

Synthesis of Nanodiamonds via Laser-Driven Shock Compression of Plastic Precursors

Dissertation
zur Erlangung des akademischen Grades
doctor rerum naturalium (Dr. rer. nat.)
der Mathematisch-Naturwissenschaftlichen Fakultät
der Universität Rostock

vorgelegt von
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geboren am 17. Mai 1995 in München

Rostock, 15th May, 2025



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Jahr der Einreichung: 2025
Jahr der Verteidigung: 2025

Abstract

This thesis explores the formation and recovery of nanodiamonds (NDs) created by laser-driven shock compression of plastics, mimicking conditions in planetary interiors. Using a combination of molecular dynamics simulations, x-ray diffraction, small-angle x-ray scattering, and microscopy techniques, it investigates the properties and behaviour of NDs during compression, on release, and thereafter. This work studies how laser pulse shaping influences ND properties and identifies pulse profiles favourable for ND stability. Cratering landscapes of high-velocity ejecta were analysed and several catcher materials investigated in regard to their recover potential, employing experimental and theoretical methods. With the use of a vacuum-compatible catcher material, this work has - for the first time - provided experimental evidence of the intact recovery of NDs from laser-driven shock compression of plastics. In this thesis, the compatibility of the used catcher material with high-repetition-rate setups is demonstrated, establishing a foundation for scalable synthesis pathways of metastable materials.

Kurzzusammenfassung

Diese Dissertation untersucht die Bildung und Wiedergewinnung von Nanodiamanten (NDs), die durch lasergetriebene Schockkompression von Kunststoffen erzeugt werden, welche Bedingungen ähnlich zum Inneren von Planeten erreichen. Mit einer Kombination aus Molekulardynamik-Simulationen, Röntgenbeugung, Kleinwinkel-Röntgenstreuung und Mikroskopietechniken werden die Eigenschaften und das Verhalten der NDs während der Kompression, bei der Freisetzung und danach untersucht. Diese Arbeit erforscht, welchen Einfluss die Laserpulsform auf die Eigenschaften der NDs hat und identifiziert Impulsprofile, die günstig für die Stabilität der NDs sind. Kraterlandschaften von Hochgeschwindigkeits-Auswürfen wurden analysiert und mehrere Auffangmaterialien hinsichtlich ihres Wiedergewinnungspotentials unter Verwendung experimenteller und theoretischer Methoden untersucht. Mit dem Einsatz eines vakuumkompatiblen Auffangmaterials konnte diese Arbeit erstmals experimentelle Nachweise für die intakte Wiedergewinnung von NDs aus der lasergetriebenen Schockkompression von Kunststoffen liefern. In dieser Dissertation wird die Kompatibilität des genutzten Auffangmaterials mit experimentellen Aufbauten für Hochwiederholrate demonstriert, wodurch eine Grundlage für skalierbare Synthesepfade metastabiler Materialien geschaffen wird.

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1. Introduction

Carbon is one of the most versatile elements in the periodic table. It is essential to all known life on Earth and exists in a wide variety of forms throughout the universe, even in its most remote regions. From the deep cores of Uranus to the surface of asteroids like Ryugu, carbon is exposed to some of the most extreme temperatures and pressures.

In addition to forming chemical bonds with a vast range of other elements, carbon alone can assemble into remarkable structures. One example is the hardest material known to mankind, diamond. Beyond its hardness, diamond is chemically stable, highly resistant to most acids and bases, and possesses exceptional thermal conductivity. Besides the remarkable properties of bulk diamond, the intriguing properties of nanometre-sized manifestations of diamond have sparked growing interest. Such Nanodiamonds (NDs) are proposed to have many exciting applications in medicine and material science [1–4]. NDs have also been found to nucleate at conditions present in the interiors of icy giants, highlighting their importance in studying planetary evolution [5–7].

The chemical and electric properties of NDs can be modified if so called dopants are involved. Dopants are non-carbon atoms, which are included in the diamond lattice and therefore cause defects which can strongly affect the NDs properties. Doped NDs are promising candidates for quantum sensing due to defect-induced electronic states. Due to their versatility, extreme properties, and relevance to celestial processes, NDs hold a special place in the realms of carbon allotropes.

Overall, the plethora of possible applications of NDs and their relevance in the inner workings of icy giant planets, positions them as a key focus in both planetary science and material research. In this work, the nucleation, growth and evolution of NDs is studied in the context of laser-driven shock compression, a technique to recreate the conditions of planetary interiors in the laboratory.

The remainder of this chapter provides the motivation for this thesis, identifying the key challenges encountered and presents relevant research efforts in this field. It closes with a detailed outline of this thesis.

1.1. Motivation

The planets of the solar system have long inspired humanity to speculate and eventually scientifically assess their movements and inner workings. Because probing of these planets is rather difficult, theoretical modelling has evolved as a powerful tool to understand their evolution. The nucleation of NDs at planetary interior conditions of icy giants like Uranus and Neptune, can have a strong effect on their internal structure. Studying the nucleation of this nanostructure is therefore an important part for their understanding. Here, laboratory astrophysics has recently developed into an important technique for benchmarking models and providing data points [8]. One major motivation for the study of ND nucleation and evolution is therefore driven by a purely scientific interest in deepening our understanding of our own solar system.

Beyond this, there is a second, more practical motivation concerning the applications of NDs. The synthesis of NDs has been available via several methods for decades. A comprehensive treatment of these synthesis procedures, along with their advantages and disadvantages is

given in Ref. [1, Ch. 2]. For now, it should suffice that the commercially available NDs are all synthesised via either 1) ball-milling of larger diamonds grown at High-Pressure High-Temperature (HPHT) conditions, 2) detonation methods of carbon containing explosives, or 3) laser ablation of carbon surfaces submerged in a liquid.

Shenderova and Nunn identify the strengths and weaknesses of these three synthesis methods as follows [1, Ch. 2]: 1) the milling of HPHT diamonds can - under certain circumstances - produce single digit NDs and even include ND doping, however, it suffers from low yields and high costs; 2) the detonation method scales well and is able to produce kg quantities of single digit nm diamonds, but requires extensive cleaning procedures; and 3) the laser ablation method is able to produce "clean" NDs due to the lack of chemical precursor treatment (although it also suffers from low yields), while its off-equilibrium nature might enable the synthesis of other novel nanostructures.

In this work, the possibility of a novel synthesis path for NDs is explored, which could unify the advantages of all existing techniques. This method has evolved from the laboratory astrophysics approach of recreating planetary interior conditions in the laboratory and will be an important addition to the currently available synthesis routes. In theory, it could even be used for synthesising other metastable high-pressure phases.

The motivation for the study of NDs forming in shock compression experiments is therefore twofold: first, it represents a fundamental scientific interest in the context of planetary science, and second, a practical drive towards novel material synthesis techniques.

1.1.1. Planetary Context

The study of the nature and evolution of planets in our solar system and beyond has long been of great scientific interest, inspiring numerous theoretical models and space missions [9–19]. Modelling relies heavily on Equation of State (EOS) data and aims at predicting planetary interior behaviour and evolution by modelling quantities like thermodynamics, transport properties and chemical reactions [20–26]. This requires knowledge of the composition of planets and the physical conditions and behaviour of their constituents for modelling and benchmarking.

Experimentally, those planets can be studied through telescopes or space missions that measure properties like magnetic or gravitational fields, providing insights into their interior conditions. An alternative to probing planetary conditions directly, is the recreation thereof in a laboratory environment. If the composition and physical regime are known, an artificial planet can be reproduced and studied in detail. Advanced laboratory diagnostic can offer a much deeper understanding of these processes than space probes.

Planetary interiors typically exist at high pressures (above a megabar $1,000,000 \text{ bar} = 100 \text{ GPa}$) and high temperatures (several thousand Kelvin) within the Warm Dense Matter (WDM) regime. This is a challenging physical regime because it lies at the edge between plasma and solid state physics and both classical and quantum effects occur at similar scales. Reaching and sustaining these extreme conditions in a laboratory framework is experimentally challenging.

Nevertheless, Diamond Anvil Cells (DACs) were first used to statically compress materials to high pressures, while simultaneous heating could provide the required temperatures [27]. However, the finite size and material strength of diamonds puts natural constraints on these kinds of experiments. Dynamic compression offers another method to create WDM conditions by

exposing the target to an explosion or a high-velocity solid pusher (usually a flyer plate) impacting the target at very high velocities. The velocities typically reach several km s^{-1} , and create a shock wave with a jump in pressure and temperature conditions [28]. By tailoring the velocity of the pusher or intensity of the explosion and the material composition of the target, various physical states are accessible experimentally for probing until the shock decays or breaks out at the rear surface.

Such dynamic compression experiments have also been realised using the ablation pressure of high intensity drive lasers [29]. Here, a short laser pulse of several nanoseconds with very high intensities in the order of TW cm^{-2} is focused on a target, ablating the laser-side surface. Momentum conservation forces a shock wave into the target, which ultimately breaks out at the rear side of the sample, releasing the pressure. While the shock state persists, it can be probed in the laboratory. Due to their highly dynamic nature, these states only persist for a very short time in the order of the length of the drive laser and require very bright diagnostic lasers to accumulate sufficient signal on such short exposure times. X-Ray Free Electron Lasers (XFELs) are typically used for probing because they provide ultra-bright x-ray sources and can penetrate the sample [30]. The interest in these kind of shock compression experiments has grown due to recent progress in the field of Inertial Confinement Fusion (ICF), which for the first time received a net positive energy balance (ignition) which utilises a similar principle [31].

Recent advancements in laser technology have elevated the repetition rates of high intensity drive-lasers to several Hertz, further increasing the interest in dynamic compression experiments [32]. Many small scale laboratories can now efficiently create WDM conditions at relatively low costs. This creates possibilities for experiments and applications that were impossible before, especially those requiring high repetition rates due to low signal-to-noise ratio [33].

Understanding the extreme conditions within planetary interiors not only helps modelling their evolution, but could also open possibilities to study the formation processes of unique material formation processes which occur at these HPHT conditions. One such process is the formation of diamonds. These diamonds, predicted to form in the deep interiors of Uranus and Neptune, have gained the attention of researchers due their formation mechanism [34]. By recreating WDM conditions in the laboratory, the diamond nucleation processes can be investigated, while also exploring the possibilities of their applications.

1.1.2. Nanodiamonds

It has long been predicted that interesting materials like diamonds can form under the WDM conditions of the interiors of Uranus and Neptune [34]. This hypothesis was backed by finding ND nucleation at these conditions in dynamic compression experiments of Polyethylene (PE) and graphite foils [5, 6]. The NDs could form in the outer planetary layers and sink towards the core, thus releasing a part of their gravitational energy and contribute to the luminosity. This might provide the internal heat source required to match the increased luminosity observed in Neptune [35]. The possibility to form these NDs from PE and other plastic foils at remarkably high nucleation rates inspired the idea to use this mechanism for dynamic material synthesis of NDs [36–38].

The term nanodiamond refers to very small diamonds with radii of a few nanometres ¹. At such small sizes, the diamonds consist of only a few thousand atoms and the properties of

¹In the literature the term can extend up to a few hundred nanometres [39].

such small particles can greatly differ from bulk material. Due to their very small size, ND-synthesis is not trivial and an entire field of research is dedicated the synthesis of NDs, trying to control their size distributions and properties [40]. Current means of production, like Chemical Vapour Deposition (CVD), HPHT-methods and Detonation Nanodiamond (DND) suffer from various difficulties like low yield, high costs or the requirement for intense chemical cleaning procedures [1, Ch. 2]. NDs synthesised via laser-driven shock compression might prove a valuable extension of current synthesis methods, especially as the so produced NDs have very small diameters below what DND synthesis is able to produce [2, 7].

NDs find applications in hygienic coatings, bioimaging, and lubricants among others [41–43]. It has been suggested that their hydrogenated versions could improve radiation treatment of cancer cells [3]. NDs modified by doping have especially promising properties. Nitrogen vacancy centres can be used as temperature sensors in living cells, single photon sources or magnetic sensors with nanoscale resolution [44–48]. Synthesis via shock compression of plastics might enable doping of NDs by modifying the plastic target.

Although NDs have formed in various plastic precursor materials during shock compression, their recovery and concentration has shown to be a challenging task [37]. This is because the created WDM states at which NDs nucleate are extreme, and after the shock wave has traversed the sample, pressure drops to ambient conditions and the compressed material is ejected at hypervelocities ($> 10 \text{ km s}^{-1}$). Collection and concentration of intact material from the release cloud in a catcher substance is one of the main challenges in dynamic material synthesis using laser-driven shock compression. NDs are not the only material which can form in a high pressure environment. Synthesis via dynamic compression can be achieved for a variety of substances [49, 50]. However, due to diamond being the hardest known material and its outstandingly wide range of applications it is an excellent starting point for attempting dynamic material synthesis via laser-driven shock compression as a proof-of-principle.

This work aims at understanding the process of ND formation and release from a laser-driven shock in plastic materials, identifying ways to maximise the amount of NDs released and recovered after shock breakout. The focus of this work is to identify the dominating factors and challenges for intact recovery and subsequent ND concentrations. Additionally, this thesis aims at determining the best ND catcher materials and the advancement of high-repetition-rate drive-laser platforms, which can be utilised to achieve the goal of dynamic material synthesis via shock compression.

