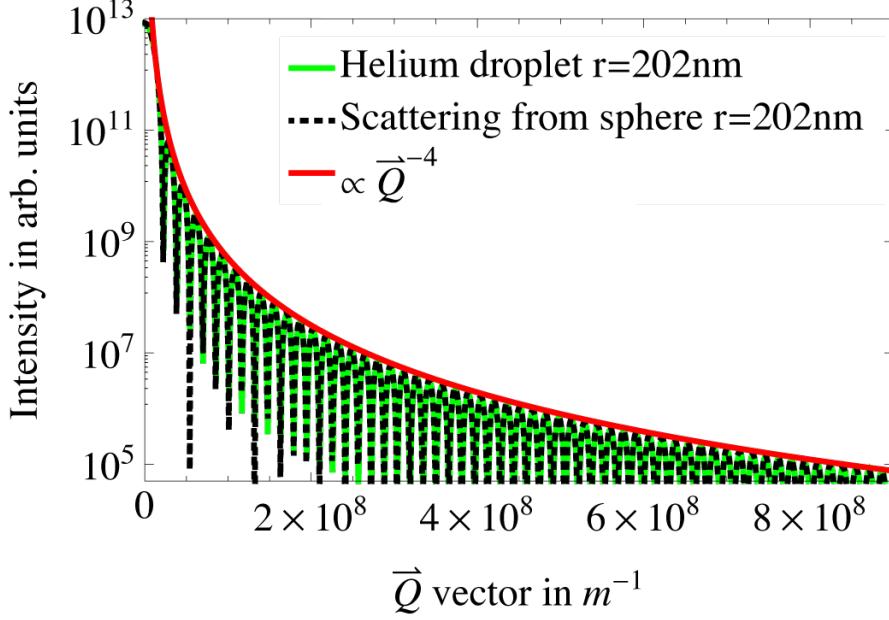


Figure 4.9.: Comparison of analytical scattering from a sphere of radius $R = 202$ nm (black curve), Equation (2.39), and scattering of a sphere of radius $R = 202$ nm from 2D simulations projected onto 1D (green, dashed curve). The envelope of scattering intensity of a sphere (Porod's law) is $\propto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

it is simple to construct the desired real space core-shell system. The electron densities of multiple spheres consisting of arbitrary radii and densities can be added together onto the 2D array. In these simulations, 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, which 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 *ifftshift* and squared.

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 $\propto |\vec{Q}|^{-4}$. The developed simulation agrees well with the analytical scattering, when $k = 0$.

4. Methods

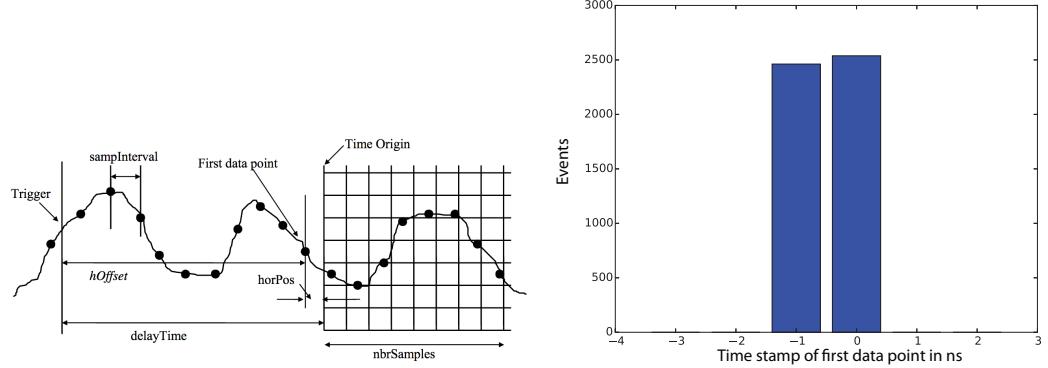


Figure 4.10.: Left image from [148], it shows the schematics of the timing system in the Acqiris. Due to the finite sampling of the trace, the *first data point* can be before time zero. Right image is a histogram of the timestamp from the *first data point*.

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 rate and the Acqiris “clock” are generally not chronologically synchronized with the electronic trigger from LCLS-EVR that starts the readout process. The electronic trigger can occur between the sampling point (1, 2, ..., or 10), as it is illustrated in the left panel of Figure 4.10. These initial 10 channels function as some sort of a “rolling” buffer for the Acqiris. When the Acqiris receives the trigger, it reads out 40,000 samples including the 10 initial sampling points, so, some sampling points may be before the trigger and are thus “unused”. The unused sampling points are removed from the trace by the Acqiris. But to avoid different trace lengths in the data analysis that vary from shot-to-shot, the LCLS DAQ group fills each array with zero entries until the trace is 40,000 points long. This simplifies the data analysis and data handling of the waveform signal. Additionally we should consider the case when the trigger comes in between two sampling points, where the time difference between the *First data point* and the *Time Origin* is within the sampling interval (see Figure 4.10). In this case, the Acqiris uses the first data point as first entry in the read out trace to avoid data loss. This first data point may have a negative time stamp attributed to it as the time origin occurs closer to the second data point. The right panel of Figure 4.10 shows a histogram of the time stamp from 5000 first data points. The time stamp is evenly distributed, which is what one would expect when the electronic trigger “ran-

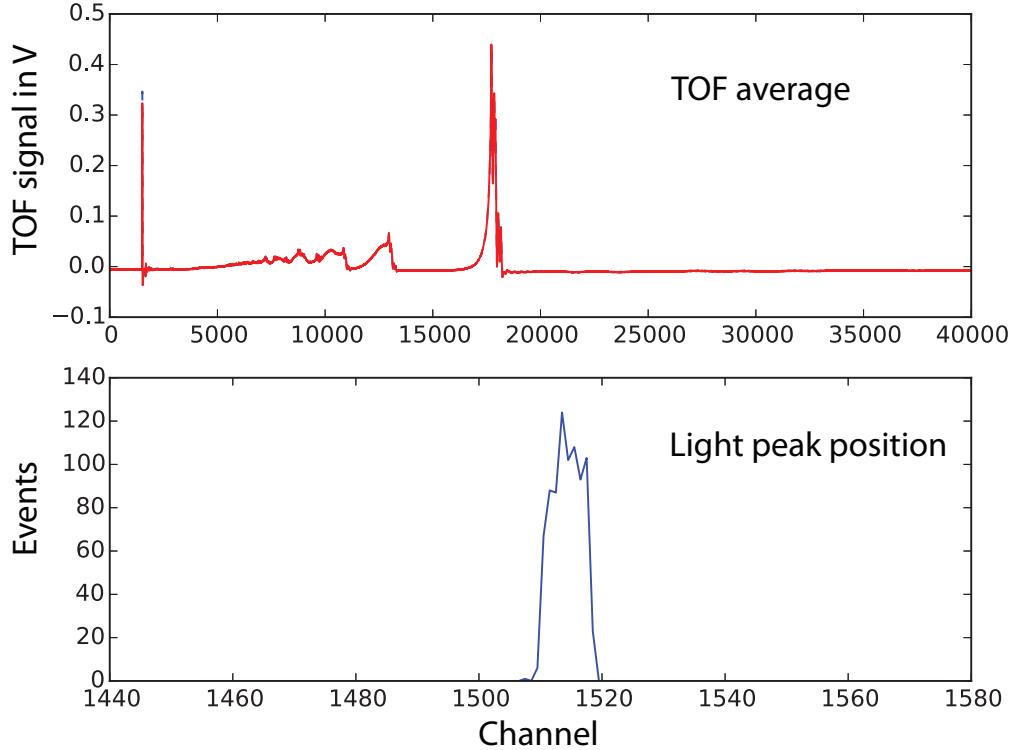


Figure 4.11.: Top plot, average TOF trace of xenon cluster upon irradiation with LCLS. Red curve, corrected run average to account for shifted light peak due to Acqiris sampling. Blue curve, uncorrected average. Bottom image, histogram of light peak channel position ranging between $\sim \pm 5$ of channel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

domly” occurs in between sampling points.

