The FEL-Simulator
Imaging Nano-Particle Injectors Using
Strong-Field-Ionisation Time-Of-Flight
Mass-Spectrometry

Christian Nikolaus Kruse

Internal Supervisor:
Professor Dr. Jon MARANGOS
External Supervisor:
Professor Dr. Jochen KÜPPER

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Abstract

Coherent diffractive imaging enables the analyses of fragile biomolecules at picometre spatial and femtosecond time resolution. While most experiments are performed with nano-crystals, the analyses of single particles and the recording of molecular movies is limited by low hit rates of the X-ray pulses and the analysed specimen. In order to increase hit rates, new particle injectors have to be developed and improved. For this challenge it is crucial to analyse the particle flows of existing injectors and validate the working principle of prototypes. In this report an experiment is introduced to characterise the particle flow of injectors, especially of gas dynamic virtual nozzles and aerodynamic lens stacks. The imaging setup contains a 1 μm microscope for optical imaging and a velocity map imaging setup for mass spectrometry. The optical measurement was successfully tested on a gas dynamic virtual nozzle. The mass spectrometry setup was simulated in SIMION® to analyse the achievable mass resolution of the setup under the influence of different injector-shapes. With the final design for the mounting of a gas dynamic virtual nozzle, masses around 100 amu can easily be distinguished. With the imaging setup introduced in this report it will be possible to characterise the full particle flow emergent from an injector. This will help in the improvement of injectors by extracting simulation parameters, comparing simulations with experiments and validating achieved results of prototypes.
**Declaration**

All work during this project was undertaken at the Centre For Free Electron Laser Science at DESY in Hamburg and under the supervision of Professor Dr. Jochen Küpper and Dr. Daniel Horke. The experimental setup and the vacuum chamber described in this report were set up during this project with the help of Nils Roth and Daniel Gusa. All measurements and data acquisition were performed by myself. All simulations were done by myself using the SIMION® version 8.0 software. The data analysis was performed by me and discussed in the COMOTION group.

I hereby declare that the planning and writing of this thesis is the result of my own research and work and that it has not been previously published or submitted as part of an academic award at another university. All ideas, data or figures from the work of others have been clearly marked as such and complete references have been given.

Christian Nikolaus Kruse

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Chapter 1

Introduction

In many areas of science it is crucial to obtain structural and temporal information about nano-scale objects. The analysis of proteins or viruses in structural biology is one very important example of this. Microscopes working in the visible light spectrum are limited to resolutions of about 0.25 µm due to the Abbe limit [1]. As for structural biology spatial resolutions on the picometre scale are desirable, shorter wavelength, i.e. X-rays, have to be used. For conventional X-ray diffraction fragile biomolecules will suffer considerable radiation damage before any structural information can be obtained.

With the development of Coherent diffractive imaging (CDI) [2, 3] it was possible to go beyond these conventional limits and obtain resolutions on the picometre scale. In CDI ultrashort (< 30 fs), coherent X-ray pulses from a X-ray free electron laser (XFEL) are used to create the diffraction pattern of the analysed object. The advantage of CDI over conventional methods is that the X-ray pulse is diffracted off the sample before any damage can be observed at the particle. Hence radiation damage is no longer a concern in these diffraction-before-destruction measurements.

The destruction of the molecule combined with the low signal-to-noise ratio makes it necessary to replace the destroyed molecule with an intact one before the next X-ray pulse arrives to repeat the measurement many times to increase the signal-to-noise ratio. One possibility to replace destroyed particles is to use a continuous flow of particles through the X-ray interaction region. In order to create such a particle beam there are many different kinds of particle injectors. So far all of these injectors share a common problem, which is the huge waste of sample and XFEL beam time due to low hit rates of the X-ray pulses with the sample molecules. As XFELs such as FLASH in Hamburg are large scale facilities, beam time is a precious and very expensive resource. In addition to that, biologically important samples are often very time intensive to prepare and only obtainable in small amounts [4]. Because the hit rates decrease further when analysing smaller objects it is so far not possible to do single particle imaging with reasonable time and sample expenses. In CDI it is also possible to analyse reaction dynamics in pump-probe experiments where a reaction is initiated by a pump laser and the response of the molecule is probed by the X-ray pulse. The recording of a “molecular movie” of single particle
reactions is due to the low hit rates also not possible so far. The huge loss of sample, money and beam time due to low hit rates and the goal of recording single particle images and molecular movies makes the research on particle injectors to achieve higher hit rates one of the key research areas in coherent diffractive imaging. In the COMOTION project (Controlling the Motion of Complex Molecules and Particles) in the Controlled Molecule Imaging group at the Centre For Free Electron Laser Science in Hamburg particle injectors are developed and improved for the use in CDI experiments. Among the reduction of the beam diameter to increase hit rates also, for example, sample delivery efficiency and background scattering of gases used in the injector are to be taken into account for the improvement of injectors.

When designing a new injector often simulations have to be used to model the expected results and the improvements that can be made. In most cases the systems for the simulations are to large to be calculated ab initio and therefore need to be calculated by using hydrodynamic models. As all of these injectors need to operate in high vacuum (HV) some of the input parameters for these models, such as downstream pressures, are quite hard to extract. Also it is very important to verify the results of the simulation by comparing them to particle beams of existing injectors. For all this it very important to have an imaging system that can analyse and characterise particle beams and at the same time can extract important parameters such as pressures or velocities of gas or liquid flows. The development of this imaging system is the goal of this project. During this project a new vacuum chamber was set up in which Nils Roth, PhD student in the CMI group, will develop and test an aerodynamic lens stack. Due to this fact the design of the imaging system was optimised for the later use with an aerodynamic lens. However, the lens stack is still being simulated and therefore all the measurements during this project were performed with a gas dynamic virtual nozzle (GDVN). The GDVN has the advantage of being a small and fairly simple particle injector which creates particle beams of similar dimensions and properties as the aerodynamic lens. Both particle injectors are explained in detail before the actual experiment is introduced.

The imaging setup for the GDVN includes three types of measurements. For the first type a microscope with 1 µm resolution was installed inside the vacuum chamber to allow optical imaging of the micrometre sized liquid jet using laser illumination. With this laser it is also possible to create a plasma from the gas flow and thus measure gas densities in the vacuum. For the third measurement a time-of-flight mass-spectrometer was installed to allow a detailed analysis of the sample flow within the liquid jet and extract velocity profiles for both liquid and gas flow.

In this report a detailed overview of the experimental setup is given before the working principle is shown on a GDVN.
Chapter 2

Theory

2.1 Particle Injectors

Particle injectors used in coherent diffractive imaging (CDI) need to produce small diameter beams of slowly moving particles to increase the hit-fraction of X-ray pulses with intact sample molecules. They also need to meet other requirements like, for example, avoiding background scattering or provide an aqueous environment for certain biomolecules. Depending on the exact experimental setup it may also be desirable to create a collimated particle beam to further manipulate the particles, for example, aligning them or selecting specific conformers [5, 6].

In order to design an efficient imaging system for particle injectors it is important to understand the working principle of the analysed injector and how the particle beam is formed.

This report focusses on two particle injectors. The first is the gas dynamic virtual nozzle (GDVN) [7] which creates micrometre sized liquid jets and was used in all the measurements during this project. The second one is the aerodynamic lens which creates a collimated beam of aerosol particles [8]. After the working principle has been proven in this project the imaging setup will first be used for an aerodynamic lens stack to extract valuable parameters for the simulation of such a lens and to validate the achieved results once the design is finished.