1.1.3. Challenges in Nanodiamond Recovery

Typical length and time scales in laser-driven shock compression experiments are a few ns during which the shocked state persists in typically tens of μm thick layers. During this time the initially bonded polymers break into their chemical constituents, carbon atoms concentrate and NDs begin to nucleate. The entire process is over after a few nanoseconds. Usual diagnostics for analysing ND properties include volume-probing methods like X-Ray Diffraction (XRD), Raman Spectroscopy or Dynamic Light Scattering (DLS), and methods that offer higher spatial resolution e.g. Transmission Electron Microscopy or Atomic Force Microscope techniques [1, Ch. 10]. Many of these methods require long integration times or very delicate sample preparation to produce conclusive data, both of which can be very hard to achieve given the dynamic nature of shock-compressed states. Therefore, *in situ* probing is required and a detailed understanding of the release and ejection process is crucial for enabling analysis of the collected material after the shock experiment. Diamond is metastable at ambient conditions,

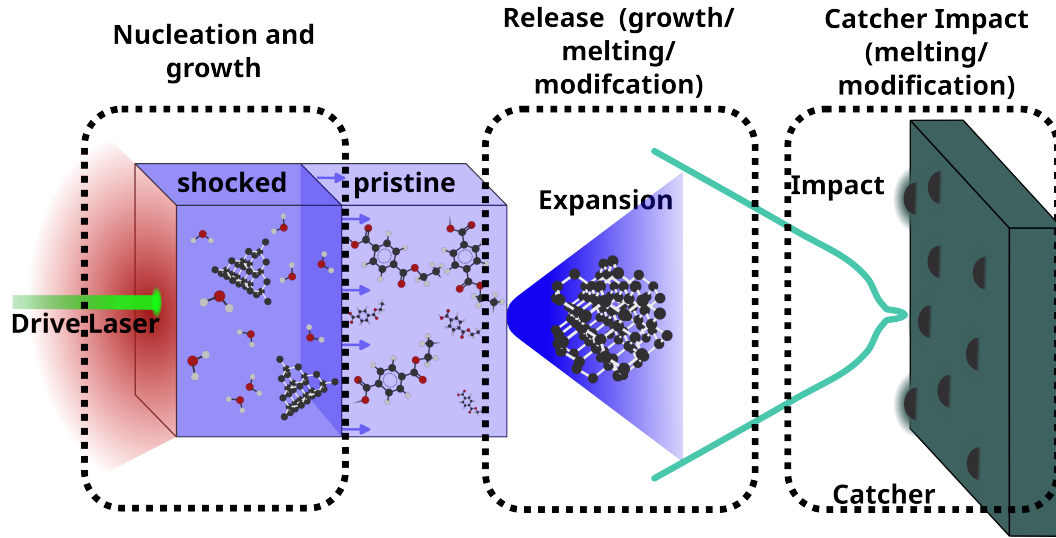


Figure 1.1.: Schematic overview of a recovery experiment. The drive laser impacts the target material from the left, forming a shock wave (dark blue region), which is travelling through the sample and ejected at the rear side. The releasing material is impacting the catcher. The three relevant stages that can influence recovery are shown as boxes.

and the fact that it releases from the extreme WDM states rapidly into vacuum poses a substantial threat to the NDs structural integrity.

To tackle some of these challenges, this work combines Molecular Dynamics (MD) simulations with experimental results. The use of MD simulations can shed light on those parts of the release and ejection process, that evade detection by experimental methods alone due to their transient nature. Combining the simulation results with experimentally measurable quantities provides a clearer picture of the entire process and can help identify key challenges in the recovery process of NDs.

Fig. 1.1 shows a schematic of a recovery experiment using dynamic compression. While the details are explained below, it is helpful to outline the process in distinct phases. Describing each of these phases requires a mix of theoretical and experimental approaches, as they all cover their own timescales.

Phase 1: Nucleation and Growth

The laser generates a shock wave through ablation, rapidly increasing the target's temperature and pressure. This shock can be single, double or more complex in shape. The key point is that the target enters a thermodynamic regime, where diamond nucleation can occur [51, Ch. 3]. This process requires sufficiently high (local) carbon concentrations.

After nucleation, the diamonds can grow depending on the thermodynamics and the surrounding material. Nucleation and growth of nanoparticles are competing processes. High nucleation rates at low growth rates typically result in many small particles, while low nucleation rates at high growth rates result in few large particles. Both nucleation and growth are complex phenomena, dependent on factors such as minimal stable cluster sizes of the nucleating phase and diffusion rates of free atoms to those nuclei. Understanding these processes requires accurate computations, often done with methods like Density Functional Theory (DFT) [51, 52], which are computationally expensive.

In the context of ND recovery, it is important to experimentally identify the materials and shock conditions where ND nucleation can occur, compare the growth of ND particles in different materials and shock regions, and provide data for comparison with theoretical predictions of ND growth and nucleation. This requires studying the material response and dynamics of carbon containing materials within the WDM regime. A theoretical description of the WDM regime, as well as an understanding of the shock dynamics is therefore required. Typical theoretical methods include DFT and hydrodynamics. The entire process takes about 10 ns and time resolved snapshots of the material need to penetrate the sample with detection methods well below that timescale. XFELs are perfectly suited due to their high brilliance (short exposure times) and their ability to probe bulk material.

Phase 2: Release

After the shock has traversed the sample, it will break out at the rear surface into vacuum, and a release wave will travel in the opposite direction. This rapidly reduces the pressure in the sample. The NDs, still compressed and at high temperatures, will expand rapidly, which can affect their size. If not all carbon has turned into diamond, the surrounding material will contain carbon atoms and the NDs could grow, shrink, or form other surface bonds depending on the nature of the expansion and surrounding material. This process is extremely fast (< 1 ns) and highly dynamic, making experimental studies challenging and adding the requirement for simulation approaches like MD. Nevertheless, understanding the release and expansion process is crucial for ND recovery.

Phase 3: Catcher Impact

After ejection, the release cloud containing the NDs travels through vacuum and impacts the catcher material. Depending on the catcher's properties, the NDs may undergo further modification. Despite diamond's exceptional hardness, the extreme impact velocities - hypervelocities of several tens of km s^{-1} - can cause ND melting upon impact. Such hypervelocities are common in cosmic environments, such as meteoric impacts or spacecraft collisions, creating a link to related areas in materials science.

Nanoparticles at hypervelocities pose a serious threat to spacecrafts and satellites as part of space debris and have been studied extensively over the past decades [53]. Experimental methods include material impact studies via acceleration of micro- and nanoparticles and subsequent studies of catchers via Scanning Electron Microscope (SEM), AFM, Transmission Electron Microscopy (TEM), Raman Spectroscopy and other microscopic imaging techniques [54–56].

The amount of shocked material that can be generated with high-repetition-rate lasers is small. To enable efficient synthesis of NDs via dynamic compression, multiple shots have to be accumulated in the same catcher at a high repetition rates. One purpose of this study is to find materials that are preferable for intact ND recovery while also enabling simple further purification and concentration. Furthermore, an efficient target and catcher design should be constructed, which allows for high repetition rates and the accumulation of material through multiple shots.

To summarize, the purpose of this work is to understand how to efficiently recover and concentrate NDs from laser-driven shock compression experiments and how tailoring the shocked material, laser pulse profile and catcher material influences the ND properties. To do so, it is important to understand which factors maximize ND yields at each step depicted in Fig. 1.1 and

how they affect ND properties. Because these processes occur on different timescales and some of them are very challenging to detect experimentally, it is crucial to make use of theoretical methods in conjunction with experiments. Combining experimental methods with simulations helps to provide a consistent picture and contributes to the research of a new method to synthesise NDs from laser-driven shock compression of cheap plastic precursors.

1.2. Previous Research

This section provides an overview of previous research. This foundation will explore the necessary scientific context required in the presented work. First, the section presents research on the nucleation and growth theories of NDs and their general properties. Thereafter, key research investigations on ND formation in the WDM regime will be presented, along with attempts at ND recovery. Finally, previous research on Hyper Velocity Impact (HVI) will be outlined.

1.2.1. Nanodiamond Nucleation and Properties

NDs have been the subject of extensive research for several decades, with a focus on their optical and mechanical properties, as well as their synthesis procedures. A comprehensive review by Mochalin et al. covers various aspects of ND formation, synthesis, purification, applications, and properties [43].

1.2.1.1. Stability and Metastability

Diamond is not the stable form of bulk carbon at ambient conditions, but is a so-called metastable phase. The diamond crystal structure is characterised by carbon atoms arranged tetrahedrally and bonded in sp^3 hybrid orbitals, representing a metastable configuration. The total energy of a graphitic arrangement with sp^2 binding orbitals is preferable for a bulk system at ambient conditions. Although the energy levels of these two phases are very similar, the energy barrier between them is substantial (order of eV/atom) in bulk material [43].

In the case of finite-size effects, the picture is more complicated. Multiple factors can influence which phase is stable. Most notably, there are surface interactions which strongly contribute to which configuration is energetically most stable. Consequently, spherical hollow carbon molecules with a closed surface (so called fullerenes) are predicted to be the most stable form of carbon, e.g. for the C_{28} isomers [57].

A finite-size diamond will inevitably have atoms on the surface that cannot be bound in regular tetrahedral fashion. If left unbound, those so-called dangling bonds would introduce additional sources of energy. Similar effects occur at the edges of a graphite sheet. Therefore, depending on the number of atoms, the stable form is the one which minimises not only the bulk energies, but also the surface interaction terms. *Ab initio* calculations using DFT suggested that ND is the stable phase of carbon in a range from 1.9 to 5.2 nm even at ambient conditions [58]. Instead of dangling bonds, those edge atoms can also bind to functional groups, atoms such as hydrogen, or can join with other diamond surface atoms. Depending on the stability of this terminating bond, growth of the ND nuclei can be inhibited or enhanced [59].

1.2.1.2. Nucleation Theories

Nucleation is the emergence of a new phase within a surrounding phase. Different theoretical approaches to describe and understand nucleation have been developed, of which Classical Nucleation Theory (CNT) is the most widely spread [60]. CNT tries to describe the nucleation process phenomenologically. In contrast to this, non-classical theories try to describe the nucleation process on a microscopic scale, usually from first principle methods [51].

CNT, developed in the early 20th century, statistically describes the formation of a nucleus from a supersaturated parent phase [61–63]. Supersaturation here means that the parent phase has a higher concentration than expected under equilibrium conditions and is usually put into context with a critical nucleus size. The parent phase would be supersaturated in regard to nuclei exceeding such a critical size. The formation of such nuclei is a statistical process and is dependent on the thermodynamics and the change of the Gibbs free energy during the nucleation of the new phase [51, Chapter 3]. CNT is based on assumptions such as local thermal equilibrium between nucleus and the surrounding phase, a spherical nuclei shape, and a planar phase-phase interface, i.e. the capillary approximation [60]. Especially at small nuclei sizes these assumptions are clearly violated.

The formation rate J of critical nuclei - nuclei of a critical size, encouraging growth - is usually expressed as:

$$J = J_0 \exp \left(-\frac{\Delta G}{k_B T} \right), \quad (1.1)$$

and depends on the temperature T , the difference in Gibbs free energy of the two phases ΔG , and a prefactor J_0 .

Heterogeneous nucleation refers to nucleation at a phase perturbation, such as a vessel wall, dust particle, or other disturbance and requires lower supersaturation for a nucleus to emerge. A widely known application of this effect is the artificial generation of rain through the introduction of, e.g. silver iodide [64].

Non-classical nucleation theories include DFT methods in which the free energy of nuclei is calculated from their radial density profile and a critical nucleus size which favours growth is calculated [60]. Other theories try to extend CNT by modelling intermediate stages which are formed between the two phases of interest [65]. The nucleation of NDs in the WDM regime could be facilitated by H-C demixing caused by an insulator-metal transition of hydrogen which makes it immiscible [66]. Such demixing could create carbon-rich areas, with locally increased supersaturation.

1.2.1.3. Experimental Studies of Nucleation

All theories require experimental validation. Thermal diffusion chambers are commonly used to determine nucleation rates. They create controlled nucleation conditions and study the formation of nuclei via light scattering and can measure nucleation rates from 10^{-3} to $10^3 \text{ cm}^{-3} \text{ s}^{-1}$ [67–69]. Expansion cloud chambers are another method for nucleation studies. Therein, a compressed vapour expands adiabatically and creates high supersaturation at uniform conditions [51, Chapter 16]. Nucleation pulse chambers are able to measure nucleation rates in the range of 10^5 to $10^{10} \text{ cm}^{-3} \text{ s}^{-1}$ via a single nucleation pulse which lasts for about 1 ms [70, 71]. This device can estimate the critical nucleus size under certain assumptions [72].

Small-Angle X-Ray Scattering (SAXS) is a technique which can resolve electron density contrast through elastic scattering. In contrast to XRD the detector setup makes it sensitive to much smaller scattering vectors q and it can resolve density contrasts in the order of up to a few hundred nm. This diagnostic is often employed when trying to estimate critical sizes in nucleation experiments [73, 74].