Due to these considerations, the origin of time in a LCLS experiment is best defined by the light peak in a TOF trace. The time-of-flight spectrometer will detect photons scattered of the sample as the pulse is traversing through the system. This light peak is typically in the beginning of the TOF trace and for well scattering samples, such as xenon clusters, the light peak is a well-defined peak (see top panel of Figure 4.11). When 40,000 channels are being read out, each channel corresponds to one sampling point at a sampling rate of 1 ns. The bottom panel of Figure 4.11 shows an analysis of the light peak position in the TOF trace. The light peak occurs within a ~ 10 ns window and is evenly distributed around channel 1514. We attribute this to the earlier mentioned

4. Methods

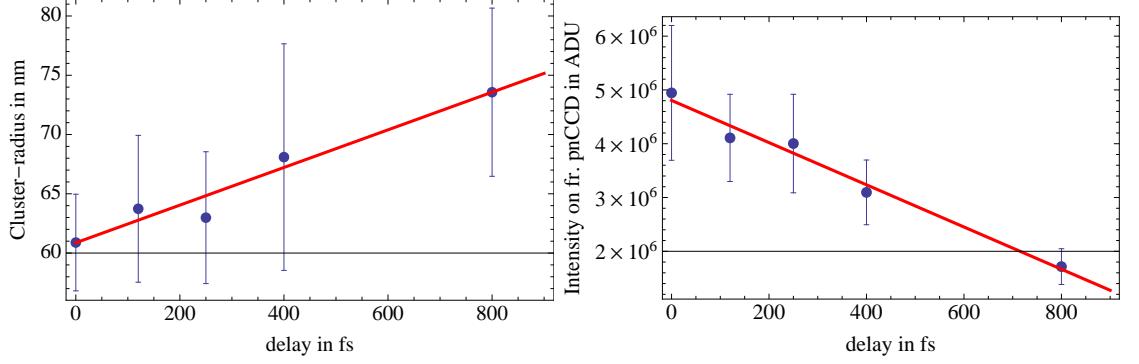


Figure 4.12.: Left: Average Xenon cluster size of intense hits as a function of pump–probe delay Δt . Right: Average intensity on the front pnCCD of intense single-shot hits from single Xe-cluster as a function of the pump–probe delay Δt .

“rolling” buffer. The top panel of Figure 4.11 shows an average of 1000 TOF trace (blue curve) and a TOF trace that has been corrected for the light peak occurring at different position (red curve). The data shows a very good agreement of both curves and indicates that at low time-resolution of a 1 ns sampling, the above considerations may be disregarded. However, for high-resolution TOF spectroscopy the above considerations will become important. The time-of-flight analysis in this thesis accounts for the above considerations 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 and plotting. The coincident detection of diffraction image and time of flight trace 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 pulse sequence with a single cluster system. On the one hand, clusters produce the most intense signal on pnCCD and TOF detectors when they are in the center of the intensity profile of the LCLS beam [33]. 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 a cluster would produce barely any signal on the front pnCCD. In order to filter on the full spectrum of interesting hits, a series of filters have been applied. Filtering on ion time of flight high-charge states has been successful in the large scale analysis of events that resolve pump–probe dynamics. In the left panel of Figure 4.12, the xenon pump–probe data has been automatically pre-filtered on xenon ion high-charge

4.6. Data filtering

states, leaving several thousand events that were then semi-automatically reduced to over 350 single-hit diffraction images. This semi-automatic process determines, 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 plotted events in Figure 4.12 indicate a linear average-Xe-cluster-radius increase of $\sim 20\%$ over the course of the first 800 fs (see more in Section 5.1). However, to perform phase retrieval and to solve the inverse problem, bright hits containing many photons are required. Therefore, another set of hitfinding has been implemented. This hitfinder determines the scattering intensity of single events automatically and the brightest hits that show signs of X-ray induced dynamics have been selected semi-automatically. These hits undergo a phase retrieval to reveal their electron density. To clarify, single He- and Xe-cluster hits show X-ray induced dynamics, when the 1d reduction of the intensity profile differs from the scattering of an intact sphere, i.e., $\frac{I}{F_{\text{intact}}^2} \ll 1$. The case of X-ray induced dynamics in HeXe-clusters is discussed in more detail in Section 5.5.

5. Results and discussion

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

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

A large scale analysis of size, scattered intensity and shape is performed on single-shot diffraction patterns of xenon cluster to investigate the nanoplasma transition. The analysis starts by selecting useful hits from an experimental run using the methods described in Section 4.6. A typical run length is 20 mins and results in a total of $\sim 36,000$ images. These events are automatically reduced to ~ 1000 events by filtering on high-charge states of Xe-ions. Then, a semi-automatic routine reduces the data to a subset of 30 to 60 single-shot diffraction patterns per run. This breakdown allows the estimation that (0.08 to 0.16) % of all imaged xenon clusters had good parameters for analysis per run. Multiple runs of data were taken as the pump–probe delay Δt was varied.

In the above mentioned high-throughput size evaluation, Equation (2.39) is used to automatically determine the cluster radii of several hundred Xe-clusters. Figure 5.1 shows a distribution of cluster radii at X-ray pump–X-ray probe delays, $\Delta t = (0 \text{ and } 800) \text{ fs}$. The size distribution of Xe-clusters follows a log-normal distribution [149] and at $\Delta t = 0 \text{ fs}$ the mean cluster radius is 61 nm. When the delay is increased to $\Delta t = 800 \text{ fs}$, the mean cluster radius increases to 74 nm and the distribution becomes more broad. The mean cluster radius increase by $\sim 20\%$ over the time delay of 800 fs is attributed to

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

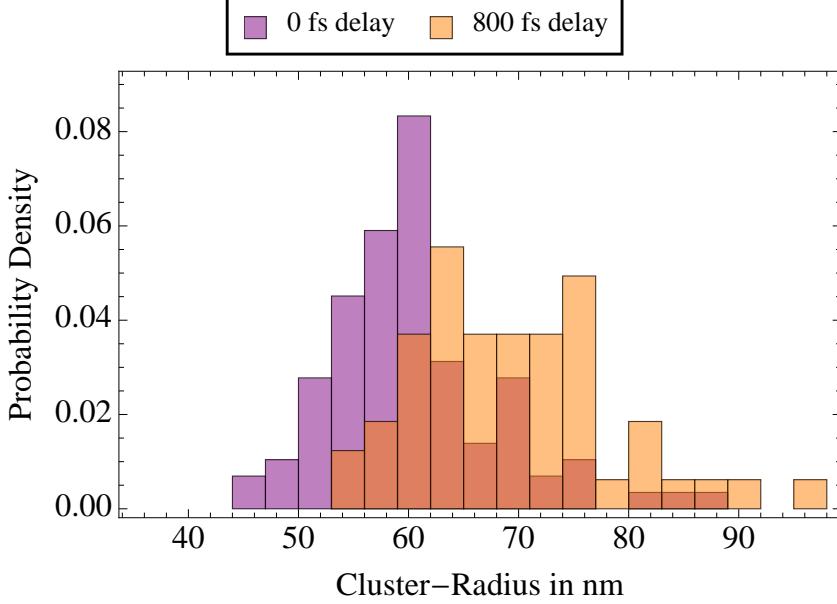


Figure 5.1.: Size evaluation of ~ 30 single Xe-cluster hits per time delay Δt step. At $\Delta t = 0$ fs, the size distribution follows an expected log-normal distribution, while at $\Delta t = 800$ fs the distribution broadens and shifts towards larger radii due to the nanoplasma transition.

the nanoplasma expansion, as the cluster source should have a stable size distribution. The Xe-cluster size distribution may become more broad due to a distribution of the pump-pulse power density that varies the expansion speed from shot-to-shot.