2.1.1 Gas Dynamic Virtual Nozzle

A gas dynamic virtual nozzle is a particle injector that has already been used in many CDI experiments [9, 10]. As shown in figure 2.1 a GDVN consists of two capillaries where the smaller one (C) is placed within the larger one (B). Any sample to be analysed in the experiment is dissolved in water or another liquid solvent and then directed through the inner capillary. In the outer capillary gas is flowing towards the orifice. This gas flow focusses the liquid flow in region (A) down to diameters on the micrometre scale by forming a virtual nozzle much smaller than the orifice of the GDVN. In most cases helium is used as a focussing gas because it leads to a low background scatter in CDI experiments. However, these nozzles work with a range of gases including all noble gases, carbon dioxide and different carbon hydrates which may be
more suitable for certain experiments [7].
A shadow image of the created particle beam is shown at the bottom of figure 2.1. After emerging into vacuum the particle beam is first a continuous jet of about 200 µm length and 5 µm diameter depending on the exact nozzle. This jet eventually breaks up into a droplet stream due to the Rayleigh instability. This instability is caused by the surface tension of the liquid, which causes the surface area of the fluid to minimise. Although this droplet break up can in principle be triggered and synchronised to the XFEL pulses [11] most CDI experiments where performed in the jet region of the liquid jet.

Figure 2.1: The top figure shows a microscope image of a GDVN. It consists of two capillaries (B and C). For the operation of this injector a sample molecule is dissolved in water and then directed through the inner capillary C. The outer capillary contains a laminar gas flow which is forming a virtual nozzle at the exit orifice of the injector. This gas causes the water to contract in region A into a small diameter (down to ca. 5 µm) liquid jet. The created particle beam of this GDVN is shown in the bottom figure. After emerging into vacuum the beam is first a liquid jet of about 200 µm length. Then the jet eventually breaks up into droplets due to the Rayleigh instability. Reprinted from [12]

2.1.2 Aerodynamic Lens
An aerodynamic lens stack is a particle injector that compresses aerosol particles into a collimated beam [8]. As shown in figure 2.3 such a lens stack consists of several axisymmetric contractions in a flight tube. The aerosol is travelling through these lenses together with a lighter carrier gas (e.g. helium). While the carrier gas quickly expands after each contraction the heavier aerosol particles tend to stay closer towards the centre of the flow field. The flow field of a light carrier gas (black) and the trajectories of particles with different masses (coloured) are shown in figure 2.2.
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Figure 2.2: These figures show an aerodynamic lens and the flow field of a light carrier gas (black lines). The focussing effect of such a lens depends on the particle mass. In the top figure the particles are lighter than the optimal mass and thus follow the flow field which results in only a small focussing effect. The middle figure shows the trajectories of particles with the optimal mass. The bottom figure shows the trajectories of heavier particles which fly straight into the walls of the lens which results in a low particle delivery efficiency and no focussing. The colour scale indicates the velocities from slow (blue) to fast (red) moving particles. Reprinted from: N. Roth, D. Horke and J. Küpper, 2015, conference Heidelberg, poster.

To understand the focussing effect of such a contraction let us first assume that the only force acting on the aerosol particles is the drag force

$$\frac{dV_p}{dt} = \frac{V - V_p}{\tau}$$  \hspace{1cm} (2.1)

where $V_p$ is the particle velocity, $V$ the velocity flow field and $\tau$ the relaxation time. This approximation neglects lift forces and Brownian motion and may be used when the local Reynolds number is not exceeding a few hundred. The Reynolds number is the ratio of a fluids inertia to its viscosity. Low Reynolds numbers are correspondent to a high viscosity in comparison to the inertia which leads to a laminar flow. Considering small particles in a flow of a light carrier gas Robinson showed that the differential in equation 2.1 can be replaced by a differential along the trajectory $\frac{DV_p}{Dt}$ of the flow field [13].

$$\frac{DV_p}{Dt} = \frac{V - V_p}{\tau}$$  \hspace{1cm} (2.2)

Introducing the average particle mass per unit volume $C_m$ with the continuity equation

$$\frac{1}{C_m} \frac{DC_m}{Dt} = -\nabla V_p$$  \hspace{1cm} (2.3)
equations 2.2 and 2.3 lead to the equation which is know as Robinson’s inequality [13]:

\[
\frac{DC_m}{Dt} > 0
\]  

(2.4)

This means that particles tend to concentrate along the trajectories of the carrier gas. For an axisymmetric, incompressible and irrotational flow this is leads to an increase of particle concentration along the centreline of the flow [8]. Although not all the assumptions, especially the assumption that \( \frac{D}{Dt} \) exists everywhere, hold in real-world applications it can be shown that in fact particles of a specific mass are concentrated near the centreline of the flow while larger or smaller particles may get defocussed by the contraction [8].

Thus lenses designed for the operation with a wide range of particle masses can not achieve the small beam diameters desired in CDI experiments. Therefore a lens stack for the operation with only one particle mass is currently designed in the COMOTION project. The particle beam of this lens stack will, in principle, only be limited by Brownian motion and the lift force acting on the particles.

The Brownian motion describes the random motion due to particle collisions and depends on the mass ratio of the carrier gas and the aerosol particles. In many applications helium is used as a carrier gas and the analysed molecules are much heavier than the helium atoms. In this case the Brownian motion only plays a small role in the broadening of the particle beam. However, in some applications, especially in single particle imaging, it might broaden the beam significantly. The second contribution to the broadening of the particle beam is the lift force which is proportional to the deviation of the particle shape from a sphere. Of course the influence of this force is strongly dependent on the form of the analysed molecule but is often much larger than the influence of Brownian motion [8, 14].

![Figure 2.3: Example setup of an aerodynamic lens stack as used in CDI experiments. A pressure gradient drives aerosol particles through a series of aerodynamic lenses which force the particles into a collimated, small diameter beam. Adapted from [15]](image)
Both of the introduced particle injectors have been used successfully in CDI experiments. The GDVN provides sample in aqueous solution which is necessary for some biomolecules but also introduces a lot of background scatter for the imaging. To achieve a good signal-to-noise ratio in such an experiment measurements can be done in the so called "water-window" in which water is transparent to the incident X-rays. However, the restriction on the possible X-ray wavelength limits the achievable resolution [16]. While in a GDVN the sample delivery efficiency (particles which reach the vacuum chamber) is close to 100% the efficiency in an aerodynamic lens stack can be considerably smaller depending on the particle size [17]. Following from this it is obvious that the "perfect" particle injector does not jet exist and that the research on particle injectors is a very important field for improving CDI measurements.

The important differences of the particle beams concerning the analyses of the created particle beams in this report are the huge amount of water and the, probably, considerably higher gas pressures at the tip of the GDVN. How this will effect the experiment will be discussed with the results of the specific measurement.

2.2 Mass Spectrometry

In mass spectrometry molecules are analysed by determining their mass or, to be more precise, the mass-to-charge ratio of ions created from these molecules. Although there are several techniques to separate ions by their masses, time-of-flight (TOF) mass spectrometry (MS) is suited best for the use in the imaging setup. This is because in TOF mass spectrometry there is no need for time intensive scans and an, in principle, unlimited mass range can be detected at the same time [18].

As the name already says in TOF MS molecules are separated by their time-of-flight after being ionised by, for example, a laser. In the TOF-setup in figure 2.4 particles are ionised in the laser-particle interaction volume and then accelerated by a static electric field between the repeller-, extractor- and ground-electrodes. Assuming equal charges the ions then all gain the same kinetic energy from the electric field:

\[ U q = \frac{1}{2} m v^2 \Leftrightarrow \frac{m}{q} = \frac{2U}{v^2} \Rightarrow \frac{m}{q} (t) = \frac{2Ut^2}{s^2} \quad (2.5) \]

where \( U \) is the voltage between the plates, \( s \) is the distance between the laser-particle interaction point and the MCP, \( q \) is the charge, \( m \) is the mass and \( v \) the velocity of the ions. Therefore heavier ions will gain a lower velocity by passing the electric field and hence arrive later at the detector. From the arrival time at the detector the mass of the ions can then be determined provided the ion charge is known or can at least be estimated [18].

Since TOF MS has been around for decades there are many different possible setups for the
Figure 2.4: Schematic drawing of a time-of-flight mass-spectrometer using a velocity-map-imaging setup. The particles are ionised in the laser-particle interaction region and then accelerated towards the detector by the electric field of the three electrodes. From the spatial distribution of the ions on the detector, 3D velocity or spatial distributions of ions can be reconstructed. To record conventional time-of-flight mass spectra the phosphor screen and CCD camera can be replaced by an anode to measure the total current from the MCP detector. Adapted from [19] electrodes and different detectors for recording the ions. The velocity map imaging setup [20] of the electrodes together with a microchannel plate detector allows also the mapping of spatial or velocity distributions onto the detector. As this is highly useful for the imaging, they are used in the experimental setup and introduced in the following sections.