In addition to volume probing techniques, microscopic diagnostic tools are also employed to shed light on nucleation processes. TEM and AFM are imaging techniques with atomic resolution that can help in understanding even complex multi-stage nucleation processes [75–78]. Different theoretical and experimental methods have been employed to study the nucleation of NDs, some of which are explored below. However, studying the nucleation process within the WDM regime requires techniques that can probe dynamic shock states *in situ*.

1.2.1.4. Nanodiamond Nucleation

To effectively control ND size distributions and nucleation, it is essential to understand the nucleation, growth, and stability regions within the phase volume. Growth experiments with defined proto-nuclei sizes have determined a critical nucleus size between 22 and 26 atoms for temperatures below 1000 K. This value is two orders of magnitude below predictions from CNT [79]. However, growth of those nuclei is in good agreement with that predicted from CNT. Interestingly, the critical nucleus pentamantane (a diamondoid with five carbon cages) does not contain a single bulk carbon atom, calling into question the assumption of surface to bulk energy trade-off used in CNT.

Ghiringhelli et al. have estimated ND nucleation rates via MD simulations and have studied different carbon concentrations along the isentropic conditions of Uranus up to 100 GPa [80, 81]. They used a critical cluster size of 110 atoms and conclude that given an ideal mixture of elements, diamond nucleation at planetary interiors would require a carbon concentration of $> 15\%$ which is beyond what is expected in planets like Uranus and Neptune [82]. Importantly, the authors do not consider demixing of the carbon phase to allow for locally increased carbon concentrations. The predicted nucleation rates along with the Uranus and Neptune isentropes from Redmer et al. [83] are illustrated in Fig. 1.2.

In situ x-ray probing of shock-compressed plastics have found diamond nucleation from different precursor materials like PS (atomic carbon fraction $\chi_C^{\text{PS}} = 0.5$) and Polyethylene Terephthalate (PET) ($\chi_C^{\text{PET}} = 0.46$) [6, 7]. For PS, Schuster et al. have estimated the ND nucleation rates at 150 GPa and 5000 K to be 10^{29} to $10^{34} \text{ m}^{-3} \text{ s}^{-1}$, with no nucleation at 70 GPa and 3000 K [36].

Theoretical calculations based on DFT by Cheng et al., based on Machine Learning (ML) potentials, suggest a "depletion zone", where a hydrogen-carbon mixture would be thermodynamically driven to demix to a hydrogen rich and a carbon enriched fluid [84]. In this region ($P > 200$ GPa and $T > 3000 - 3500$ K) the formation of diamond would be thermodynamically favourable and nucleation could be possible even at (macroscopically) relatively low carbon concentrations. Such demixing phenomena have also been predicted for other planetary systems like Saturn and Jupiter (hydrogen-helium) and can by themselves be a source of internal heat [85, 86, 22]. Demixing can result in locally increased carbon concentrations and certainly plays an important role in the nucleation process. However, at the extreme WDM conditions, diamond can also become permeable to hydrogen [87, 88].

Furthermore, kinetics can play an important role in the nucleation process. This is highlighted by the different experimental results obtained from dynamic, laser-driven shocks, and static

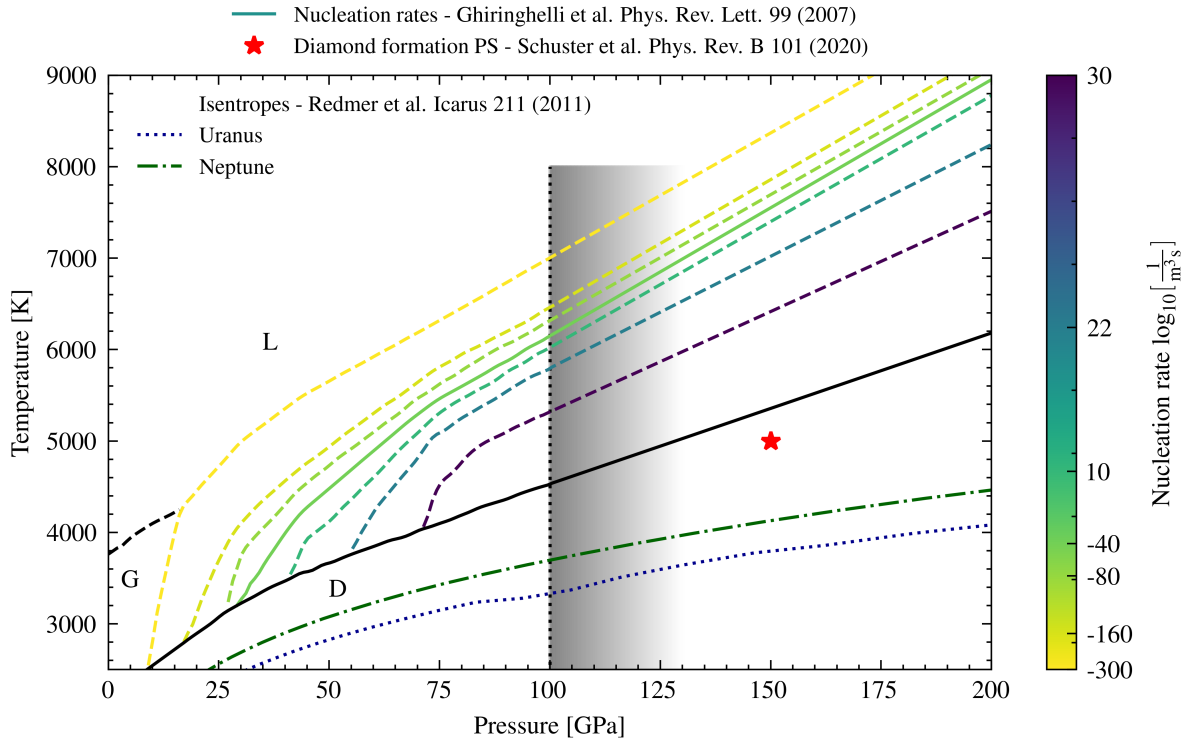


Figure 1.2.: ND nucleation rates in pure carbon at different P - T conditions with the stability regions for diamond (D), liquid (L) and graphite (G), reproduced from Ghiringhelli et al. [81]. The continuous green line is the nucleation rate corresponding to a single critical nucleus forming in Uranus within the life time of the universe. On the right side of the gray-shaded area, the data was obtained by extrapolation. The red star is the point at which ND formation at high rates has been observed from shock-compressed Polystyrene (PS) by Schuster et al. [36]. The isentropes of Uranus and Neptune are taken from Redmer et al. [83].

compression experiments in DACs. One such experiment observed diamond nucleation at significantly lower pressures (19-27 GPa) from PS after 30 to 40 ms, compared to the nanosecond timescales of dynamic experiments [89]. However, due to the nature of DAC experiments, which require close contact between the sample and the surrounding materials (anvils, gaskets, sensors), heterogeneous nucleation - which is known to occur much earlier than homogeneous nucleation - might be induced [84].

The question of the potential diamond sizes in planetary interiors is yet unanswered. One theoretical study has tried to combine a nucleation and growth model to obtain size distributions within a shocked sample, which could provide a valuable benchmark if it could be tested experimentally [90]. The corresponding conference contribution is displayed in Fig. A.1.

In summary, understanding the nucleation process of diamond is a challenging task and requires a multitude of theoretical methods and experiments. As it is not purely thermodynamic, but includes kinetic effects, knowing the nucleation region in phase space is not enough to model nucleation. Local carbon concentration can be affected by demixing phenomena and further complicate the picture. The atomic composition of the precursor material might differ substantially from the nucleation region in the shock compression experiment. Current experimental methods are not capable of resolving atomic concentrations within the shocked sample. Nevertheless, time resolved XRD and SAXS experiments can inform us about the materials and conditions where nucleation occurs. Such experiments are vital to be able to control size distributions in potential shock-synthesised NDs as the following section will explain.

1.2.1.5. Nanodiamond Growth

As mentioned above, nucleation and growth are two competing processes. Like nucleation, growth dynamics depend on the available free carbon close to the critical nucleus. Typically, the growth process is described as a kinetic process, where a growth unit - sometimes a single atom - diffuses towards the crystal surface and forms corresponding bonds to integrate into the lattice [91, Chapter 3]. Factors like the surface structure of the critical nucleus and diffusion rate of growth units influence the magnitude of the growth rate [92]. Since both processes - nucleation and growth - compete to exhaust free carbon atoms, they are closely related.

The size of NDs can be assessed *in situ* by techniques like XRD or SAXS. Here, the width of the diffraction peak is dependent on the size of the crystallites. Because small crystallites cannot compensate for small deviations of incident angles by a matching destructively interfering lattice plane, they result in broader peak shapes [93]. Time resolved measurements of the peak width are able to determine size distributions from *in situ* XRD patterns. Another method to determine growth are high resolution TEM micrographs, which directly visualise ND sizes. The growth dynamics and rates depend strongly on the synthesis method. The most commonly synthesised NDs are HPHT NDs, DNDs, and CVD NDs. An overview over their respective properties will be given below. Each method is unique and expresses different growth dynamics.

A systematic study of ND growth from 1-fluoradmantane ($C_{10}H_{15}F$) found the growth of HPHT synthesised diamonds to be dependent on the temperature [94]. NDs grew to sizes of up to 5 nm over a time of tens of seconds, with higher temperature resulting in larger NDs. Significantly larger NDs (< 457 nm) have been synthesised in a two step HPHT experiment over the course of up to 3 hours [95].

Another study investigated the annealing of DNDs and found a similar trend to the HPHT results with higher annealing temperatures resulting in larger crystallite sizes [96]. The an-

nealing was performed at 5 GPa over a time of 60 s from commercial DNDs. *In situ* SAXS probing of DNDs forming in a detonation chamber suggested that the entire growth happens within a time of 0.3 μ s with most of the growth already happening before 0.1 μ s [97]. Reaction temperatures here reached up to 4000 K. Termination of growth of DND is believed to not only depend on temperature and pressure, but also on the decrease of carbon radical concentration [98]. It was also suggested that there exists an upper limit for DND growth due to accumulation of defects towards larger diamond sizes, which inhibits growth above diameters of 8 nm [99].

CVD diamonds can be grown to very large sizes beyond the realms of the nanoscale. Some can be as heavy as 1 ct (200 mg) [100]. Growth rates in CVD synthesis can reach several ct/h and are dependent on the input power in the CVD reactor [101]. Other factors influencing CVD growth rates are stress of the growing wafer (this can negatively affect growth rates), synthesis temperature, gas flow rates and plasma parameters [101]. At these growth rates, a spherical diamond of diameter 200 nm would take about 200 ps to grow. In CVD, growth is heavily affected by surface termination of dangling carbon bonds on the ND surface. Mostly, the dangling bonds are stabilised by hydrogen which helps incorporating carbon into the lattice [102]. Compared to other growth regimes, pressures and temperatures in CVD growth are relatively low (< 1 bar and < 1600 K) and growth generally relies heavily on chemical reactions.

Growth in laser-driven shock compression is the least investigated. Few experiments have investigated ND growth in laser-driven shocks and the focus of most of those experiments was on evidence for diamond formation and not growth dynamics. However, He et al. used SAXS on NDs forming in a laser-driven shock compression of PET to study the formation kinetics. They found size distributions centred at $d = 2.2$ to $d = 6.4$ nm over a time of several ns [7]. The ND formation occurred at temperatures around 4000 K and pressures between 72 and 125 GPa. The growth process here is several orders of magnitudes faster than in the HPHT context (where NDs takes seconds to form), while it is below what can be achieved with CVD.

Unlike DND, where growth is suspected to be limited by defect incorporation and CVD which is dependent on chemical reactions and surface termination of carbon bonds, it is not yet clear what limits the growth of NDs in shock compression, or if the growth is even limited. The short persistence of the shocked state is a natural limitation for ND size, but the question remains whether longer shock durations in the order of seconds (which require much stronger lasers than currently available) could result in larger diamonds. Answering this question is relevant for planetary contexts as well as material synthesis, because it would strongly affect the diamond size in planetary interiors.

1.2.1.6. Nanodiamond Synthesis

The state of the art ways of ND synthesis differ depending on the size distribution of the crystallites [1, Chapter 2]. A standard way to synthesise NDs of a few nm in diameter is the detonation method [103]. The synthesis process of DNDs has been continuously advanced and they are now easily available commercially.

NDs with diameters of 4 nm were synthesized by Greiner et al. using detonation of different Trinitrotoluene (TNT) based explosive compositions [104]. It has been suggested that the nucleation process happens not in the shock wave itself, but in the rarefaction wave following the detonation shock wave [59].

ND synthesis was first discovered from shock compression of graphite via explosives and it was later found that it also occurs in graphite-free detonation [105]. In the dynamic compression experiment producing DNDs, the nucleation conditions persist only for a short time and efficient nucleation is required to achieve high yields. It was found, that efficient prevention of oxidation and graphitisation of NDs is very important for ND formation and growth [105].