Figure 4.12 summarizes the mean cluster radii data over several pump-probe delay steps, $\Delta t = (0, 120, 250, 400, \text{ and } 800)$ fs. This data suggests that the nanoplasma expansion speed, v_{exp} , is constant. With the mean cluster radii at $\Delta t = (0 \text{ and } 800)$ fs, we note $v_{\text{exp}} \approx 15\,250 \text{ m s}^{-1}$. We may use this expansion speed to estimate the electron temperature of the nanoplasma. Here, it is assumed that electrons thermalize with the nucleus within a few femtoseconds such that the velocity distribution of the hot electron gas in the nanoplasma follows a Maxwell-Boltzmann distribution. If we use v_{exp} as mean velocity of a Maxwell-Boltzmann distribution the electron temperature is ~ 125 eV, which compares to temperatures that can be found inside the sun. We can also compare the electron temperature to a similar IR pump-X-ray probe nanoplasma study on Xe-clusters [16], where electron temperatures of ~ 200 eV have been found. The difference in expansion speed and electron temperature is attributed to the different pump-pulse parameters. Although the IR-pump pulse had power densities of only $\sim 10^{15} \text{ W cm}^{-2}$ compared to the $\sim 10^{17}$

5. Results and discussion

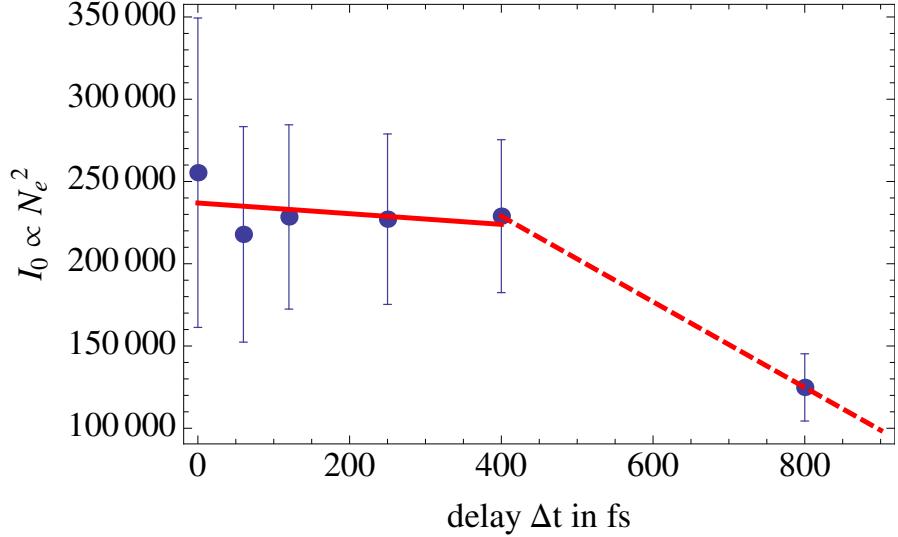


Figure 5.2.: Intensity I_0 in arb. units at $\vec{Q} \rightarrow 0$, which is proportional to the total number of scatterers squared N_e^2 , here electrons. The data show that the expanding cluster Coulomb traps electrons steadily in the initial stages of the nanplasma expansion but as the trapping potential decreases due to the multi-step ionization a sudden decrease of $\sim 65\%$ electrons is observed.

W cm⁻² of the X-ray-pump pulse in this study, the X-ray absorption cross-section is much smaller than the IR cross-section. Ultimately, the Xe-clusters absorb more energy from IR-pump pulses than X-ray-pump pulses of similar power density.

The total number of scatterers, i.e., electrons that interact with the LCLS pump-pulse, is deduced from the diffraction patterns via an intensity analysis. As described in the theory Section 2.3.1, when

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

where I is the distribution of the scattered intensity as a function of the scattering vector \vec{Q} , we can determine the number of electrons, N_e , that contribute to the scattering process. Figure 5.2 shows the parameter ρ_0^2 , from Equation (2.39), as a function of the time delay Δt (blue dots). As the incident beam intensity, I_0 , remains constant in the X-ray pump-X-ray probe setup $\rho_0^2 \propto N_e^2$. Two linear fits (red lines) have been added to the figure to visualize the effect. The data show that up to a delay of $\Delta t = 400$ fs the amount of electrons N_e in the interaction region rather constant (solid red line). However, at a time delay of $\Delta t = 800$ fs, the number of scattering electrons decreases on average by $\sim 26\%$ (dashed red line). This supports the idea that the Coulomb

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

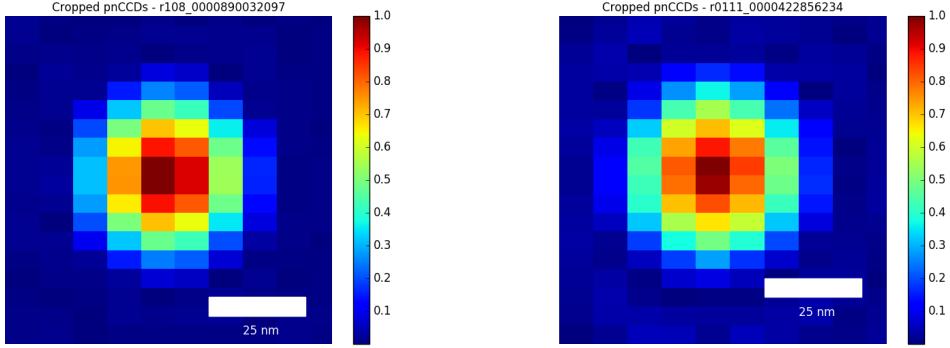


Figure 5.3.: Single-shot 2D reconstructions of diffraction patterns from single Xe-clusters. The left image shows a ~ 25 nm radius Xe-cluster at a pump–probe delay $\Delta t = 0$ fs. The cluster has a spherical or arguably icosahedral electron density distribution that is distinct compared to the background. The right image shows a ~ 25 nm radius Xe-cluster at a time delay $\Delta t = 800$ fs that shows a similar symmetry but due to the loss of scatterers (see fig 5.2), the signal-to-noise ratio decreases and a ringing appears that is likely generated by the support structure in the iterative process.

barrier 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 and dissipate the interaction region, such that they do not contribute to the diffraction image anymore. The key driver that lowers the trapping potential, thus releasing the electrons, is the expansion of the cluster. The effect of trapped electrons has been simulated in, e.g., [19]. Trapped electrons contribute drastically to the radiation damage process due to secondary collisional ionization.

In a thought-experiment, where SPI is performed using long X-ray pulses of ~ 100 fs, the sample would get ionized and efficiently traps electrons. The trapped electrons can be treated as non-relativistic, thus they do contribute coherently to the scattering pattern. However, their contributions reduce the contrast as their positions are not related to the structure. A similar damage effect is described in [17] and it is shown that computational methods may compensate for such damage.

Figure 5.3 shows 2D reconstructions of single Xe-clusters at $\Delta t = 0$ fs in the left panel and $\Delta t = 800$ fs in the right panel. The clusters appear generally spherical, however, an icosahedral shape is imaginable. Both clusters have a radius of $r \approx 25$ nm. The

5. Results and discussion

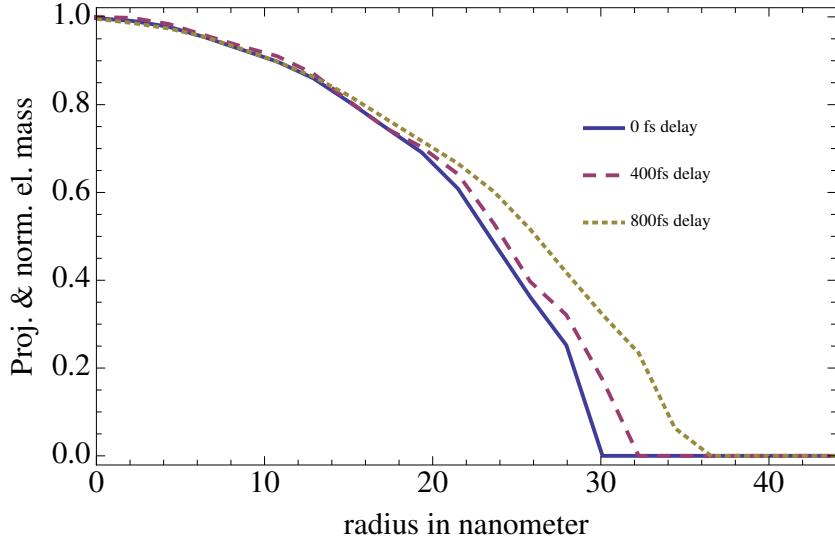


Figure 5.4.: Single shot 1D reconstruction of Xe-cluster at various time delays Δt . The figure shows the projected and normalized el. mass as a function of the radius, i.e., the electron density. These real-space images of a nanoplasma transition show that, at first, outer atomic layers are shed off, here imaged at $\Delta t = 400$ fs. And over time, more inner atomic layers follow, here imaged at $\Delta t = 800$ fs.

reconstructions constitute some of the smallest objects recovered with diffraction imaging at the time of writing. The minimal resolvable feature size in these images is $\sim 14 \times \sim 6 \text{ nm}^2$ 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 a lower signal-to-noise ratio, which is due to the described loss of electrons in the interaction region. Due to the resolution limitation, a nanoplasma expansion, i.e., the earlier discussed 20 % increase in Xe-cluster radius, may be difficult to see. Also, 2D reconstructions of nanoparticles of that size are challenging and the number of successful 2D reconstructions is low. We thus analyze the xenon imaging data in 1D in the following paragraphs.