### 2.2.1 Strong-Field-Ionisation

Classically an atom or molecule can only be ionised by radiation if the photon energy exceeds the ionisation energy. While this is often the case in the short wavelength regime of, for example, X-rays, the photon energy of 800 nm light from the Ti:Sa laser is only about 1.6 eV and lower than the ionisation energies of many particles. However, for very high intensities reached in a focussed laser beam other processes play a significant role in the ionisation of molecules. These processes include, for example, multi-photon ionisation, tunnel ionisation and the Stark shifting of atomic potentials and depend strongly on the exact laser parameters. All these processes rely on strong fields that can be reached in, for example, a laser beam and are therefore referred to as strong-field-ionisation (SFI) [21].

Due to SFI and depending on the laser power it is possible to achieve different levels of ionisation from singly charged ions to fully ionised plasma with the Ti:Sa laser in the particle flow of, for example, an injector. Another important aspect of the ionisation process in mass spectrometry is the fragmentation of particles due to the laser radiation. Molecules which break up in the ionisation process have to be determined from the mass spectrum of their fragments and, as not necessarily all the fragments are ionised, information might be lost in this process. However, for the imaging setup fragmentation is not a major concern since the initial positions need to be measured and not the exact configuration of the parent molecule.
2.2.2 Velocity Map Imaging

As explained above the ions in TOF MS are accelerated by an electric field which can, for example, be created by a three plate electrode setup. While in conventional TOF MS often grid electrodes are used, there is an alternative setup using electrostatic lenses. With such an electrostatic lens it is possible to map the velocity vectors of the ionised particles onto the MCP detector, regardless of their initial position in the ionisation region. Setups with this feature are referred to as velocity map imaging (VMI) setups [20].

When connecting a simple oscilloscope to the MCP detector of the setup it is possible to use a VMI setup in the same way a conventional TOF setup is used. In this case the mass of the ionised particles is determined by their arrival time at the detector. However, in many applications of TOF MS not the mass of the particles but their initial spatial and/or velocity distribution is the primary information desired.

In that case the VMI is operated with a spatially resolved detector, in this setup a MCP in combination with a phosphor screen and CCD camera. From the spatial distribution of the ions on the detector, 3D velocity or spatial distributions can be reconstructed using the Abel transform [22].

In the case of analysing particle injectors there are mainly the three masses of the focusing gas, the liquid and the sample itself which are known for each experiment. With the setup shown in figure 2.4 it is now possible to measure detailed spatial and velocity information for each of those masses by gating the MCP detector to record only ions with a specific arrival time. Of course the analysis is not limited to these masses and especially for sample molecules the fragmentation might also be of interest which can be analysed using this setup.

2.2.3 Microchannel Plate Detector

As described in the previous section the VMI setup requires a detector that can detect ions on impact with not only a good temporal but also a good spatial resolution. This is to perform mass spectrometry for the particles and at the same time reconstruct 3D spatial and velocity distributions.

As with most VMIs a microchannel plate detector (MCP) is used in this imaging setup. This is because of its capabilities in achieving good spatio-temporal resolutions and its popularity which leads to highly reliable commercial devices.

A microchannel plate detector consists, as the name says, of a plate with many microchannels leading from one surface to another. When a voltage is applied between both sides of the MCP each of these channels acts as an electron multiplier. When an ion hits the wall of the channel it starts a cascade of secondary electrons each of which then starts additional cascades when hitting the walls. This secondary electron emission increases the signal by orders of magnitude. After emerging on the other side of the MCP the electrons can either be recorded by an anode
just measuring the total current or on a phosphor screen in combination with a CCD camera allowing the measurement of spatial information needed for the VMI. In order to assure reliable signal amplification the channels are often in a slight angle to assure that every ion hits the channel wall [23, 24].

MCPs have the advantage of being very fast and very precise detectors which makes them very popular. However, the emission of secondary electrons is decreasing with lower velocities. Hence for very heavy ions the detection efficiency decreases [25]. Also the channels in a MCP are only about 10μm wide and high voltages in combination with high pressures in the vacuum chamber can lead to voltage breakthroughs which can damage the detector. Therefore a MCP should only be operated in a low pressure vacuum (at least $<10^{-5}$mbar).
Chapter 3

Experimental Setup

Improving and developing particle injectors often requires extensive simulations which can not be done ab initio. While many operation parameters are known or can be easily measured, especially down stream parameters like the pressure at the outlet are difficult to determine, as all of these particle injectors work in high vacuum (HV). An example of this is the simulation of the aerodynamic lens: Using hydrodynamic modelling the flow fields of the carrier gas and hence the trajectories of the sample particles can be calculated. However, to perform accurate simulations it is necessary to not only know the inlet pressure but also the pressure at the injector tip directly after emerging into vacuum. For the extraction of these parameters and to analyse achieved results it is important to have a good imaging system which is ideally also capable of measuring pressures and velocities. The experimental setup of an imaging system, to measure this and other parameters of the particle flow, is introduced and explained in detail in this chapter before the results of first measurements are discussed in the following chapter.

The imaging was realised in three different types of measurements:

In the first measurement the particle beam is illuminated with a laser and the scattered light is recorded by a microscope with 1 µm resolution. This allows the measurement of the beam diameter which is one of the most important characteristics of a particle beam for the use in CDI experiments (section 3.4.1).

By increasing the laser power in the second measurement it is possible to create a plasma from the gas flow of the injector and by the recorded light intensity determine the gas density and hence the pressure (section 3.4.2).

To perform a detailed analysis of the sample within a liquid jet and also to record velocity profiles a time-of-flight mass-spectrometer was set up. In this third measurement the laser is used to ionise the particles and record the ions on a microchannel plate detector with the use of a velocity map imaging setup (section 3.5).

The experimental setup for these measurements is shown in figure 3.1a. Figure 3.1b shows a photo of the vacuum chamber that was set up during the project to contain the imaging setup.
3.1. THE LASER

### Chapter 3. Experimental Setup

(a) Overview of the experimental setup. A 800 nm Ti:Sa laser (section 3.1) is used to ionise the particles in the particle-flow emergent from the particle injector (section 3.3). Depending on the laser power the scattered light or the fluorescence emittance of the plasma can be analysed by the microscope (section 3.2). The ionised particles can also be analysed with the three-plate velocity-map-imaging setup in combination with a MCP detector (section 3.5). Both optical and mass-spectrometry analyses can be performed at the same time.

(b) Photo of the vacuum chamber in which the experiment was set up.

**Figure 3.1:** The Experimental Setup

### 3.1 The Laser

All three types of imaging explained above rely on a laser to either illuminate or ionise the particles in the beam or gas flow. For convenience one laser was used for all experiments for which the power was adjusted by using filters. As mass spectrometry depends on the timing of ion creation and detection at the detector (see section 3.5) it is necessary to use a pulsed laser. Furthermore the creation of plasma in low density gases requires high intensities within the laser focus. To meet these requirements a 800 nm Ti:Sa laser with an output power of 4 W at 1 kHz repetition rate in 35 fs pulses was used. As this laser was used for several experiments at the same time, the maximum output power for the imaging setup was 1.8 W corresponding to 1.8 mJ per pulse.