1.2.1.7. Nanodiamonds from Laser-Driven Shocks

The formation of NDs from laser-driven shock compression has been observed experimentally in graphite and plastic samples at WDM conditions. A first study found the formation of NDs from pyrolytic and polycrystalline graphite as well as the formation of lonsdaleite - although only from compressed pyrolytic graphite - via *in situ* x-ray probing [5]. Both occurred on the nanosecond timescale at pressures of tens to hundreds of GPa. Another study, which investigated the behaviour of hydrocarbons at the interior conditions of Uranus and Neptune through laser shock compression of PS, found NDs to form only under double compression [6]. The nucleation conditions were 5000 K at 150 GPa. With the addition of oxygen to the plastic, the diamond nucleation was found to occur already in single shocks of PET, at 72 GPa at 3500 K [7]. Although dynamic compression experiments have confirmed the formation of NDs in shock-compressed plastics with different C-H-O stoichiometries via *in situ* probing, recovery attempts to ambient conditions have yet been unsuccessful [38, 37].

1.2.2. Catcher Impact

In the context of ND recovery it is important to understand the ND-catcher interaction at high velocities. The goal is to find a catcher material which satisfies a set of requirements: The NDs have to stay intact after the impact and the material should be biocompatible with many of their applications being of a medical nature. To have a real advantage over other techniques, the concentration and extractions of NDs from the catcher material should not require complex methods or expensive chemical procedures.

The catcher medium also serves as an indirect detection method for the formation of NDs. As will be explained later, *in situ* XRD to prove ND formation can be difficult in some experiments, including those where catchers are mounted behind the target. Previous experiments have not found experimental evidence for NDs in catcher materials [37]. It is important to understand if this was due to low concentrations of NDs in the catcher, ND melting before catcher impact or because the impact itself was responsible for ND destruction. A detailed understanding of ND impact dynamics can help identify the cause for the lack of NDs in catchers. This section will explore previous research of hypervelocity impacts into different media and how it might be possible to differentiate between ND and non-diamond impactors in a recovery experiment.

As mentioned before, the ejected NDs will reach tens of km s^{-1} and impact the catcher material as part of a released plasma cloud. This HVI scenario is not unlike what happens to satellites flying through interplanetary dust clouds in outer space and National Aeronautics and Space Administration (NASA) and other space agencies have had great interest in understanding such possible threats to their precious spacecrafts. Therefore, much research has investigated the phenomenon of HVI [53]. Nanoparticles comprise a large part of interplanetary dust and many experimental and theoretical studies have investigated the interaction between solids and such nanoparticles of different materials [106].

The Stardust mission by NASA collected dust particles from a comet (81P/Wild 2) into low density silicon aerogel collectors and aluminium foil [107]. Extensive experimental studies were performed to relate the penetration tracks within the aerogel to qualities such as impactor mass, density and impact velocity [108–111]. The aerogel was chosen as a low density medium to minimize damage on the collected particles and thus study the cosmic particles unmodified. The impact velocities in the Stardust mission reached 6.1 km s^{-1} and revealed a diverse impact spectrum in the catcher material [112]. The studies found that the crater and track diameter and shape in the aerogel can give direct information on the size distribution of the impactors as well as their aggregation properties [112]. It is important to note, that the craters in these studies are very defined and can be clearly separated from each other, which is difficult to achieve in a shock experiment, where hundreds of thousands of nanoparticles form in an area in the order of the laser spot size.

Schuster et al. have studied the impact of laser-driven shock ejecta from plastic samples (which is expected to contain NDs) into BN, SiO_2 , Al_2O_3 and ZrO_2 aerogels with different levels of zirconium doping and found spherical objects using microscopy techniques [37]. They also used a high-speed camera to understand the ejecta cloud dynamics and the impact phenomenon.

Price et al. have taken a special interest in the crater shape by means of hydrocode modelling of the impact from different mediums and velocities into aluminium [113]. They have focused on the crater morphometry as a means to determine the approximate impact velocity. The simulations were benchmarked against experiments and interpolation functions to predict the crater depth and diameter for solid impactors. Experimental cross sections of the craters were determined via Focused Ion Beam (FIB) cutting of impact sites (see Sec. A.8). Price et al. have found phenomenological functions to predict the crater depth d and diameter D_c from the impact velocity ν , impactor density ρ and impactor diameter D_p :

$$D_c = A\rho^\alpha D_p^{B\rho^\beta} \nu_p^{CD_p^\gamma}, \quad (1.2)$$

$$d = A_2\rho^\chi D_p^{B_2\rho^\psi} \nu^{C_2\rho^\omega}. \quad (1.3)$$

Under the assumption that the impactor velocity is well known, the ratio of crater radius to diameter can give information about the impactor density. In a shock experiment, this can provide valuable information about the presence of NDs in the impacting material.

A Bachelor thesis by Kuhlke, supervised in conjunction with this work, studied impact crater landscapes in aluminium plates with AFM, SEM, optical imaging, and TEM scans [114]. The aluminium plates were used as catcher material for the release of shock compression experiment of PET at different impact velocities. The author found that the cratering landscape varies depending on the impact velocity. High velocities resulted in well separated craters with a clearly defined profile. Lower velocities produces landscapes of overlapping craters with a less clearly defined cross section. Kuhlke found that the crater morphologies at high impact velocities could be consistent with ND impactors from the results in Price et al. [113].

1.2.3. Molecular Dynamics Simulations

MD are a well suited tool to study experimentally inaccessible processes. Nucleation is such a process and MD simulations sometimes in conjunction with DFT have been widely used to

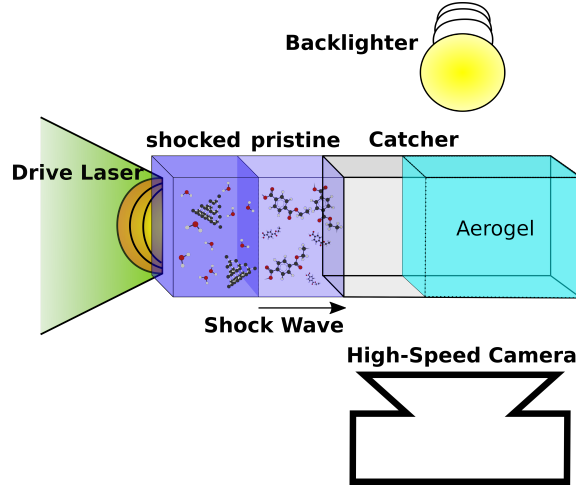


Figure 1.3.: Recovery setup for a laser-driven shock experiment with an aerogel catcher as it was used by Schuster et al. [37]. The drive laser hits the target from the left, forms the shock wave, which traverses the sample and is ejected into the catcher volume. Here, Schuster et al. imaged the dynamics with a high-speed camera with and without backlighter to image shadowgraphy and self-emitting particles respectively. The release cloud was found to oscillate back and forth in the confined volume breaking the aerogel catcher material into many pieces and not leaving defined tracks.

model the formation of crystals. As MD simulations are evolving in time they can go beyond what is possible in CNT (compare Ref. [65] for details).

In terms of ND recovery, MD was previously used to determine the expansion process as well as the impact into the catcher material [38, 37]. In Ref. [38], Schuster describes ND cubes, which have been equilibrated at WDM states in a fixed wall setup. After equilibration the spatial constraints were suddenly removed and the evolution of the system modelled. The ND particles showed an oscillation motion with increasing frequencies for higher initial pressures. The expansion simulations show largely intact diamonds for initial conditions of 50 GPa at 1000 K and 200 GPa at 1000 K, while most of the diamond disintegrates at 50 GPa at 4000 K. Schuster highlights the importance of temperature for the diamond stability during release. However, the simulations were conducted without explicitly modelling the expansion process which might contribute to cooling.

The impact simulations described in Ref. [38] model a ND cube impacting into an aluminium block at velocities of 4, 10, and 20 km s⁻¹. The analysis focused on catcher stability and crater shapes. They showed that at an impact velocity of 20 km s⁻¹ the diamond cube and parts of the catcher evaporated. The crater depth increased substantially with increasing impact velocity as did the crater width.

The quality of MD simulations strongly depend on the choice of interaction potential. An in-depth comparison of different carbon interaction potentials was studied by de Tomas et al. [115]. They studied the accuracy of six different interaction potentials used to describe the graphitisation of amorphous carbon by annealing at densities ranging from 1.5 to 3.0 g cm⁻³. The authors found that the Environment Dependent Interaction Potential (EDIP) performs best at reproducing the *sp*³ fraction. The potential was also able to describe the inter-layer stacking which the authors attribute to the inclusion of long-ranges π -repulsion in EDIP. Both quantities are highly relevant when considering ND release as the *sp*³ bonding nature might change and form graphitic structures like carbon onions, which were previously described as results of annealing ND [116]. Therefore, the EDIP potential was chosen for the MD simulations in this work [117, 118].

Previous work on ND formation from molten carbon was performed by Ileri et al. [119]. Therein they studied the free expansion of shocked carbon via DFT, and assessed the ratio of ND to graphite formation in an adiabatic expansion process. The authors found that the amount of carbon atoms bound in sp^3 orbitals increases with the pressure of the shock state. The MD simulations performed in this work draw upon their methodology.

1.2.4. Small Angle X-ray Scattering and Shock Compression

SAXS is a powerful technique that can resolve electron density contrasts in the order exceeding a few nanometres. In the context of dynamic shock compression, the *in situ* diagnostics are very important and SAXS has contributed to understanding the larger structures forming in this regime. It is especially sensitive to the long-range order and is commonly used to determine the sizes and structures of proteins. Some efforts have been made in using SAXS for the purpose of diagnosing WDM states.

In Ref. [120] Rödel discusses SAXS as an *in situ* diagnostic for WDM states in detail. The reference establishes the basic assumptions and theories behind SAXS as well as its potential to observe ND size and volume fraction during the shock. It also highlights the potential of SAXS to resolve demixing experimentally via the electron contrast. It argues convincingly that the main source for electron contrast leading to SAXS signal can be attributed to the formation of NDs. Rödel used SAXS to estimate ND diameter in shock-compressed PS to lie below $r < 5$ nm [120].

He et al. have continued this work to study the size distributions of NDs formed in shock-compressed PET, which, in contrast to PS also contains oxygen [7]. An analytical method for fitting the SAXS signal was used as well as Monte Carlo (MC) sampling of the distribution using McSAS [121]. The authors have determined the ND diameter to $\bar{r} = 1 - 3$ nm. The NDs appear to be growing with increasing probing delay. The longer the shock conditions persist, the larger the NDs become.

Another way to interpret the results from SAXS in WDM states makes use of Neural Network (NN). In Ref. [122] He et al. present a method to train a NN on synthetic data to reconstruct a nanoparticle size distribution based on the signal. The network was trained on three superimposed Schulz-Zimm distributions by calculating the theoretical scattering signal. The SAXS signal was used as the input signal and the size distribution was the target variable. The article showed a good agreement of the NN predictions with MC sampling, which takes significantly longer to perform inference. The fast inference time and good abstraction of NN predictions can make it a valuable tool for studying SAXS from nanoparticles. The NN method was also proven to be successful in significantly more difficult non-radial-symmetric scatterers [123].

Lindqvist has studied the size distributions of NDs forming in shock-compressed PET and Cellulose Acetate (CA) via double shocks [124]. Therein, the author uses an analytical SAXS model, as well as McSAS, the NN designed during this work (compare Section 3.2.2) and XRD results [125]. The overall agreement of the method was good and they argued, that the NDs show clear signs of growth over the course of the shock progression. They show distributions starting at $r \approx 1$ nm and reaching distributions with maxima around $r \approx 2.2$ nm. Slightly higher growth rates were found for CA, which was attributed to the higher oxygen content compared to PET.

1.3. Thesis Outline

This thesis is structured into three main chapters. Ch. 2 provides an overview of the theoretical background, necessary to understand the physical regime, experiments, and simulations that were studied and conducted in this work. Thereafter, Ch. 3 contains the detailed descriptions of the simulations and experiments, which were performed in this work. Ch. 3 presents all relevant information to reproduce the experiments, as well as the simulation procedures and methods used to evaluate the data. Subsequently, Ch. 4 presents the results of the simulations and experiments along their discussion and interpretation. Finally, a conclusion of the results of this work along with an outlook for future research is provided in Ch. 5.

In the theory part (Ch. 2), the WDM regime is briefly defined and the main simulation frameworks to access physical quantities therein are presented. Next, the concept of shock experiments along with the theoretical descriptions are outlined, followed by an introduction of the relevant diagnostics used to determine pressure and temperature conditions in a shock compression experiment. Subsequently, the foundations of x-ray scattering techniques are presented. This includes XRD and SAXS. Sec. 2.3 discusses the theoretical descriptions commonly used to describe HVI. In Sec. 2.4 the different microscopy techniques, which were used to find evidence of ND in the catcher materials are briefly outlined.

The experiments and methods part of the thesis (Ch. 3) begins with presenting the simulation setup of the MD simulations conducted to model ND release and cooling processes. The description of simulations of NDs impacting catcher materials at high velocities follows. The chapter continues, by providing a detailed description of the shock experiments covering *in situ* x-ray diagnostics, performed to determine ND formation in PET at WDM conditions. This includes the experimental setups, materials and laser parameters, as well as the models used to describe the results. Therein, the description of the NN used for determining ND size distributions from the SAXS signal is provided. After that follows a section, which contains information about the Raman, TEM, high-speed camera, cratering, and high-repetition-rate experiments. The focus of these experiments was to achieve the intact recovery of NDs in different catcher materials.