Real-space images of single Xe-clusters have been recovered in 1D in Figure 5.4 (see methods Section 4.3.3). The 1D reconstructions show normalized and projected electron density from single xenon cluster at time delays $\Delta t = (0, 400, \text{ and } 800)$ fs. At $\Delta t = 0$ fs, the electron density follows the density projection of a sphere (compare Figure 4.8). With a delay of $\Delta t = 400$ fs, an expansion of the outer atomic layers of the cluster is

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

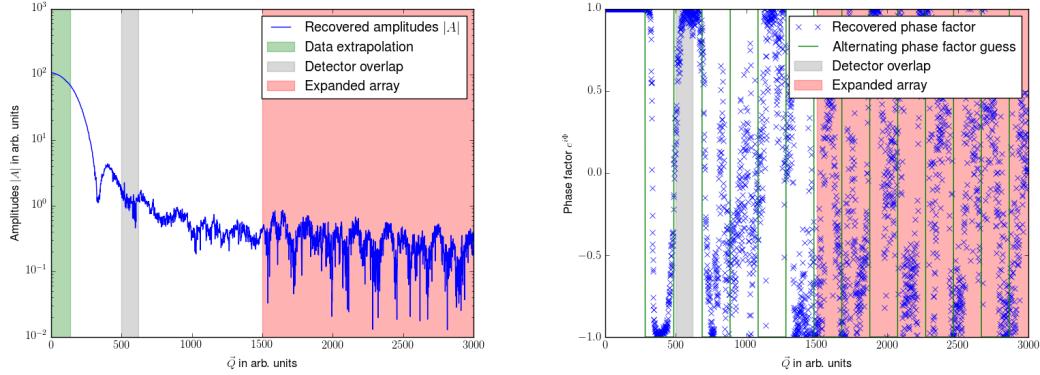


Figure 5.5.: The left panel shows the recovered amplitudes $|A|$ and the right panel shows the phase factor of the 1D phase retrieval. The green and red background indicates the space where initial data points were extrapolated. The gray area discloses the detector overlap. See Section 4.3.3 for more details.

observed. At $\Delta t = 800$ fs, outer layers continue to expand and inner atomic layers start to follow. Over the time delay sequence $\Delta t = 0$ to 800 fs, the cluster radius expands $\sim 20\%$, or from $r \approx 30$ nm to $r \approx 36$ nm. This sequence of events gives insight into the shape of the Xe-cluster as it undergoes the nanoplasma transition and directly confirms theoretical predictions, e.g., [19]. The images clusters have comparable initial sizes as they are selected from the lower end of the cluster size distribution.

For the sake of completeness of these 1D reconstructions, the recovered modulo of the amplitude, $|A|$, and the recovered phase factor are shown in Figure 5.5 for the data at $\Delta t = 800$ fs. The amplitudes $|A|$ have been replaced in the space with white background. The data with the green background was interpolated using the anticipated scattering of a sphere. The grayed area indicates the pnCCD detector overlap and the red background data is extrapolated 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.

We may also analyze the Xe-cluster in reciprocal space and analyze the radial projections of the measured diffraction patterns directly. Radial projections of single-shot diffraction

5. Results and discussion

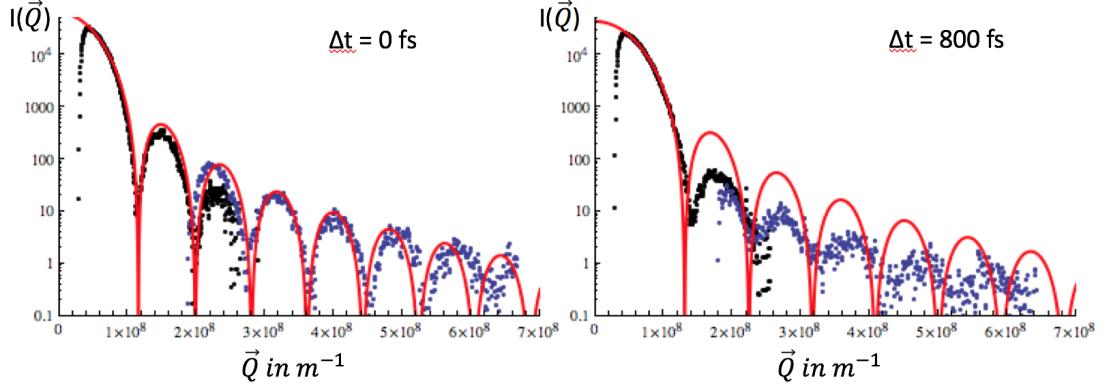


Figure 5.6.: Single shot diffraction pattern at certain pump–probe delays Δt . The red curve simulates the scattering of a sphere, the black data points are from the rear pnCCD detector and the blue data points are from the front pnCCD. The nanoplasma expansion manifests in the scattering intensity I at large spatial frequencies $|\vec{Q}|$, where I decreases as described in [16].

patterns from single Xe-cluster can be found in Figure 5.6. 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 and the incident beam intensity variable. The black data points are projected from the rear pnCCD and 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. Hence, the fit (red line) agrees well with the data points up to scattering angles of $\Theta \approx 9^\circ$ or $|\vec{Q}| \approx 6.8 \cdot 10^8 \text{ m}^{-1}$. However, it should be noted that this comparison becomes less good at very large scattering angles due to the flat detector [100] and deviations in the diffraction pattern from a perfect sphere. As the time delay Δt increases, the large- $|\vec{Q}|$ scattering signal decreases and the scattering of a plain sphere does not fit the scattering well anymore. A similar effect is also observed in the previously mentioned IR pump–X-ray probe study [16]. Due to the nanoplasma transition, the Xe-cluster is expanding with the outer layers expanding faster than the core. A mathematical description of this damage model, namely an expanding sphere, has been introduced in Section 4.4. It generally fits the data well, as it is shown in great detail in [16, 150]. Note that the X-ray pump–X-ray probe considerations from Section 4.2.2 would minimize the effect of a decreased scattering at large scattering angles.

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

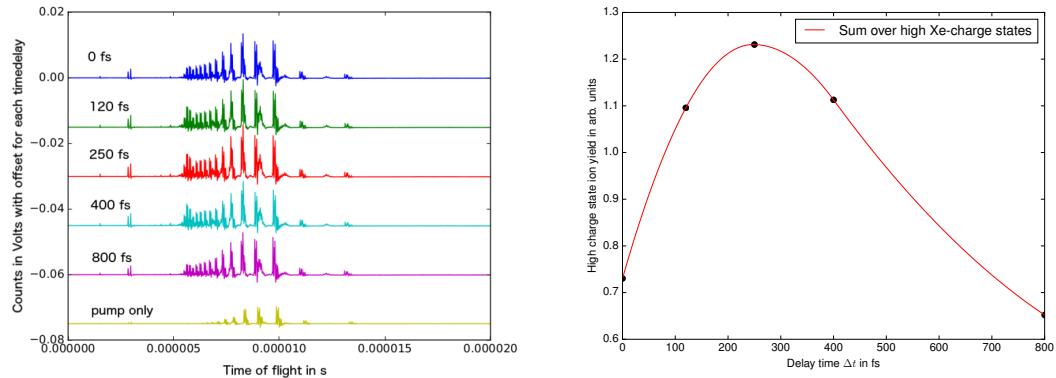


Figure 5.7.: Atomic xenon ion time-of-flight data shows resonant type behavior. As the X-ray pump-pulse traverses through the xenon ions, the 3d-subshell becomes highly ionized and thus the atom becomes increasingly transparent for the probe-pulse ($\Delta t \approx 0 - 120$ fs). The electron-holes have 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 probe-pulse efficiently ionizes the atoms ($\Delta t \approx 250$ fs). Eventually, relaxation processes dissipate energy leading to fewer high-charge states.