The setup of the laser beam line is shown in figure 3.2 together with the microscope setup explained in the next section and the VMI setup for mass spectrometry. The laser beam is focussed by a 800 mm lens into the vacuum chamber. This lens is mounted on motorised translation stages which allow the laser focus spot to be scanned across the particle beam. In order to reduce power losses and dangerous back-reflections on the way to the laser particle interaction region (green) coated mirrors and windows where used to guide the laser inside the vacuum chamber.
Figure 3.2: Schematic drawing of the microscope setup. The 800 nm Ti:Sa laser (red) is guided by two mirrors and a 800 mm focussing lens through an anti-reflex coated window into the vacuum chamber. The lens is mounted on motorised translation stages to allow the movement of the laser focus inside the chamber. In the laser-particle interaction region (green dot) the focussed laser beam intersects the particle beam. The scattered light or fluorescence emittance (yellow) is recorded by a 4x objective and guided to the camera through a clear vacuum window by a mirror and a focussing lens. The additional setup for the VMI spectrometer is shown in blue. Ions created in the interaction region (green) are accelerated by the electric field between repeller-, extractor- and ground-plate towards the MCP detector.
Considering the 800 mm focussing lens and an initial beam diameter of 16 mm it is possible to estimate the focus spot size and the Rayleigh length of the laser in this setup. The Rayleigh length is the distance from the beam waist to the point where the area cross section of the laser beam has doubled and is a measure for the depth of the laser focus. To estimate the laser spot size an ideal, diffraction limited Gaussian beam is assumed. The laser spot size is then:

\[ w = \frac{\lambda f}{\pi w_{\text{input}}} \]  

(3.1)

where \( f \) is the focal length of the focussing lens, \( w_{\text{input}} \) is the input beam radius and \( \lambda \) is the laser wavelength.

The Rayleigh length is then

\[ z_R = \frac{\pi w_{\text{waist}}^2}{\lambda} \]  

(3.2)

where \( w_{\text{waist}} \) is the beam radius at the waist, i.e. the focus spot size [26].

For the laser parameters of the Ti:Sa laser and the 800 mm focussing lens used in the experimental setup this results in a focus spot size of about 13 \( \mu \text{m} \) and a Rayleigh length of about 640 \( \mu \text{m} \).

It is now also possible to calculate the peak intensity reached in the focus spot. Starting from a 1.8 W laser power it immediately follows that each pulse contains an energy of 1.8 mJ. For a 35 fs pulse focussed on a \( 1.3 \cdot 10^{-6} \text{cm}^2 \) focus spot this results in a peak intensity of \( 4 \cdot 10^{16} \text{ W/cm}^2 \).

### 3.2 The Microscope

In order to allow observation of the scattered light and the created plasma it was necessary to install a microscope with \( \mu \text{m} \) resolution inside the vacuum chamber. The setup of this microscope is shown in figure 3.2. A 4x objective with a working distance of 18.5 mm and 0.10 NA is used to magnify the objects in the field of view. After the collimated light rays are reflected at a silver coated mirror and directed through a clear window of the chamber they are collected on a 5 megapixel camera by using a focussing lens. The distance between the focussing lens and the camera is adjustable to correct for objects out of the focal plane of the objective.

To determine the achievable resolution of the microscope setup, a calibration slide with 50 \( \mu \text{m} \) spacing was used (see figure 3.3). The approximated resolution of the microscope is about 1 \( \mu \text{m} \).
3.3 Injector Operation

During all measurements in this report a gas dynamic virtual nozzle was used. As described in section 2.1.1 this injector consists of two capillaries. The outer capillary is connected to the pressure regulator in the bottom gas line shown in figure 3.4. The inner capillary has to be operated with water for simple testing, dissolved sample molecules for a detailed analysis or gas to clear the line from residual liquid and for the plasma measurement (see section 3.4.2). Residual liquids need to be cleared out of the inner capillary after jet operation in order to avoid the formation of ice at the nozzle tip once the pressure is reduced. In order to allow this operation, the upper gas line and pressure regulator is connected to an electronic line-switch over three lines: The first line is connected directly to the switch to allow gas operation of the inner capillary. The second line is connected to a 2 ml water reservoir and a flow meter in order to allow water-jet operation of the GDVN and simultaneous measurement of the liquid flow. Both of the lines are connected to the valve labelled “H2O” as shown in figure 3.4. The last line is connected to a 2 ml reservoir containing the water-sample solution and the valve labelled “SAMPLE” in figure 3.4. While in CDI experiments single biomolecules or nano-crystals are used as a sample, the sample for testing the imaging setup are latex or polystyrol spheres of micrometer diameters which is about the size of nano-crystals used in CDI experiments.

Depending on the GDVN, the focus-gas line (outer capillary) has to be operated at pressures between 10 and 200 PSI for successful jet operation. The liquid line (inner capillary) has, in most cases, to be operated at pressures >100 PSI. Higher pressures in the liquid line lead, in most cases, to a more stable jet and higher flow rates. For most GDVNs used in this project the flow-rate was about 15-20µl/min which allows a jet operation of about 100 min before refilling the liquid reservoir.
3.3. INJECTOR OPERATION

Figure 3.4: Picture of the gas panel to operate the GDVN. Both lines are connected to the laboratory gas line of either Helium, Argon, or CO$_2$ depending on the experiment. The bottom line is connected to the outer capillary of the GDVN. The upper line is connected to two valves. The right valve labelled “H2O” is connected directly to a line switch and to a water reservoir which is then connected to the line switch via a flow-meter. The left valve labelled “SAMPLE” is connected to a reservoir containing water-sample solution which is then connected to the line switch. The pressure in both lines can be reduced by operating the valves in the line labelled “VACUUM”, which is connected to the roughing pump of the experimental setup.

The GDVN can be operated with different gases. In this report the jet-operation was successfully tested with Helium, Argon and CO$_2$, but also other gas could be used if necessary. The operation with CO$_2$ as a focusing gas made it necessary to vent the gas lines into an exhaust in case the pressure in any of the lines needs to be reduced. This was achieved by connecting the lines over different valves to the pre-vacuum line. As shown in figure 3.4 the line is labelled “VACUUM” and contains a needle valve to allow controlled pressure reduction. It can later also be used to flood the chamber to a certain pressure for calibration measurements (see section 4.2).
3.4 Optical Imaging

After the experimental setup for optical imaging was introduced in the previous sections and figure 3.2 the experiment-procedure itself is explained in this section. Section 3.4.1 describes the measurement of liquid jet parameters using laser illumination and in section 3.4.2 the measurement of gas densities using plasma creation and fluorescence emittance is described.

3.4.1 Scattering

To visualise the liquid jet emerging from a GDVN a 1 μm resolution microscope was installed inside the vacuum chamber (section 3.2).

With the laser used as a light source for optical imaging it is possible to measure the jet diameter which is one of the most important characteristics of a particle beam. The laser power for an optimal illumination is in the range of 10-20 mW which is about two orders of magnitude lower than the maximum laser power in this experimental setup.

However, it is not possible to record an entire image of the jet in the field of view at once. In order to create such an image it is necessary to record several pictures at different positions in the jet and add up the pictures to create a full jet image. In most measurements in this report 80-120 images (2 at each position) were taken at different distances from the injector tip in the particle beam. These were in most cases in this report spaced by about 12 μm (10 steps of the step-motor) which is approximately the size of the laser focus, to ensure observed structures are characteristics of the particle beam and not of the image acquirement itself. However, good jet images can be obtained with larger step sizes as well. This can be beneficial for injectors with unstable particle beams, as the recording of fewer images due to larger step sizes takes less time. However, injectors producing very unstable jets with frequent jet break-ups and beam movement can not be analysed with this technique because the characteristics of the particle beam will change during the measurement. As only injectors with stable and reproducible particle beams are useful for CDI experiments this should be no concern for the imaging of CDI-relevant injectors.

While the general working principle has been established there are still some issues left to be discussed. The inside walls of the metal vacuum chamber in fact act as mirrors and with that a double image appears on the camera which needs to be taken care of (see figure 3.5a). In order to reduce these reflections to a minimum black anodised aluminium foil was used (see figure 3.5b). Unfortunately this setup can not be used once the VMI (see section 3.5) is build in and other ways of reducing the double images need to be found (see section 4.1).
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3.4.2 Plasma Creation

Although the flow of the focussing or carrier gas of the particle injectors is not of direct interest for the application in CDI experiments, it is very important to extract parameters like the gas density for performing simulations. This simulation parameter is not trivial to measure but in the following section an experiment is introduced which can do exactly this.

For this experiment any filters in the laser line are removed to achieve the maximum laser power of 1.8 W. The inner capillary is switched to gas operation at a low constant pressure to assure all measured effects result from the gas flow in the outer capillary.