The results of the experiments and simulations introduced in Ch. 3 are presented and discussed in Ch. 4. They follow the same order as they are introduced in the Experiments and Methods chapter.

Throughout the thesis, references to the Appendix are made, where lengthy derivations or detailed method descriptions are necessary for completeness or reproducibility but would otherwise interrupt the flow of the main text.

2. Theoretical Background

As mentioned, recovering NDs from laser-driven shocks is a challenging task, due to the inherently elusive field of WDM, but also due to the need for NDs to survive these short-lived extreme states. Furthermore, NDs need to transition to ambient conditions within nanoseconds, which poses an additional difficulty. The following chapter provides a brief overview over the theories and experiments regarding the relevant physical regimes. This spans the phases of nucleation, release and impact (see Sec. 1.1) which are important for ND recovery from laser-driven shock states.

First, the WDM regime is introduced, along with relevant simulation techniques to access physical properties therein. A brief introduction into the framework of shock physics, as well as the relevant diagnostics used in this work is presented. Second, the basics of several x-ray scattering techniques are explained, which are used in this work to perform *in situ* measurements. Third, the concepts relevant for HVI are outlined as they are relevant to understand the ND catcher impact. At last, the foundation of various microscopy techniques are presented, all of which were used in the course of this work to find evidence for NDs present in the catcher material.

2.1. Warm Dense Matter Regime

The ND formation occurs in the WDM regime. This is the physical regime which lies in between condensed matter, gases and plasma [126]. It is not clearly defined but rather identified by the region where electromagnetic interactions and quantum effects are in the order of the thermal energy of the system close to the Fermi energy. Typical temperatures and densities lie between $1\text{eV} \lesssim T < 100\text{eV}$ and $0.01\text{g cm}^{-3} < \rho < 100\text{g cm}^{-3}$. Many systems across the universe exist in this thermodynamic regime. In our solar system the planetary interiors of many planets cross points at the low end of the WDM regime [127]. It was in this context, that researchers first predicted the formation of NDs to solve a long standing problem with the energy balance of Uranus and Neptune [34]. The difficulties regarding the description and understanding of the WDM regime are twofold: First there is the challenge in finding a theoretical model to describe the relevant physics; and secondly there is the challenge to study such an extreme state of matter experimentally.

2.1.1. Molecular Dynamics Simulations

From a theoretical point of view, the complications of describing the WDM arise from the fact that neither ideal plasma nor ideal condensed matter theory are valid in this regime. The usual simplifications, like assuming very low temperatures in condensed matter and assuming high ionization degrees and negligible strength of quantum interactions in ideal plasmas, are no longer valid. To describe the physics of materials at WDM conditions, quantum effects of the electrons need to be explicitly included and combined with Coulomb interactions.

One successful approach in this regard is the combination of DFT with classical MD to DFT-MD methods. In DFT - an *ab initio* method - the complete exchange and correlation interactions of the electronic part of the Hamiltonian are put into a so-called exchange and correlation functional of the electron density. This reduces the computational dimension to a manageable amount by representing the high-dimensional electronic system with a three-

dimensional electron density. This way, the electronic ground state solution of a system can be obtained numerically.

As the most interesting quantities require an understanding of the dynamics of such a system, DFT is combined with classical MD simulations.

MD is a method developed in the 1950s which uses iterative methods to solve Newton’s equations of motion for a molecular system in the Born-Oppenheimer approximation [128]. To obtain a physically meaningful result, an exact description of the interactions of species (here assuming atoms) is required. MD simulations are only able to simulate phenomena that the interatomic potentials, which are used, can describe. This is of particular importance if interatomic bonds are formed or broken.

Here, the nature of the interaction - e.g. whether it is repulsive or attractive - usually depends on the surroundings of the atoms themselves. In the classical chemical picture, a carbon atom forms exactly four covalent bonds. In MD, this is represented by the interatomic potential. A bond would be represented as a local minimum in the Potential Energy Landscape (PEL) for a configuration representing that bond. Importantly, MD generally treats atoms as point masses without explicitly including any electronic or charge exchange interactions. However, these interactions can be included implicitly in the way the interatomic potentials are constructed or explicitly added.

The choice of the interatomic potential is extremely important to obtain accurate predictions from MD simulations. Simplified, the quality of an MD simulation is largely dependent on the accurate description of the PEL of the molecular configuration.

The most simple forms of interatomic potentials are functions that only depend on the distance between two atoms to determine the energy. One of the simplest potentials is the widely used Lennard-Jones (LJ) potential. It includes a repulsive part for very small distances, and an attractive long range interaction [129]. A common functional, computationally efficient formulation is:

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.1)$$

The minimum of the LJ potential can be identified as the bond distance and is given as $r_{\text{min}} = 2^{\frac{1}{6}}\sigma$. Such a potential is strictly influenced by the interatomic distance. The surrounding atoms do not influence the PEL. Therefore, it should only be used if complex bond structures are either negligible, or of little interest/importance to the results. For other cases, more complex potentials need to be employed.

There are different approaches to obtain functional descriptions for the PEL of atoms. One way is to first find a functional shape by heuristically considering bond formations in the classical chemical picture and choose parameters which define the strength and shape of the interaction. Then, the values of the parameters can be fit by modelling physical phenomena to obtain quantities for which experimental values are available. Within the previously introduced picture, one obvious example could be bond lengths of the system [130].

More advanced methods include the computation of energetic values with computationally expensive, high-accuracy methods like Coupled Cluster (CC), DFT or Quantum Monte Carlo (QMC) methods, and fitting a computationally cheap potential to these high accuracy data

points. Recently this has been extended to methods using ML techniques, such as NNs [131–134].

In DFT-MD the classical interatomic potential is replaced by finding the ground state solution to the electronic system with DFT. The classical interatomic forces are then derived from the DFT solution and a MD time integration step is performed. Here, DFT provides reliable solutions of the electronic system and includes quantum effects, while MD provides the time evolution of the ionic system. However, DFT methods are also limited by computational constraints. Systems beyond a few thousand atoms are not easily accessible.

Many interatomic potentials are limited to certain regimes or have strengths and weaknesses in describing certain properties. Most are not valid over arbitrary conditions but are fit to certain regions in the phase diagram, or to match some quantities accurately while others suffer. It is extremely important to choose a potential which is well suited for the problem at hand. In this work, MD simulations are mainly employed to assess ND stability during release and impact. Thus, an interatomic potential should be chosen which is benchmarked to describe carbon bonds accurately across a wide range of pressures and temperatures.

An MD simulation is essentially an integration scheme for Newton’s equations of motion using, e.g. the velocity-Verlet integration method [135, 136]. The obtained estimates for the positions and velocity of a particle i after a timestep Δt are:

$$x^i(t_0 + \Delta t) = x_0^i + \dot{x}_0^i \Delta t + \frac{F_0^i}{2m^i} \Delta t^2 \quad (2.2)$$

$$\dot{x}^i(t_0 + \Delta t) = \dot{x}_0^i + \frac{\Delta t}{2m^i} (F_0^i + F^i(t_0 + \Delta t)). \quad (2.3)$$

The error made in the positions and velocity using the Verlet algorithm is $O(\Delta t^2)$. Therefore, the timestep should be as small as possible. However, computational limitations require finite timesteps to obtain a solution within reasonable computing time. A common trade-off is to choose a timestep as large as possible, while still maintaining energy conservation [137]. In practice, this should be tested under the corresponding simulated conditions.

To define a system in certain thermodynamic conditions it can be coupled to a thermostat or barostat to maintain a pre-set temperature or pressure during the simulation. The Nosé-Hoover thermostat is a commonly used method to simulate the Canonical Ensemble - Fixed Particle Number, Volume, and Temperature (NVT) [138, 139]. Here, an external heat reservoir is introduced which acts as a friction force on every single particle in the simulation, scaled by a coupling constant. This introduces an additional degree of freedom. A barostat, keeping the pressure constant can also be implemented to keep the pressure constant. Any MD simulation needs to start in a physically meaningful state. This means, that in addition to a correct description of the forces, a so-called equilibration phase is required. In the case of using a thermostat, this guarantees that the particles in the simulation domain follow Maxwellian velocity distribution of the set temperature. The length of the equilibration phase can vary. It should be verified that after the equilibration the systems thermodynamic properties (pressure, temperature,...) oscillate around the required values.

There are different ways of implementing MD simulation boxes. It is impossible to simulate an infinite number of particles, therefore, the simulation box is usually restricted to a couple of thousand atoms in a finite simulation cell. Special care needs to be taken to choose the correct interaction with the simulation cell walls. To simulate a domain of virtually infinite size, it is

common to use so-called periodic boundary conditions. With periodic boundary conditions, a particle at the edge of the simulation cell will see the particles on the other side of the simulation cell as a periodic image. The forces will therefore translate through the simulation cell walls and the system mimics an infinite domain size. To simulate finite domains, the walls of the simulation cell can be set to reflect incoming atoms.

It is important to ensure the convergence of the MD simulation. Essentially, this means that the system is large enough to actually represent the required domain (e.g. infinite box size). The simplest way to determine a minimal domain size, which is able to represent the required domain, is by gradually increasing the simulation cell volume and comparing the evolution of certain quantities. If these quantities stop changing with increasing simulation cell volume, the system can be assumed to have converged.

After timestep length, equilibration time, and convergence have been confirmed, and the interatomic potential of choice has been implemented, the actual MD simulation can be performed.

2.1.2. Hydrodynamic Simulations

When studying dynamic compression and ND formation, the pressure and temperature conditions are of particular importance and even DFT-MD methods are prohibitively computational expensive. Temperature is particularly challenging to measure in short-lived states. Therefore, another theoretical approach to estimate the shock conditions is required. Such a tool are Hydrodynamics Simulations (HDSs). Contrary to DFT, HDSs are not an *ab initio* method, but require intricate knowledge of the simulated materials, especially the EOS and opacity. HDS relies on solving the Navier-Stokes equations of fluid dynamics with the inclusion of effects of radiative energy transport and electromagnetic interactions.

The strength of HDS are that they explicitly model the laser pulse used in dynamic compression, that they are able to resolve the dynamics of the sample during the shock, and that they are very fast (usually only taking a few seconds on consumer hardware). Given an EOS of the material, HDS can help estimate the conditions in the sample even during beam time of an experiment. This way, it is possible to obtain an idea of the thermodynamic state of the samples without diagnostics. However, the results of HDS are heavily dependent on the EOS used. Especially with more exotic materials, a suitable EOS might not be readily available. Validating such simulations is difficult because benchmarking in the WDM regime is a challenging task.

Fig. 2.1 illustrates the output of an HDS for a 75 μm thick PET sample calculated with HELIOS [140]. The upper row includes the ablation plasma region, with its extremely high temperatures. This off-streaming plasma creates the shock wave propagating into the sample. The shock front moving into the pristine sample is indicated as a red arrow, and so are the two release waves. Once the drive laser stops, the compressed sample will expand into vacuum. The same happens if the shock wave reaches the rear side of the sample. Behind the two release waves, pressure and density are rapidly reduced. Any penetrating probing method, will always probe a horizontal slice through the entire target. This can mean probing several conditions within the sample simultaneously. Especially in more complex shocks this yields results, which can be difficult to interpret.