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

Ion time-of-flight traces of atomic xenon at different time delays $\Delta t = (0, 120, 250, 400, \text{ and } 800)$ fs and X-ray pump-pulse only data is shown in Figure 5.7. The time-of-flight data show a resonance behavior as the atomic xenon high-charge states peak at $\Delta t = 250$ fs. The xenon high-charge states start low at $\Delta t = 0$ fs and then peak due to intensity-induced X-ray transparency [15, 151]. 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 and the Xe-atoms become increasingly transparent as the X-ray pulse propagates. 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, relaxation processes catch up and effectively dissipate energy, thus reducing the average ionization level.

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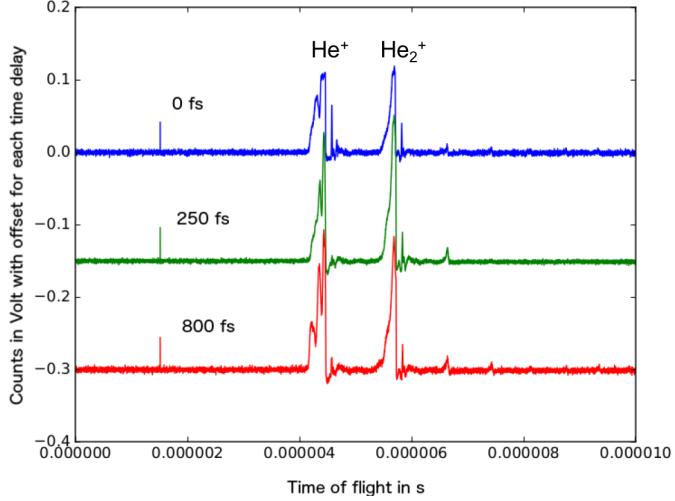


Figure 5.8.: Ion time-of-flight traces of He-cluster with a radius of $r_{\text{He}} \approx 810$ nm. Although minor changes in the charge fragmentation are observed, we shall note that there are no He^{2+} ions in this data. The absorption cross-section of helium are too low to lead to doubly-charged states [84].

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

The response of clusters in highly intense X-ray radiation is more complex than the atomic signal. Size-dependent [151, 152] and recombination effects in the nanoplasma [153] 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 $\Delta t = (0, 250, \text{ and } 800)$ 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 [75]

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

The data show an overall similar behavior regardless of the delay Δt , although minor changes in the charge fragmentation distribution can be seen. More importantly for referencing purposes, the traces indicate no contribution of doubly-charged helium atoms. The lack of double-charged helium can be explained by the comparably low absorption cross-sections of helium (see Table 2.3) [84].

Xenon doped helium cluster time-of-flight traces are shown in Figure 5.9. Here the He-droplets have a radius of $r_{\text{He}} \approx 600$ nm or $\langle N_{\text{He}} \rangle \approx 2 \cdot 10^{10}$ particles with a $\sim 0.6\%$ doping

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

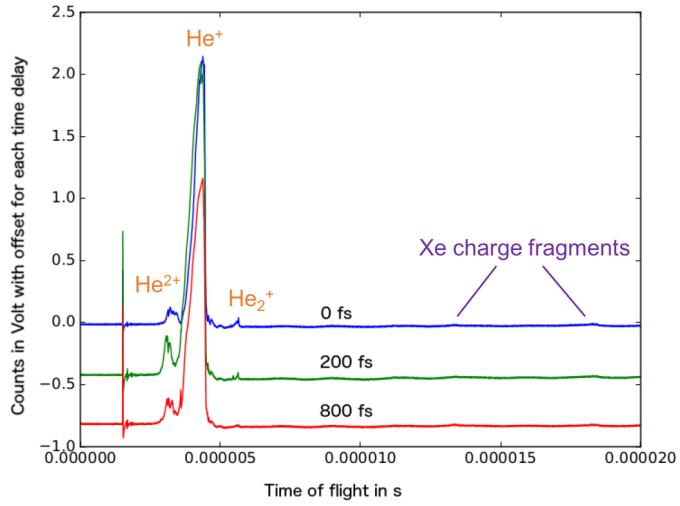


Figure 5.9.: Ion time-of-flight spectra of He-cluster with $r_{\text{He}} \approx 600$ nm radius and Xe-doping levels of $\sim 0.6\%$. The Xe-atoms absorb X-rays efficiently and transfer the absorbed energy to the He-atoms. The Xe-ions recombine and only a few xenon charge fragments are observed. Due to the energy transfer, doubly-charged He-ions are detected and the *kinetic energy release* is increased as well. As the delay time, $\Delta t = (0, 200, \text{ and } 800)$ fs, is varied sequentially, the system undergoes a resonant type behavior that is attributed to the ionization dynamics of Xe-atoms.

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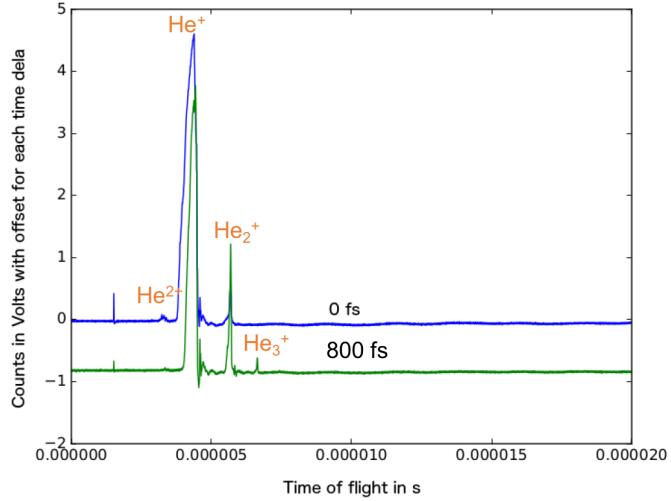


Figure 5.10.: Ion time-of-flight spectra of He-cluster with $r_{\text{He}} \approx 775$ nm radius and $\sim 0.06\%$ xenon doping. These weaker doped HeXe-clusters show a lower He-ion count and kinetic energy release due to overall less absorption from the lower xenon doping. However, He^{2+} , which indicates an energy transport from the xenon to the helium, is still observed.

level of xenon. For the sake of completeness, the helium depletion at this doping level is $\sim 62\%$ (see Section 2.2.2). Most notable is the presence of He^{2+} ions and a strongly increased signal from He^+ ions. But, 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 hypothesize two points. One, there must be an efficient, ultrafast energy transfer process from the Xe-particles to the He-droplet; two, that the helium atoms function as electron reservoir as the initially photoionized xenon atoms must recombine with trapped electrons to be neutrally charged and thus not detected by the ion TOF. As the time delay Δt is varied, we observe that the He-ion signal shows a resonant 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 around the data shown in Figure 5.8 and 5.7 and conclude that this behavior does not originate from the absorption and ionization dynamics of the He-droplet but rather from the Xe-atoms with which the He-droplet is doped. In a theoretic study of HeXe-clusters using optical laser pulses a similar resonant behavior is found [154].

Figure 5.10 shows ion time-of-flight data of with $r_{\text{He}} \approx 775$ nm He-droplets and a 0.06%

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

doping at pump-probe delays $\Delta t = (0 \text{ and } 800) \text{ fs}$. 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, compared to the higher doped data these peaks are less intense. Qualitatively this can be explained with the less strong xenon doping. The X-ray absorption from the xenon atoms and subsequent energy transfer to the helium atoms dominate the helium ion characteristics, although the He-droplet is larger in this case. So, less doping results in fewer photon absorption processes and thus less energetic helium ion characteristics. Again, 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 support this hypothesis.