To measure the density profile within the gas flow, the laser focus is moved as close as possible to the tip of the nozzle. It is, however, not clear how resistant the GDVN ceramic is to the laser radiation. As the laser has a Gaussian beam profile, the outer areas of the beam still contain a high intensity which might damage the ceramic. Therefore the measurement was started at about 150 μm away from the nozzle tip.

The full image of the gas expansion is then acquired by moving the laser focus down in steps of 12 μm (10 steps of the step-motor) similar to the measurement described in the previous section. While for the illumination of the jet larger step-sizes are also possible, a plasma can only be created in the centre of the laser beam and it is therefore necessary to move the laser down in small steps. Nevertheless, there are no concerns about measurement-time for the plasma imaging, as the gas flow from the GDVN is very stable over time.
3.5 Mass-Spectrometry

With the optical imaging introduced in the previous section it is already possible to measure important characteristics of an injector. This includes the width of the particle beam and the pressure of the gas flow after emerging into vacuum. However, important characteristics of the sample within the flow and velocity profiles of gas and liquid are still not measurable. In order to perform a full characterisation of the particle beam and the surrounding gas flow it is therefore necessary to set up an additional imaging experiment. In this experiment the particles in the flow are ionised by the Ti:Sa laser and then analysed with mass spectrometry. For this the experimental setup of the optical imaging was extended by velocity map imaging electrodes (see section 2.2.2) and a MCP detector (see section 2.2.3). The mass-spectrometry-addition to the experimental setup is shown in blue in figure 3.2 and a photo of the setup inside the vacuum chamber is shown in figure 3.6. It should be noted that it is possible to perform optical imaging and mass spectrum analysis simultaneously.

![Figure 3.6: Photo of the VMI setup inside the vacuum chamber for the imaging setup.](image)

The electrostatic lens of the VMI setup consists of three plates, where the repeller electrode is a 12 cm by 12 cm square plate with an aperture of 10 mm diameter and the other electrodes are plates of the same size with aperture diameters of 25 mm (see figure 3.6). The distance of the repeller electrode and the MCP detector will be about 16 cm. However, the MCP detector is not set up jet due to high chamber pressures during GDVN operation (see section 5.2.2).
Chapter 4

Results And Discussion

After the experimental setup was introduced and explained in the previous chapter, first results are presented in the following chapter. In this chapter the results of the optical measurements using the setup shown in figure 3.2 are presented and discussed. It should be noted that all raw data were recorded as 5 megapixel "*.tif" images. In this format each pixel is assigned three RGB values between 0 and 1. Values <0 are displayed as 0 and values >1 are displayed as 1.

4.1 Water Jet

To operate the microscope (section 3.2) an, in principle arbitrary, light source is needed to illuminate the jet. However, the illumination of the liquid jet with a commercial LED proved to be not beneficial for the imaging of the jet. As shown in figure 4.1a the jet appears to be very thin which proves to be not the case as shown in figure 4.1b. The low contrast and the thin line of the liquid jet show that LED illumination is not sufficient for particle beam imaging. This is probably due to the fact that the light is only scattered at one side (right side in this case) but does not penetrate the jet and therefore does not illuminate every part of it.

Although very hard to see, the jet in figure 4.1a not only appears very thin but is also divided into different colours. It was so far not possible to determine the origin of this "rainbow effect". Possible candidates for causing this effect are the objective, the chamber window or the focusing lens. However, the scattered light using laser illumination has only a small wavelength bandwidth (ca. 750 nm-850 nm) and thus no broadening of the image can be observed in this measurement. Nevertheless this should be kept in mind for measurements in which more than one wavelength is measured. As a first simple solution a colour filter can be used if only one wavelength at a time is of interest.

In order to measure the size of the particle beam it is illuminated with a Ti:Sa laser with a focus spot of 13 μm diameter (see section 3.4.1). A single shot measurement is shown in figure 4.2a.
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(a) LED illuminated image of a liquid jet and (b) Laser illuminated image of a part of a jet. The GDVN. The liquid jet appears as a very thin line. illuminated section of the jet is about 170 µm wide. It emerges from the middle of the nozzle tip and is slightly tilted. Also the colours in the image are slightly separated. This can be seen best at the blue right edge of the nozzle.

Figure 4.1: Comparison of LED and laser illumination

In order to create a full jet image the laser focus spot is moved down by moving the lens with the motorised translation stages. The full jet image corresponding to the single image 4.2a is shown in figure 4.2b. It was created by taking 86 pictures at 43 different positions. The spacing between the positions was 10 motor-steps which corresponds to 12.5 µm. Together that leads to a scanning range of 0.54 mm.

In order to add multiple pictures together it is necessary to subtract the background of each picture first. The background rises from non-zero pixel values for not illuminated areas probably from stray light or the camera software itself.

For the visible light, i.e. LED illumination, the reflections and hence the double image was reduced significantly by surrounding the imaging area with black anodised aluminium foil (see figure 3.5). However, for the laser illumination in figure 4.2b there is still a double image visible. This is because of a higher light intensity for the laser illumination and because of different reflectivities for the 800 nm light.

Both of these problems can be addressed by subtracting values a little higher than the background from each image. The background (taken as the pixel value of the top-left corner) is about 0.05 as a pixel value for each of the RGB values. By subtracting instead values of the order 0.07 it is already possible to reduce the double image significantly. In comparison to that the pixel values in the actual jet area are all >0.3. Also when only subtracting the background as defined here there are many coloured pixels throughout the image rising from slight differences of the RGB values at certain positions. To compare both created images compare figure 4.2b (0.047 subtracted) with figure 4.3 (0.07 subtracted). The comparison shows that the liquid jet looks exactly the same while the double image and coloured pixels disappear mostly.

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(a) Single picture of the laser illuminated jet at the position nearest to the nozzle tip.

(b) Laser illuminated full jet image. The image was created by adding up 86 images from 43 different laser positions in the jet. From each of these images the background, taken as the top left pixel value of each image, was subtracted first. Because the jet broke up due to instabilities the part of the jet farthest away from the tip of the nozzle could not be measured.

Figure 4.2: Creation of full jet images from single images

As demonstrated in figure 4.3 it is now possible to measure the jet size with an accuracy of about 1 µm. For the example measurement shown in figure 4.3 the jet size was about 15 µm which is quite large. The large diameter of the jet results from the high flowrate (15-20 µl/min) of the tested nozzle. However, this nozzle produced a very stable jet which made it a good candidate for testing the imaging setup while, at the same time, this particular nozzle is not well suited for the use in CDI experiments because of the large jet diameter.

The working principle of jet size measurements using laser illumination has been proven in this project. However, there are still some issues with double images, reflections and background subtraction which, so far, need to be addressed manually while creating the full jet image. It would be very helpful to reduce these for future measurements or at least systematically analyse and implement these in the final image creation. Although it is not entirely clear where these effects are caused, it might be helpful to use an anti-reflex coated window for the microscope setup.
4.2 Gas Flow

After the beam diameter was measured in the previous section, the gas flow from the particle injector is characterised in this section. In order to analyse the gas, a plasma is created, again with the setup shown in figure 3.2 but now with a laser power of 1.8 W corresponding to 1.8 mJ per pulse. During all measurements in this report the GDVN was operated with CO\textsubscript{2} as the focussing gas.

Increasing the laser power to maximum enables the creation of plasma even from low density gas flows. The recombination processes within the plasma lead to fluorescence emittance which is then captured by the microscope. The light intensity emitted by the plasma is dependent on the gas density as shown in figures 4.4a and 4.4b. In figure 4.4a a plasma is created from the gas flow of a GDVN with an inlet pressure of 300 psi for the focussing gas. Figure 4.4b is a picture of the same situation only with an inlet pressure of 400 psi. The inner capillary was in both cases switched to gas operation at a low constant pressure. The emitted light intensity for the 400 psi inlet pressure is considerably higher than for the 300 psi operation. This is due to the fact that the gas density is also higher in the 400 psi operation. This measurement was performed to show the connection of emitted light intensity an gas density. It should be noted that the pressures for successfully operating a GDVN are much lower and that the plasma intensity will therefore also be lower.