It is important to benchmark the output of HDSs to experimentally accessible quantities and, if possible, augment the results with measurements. Although most quantities are hard to determine experimentally in dynamic compression experiments, there are exceptions. One

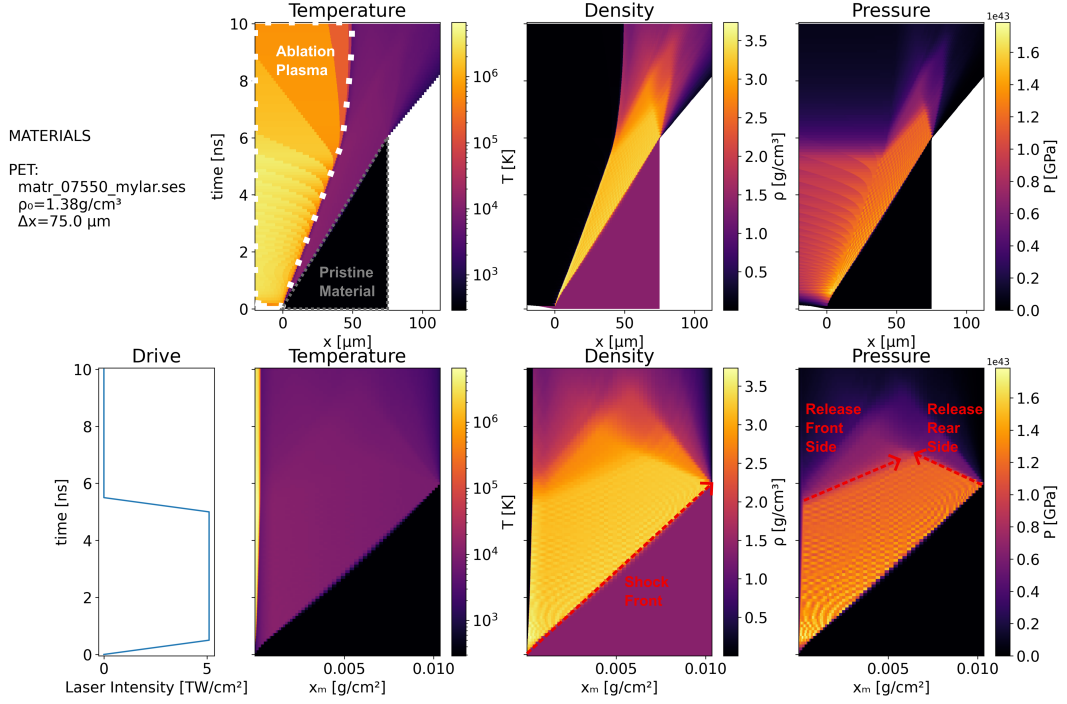


Figure 2.1.: HDS of a PET target of 75 μm thickness hit with a laser pulse with a nominal duration of 5 ns. The upper row is plot in Eulerian coordinates while the lower row shows the area of the shocked target, omitting the ablation plasma region and is plotted in mass coordinates (Lagrangian). Simulation was done using HELIOS [140].

very important quantity in HDSs is the transit time, i.e. the time that passes between the laser hitting the front side of the target and the breaking out of the shock wave at the rear surface. This time is related to the shock speed, which is a very important quantity in dynamic compression. This transit time can be measured by optically imaging the rear surface of the target. By comparing the experimentally observed transit times with the output of the HDSs one can adjust the laser parameters in the simulation to match the two times.

2.1.3. Shock Physics in Dynamic Compression

In dynamic compression a shock refers to a rapid change in material conditions. Here, the shock takes the form of a shock wave which can be created, e.g. from explosions or lasers, and transports large amounts of energy through the sample while heating it and increasing the entropy [141]. The speed of the shock wave in the sample must exceed the speed of sound of the un-shocked material so disturbances in the medium can not propagate ahead of the shock front. This way a jump in material conditions occurs at the shock front.

Fig. 2.2 shows on the left the schematics of a shock wave propagating through the sample, assuming there is a "piston" pushing the material with the supersonic velocity u_p . The pressure and temperature behind the shock front - in the shocked region - experience a sudden jump associated with a shock. Importantly, the speed of the shock wave is *subsonic* in respect to the shocked material. The left image shows the material at rest (top) and after the start of the shock (bottom). On the right, the jump of pressure and temperature are shown. u_0 and u_1 indicate the velocity of the un-shocked and shocked material.

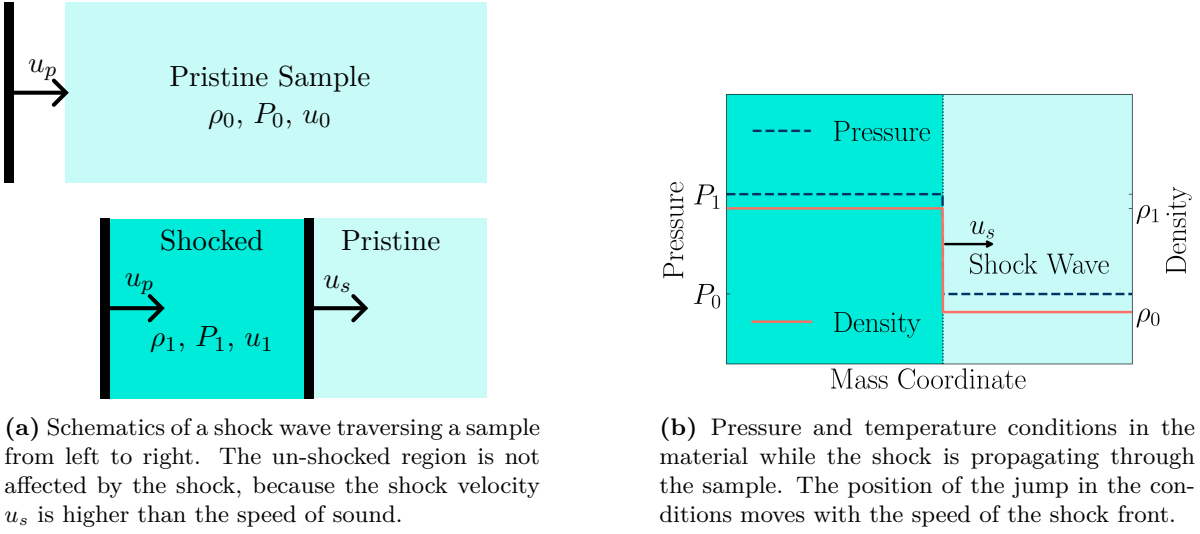


Figure 2.2.: Schematics and $P - T$ conditions of a shocked sample. Un-shocked conditions have a subscript 0 while shocked conditions have a subscript of 1.

The mass, energy and momentum have to be conserved across the shock front. By applying the conservation laws, a set of equations can be derived that relate the quantities before and after the shock to each other, the so called Rankine-Hugoniot equations [142–144]:

$$\rho_1 v_1 = \rho_0 v_0 \quad (2.4)$$

$$P_1 + \rho_1 v_1^2 = P_0 + \rho_0 v_0^2 \quad (2.5)$$

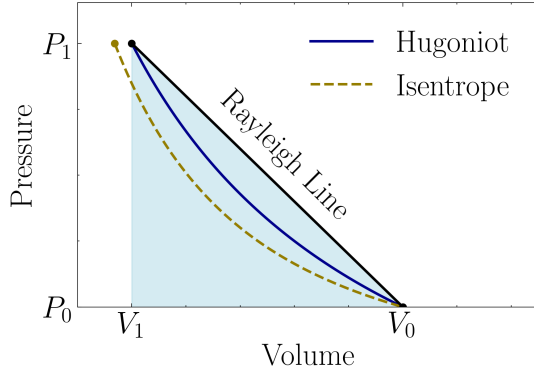
$$E_1 + \frac{P_1}{\rho_1} + \frac{v_1^2}{2} = E_0 + \frac{P_0}{\rho_0} + \frac{v_0^2}{2}, \quad (2.6)$$

with the densities ρ_0, ρ_1 , velocities v_0, v_1 , pressures P_0, P_1 , and the specific energies E_0, E_1 . The velocities are in the frame of reference moving along with the interface. Transformation to the laboratory frame of reference can be obtained by using the velocity of the shock front u_s , of the particles/piston u_p after the shock is done via [145]:

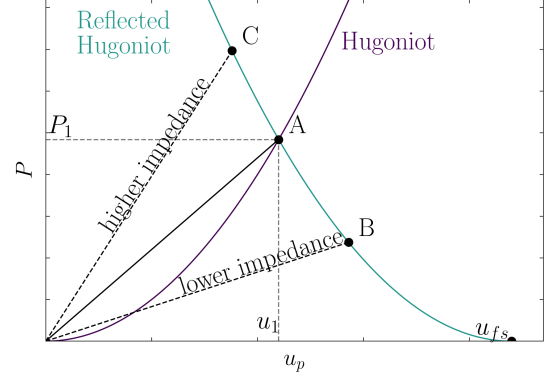
$$v_0 = -u_s, \quad v_1 = -(u_s - u_p). \quad (2.7)$$

Usually in shock experiments the initial conditions are well known. Therefore three equations are used to describe the five unknown quantities ρ_1, P_1, u_s, u_p and E_1 . To determine all values, two quantities need to be measured. If the EOS is known, only a single quantity needs to be measured experimentally to obtain all quantities of a shocked material. In any case, by combining these equations, a so-called shock Hugoniot can be defined. This shock Hugoniot is a material specific curve which defines all possible jumps in density, pressure and energy that a single shock wave can cause. Importantly, the entropy is not a conserved quantity, but increases in a shock.

Fig. 2.3 shows the shape of a Hugoniot curve next to an isentropic compression curve. The intersection of the Rayleigh line (black line) with the Hugoniot curve defines the conditions



(a) Hugoniot curve with the isentropic compression curve and the Rayleigh line. The coloured area visualises the increase in internal energy through the shock.



(b) Release wave in case of higher (C) and lower (B) impedance of second material. Release into vacuum will result in a doubling of the free surface velocity. Reproduced from [145].

Figure 2.3.: Hugoniot curve with compression isentrope and visualisation of the velocity doubling rule at shock breakout.

which are reached behind the shock front. It is convenient to use the specific volumes $\nu_i = V_i/m_i = \rho_i^{-1}$ to express the pressures increase across the shock front as:

$$P_1 - P_0 = u_s^2 \cdot \left(\frac{1}{\nu_0} - \frac{\nu_1}{\nu_0^2} \right). \quad (2.8)$$

If the initial pressure and density are known, the pressure can be directly inferred from the shock speed u_s . It was experimentally found that many materials show a linear relationship between shock-speed u_s and particle velocity u_p in the form [146]:

$$u_s = c_0 + \alpha u_p, \quad (2.9)$$

with the ambient speed of sound c_0 and the coefficient α . Neglecting the initial pressure (which is justified in strong shocks) we can combine Eq. (2.8) and (2.9) to obtain an equation for the shock pressure which is hyperbolic in u_p .

In case a shock wave is exiting a material and entering another, either solid or vacuum, the nature of the transmitted state is defined by the relation of the two shock impedances of the material $Z = \rho_i u_s$. In analogy to electrical impedance, this is the opposition a material expresses towards compression. If the impedance of the material the shock wave is transmitted into is higher than the original materials impedance, a second shock wave is reflected back into the original material (in opposite direction). If the original materials impedance is higher, a rarefaction wave is reflected into the original material. Intuitively speaking, transmitting a shock wave into a sample with *lower* impedance will result in an *increase* in particle velocity. The pressure and particle velocities of the original material in both cases can be constructed in the way depicted in Fig. 2.3b. Here, the impedance $Z = \rho_0 u_s$ describes the slope of the line on which the shock pressure can be found:

$$P = Zu_p = \rho_0 u_s u_p \quad (2.10)$$

By mirroring of the Hugoniot curve at the shocked conditions and intersection of that curve with the impedance line of the secondary material, an approximation of the release isentrope of the material can be found. Using this approximation a release into vacuum (no impedance) will result in a doubling of the velocity [145]:

$$u_{fs} = 2 \cdot u_p. \quad (2.11)$$

In this way, the particle velocity can be inferred by measuring the free surface velocity, an experimentally routinely accessible quantity.

2.1.4. Shock Wave Creation

Historically, shock wave generation used to be done by using explosives or light-gas guns, in which a piston is propelled into a light-gas (He, CO₂, etc.) which is connected to the projectile chamber via a pressure valve. The projectile is usually a flyer plate which then impacts the sample, creating the shock wave as described above. Projectile speeds can reach up to 10 km s⁻¹ using elaborate designs [147]. This method leads to very planar, homogeneous and well characterised shock conditions in the sample but is limited in compression.

Higher flyer plate velocities, and thus compressions, can be reached using magnetically driven impactors. The Sandia Z-machine is such a device, which can accelerate flyer plates to over 30 km s⁻¹ through the use of very strong currents (20 MA) in the presence of strong magnetic fields (1000 T) [148]. This results in peak pressures of up to 2.7 TPa [149].

Another way to drive shocks into samples are lasers. Since the late 1970s, intense laser pulses in the order of $> 10^{13} \text{ W cm}^{-2}$ have been used to dynamically compress targets [29]. In laser-driven compression, the front side of the target is illuminated with a high intensity laser pulse. The high field intensities of the laser pulse can partially ionize the sample and produce a thin plasma layer. The plasma is expanding in laser direction transferring momentum away from the target. The plasma density increases towards the sample surface. Incoming laser light is absorbed by the plasma as it passes through the - more and more dense - plasma until it reaches a region of critical plasma density. The photons are absorbed along the path through inverse Bremsstrahlung until reflection at the critical surface. Thus, the energy is transferred to the plasma and it continues heating and expanding. To conserve momentum, material has to move into the sample creating the shock wave travelling in laser direction. Fig. 2.4a illustrates this process and the electron density during the laser absorption.

Importantly, not the entire energy of the laser pulse is transformed to the shock wave. Depending on the material on the surface, the absorption process varies in efficiency. The choice of ablation material is therefore very important. As this so-called ablator is generally not the material of interest, this leads to the assembly of layered targets. The ablator is glued onto other components (pusher, target material, heat-shield, windows, etc.) and the entire sandwich target is shocked. This ensures efficient laser absorption and high shock pressures. The ablator material is usually some form of plastic, which is an efficient thrust generator and avoids signal contaminations by high-Z materials [150, 151].