Summarizing, pristine He-droplets show few dynamics as the time delay Δt is varied and only singly-charged He^+ ions are measured. If the He-droplets are doped with xenon, doubly-charged He^{2+} ions are detected, the kinetic energy release 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 is more frequent. This data suggests an ultrafast and efficient energy transfer from the xenon atoms to the helium atoms. Collisions could drive this transfer. The helium particles furthermore act as an electron reservoir. The 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 an electron supplier for the high-Z material has also been studied in [105].

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

It is not well known how heterogeneous helium-xenon clusters form a core-shell system. As described in Section 2.2.2, the superfluid 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. [10] reports that at a doping level of 0.02%, i.e., when there are 5000 more helium atoms than xenon atoms, multiple smaller clusters form and locate at vortexes within a 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-

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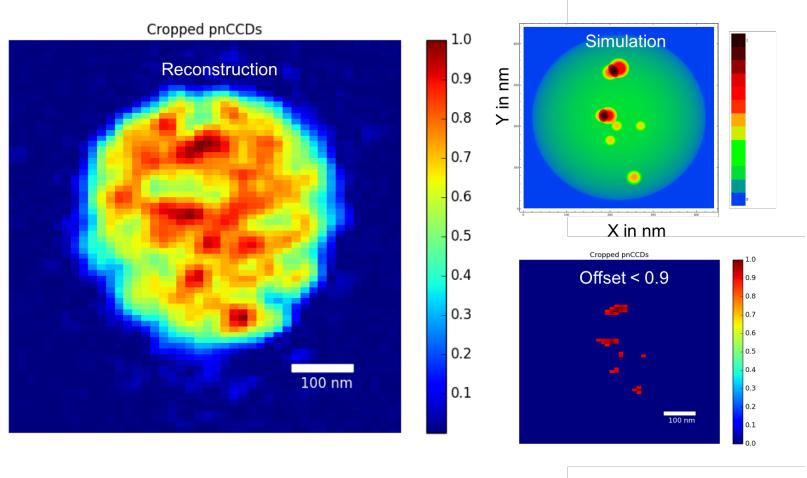


Figure 5.11.: Real-space reconstruction of a HeXe-cluster that has a radius of $r \approx 210$ nm and a Xe-doping level of $\sim 0.5\%$ (left). The electron density indicates a Xe-cluster arrangement of the plum-pudding few scatterer case discussed in Figure 5.12. The normalized intensity map is offset (bottom right image) and mimicked by 2D electron density simulations (top right image).

clusters form within a droplet. Let us call hypothesis two a *plum pudding core-shell system*¹ that we can further divide into a case of few and larger scatterers, or many and smaller scatterers.

Fortunately, single particle imaging is a direct structural measurement technique that allows us to investigate the actual structure of a HeXe-cluster. The left panel of Figure 5.11 shows a reconstruction of a HeXe-cluster that has a radius of $r \approx 210$ nm at a Xe-doping level of $\sim 0.5\%$. The reconstruction indicates a plum-pudding arrangement, where a few Xe-cluster (intense, dark red spots) appear randomly distributed within the He-droplet (less intense, green to orange area). The normalized intensity map from the reconstruction is offset to guide the eye to dense centers (bottom right panel) and these dense center can be used to reverse-engineer the electron density. The reverse engineered electron density can be Fourier transformed to yield a diffraction image that can be compared to data (top right panel). To verify the success of the HeXe-reconstruction, several core-shell arrangements are shown in Figure 5.12 along with their Fourier-space representations in 1D. The shown He-droplet has a radius of $r \approx 125$ nm and a constant xenon doping level of $\sim 20\%$ and the figure shows an artistic representation of

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

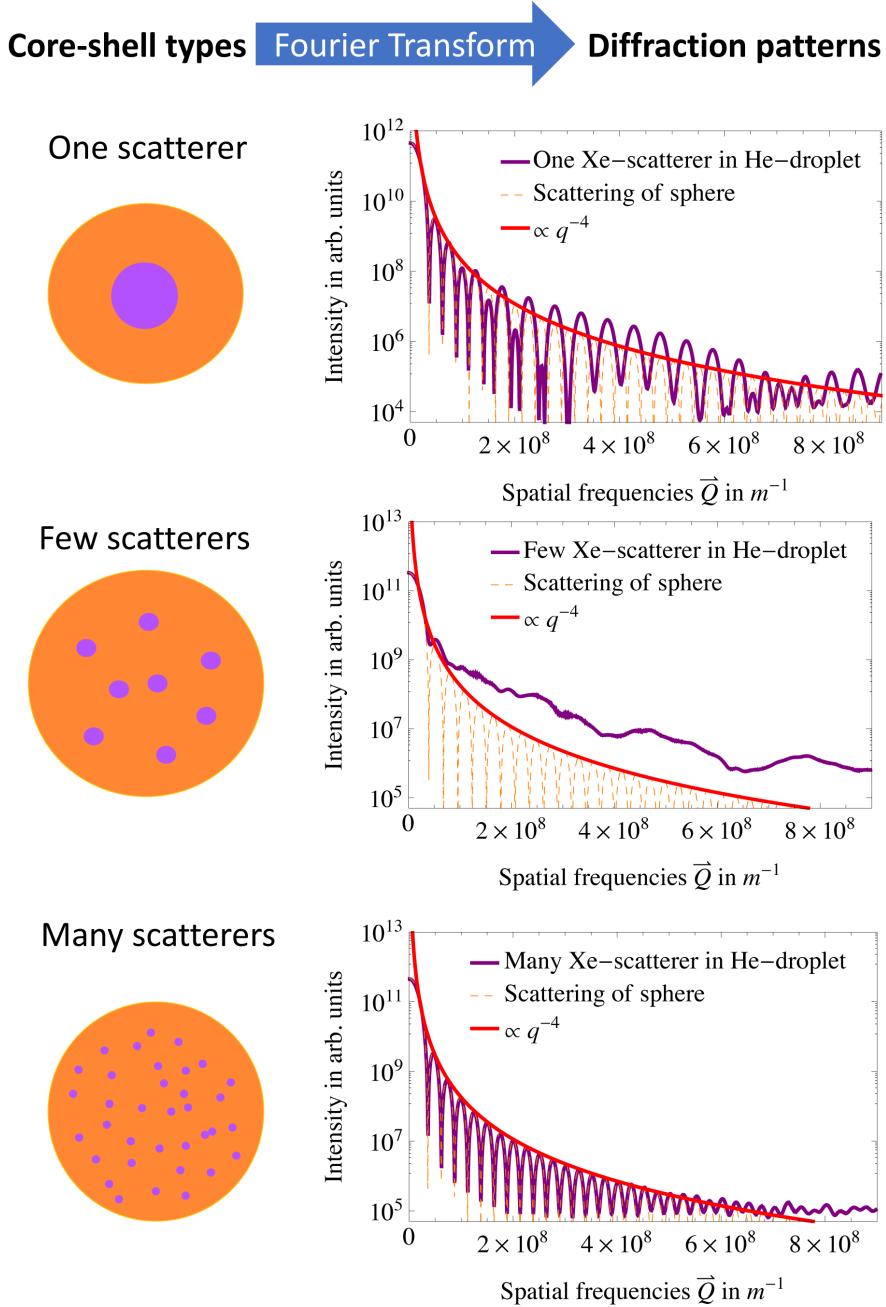


Figure 5.12.: Hypothetical arrangement of xenon atoms in superfluid helium droplets and corresponding 1D diffraction patterns. The He-droplet has a radius of ~ 125 nm and the Xe-doping level is $\sim 20\%$. The case of one xenon scattering center $N_{sc} = 1$ (top), few scatterers $N_{sc} = 8$ (middle) and many scatterers $N_{sc} = 100$ (bottom) are shown (left) to illustrate their impact on diffraction pattern (right). 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 dominated by the Xe-clusters. This is mostly due to the size of the Xe-clusters; smaller scattering centers are resolved at larger scattering angles.