Similar to the creation of a full jet image, the image of the entire gas expansion has to be created.

Figure 4.3: Final full jet image with higher back ground subtraction. This image was created in the same way as figure 4.2b but the background subtraction was increased from 0.047 to 0.07 to reduce the double image. The measured beam diameter is 15 µm.
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Figure 4.4: Comparison of plasma fluorescence emittance at different gas pressures. Both images were taken at the same distance from the tip of the nozzle. While all other parameters were exactly the same, the inlet focusing pressure in (a) was 300 PSI and the pressure in (b) 400 PSI. Since the fluorescence emittance is higher for 400 PSI it is clear that the emitted intensity corresponds to the plasma density.

from single images as shown in figure 4.5. As the outer areas of the focussed Gaussian laser beam still carry enough intensity to illuminate the jet, the laser spot appeared quite large in the optical jet measurement (see figure 4.2a). However, for plasma creation, especially in low density gases, a high laser intensity is required. Therefore, plasma is only created in the centre of the laser beam. While in the optical measurement larger step-sizes (>10 steps per picture) may be used in order to speed up the measurement, the plasma imaging relies on small step-sizes. However, as the gas expansion is very stable over time, measurement time is no concern in this case.

In figure 4.5a the plasma measurement nearest to the nozzle tip is shown. It can already be seen that the nozzle is illuminated very brightly, although the laser focus is still quite far away. It should be kept in mind that even the edges of the laser beam profile carry a high intensity which may damage the ceramic nozzle. Therefore the pressure directly at the tip was not measured so far. It should however, be possible to get a good estimate for the density and pressure by starting the measurement at the position shown in figure 4.5a.

The full plasma image shown in figure 4.5b was created by adding a total of 120 measurements at 60 different plasma positions. Similar to the discussion above, the background of each picture needs to be subtracted first. However, the light intensity scattered from the liquid jet was high in comparison to the intensity emitted by the plasma. Therefore, overshooting the background subtraction to get rid of double images, reflections and coloured pixels is no option here as it would alter the overall result considerably. Hence, the background was taken to be the pixel value of the top left corner of the image. The complete result of the plasma imaging is shown
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(a) Single picture of the CO\textsubscript{2} plasma at the position nearest to the nozzle.

(b) CO\textsubscript{2} gas expansion profile. The image was created by adding up 120 images from 60 different laser positions in the gas expansion. From each of these images the background, taken as the top left pixel value of each image, was subtracted first. A slightly asymmetric cone of the gas expansion can be observed.

Figure 4.5: Creation of full density-profile images from single measurements

Although there is a bright double image from the illumination of the nozzle, there is no observable double image from the actual plasma. This is due to the fact that the emitted light is of low intensity and that the reflections within the chamber where reduced as described in section 3.4.1. However, the appearance of coloured pixels is still observable similar to the measurement in the previous section.

The coloured pixels can be reduced by applying a blue filter to the jet image in figure 4.5b. The result is shown in figure 4.6a. However, this only reduces the number by about one third. More importantly it changes the overall result as not all emitted light in the lower region of the image is blue. In order to analyse the result produced in this way a more detailed analysis of the plasma creation process and the effects on the imaging is needed. A second approach is to take the measurement farthest away from the nozzle tip and subtract this image from the others to get a uniform background subtraction and a good result in the upper area of the image. However the appearance of coloured pixels seems to be dependent on the plasma position and thus the achieved result shown in figure 4.6b is no improvement over the original result.

So far the appearance of coloured pixels throughout the plasma profile image could not be reduced. In order to do so the reason for the effect need to be determined in the experimental setup and treated there.

Nevertheless the measurement shows already good and usable results for the characterisation of the gas flow emerging from a GDVN. The density profile appears to be a cone emerging from
4.2. GAS FLOW

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(a) CO₂ gas expansion profile with only blue values taken into account. The background of randomly coloured pixels decreases but at the same time the appearance of the gas-expansion-cone changes.

(b) CO₂ gas expansion profile with last image as background subtraction. With this background subtraction the upper part of the cone appears as before but the lower part vanishes. In addition to that more coloured pixels appear throughout the image so no improvement can be observed in comparison to figure 4.5b.

Figure 4.6: Tests of background improvements.

the tip of the nozzle which agrees well with gas expansions observed in other areas of physics. However, there is a slight asymmetry to the visualised gas flow. This could be due to the design of this particular nozzle, as also the jet is slightly tilted (see section 4.3). It is however possible that this is an effect of different laser intensities at different positions inside the plasma. This could either be caused by absorption effects or by the change of the laser intensity moving away from the beam waist. To rule out this last possibility multiple measurements of the same gas flow should be performed while scanning the laser focus from left to right (or vice versa). By comparing the results, the influence of changing laser intensities can be analysed and if necessary implemented in the future analysis.

This experiment already gives an idea of the relative densities in the measurement. However, the recombination process of electrons and ions in the plasma is not easily predictable. Hence the dependence of the light intensity of the gas density is most certainly not linear but another unknown function. To measure absolute values for the pressure or the density at a certain point it is therefore necessary to calibrate the measurement first. This can be done by flooding the chamber to a known pressure with the gas used in the injector. The emitted light intensity from the plasma for the current camera settings is then recorded for the chamber pressure. After repeating this measurement for several pressures the dependency of emitted light intensity and gas pressure can then be interpolated. It is convenient to use the same camera settings (capture time, gain etc.) for all the measurements as a change of these parameters must be taken into account for the calibration measurement.
In this section the working principle of the plasma measurement was proven. Although there are some issues left, as discussed above, it will be possible to measure gas densities and pressures and obtain valuable parameters for future simulations.

### 4.3 Simultaneous Measurement

The working principle of optical imaging using laser illumination and density measurements using plasma fluorescence emittance was demonstrated in the previous chapters. However, these measurements were not related to each other so far. In this chapter the possibility of measuring the liquid jet and the corresponding gas flow at the same time is discussed.

In figure 4.7a the GDVN was producing a liquid jet which was illuminated by the 1.8 W laser pulses of the gas flow measurement. It is obvious that too much light intensity is scattered into the microscope causing an over saturation and other effects in the image. As this scattered light has a wavelength of 800 nm and the light emitted from the plasma is in the blue range of the visible spectrum a blue filter between the objective and the focusing lens was used. The overall result of 120 images is shown in figure 4.7b. Although there are still many issues with the over-illuminated jet and additional reflections from the new setup, the jet and the gas expansion can be measured at the same time. Of course from figure 4.7b no data can be extracted, but with the help of more suited 800 nm filters and anti-reflex coated windows it should be possible to perform both measurements at the same time. With this measurement it would be assured that the gas flow profile is imaged during jet operation.

As an alternative to the measurement proposed above it is also possible to make both measurements separately and then add both images. For the image in figure 4.8c the GDVN was first operated with a liquid jet and as described in section 4.1. The image was created by adding 120 images at 60 different positions with higher background subtraction. After the jet measurement was completed, the inner capillary was switched to contain CO$_2$ at a low pressure. In this configuration the gas flow imaging was performed again taking 120 images at the same positions the jet images were taken. Both images were added to get the overall image shown in figure 4.8c. Although this measurement already gives good and probably very accurate results it is not showing both the jet and the gas flow during jet operation. To analyse possible differences between both measurements the first experiment explained above first has to be improved.
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(a) Single picture of simultaneously measured jet and gas density. The plasma from the gas expansion can not be observed due to the over-illuminated jet. In addition to the large and very bright appearance of the jet, other spots can be observed which may results from diffraction off objects in the particle flow from the injector (droplets, ice crystal etc).

(b) Full image of simultaneously measured jet and CO$_2$ density with a blue filter in front of the camera. The image was created by adding 120 images at 60 different positions and subtracting the background, taken to be the value of the top left pixel, from each of these images. The blue cone of the plasma expansion and the liquid jet can be observed at the same time. The liquid jet appears very brightly and no diameter can be extracted in the jet region of the particle beam. Also many unwanted reflections can be observed in the image.