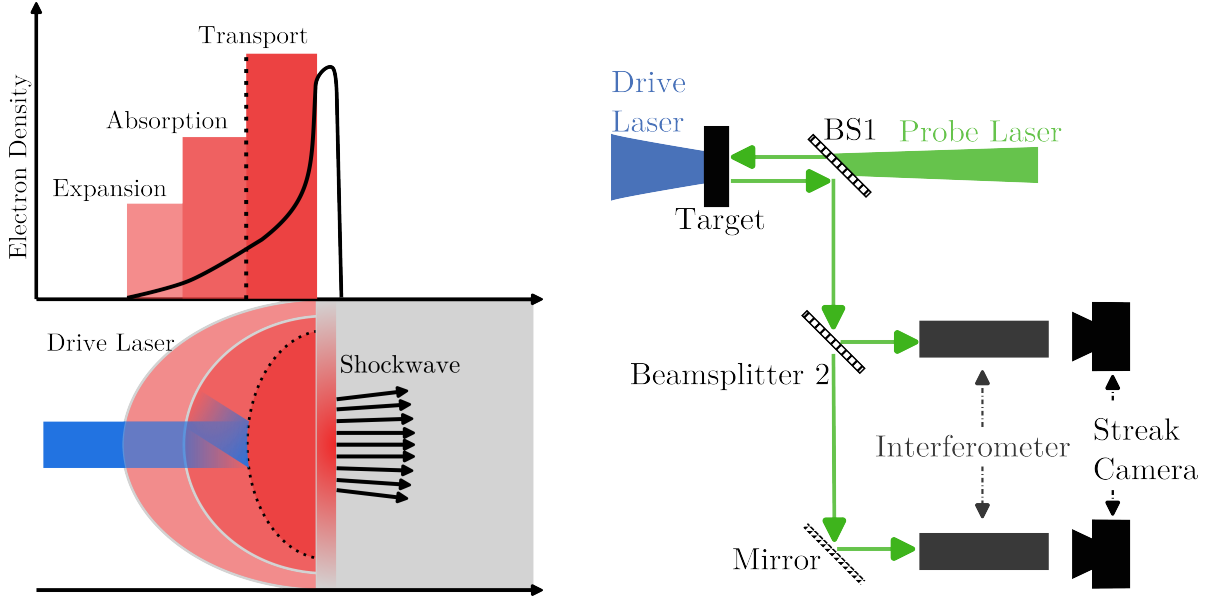


Figure 2.4.: Domains in laser absorption during shock wave creation and sketch of VISAR diagnostic setup.

2.1.5. Shock State Diagnostics in Dynamic Compression

As explained above, in the Hugoniot framework, quantities of the shocked state - like pressure, energy, and density - can be calculated when both velocities (particle and shock) are known, or when one velocity is known along with an EOS of the material. Therefore, velocity measurements are very important in characterising the shock state. One experimental tool to determine the speed of a moving (reflective) surface is the VISAR. Here, the velocity of the surface is measured by using an interferometer to determine the Doppler shift in respect to a probe laser by the moving surface. A one-dimensional interference pattern is created by the reflection of the rear surface of the sample. One arm of the interferometer is passed through an optical delay before recombination to adjust the VPF and thereby the VISAR's sensitivity. As the surface starts to move, the fringes in the pattern shift according to the surface velocity [152]:

$$\text{VPF} = \frac{c\lambda}{4(n - \frac{1}{n})(1 + \delta)}. \quad (2.12)$$

The VPF depends on the thickness h , refractive index of the etalon n , and the probing laser wavelength λ . c is the speed of light. The factor δ is a dispersion correction for the etalon [153]. Fig. 2.4b shows the setup of a VISAR. By using a streak camera the time evolution of the one-dimensional interference pattern can be recorded. As the velocity by measuring the fringe shift is only defined between integer multiples of fringe shifts, a second system is employed with different VPF to uniquely determine velocities.

If a materials response to shock compression is well known, e.g. the Hugoniot curve is well characterised in terms of pressures and temperatures, a single measurement can be sufficient to determine the point on the Hugoniot curve, and thus the shock conditions.

While the VISAR method is extremely powerful, it requires reflective surfaces and transparent rear sides in sandwiched targets. Metallic coatings are a convenient way to make materials reflective without strongly changing the shock transmission dynamics. The same streak camera setup can be coupled with a self emission measurement, to measure the temperature under a gray body assumption, called Streaked Optical Pyrometry (SOP) [154].

2.2. X-Ray Scattering Techniques

A powerful method to probe structures of WDM samples is x-ray scattering. Here, the sample is probed with a high intensity (several mJ) short (tens of fs) x-ray pulse, and the scattering at small and wide angles is recorded on areal detectors. Depending on the angular range of the detector, the structure of the bulk sample can be probed on different orders of magnitude ($\text{\AA}$ to hundreds of nm). It is very important to use short pulses to resolve the fast evolving processes. To accumulate sufficient signal on the detector highly brilliant sources like XFELs are usually required.

In general, the azimuthally averaged detector intensity of x-ray beams, which coherently scattered on N electrons (e.g. in atoms) can be described by the double sum over each electron-electron scattering interaction¹ [155, 156]:

$$I(q) = \sum_m^N \sum_n^N f_m(q) f_n(q) \frac{\sin(qr_{mn})}{qr_{mn}}, \quad (2.13)$$

with the atomic form factors $f_i(q)$ and the momentum transfer $q = 4\pi \sin(\theta)/\lambda$, dependent on the scattering angle θ and probing wavelength λ . An illustration of the involved vectors can be found in Fig. A.6. The so-called Debye scattering equation can be simplified for several special cases, such as monoatomic liquids (same form factors), or - especially - when probing crystals (discrete r_{mn}). The following sections introduce two cases heavily used in this work: the first is XRD, which makes use of short-range crystal structure and symmetry, while the second, SAXS, is dominated by long-range order.

2.2.1. X-Ray Diffraction

XRD refers to the elastic scattering of x-rays by the atoms in a crystalline sample. As electromagnetic waves, the incident x-rays interact with the electron clouds of atoms in the crystal lattice, producing scattered waves that interfere constructively or destructively depending on the x-ray wavelength and the spacing between lattice planes. For a sufficiently large number of randomly oriented microcrystals, this interference results in radially symmetric diffraction rings. Assuming that the primary scattering occurs exclusively at atomic positions within the crystal, the scattering angles θ must satisfy the Bragg condition:

¹For a detailed description compare Sec. A.4.1

$$n\lambda = 2d \sin(\theta). \quad (2.14)$$

This relation has been used in powder diffraction for crystal structure determination since the early 20th century [157, 158]. In the beginning, it was limited due to the broad source spectra and low instrument resolution [159]. With the advancement of available instruments and the advent of computers, Rietveld introduced a method to match the entire powder diffraction pattern by a refinement procedure [160]. Here, many parameters that can influence the diffraction peak shapes, like crystallite size, sample temperature or microstrain are used in combination with a source function of the instrument (the Instrument Resolution Function (IRF)) to produce a forward model of the expected diffraction pattern. To determine the IRF a so-called calibrant is used. This is a standard material, for which the diffraction pattern is well known. The Rietveld model is then computationally refined to minimize the discrepancies between data and prediction and find the best matching set of parameters. An outline of this process is given in Sec. A.4.3.

After the IRF has been fit to match the calibrant, the different effects of the sample can be convoluted with the IRF. The most influential contributions in the context of NDs are size broadening and intensity reduction due to temperature, which will shortly be described below. To obtain a good fit, all contents of the sample need to be described by the model. Following the Bragg Eq. 2.14, the peak position can inform the crystal lattice plane spacings using the Miller indices, which for cubic systems (like diamond), simplifies to:

$$d_{hkl} = \frac{a}{h^2 + k^2 + l^2}, \quad (2.15)$$

with the lattice constant a . By knowing the peak positions, the lattice constant can be inferred. Stress and strain can also be inferred from the peak positions as they influence the crystal structure and lattice spacings. In the context of this work on NDs, only stress in the form of isotropic compression will be considered. Due to the averaging using powder diffraction, non-isotropic effects would be obscured in the diffraction pattern. Compression influences the peak positions and can also inform the density of the material trivially:

$$\rho = \frac{\sum_i n_{UC}^i \cdot m_{UC}^i}{V_{UC}}, \quad (2.16)$$

with the number of atoms i in the unit cell n_{UC}^i , their molar mass m_{UC}^i and the volume of the unit cell $V_{UC} = a^3$ for cubic systems. The compression influences the lattice spacing and therefore the peak positions. Asymmetries in the peak shapes could be a result of inhomogeneous sample conditions as some crystallites might experience different compressions than others. By using an EOS the density can be related to pressure and temperature. However, the crystallite material might not be at thermodynamic equilibrium so other measurements are required.

When performing diffraction experiments on dynamically compressed targets with ND nucleation, the sample consists of crystalline diffractors and a surrounding material (liquid). The complete diffraction signal will be a superposition of the liquid and crystalline diffraction.

Therefore, in addition to the model for the crystal, a liquid diffraction model needs to be included to match the XRD pattern. Details can be found in Sec. 3.2.

The broadening of the diffraction peak is the result of finite crystallite size. The lack of intensity at diffraction angles that do not satisfy Eq. 2.14, is essentially assured by destructive interference. For an angle $\theta' = \theta + \epsilon$ - common in an imperfect source - the reflected light would travel an additional distance Δ_d when reflected on the second plane and not be cancelled out by destructive interference. However, for each consecutive lattice plane into the target, another $\Delta_{\Delta d}$ will be accumulated. Given an infinite number of crystal planes, eventually one of them will destructively interfere with the reflected beam. Fig. A.7 shows a visualisation of this.

However, this is not the case for a finite domain size. In case that the number of lattice planes of a reflection hkl are finite, the peak will also have a finite Full Width Half Maximum (FWHM), which can be related to crystallite size via the Scherrer equation [161]:

$$L_{hkl} = \frac{K\lambda}{\text{FWHM}_{hkl} \cos(\theta)}, \quad (2.17)$$

with the shape factor K of the particles ($K_0 = 89$ for spherical particles), the probing wavelength λ , scattering angle θ and the FWHM of the angular diffraction in radians.

The sample temperature is the second factor that can strongly influence the diffraction peak intensity. Thermal vibrations of the atoms at finite temperatures will result in a reduction in peak intensities. The peak reduction due to the motion of the atoms can be described with the so called Debye-Waller factor [162–164]:

$$2W = \frac{3\hbar^2|q|^2}{Mk_B\Theta} \left[\frac{T}{\Theta} \phi\left(\frac{\Theta}{T}\right) + \frac{1}{4} \right] \quad (2.18)$$

$$\phi(y) = \frac{T}{\Theta} \int_0^{\frac{\Theta}{T}} \frac{x}{\exp(x) - 1} dx, \quad (2.19)$$

with the Debye temperature Θ , molar mass M , for each momentum transfer q . In the limit when $T \gg \Theta$, $\frac{\Theta}{T} \mapsto 0$ and $\phi(y)$ can be approximated by the Taylor series of $\phi(y)$ around $y_0 = 0$ (see Sec. A.4.5). This yields for the high temperature limit:

$$2W = \frac{3\hbar^2|q|^2}{Mk_B\Theta} \left[\frac{T}{\Theta} \right]. \quad (2.20)$$

A diffraction peak under the angle θ by a sample of temperature T would be reduced in intensity to:

$$I(\theta) = I_0 e^{-2W}. \quad (2.21)$$

This way, the peak intensities can be related to sample temperatures. Notably, the Debye temperature is a function of the Debye frequency, which itself is dependent on the speed of sound in the material. As this can change with varying temperature and pressure, so can the Debye temperature. The uncertainties in temperature estimation from peak reduction are therefore substantial, if the exact Debye temperature is unknown.

To summarize, XRD is a powerful tool that can inform on the structures, density conditions and sample parameters, such as temperature. Even the domain size of the scatterers can be estimated from the XRD signal. In combination with the high brilliance and photon energy of an XFEL, XRD can provide crucial insights into the formation, size and some thermodynamic parameters of NDs of *in situ* WDM states. The following section will shed light on the small angle limit of x-ray scattering, which contains information about different length scales.

2.2.2. Small Angle X-Ray Scattering

SAXS is another special case of elastic x-ray scattering. As the name indicates, SAXS concerns itself especially with small scattering angles and therefore small q vectors and is thus much more sensitive to larger structures. It is a commonly used method to determine contrast in the electron density in the order of up to a hundred nanometres. Because the underlying physics, are the same as for XRD, the process follows the same illustration as Fig. A.6.

In contrast to XRD, which resolves the electron density contrast due to the atomic distribution, the electron density contrast on the length scale that SAXS is sensitive to, is due to the particle-substance interfaces. The scattering centres relevant for SAXS are therefore the contact surfaces between particles and solution.