5. Results and discussion

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 distribution 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. The purple curve in the one-scatterer case consists of 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 the orange, dashed line). At low spatial frequencies, the He-droplet dominates the signal on the diffraction image and at large spatial frequencies, the Xe-cluster influence is more prominent. Ultimately, this is related to the size of each cluster and the contributions of their spatial frequencies to modulations in Fourier-space. In the few scatterers case, with $N_{sc} = 8$ scattering centers, the diffraction pattern (purple line) at low spatial frequencies \vec{Q} is still dominated by the He-shell and at large spatial frequencies \vec{Q} by the Xe-cores. However, the diffraction image appears to contain a more complex structure at large \vec{Q} -values due to the delocalized scatterers. Also, the average scattering intensity is well above the envelope of the scattering of a sphere (red line) that has been fitted onto the zeroth diffraction order. The location of the few scattering centers 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. In the many scatterers case, $N_{sc} = 100$ scattering centers are randomly distributed within the He-droplet. The Xe-clusters 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 a 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 do the Xe-scatterers start to dominate the signal, i.e., signal is above the envelope function of the scattering of the sphere.

To quantify and estimate the effect of Xe-cluster of a certain size contributing to the spatial frequencies, we can make use of Abbe's criterion (4.9) and the wave vector definition (2.31). In vacuum, we can write down the minimal resolvable feature size d as

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

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. 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

5.5. Understanding structural damage in the plum-pudding type clusters

the one-scatterer case $r_{\text{Xe}} \approx 15$ 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 scatterers case and ~ 10 times larger in the many scatterers case than its individual, simulated Xe-cluster components.

5.5. Understanding structural damage in the plum-pudding type clusters

Figure 5.13 shows a diffraction pattern from the simulated plum-pudding type electron density shown in Figure 5.11 that illustrates 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 effects of structural damage. 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 the Xe-cluster intact are intact. Conversely, the green, dashed curve shows the effect where the last 15% of the radius from Xe-clusters expand, but the He-shell stays intact. Lastly, all spheres are expanding in the last 15% of their radii. 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 frequencies when the (much smaller) Xe-cluster are expanding. The vast size difference of the Xe-clusters to the He-droplet, which are $r_{\text{Xe}} = (25, 22, 20, 18, 17, 14, 14, \text{ and } 13.5)$ nm versus $r_{\text{He}} = 210$ nm, allow a strict separation between the spatial frequency contributions from the He-droplet, e.g., the expanding shell, and the contributions from the Xe-clusters, e.g., the intact cores, in the diffraction pattern analysis.

These insights can be used to compare the 2D-simulations to the measured diffraction patterns. 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

5. Results and discussion

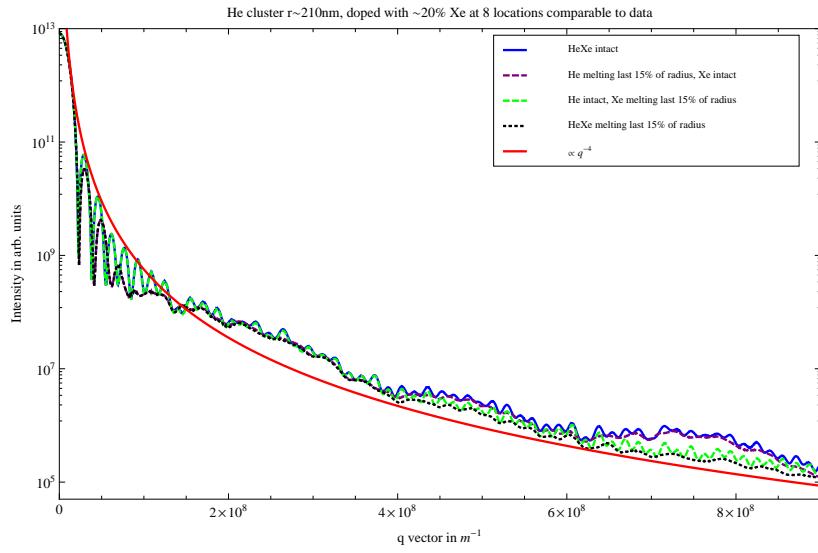


Figure 5.13.: Diffraction images from 2D electron density simulations that illustrate structural damage in HeXe-cluster. Electron densities as per Figure 5.11. In reciprocal space: The blue curve shows the helium droplet as well as Xe-clusters intact. The purple, dashed curve shows an expanding He-droplet, 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 the plum-pudding type clusters

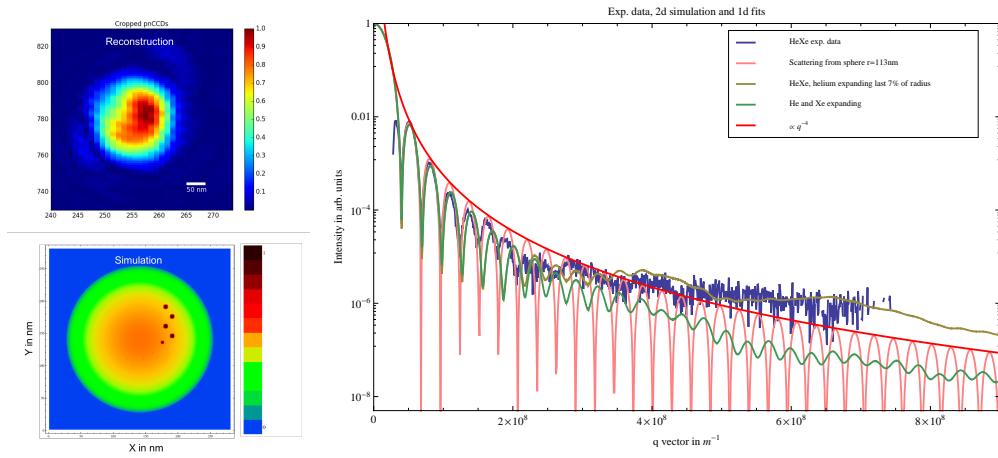


Figure 5.14.: 2D simulations fitted to real-space and Fourier-space data. HeXe-arrangement of 2D simulations (bottom left) matches recovered electron densities of a HeXe-cluster (top left). The diffraction pattern (right) shows the 1D-projected experimental data (blue curve) from the same HeXe-cluster with $r_{\text{He}} \approx 113 \text{ nm}$. This HeXe-cluster was imaged at $\Delta t = 800 \text{ fs}$ and undergoes a nanoplasma transition. 2D simulations showcase several damage scenarios; in reciprocal space: Xe-cluster are intact (yellow curve) and Xe-cluster expanding (green curve). The simulations of an expanding He-droplet and intact Xe-cluster fit the experimental data best.

5. Results and discussion

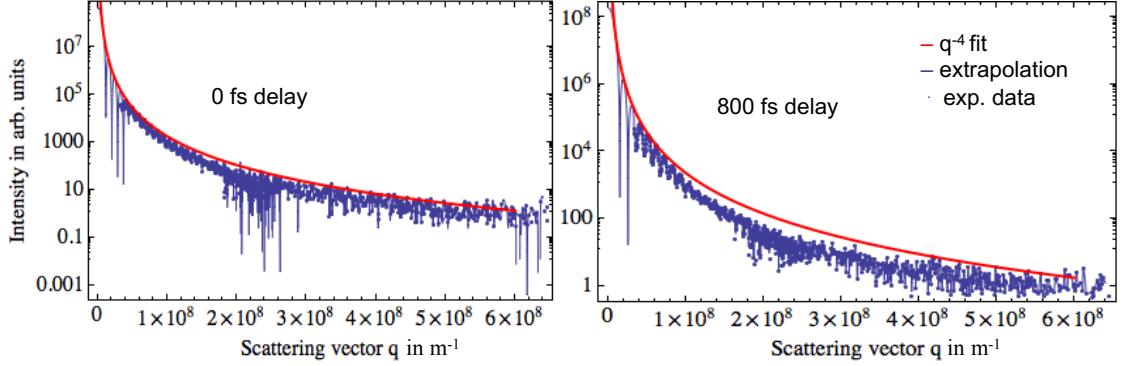


Figure 5.15.: Single-shot diffraction images of pristine He-droplets at various Δt spherically projected into 1D.

HeXe-cluster has a radius $r_{He} \approx 113$ nm. The dense spots in the reconstruction have been simulated with nine Xe-cluster of radii $r_{Xe} = (4, 4, 4, 4, 3, 0.5, 0.5, 0.5, 0.5)$ 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 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 structural damage in the Xe-cluster is still possible, but may not be detectable due to current resolution limitations.