Figure 4.7: Test of simultaneous measurements.
4.3. SIMULTANEOUS CHAPTER 4. RESULTS AND DISCUSSION

(a) Full jet image of the GDVN created from 120 images at 60 different positions.

(b) Full plasma image of the GDVN created from 120 images at the same positions used for (a). For this measurement the inner capillary was switched to CO$_2$ at a low pressure with otherwise unchanged nozzle parameters.

(c) Combination of both measurements. For this image both images from (a) and (b) were added to show the liquid jet and the corresponding gas expansion.

**Figure 4.8**: Complete characterisation of a GDVN in two different measurements.
4.4 Comparison With An Aerodynamic Lens

The optical imaging discussed in this chapter enables the measurement of liquid jet sizes and the density profile of the gas flow of a GDVN. However, the imaging setup introduced in this report is not primarily designed for analysing gas dynamic virtual nozzles but for an aerodynamic lens stack. The particle beam created by an aerodynamic lens stack is a collimated beam of aerosol particles. These particles will scatter light differently and thus may not be visible by using the same parameters as for the liquid jet. Nevertheless it should be possible to record scattered light from aerosol particles when an appropriate laser power is used.

The plasma creation and gas flow measurements depend on the gas density at the injector tip. The aerodynamic lens stack is operating with lower gas pressures and hence it is expected that the density in the gas flow is also lower than in the gas flow of a GDVN. It remains to be measured if a plasma can actually be created in this low density gas flow with the actual setup. It should however be possible to create a plasma when going to even higher laser powers. Also, even if no plasma creation is possible at all, a upper limit for the pressure can still be determined, which may already help to improve the simulations.

In conclusion the optical measurement should work in similar ways for both a gas dynamic virtual nozzle and an aerodynamic lens stack.
Chapter 5

Outlook

5.1 Optical Imaging

Although optical imaging provides already a good basis for analysing particle injectors, there are several parameters that can not be measured or analysed so far. As shown in the fast-cam shadow image in figure 2.1 the liquid jet of a GDVN eventually breaks up into droplets. While the optical measurements performed in this report show a broadening at the distance where the droplet breakup is expected, it is not possible to resolve single droplets as in figure 2.1. This is not due to the setup itself but to the long exposure times of the camera used for the imaging. When replacing the camera with a (much more expensive) fast-cam it should also be possible to image the droplet breakup.

Secondly, while measuring spatial dimensions and densities works well, it is so far not possible to retrieve any information about the velocities in the particle flow. This is not only an important parameter in CDI experiments but can also be highly useful to compare experiments and simulations. To optically measure the velocity it might be possible to use a higher frequency laser (100 kHz - 1000 kHz) and illuminate the same particle multiple times during one capture time of the camera. By the distance of the created points it would then be possible to calculate the velocity of the illuminated particle.

However, there is a different approach to measuring velocities which was explained before. The use of a velocity map imaging setup in a time-of-flight mass spectrometer is designed for this application.

5.2 Mass Spectrometry

Optical imaging of particle beams and gas flows has proven to be highly useful for characterising particle injectors but not all parameters can be measured so far. In order to improve the imaging setup further, a velocity-map-imaging (VMI) time-of-flight (TOF) mass spectrometer (MS) was installed in the setup. This additional feature allows to measure velocity and spa-
tial distributions of the molecules in the particle flow. While the spatial imaging of water and CO$_2$ was also possible with optical imaging, the MS setup provides the additional features of measuring velocities and allows also a detailed analysis of the particle flow within the beam. This allows to analyse the essential sample flow and delivery efficiency which is very important for CDI experiments.

It is possible in this setup (see figure 3.2) to measure mass spectra at the same time the optical images are recorded with the microscope. This allows a detailed comparison of both measurements in order to validate achieved results and to further improve the imaging setup.

In order to validate the working principle and to analyse the influence of the particle injector on the electric field a detailed simulation of the setup was performed using the SIMION® software. The performed simulations are explained and discussed in section 5.2.1.

It was, however, not possible to record mass spectra during the duration of this project. This is because of high pressures in the vacuum chamber during GDVN operation. Even the best pressures achieved where $> 10^{-4}$ mbar while for successful MCP operation pressures of the order $10^{-5}$ mbar are needed. Nevertheless all pressure-reduction methods are explained in section 5.2.2 and possible additional methods are discussed.

### 5.2.1 Simulation

In order to validate the working principle and to determine the optimal voltages for the electrodes, the setup was simulated using the SIMION® software. In SIMION® an electrode setup is created by the user for which the electric field is then calculated. The user can then determine the initial parameters for any charged particles for which the trajectories are then calculated by SIMION®. In order to analyse the VMI setup, the CAD file of the experimental VMI setup was imported into SIMION®. A cross section of the configuration is shown in figure 5.1a. The black lines indicate the ion trajectories where the ions are created as a 3D Gaussian distribution (standard deviation 0.167 mm) with an initial speed of 100 m/s downwards in the middle between repeller (left) and extractor (middle) electrode. The red lines are indicating the electric field in the setup.

To determine the optimal voltage a user program was written, which was running the simulation for 200 ions (mass = 100 amu, charge = 1 e) with different voltages on the extractor electrode while keeping the repeller fixed on 1000 V and the right electrode on ground. For each voltage set the standard deviation of the arrival times at the MCP was calculated as this is a good measure for the mass resolution of a TOF MS. The result of this simulation is shown in figure 5.1b. In order to analyse the best achievable mass resolution, a simulation with the optimal voltage set was run. In this simulation 1000 ions where created for each of the masses from 100 to 105 amu and the arrival times at the MCP recorded. Figure 5.1c shows a histogram of the acquired data. Each of the masses appears as a very thin line in the histogram which is corresponding to a very good mass resolution for this particular setup.
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(a) Cross section of the simulated experimental setup with the electric field (red lines) and the ion trajectories (black) of 200 ions.

(b) Dependence of the resolution (standard deviation of arrival times) at different extractor voltages (repeller voltage = 1 kV).

(c) Best achievable mass spectrum for adjacent masses. Simulation of 1000 ions for each of the masses from 100 amu to 105 amu with the best voltage parameters obtained from (b). This figure is a histogram of the obtained data.

**Figure 5.1:** Analysis of the VMI TOF setup without particle injector.

This proves that in this configuration the VMI setup is well suited for the use as a time-of-flight mass spectrometer. As shown in figure 5.1a, the VMI setup is designed for the ionisation region to be on the centreline of the setup in the middle between repeller and extractor electrode. As a GDVN produces liquid jets of about 200 µm length, the nozzle must be placed between the VMI electrodes. Since the nozzle tip is made of ceramic it is possible that it is charged during the operation of the spectrometer. This would lead to unpredictable effects on the ion trajectories and the mass resolution of the setup. The charging or the charge effects on the electric field can be prevented, however, if the GDVN is placed inside a metal tube to which a voltage can be applied.

Such a design is shown if figure 5.2a. The nozzle-holder is a 8 mm metal tube in which the
GDVN (1.6 mm outer diameter) is placed. To determine the optimal mass resolution of this setup, the simulation is run with different voltages on the extractor electrode and on the nozzle-holder while keeping the repeller electrode on 1000 V (200 ions, mass = 100 amu, charge = 1 e). Analogue to the simulation above the standard deviation of the arrival times is plotted as function of both voltages (figure 5.2b) and for the best voltage set a simulation with different masses was run to analyse the achievable mass resolution (figure 5.2c). In contrast to figure 5.1c where all masses from 100 amu to 105 amu were plotted, in figure 5.2c only the masses 100 amu and 105 amu are plotted. As even these masses have overlapping particle arrival times it is clear that the mass resolution is reduced considerably. This is caused by the strong perturbation of the electric field at the place where the ions are created (see figure 5.2a). The white areas in figure 5.2b correspond to voltage sets for which not all the ions reached the MCP, black areas represent voltage sets for which the standard deviation of arrival times was $>0.1 \, \mu$s. This can be caused by low nozzle-voltage which cause the ions to hit the nozzle-holder or by high nozzle voltages which cause the ions to hit the electrodes. Statistic deviations of ion creation coordinates in the original VMI setup are compensated by applying the appropriate voltages to the electrodes. In the setup shown in figure 5.2a this is only possible up to a certain limit due to the strong perturbation of the electric field and the small parameter space for the voltages (see figure 5.2b).