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

Single-shot diffraction images of He-droplets with radii $r_{He} \approx (379$ and $302)$ nm, at time delays $\Delta t = (0$ and $800)$ 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) are 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

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

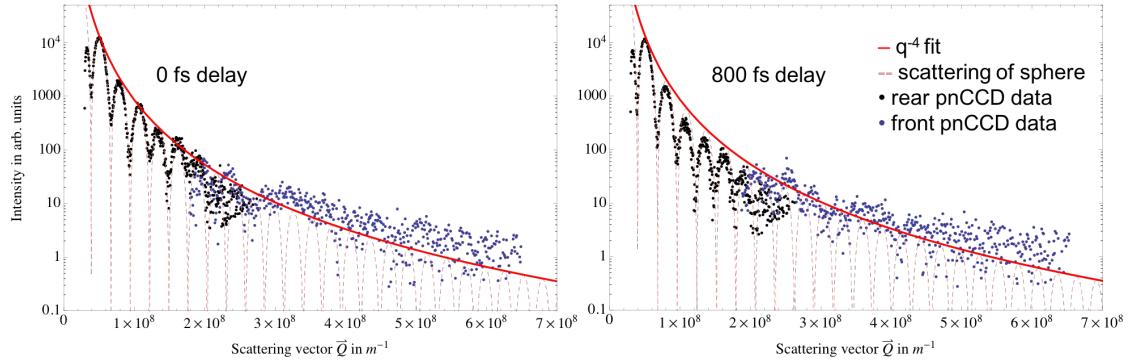


Figure 5.16.: Single-shot diffraction pattern of HeXe-cluster at time delays $\Delta t = (0$ and $800)$ fs. At $\Delta t = 0$ fs, the diffraction pattern follows the scattering pattern of a sphere at low spatial frequencies \vec{Q} but stays well above the envelope function \vec{Q}^{-4} at high spatial 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. This suggests that the He-droplet functions as sacrificial shell keeping the Xe-nanoparticles intact. More in text.

between $\vec{Q} \approx (1$ to $4) \cdot 10^8$ m⁻¹ are well below the envelope. As shown in section 5.5, this indicates damage.

Single-shot diffraction images of HeXe-cluster with radii $r_{\text{He}} \approx (116$ and $113.5)$ nm, at time delays $\Delta t = (0$ and $800)$ 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 $(0$ to $800)$ fs provide as another indication that helium functions as a sacrificial 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 envelope 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, indicating 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 scat-

5. Results and discussion

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 at large \vec{Q} -values. More in text.

tering versus 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 easily compared to the scattering curve of a sphere $f(\vec{Q})$. Hence, we can introduce a function $h(\vec{Q})$ that interpolates between the data points of pristine He- and Xe-cluster. We can calculate a relative difference in the scattering at a certain time delay using the $\frac{\sum h(\vec{Q})}{\sum f(\vec{Q})} |_{\Delta t}$. Since the effect is most visible at large \vec{Q} -values, the functions h and f total between $2.8 \cdot 10^8 \text{ m}^{-1}$ to $6.4 \cdot 10^8 \text{ m}^{-1}$. For Xe- and He-clusters, 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 $65\%|_{\Delta t=800\text{fs}}^{\text{He}}$. The interpolating function seems to underestimate the actual scattering by $\sim 10\%$, which gives us an idea of the error of this estimate. Some other error sources such as electronic noise would make up for the underestimate of the interpolating function. HeXe-clusters cannot directly 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 represent similar data points, as they have the same incident beam variable I_0 in the $I_0 |\vec{Q}|^{-4}$ fit and a size difference of only $\sim 2\%$ at the same source and doping conditions. When comparing the interpolating functions $h(\vec{Q})|_{\Delta t=800\text{fs}}^{\text{HeXe}}/h(\vec{Q})|_{\Delta t=0\text{fs}}^{\text{HeXe}}$ at different time delays Δt , 33 % more scattering at large \vec{Q} -values is measured. This leads to the conclusion that Xe-clusters exhibit no measurable damage despite the fact that damage in the He-droplet is visible at low spatial frequencies \vec{Q} . The error in the estimation originates likely from a varying pickup pattern of Xe-atoms and 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 damages in the sample². If Xe-clusters are embedded in a

²The actual intensity loss must be larger due to the loss of electrons that is described in Figure 5.2.

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

He-droplet, no damage is detected in Xe-clusters 800 fs after the nanosample has been pumped by LCLS, although the He-droplet shows damage. The He-droplet appears to shed atomic layers, which transports energy away from the Xe-clusters and enables them to exhibit no measurable damage patterns that were discussed in Section 5.5.

6. Summary and outlook

For the present study, a novel, accelerator-based X-ray pump–X-ray probe technique was pioneered [51] and the new soft X-ray end-station LAMP was built and commissioned [112]. Using this new experimental setup, a coincident single particle imaging (SPI) and time-of-flight mass spectroscopy method 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 increased the “numerical aperture” and extended the dynamic range of the detector system. The developed coincident imaging and spectroscopy, X-ray pump–X-ray probe technique allowed the study of X-ray-induced dynamics on the few-ten-femtosecond timescale with a spatial resolution in diffractive imaging on the few nanometer lengthscale.

The work experimentally investigates the nanoplasma transition in rare-gas clusters. Single, nanometer-sized, rare-gas clusters, namely superfluid He-, solid Xe- and mixed HeXe-cluster are “pumped” with an X-ray pulse to undergo the phase transition to a nanoplasma. This transition is nothing different but the radiation damage that a typical biological sample receives due to the interaction with highly intense X-ray pulses. This transition is “probed” with another X-ray pulse at a later time delay. The here studied delay range is $\Delta t = 0$ to 800 fs. The coincident imaging and spectroscopy measuring method reveals that pristine He- and Xe-clusters become highly ionized and form a nanoplasma. The nanoplasma from Xe- and He-clusters exhibits stark radiation damage due to an expansion of the plasma. Xe-clusters, for example, undergo a radial expansion that shows in diffraction images at the first delay step at $\Delta t = 120$ fs. Over the course of 800 fs, the radial expansion manifests in a $\sim 20\%$ increase of their initial average radius, which is $r \approx 61$ nm. The hot Xe-nanoplasma is heated to electron temperatures of ~ 125 eV. This thesis then shows that mixed HeXe-clusters, generated through the pickup-principle at doping levels up to 0.5%¹, arrange in a *plum-pudding* configuration. In a plum-pudding cluster structure, multiple Xe-clusters condense within a larger He-droplet at different locations. When these mixed HeXe-clusters are pumped with intense

¹0.5% as many xenon atoms as helium atoms.

X-rays from LCLS, Xe-clusters are the main absorbent of the radiation. But, data show that Xe-clusters are barely ionized and, at current resolution, appear to be undamaged inside the He-droplet. The weak absorbing helium experiences stark ionization and the He-droplet shows signs of radiation damage. This suggests that the He-droplet functions as a sacrificial shell around the Xe-particles. Two processes are identified that protect the Xe-clusters within the He-droplet; one, a kinetic energy transport from the Xe-clusters to the He-droplet; two, the He-droplet supplies electrons to the initially ionized Xe-particles, minimizing their ionization level.

These results of this work are beneficial to a variety of fields. First, the work from [16, 105] are expanded to include reconstructions of nanoparticles and a time-resolved X-ray pump–X-ray probe study. This study shows that a tamper layer can be used to inhibit effects of radiation damage in the diffraction pattern. This may be interesting for the SPI community, where it is foreseen that radiation damage will be a limiting factor in the ultimate achievable resolution [8]. 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 [104]. This allows an orientation and averaging of diffraction images, thus enabling a high-resolution 3D reconstruction of the sample while making use of the asymmetric detector geometry. 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 [30, 48, 53, 155, 156], allowing entirely new insights in previously 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/photon
                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/photon
                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
```

```

    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. Appendix

```

### 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)

```

7.2. Python code on combining detectors

```
# 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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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 11. Januar 2017

Maximilian Jakob Bucher

Ort, Datum

C. Acknowledgment

This has to be written.

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