In order to improve the mass resolution for the setup, the influence of different nozzle-holder setups was investigated and a new design was obtained. As the perturbation of the electric field at the ionisation region is mainly responsible for the low mass resolution of setup 5.2a, it was the goal to reduce the perturbation at that point. In order to do that the nozzle-holder in the simulation was first moved up by 13 mm to the edge of the aperture in the extractor electrode. All the simulations were performed in the same way as described for figure 5.2. The results for the first simulation are shown in figure 5.3a. The mass resolution for this setup is nearly as good as with no nozzle-holder at all, which proves that only the design of the nozzle-holder near the ionisation region has a strong influence on the mass resolution.

In order to analyse this influence further a nozzle-holder with 2 mm diameter was also simulated. The result of this simulation is shown in figure 5.3b. Although the peaks of each mass in the histogram appear considerably broader, it is still easily possible to distinguish between the masses. It follows from this simulation that the diameter of the nozzle-holder is crucial for the perturbation of the electric field.

However, not only the influence on the electric field but other factors like stability are important for the design of the nozzle holder. From the simulations in figure 5.3a and 5.3b a new design for the nozzle holder was obtained. For this design the ceramic nozzle was coated with chromium and then fixed in the original nozzle-holder but with the tip sticking out 13 mm. The simulation for this design is shown in figure 5.3c. Although the peaks in this simulation are slightly broader then for the 2 mm diameter design, still a good mass resolution can be achieved.
The nozzle-holder is already used in the experimental setup and also a GDVN was coated with chromium and the jet operation was tested. In conclusion, the VMI setup together with the nozzle-holder and the coated GDVN are prepared and can be tested once the pressure is reduced to allow MCP operation (see next section).
5.2. MASS SPECTROMETRY

(a) Setup with the original planning of the nozzle-holder and the corresponding electric field (red lines) for the best voltage set (see (b)).

(b) Dependence of the resolution on different extractor and nozzle voltages (repeller voltage $= 1 \text{kV}$). In black areas the standard deviation was $>0.1 \text{ µs}$. In white areas ions did not reach the MCP.

(c) Histogram of the best achievable mass spectrum for the masses 100 amu and 105 amu.

Figure 5.2: Analysis of the VMI TOF setup with the original design of the GDVN-holder
5.2. MASS SPECTROMETRY

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Figure 5.3: Analysis of the VMI TOF setup for optimal injector design. The figures were created analogue to figure 5.2 but with masses from 100 amu to 105 amu in the histograms of ion arrivals on the right side. The simulated setups are shown as a inset on the left side.
5.2.2 Chamber Pressure

As explained in section 2.2.3 the pressure for successful MCP operation has to be $10^{-5}$ mbar or lower. The vacuum chamber has a total volume of about 30 l and is pumped by a 2200 l/min turbo pump. While under normal conditions this easily allows pressures on the order of $10^{-8}$ mbar, the pressures during the operation of the GDVN are $10^{-3}$ mbar $- 10^{-4}$ mbar.

Originally the GDVNs were operated with helium and in order to improve the chamber pressure a catcher was installed. This catcher was a small differentially pumped orifice into which the jet was shooting. However, this lead to no measurable improvement of the chamber pressure which lead to the conclusion that the focussing gas is mainly responsible for the pressure increase in the chamber.

In order to reduce the influence of the focussing gas, the GDVN was first operated with argon and then with CO$_2$ in combination with a cooling trap to freeze out the gas. This cooling trap was cooled with liquid nitrogen. The cooling trap was originally a blank copper plate placed directly underneath the VMI. To increase the copper surface, a copper mesh was attached to this plate. The setup can also be seen in the photos of the setup (for example figure 3.6).

For argon the freezing point in vacuum is below the temperature of liquid nitrogen, which diminished the sticking probability of argon on the cooling trap. Therefore, CO$_2$ was used as a focussing gas as the freezing point of CO$_2$ in vacuum is about 130 K while liquid nitrogen is at a temperature of 77 K. While using CO$_2$ as a focussing gas the pressure did get better, but the results were neither reproducible nor did the pressure stabilise at one value (pressure jumps). After the pressure was falling for several seconds it suddenly jumped up to about the value it was before falling. This is probably due to CO$_2$-ice either hitting the turbo pump or the pressure gauge. However, the ice is not necessarily formed at the cooling trap but already in the gas expansion at the GDVN tip. Since the CO$_2$ gas is in this case already in crystal form, it wont stick permanently on the cooling trap which then leads to the described pressure jumps. Also all of these effects depend strongly on the GDVN and on the exact focussing gas pressure. This makes reproducible measurements very difficult.

Although mass spectrometry in general benefits from low pressures due to a longer mean free path of the ions, the main issue in this setup is the operation of the MCP at high pressures. In order to allow the operation of the MCP the pressure at the detector has to be reduced by about one order of magnitude. This will be done by a differential pumping stage for the detector. However, time did not permit to plan and install this pumping stage during this project.

Nevertheless, it might already be possible to use the mass spectrometry setup with an aerodynamic lens stack, as the pressures for the operation of this injector are smaller then in a GDVN and thus chamber pressure should also be lower. This needs to be determined once an aerodynamic lens is ready to be tested in the imaging setup.
Chapter 6

Conclusion

During this project a vacuum chamber with an imaging setup for analysing and characterising particle injectors for coherent diffractive imaging experiments was developed and set up. The imaging setup allows three different measurements to be performed:

1. optical particle beam imaging using laser illumination
2. gas density measurements using plasma creation and fluorescence emittance
3. mass spectrometry in combination with a velocity map imaging setup to measure spatial and velocity distributions of particles.

The optical imaging enables the measurement of particle beam dimensions such as the beam diameter which is an important parameter in CDI experiments. The working principle was proven by measuring a liquid jet with 15 µm diameter of a gas dynamic virtual nozzle. When using a laser with a different frequency (0.1 MHz - 1 Mhz) it might also be possible to measure velocities of particles by illuminating the same particle several times during one capture time of the camera. Also when using a fast camera it should also be possible to observe the droplet breakup in the particle beam of a GDVN.

The density measurement was performed by creating a plasma in a low density gas flow like the focussing gas flow from a GDVN. The fluorescence emittance was recorded by the same microscope which was used for the optical imaging. The emitted light intensity is a measure for the gas density at that point. While the working principle was also shown on a GDVN, calibration measurements still need to be performed in order to extract numerical values for the measured densities. There are also still some issues with unwanted reflections that lead to double images or randomly coloured pixels. The reason for these reflections needs to be found and further reduced. Also the possibility of measuring the liquid jet and the CO₂ gas expansion at the same time was discussed. While this should be possible, there are still many reflections and over-illuminations which need to be treated before a successful measurement can be performed. Although it was so far not possible to record any mass spectra due to high chamber pressures, the simulation of the setup using SIMION® shows promising results. While several approaches
to reduce the chamber pressure during jet operation were tried, none has provided significant pressure reduction so far. As the pressure only needs to be reduced at the MCP and only by about one order of magnitude it is expected that a differential pumping stage will provide the necessary pressure reduction. However, time did not permit to install and test this during the project time.

The goal of performing single particle imaging and recording molecular movies in CDI experiments is mainly limited by the low hit rates of currently used injectors. The imaging setup introduced and tested during this project can characterise and analyse particle beams and gas flows from these injectors. A detailed analyses of these injectors is crucial in the development and improvement of new injectors.

The imaging setup can already characterise spatial dimensions of particle beams which is very important for the injector performance in CDI experiments. Furthermore, valuable simulation parameters, like downstream gas pressures, can be extracted to further improve the simulation of injectors during the development. Once the differential pumping stage has been installed and successfully tested, the imaging setup can provide a full characterisation of the particle beam and the gas flow from an injector. This includes velocity profiles for the different masses, which are highly useful for the comparison of simulation and experiment.

The imaging setup will enable the development, improvement and testing of new particle injectors.
Bibliography