A more general description of the intensity, than in the special case of XRD, is the description via the form factor $F(q)$ and structure factors $S(q)$, as derived, e.g in [165]. For the SAXS signal of a collection of particles of volume V , concentration c which have an electron density of ρ , the intensity is then calculated as:

$$I(q) = c\rho^2V^2F(q)S(q). \quad (2.22)$$

In the special case of a dilute solution, or an isolated particle, the concentration and the structure factor are set to $c = S(q) = 1$:

$$I(q) = \rho^2V^2|F(q)|^2. \quad (2.23)$$

In case this single particle is a sphere of radius R , the form factor can be analytically computed to [166]:

$$F(q) = \frac{3}{(qR)^3} [\sin(qr) - qR \cos(qR)]. \quad (2.24)$$

The structure factor is substantially more difficult to obtain than the form factor because it encapsulates the inter particle interactions. It involves solving the Ornstein-Zernike equation and requires a so called closure relation, which describes the pair correlation function $g(r)$

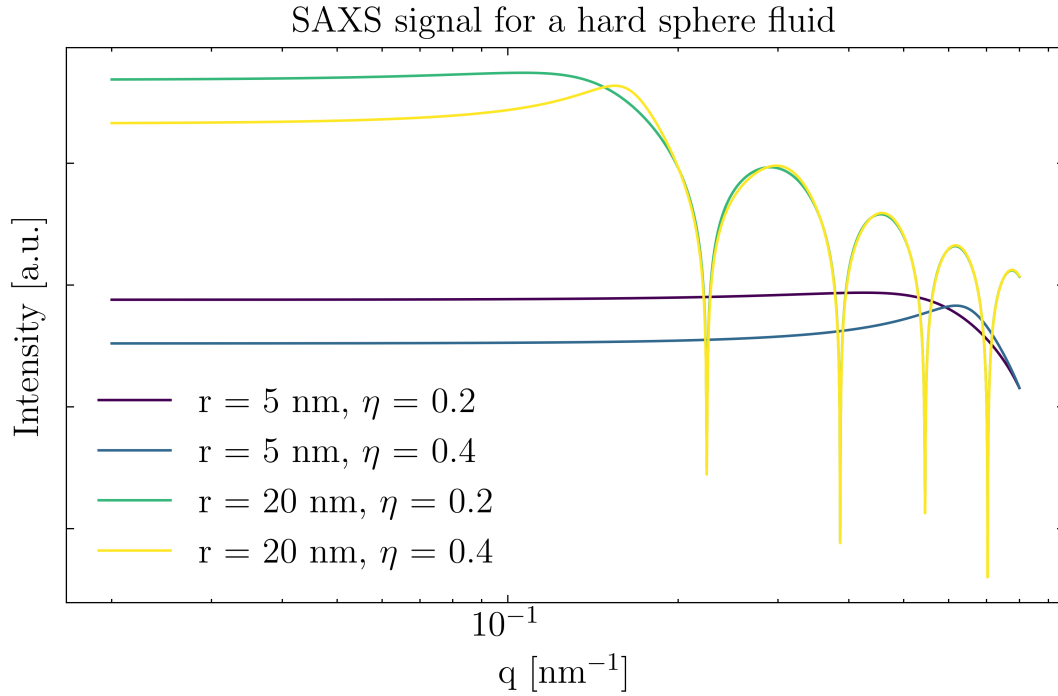


Figure 2.5.: Simulated SAXS signal for monodispersed particles of radius $r = \{5, 20\}$ nanometre and the volume fractions $\eta = \{0.2, 0.4\}$. A PY hard-shell model is assumed to model the signal. It becomes clear, that the lower q range is more sensitive to the volume fraction, while the higher q oscillations inform about the particle radius.

of a system [167]. Assuming particles of a single radius and using the Percus-Yevick (PY) approximation, an analytical expression for the structure factor of hard spheres can be found [168]. The derived equation for the structure factor can be found in Sec. A.5.1.

Combining such a structure factor with a form factor of spherical particles, the scattering signal depends only on the electron density contrast between particle and surrounding material $\Delta\rho$, the particle radius r and the volume fraction η . Example plots of different simulated signals can be found in Fig. 2.5. From the graph it becomes clear that there is a minimal radius $r_{\min}$ that the SAXS signal is sensitive to, depending on the maximal $q_{\max}$ value on the detector and vice versa. The relationships are [169]:

$$r_{\min} \approx \frac{\pi}{q_{\max}} \quad (2.25)$$

$$r_{\max} \approx \frac{\pi}{q_{\min}} \quad (2.26)$$

For polydispersed particles, which follow a certain distribution, the situation complicates further. For a distribution of particles the structure factor is rather complicated to derive. It involves solving the Ornstein-Zernike equation and requires a closure approximation [170]. Efforts have been made to derive analytical expressions for distributions which occur regularly in the context of common SAXS applications. A collection of analytical expressions for structure factors of distributions can be found in [171]. A common distribution for the length of polymeric chains is the Schulz-Zimm distributions (compare Sec. A.5.2) which is often used to model SAXS signal. One way to obtain a model for a polydispersed system is the assumption of local monodispersity. Essentially, this means that the local variation of particle radii is neg-

ligible, or, in other words, a complete correlation of particle radius and position. Under this assumption, the form factor is assumed to be well represented by a mean form factor which can be found in Sec. A.5.2 and the PY structure factor.

By using the local monodispersity approximation, the signal can be constructed for any given particle radii distribution. The sample is then assumed to consist of particles of different radii following a radius distribution function $n(r)$. It can be locally approximated with the PY structure factor, the local form factor $F(r)$ of a spherical particle and a global volume fraction φ . In this manner the entire signal can be created by integrating over the entire sample distribution. Considering the nature of shock experiments, where the nucleation conditions are locally reached in slices along the direction of the shock wave, this might be a case in which the assumption of local monodispersity is indeed appropriate.

Once the physics of the underlying process is understood, the data obtained in experiments can be interpreted using the same method as described in Sec. 2.2. The model is fit to minimise the residual error and to find the most likely set of model parameters to reproduce the experimental data. A more general way of fitting a model to the data is MC sampling. It is possible to use MC sampling to obtain size distributions from high quality SAXS data via software like McSAS [121, 169]. This method essentially follows the same assumptions of a monodisperse hard sphere fluid with a structure factor of $S(q) = 1$.

To recap, the SAXS signal contains information about the particle radii distribution, the radial distribution function, and volume fractions of nanoparticles in the sample. In contrast to XRD, it is sensitive to electron density variations in the order of up to several hundred nanometres. In conjunction with XRD, SAXS can inform about the sizes and size distribution of the nanoparticles and thus help our understanding and to differentiate between nucleation theories.

2.3. Hyper Velocity Impacts

In recovery experiments, NDs are ejected and impact the catcher material at velocities of several km s^{-1} . To achieve successful recovery, a solid understanding of HVIs is required. The term HVI usually refers to impacts at velocities in the order of the speed of sound of either the impactor or the impacted target. At these high velocities the objects experience severe shock pressures and can be strongly modified or even vaporised upon impact. Theoretical descriptions of HVIs have been motivated by geological research (e.g. meteorite impacts) [172].

This section will cover the theoretical basis for the description of cratering in HVIs. After introducing the cratering process, outlines for the experimental methods to determine crater morphologies will be given.

The entire impact process is commonly divided into three steps: (I) contact and compression, (II) excavation, and (III) modification [173]. Each of these processes covers a different time domain depending on impact velocity and projectile size.

(I) Contact and Compression

This first stage starts as soon as the projectile contacts the target. As the projectile is decelerated, shock waves are launched into the target and into the projectile. The physics follows the same Hugoniot framework outlined in Sec. 2.1.3.

The pressures in projectile (p) and target (t) can be obtained by using the respective particle velocity. By construction, the peak pressure at the interfaces of the two materials are equal and can be calculated from Eq. 2.10 and 2.9:

$$P_1^{p,t} = \rho_0 u_p^t (c_0^t + \alpha^t u_p^t). \quad (2.27)$$

This equation is valid for a trivialised impactor/target of infinite, flat shape. Such a description neglects the large pressure gradients typical for real-world impacts of often spherical projectiles. In a spherical impactor scenario, the pressure gradients result in so-called jets, referring to material which is strongly compressed and ejected as a material stream.

The compression wave will traverse the projectile until it reaches the rear surface; here, the pressure will be unloaded and a release wave will travel in the opposite direction back towards the projectile-target interface. When the release wave reaches this interface, the second stage begins.

(II) Excavation

During the excavation stage, the shock wave is expanding in the target, dispersing its energy until it decays to an elastic wave. During this stage, the crater is excavated by material flow away from the impact point. With spherical projectiles, this upwards and outwards directed flow from the point of impact creates a so-called ejecta curtain, a cone shaped flow of material with an opening angle of about 45° [174]. The duration of this stage varies depending on the impact parameters as well as on the strength of gravity in the target, but is considerably longer than the first stage. In the case of nm-sized impactors, the effect of gravity can be neglected. The excavation stage ends when the excavation process has finished.

(III) Modification

When the out-flowing material slows down, elastic relaxation processes start to dominate the material's behaviour. This leads to a collapse of the ejecta curtain, which forms crater crests and ejecta deposits in an area around the impact site (ejecta blanket). The crater's walls can collapse during this stage, reducing its depth and increasing the diameter. An estimation for the crater diameter over projectile diameter after the end of modification stage is $\frac{d_c}{d_p} \approx 20$ [174]. The modification stage determines the final crater morphology. The release of impact stress can lead to phase transitions and chemical reactions at the impact site. In geological cratering this stage is more impactful than in micro-cratering due to much stronger effects of gravity.

The crater morphology is dependent on the projectile and target material as well as on the impact velocity. It is common to categorize craters into simple craters, complex craters or multi-ring basins, depending on their morphology. Simple craters are bowl shaped depressions in the surface and have a depth-diameter ratio between $h/d \approx 0.2-0.33$ [174, 172]. Such craters usually form when only negligible collapse of craters walls occurs during the modification stage. The term complex craters refers to very large craters (> 20 km on Moon and > 3 km on Earth), which differ from the bowl shape [173].

To understand the process of recovery, knowledge of the conditions of the NDs at breakout is required. Such information can be obtained from the crater impact landscapes, independently from whether the diamonds survive the impact. Hence, a careful study of the crater surface

yields information not only for experiments where NDs can be recovered, but also for those in which they fully evaporate during impact.

2.4. Nanodiamond Diagnostic Techniques

To determine the success of a recovery method, a reliable technique for finding evidence of NDs in the catcher material is required. It was already explained that the created diamond material per shot is very limited due to the required intensities to create them. Multiple different techniques were used in this work to find evidence of the survival of NDs in the catcher material. Some involve dissolving the catcher material, while others look for discrete impact sites, or simply probe a large volume of the catcher.

This sections aims at introducing the employed methods, and highlights how they can be used to determine the existence of NDs in catchers. It does not aim at providing a rigour introduction to all of them, but a brief overview that puts each method into the context of finding evidence for NDs. The interested reader is referred to the literature to read more about the intricacies of the methods described below.

2.4.1. Raman Spectroscopy

In Raman scattering, the energy change of the incoming photon is caused by an excitation or annihilation of a molecular mode [175, 176]. In this process, a sample is probed with a laser and the scattered radiation is recorded with a spectrometer. The resulting spectrum is a molecule specific pattern, in which molecular modes, such as stretching, rotation or vibration, appear as peaks. The final energy $\hbar\omega_f$ of the emitted photon is dependent on the initial photon energy $\hbar\omega_0$ and the energy of the created or annihilated phonon $\hbar\omega_{ph}$:

$$\hbar\omega_f = \hbar\omega_0 \pm \hbar\omega_{ph}. \quad (2.28)$$

In graphitic carbon, the atoms are bound via sp^2 hybrid orbitals, while diamond is bound tetrahedrally via sp^3 hybrid orbitals. The most prominent feature of the graphite Raman spectrum are the so-called *G*-band around 1580 cm^{-1} and the *2D*-band around 2700 cm^{-1} [177–179]. The *G*-band is attributed to in-plane stretching of the benzene rings [180]. The so-called *D*-band around 1350 cm^{-1} is usually suppressed in perfect graphite, but can be active in the presence of defects, at the edges or a result of inter-layer rotation [181]. An in-depth treatment of the interpretation of Raman spectra of a transition from amorphous carbon to graphite is given in [182].

Contrary to graphite, the diamond Raman spectrum shows an absence of the *2D* and *G*-bands. Instead it contains a strong peak at the so-called diamond band at 1332 cm^{-1} [183–185]. Although the *G*-band reappears as the crystallite size approaches the nm scale due to surface effects [1]. However, the exact Raman spectrum depends on the production method. HPHT ND Raman spectra differ from DND spectra and others. An overview of the individual spectra can be found in [1].

Even though the exact spectra vary, and it is unknown how exactly the Raman spectra of NDs created in laser-driven shocks would look like, all ND spectra have the diamond band and a second broad peak just above 1580 cm^{-1} [1]. However, this peak can shift to higher wavelengths above 1590 cm^{-1} depending on the exact surface chemistry and excitation wavelength [1].

These are the important features to look out for in a Raman search for NDs. A detailed consideration of Raman spectroscopy is given in reference [176].

2.4.2. Scanning Electron Microscopy

Another technique that was used in this work is SEM. It was primarily used to determine impact crater morphologies and to look for potential ND candidates. SEM as the name indicates, uses a beam of accelerated electrons to scan the sample surface by directing the electron beam on a raster pattern. The target then emits secondary electrons, as well as backscattered electrons. The secondary electrons can be detected to recreate a high resolution two-dimensional image comparable to an optical microscope with magnification factors up to 3,000,000 [186]. If a sample is non-conductive, it accumulates an electric charge over time, which eventually makes measurements impossible. Therefore, non-conductive samples are usually coated by sputtering a conductive layer on them [187]. By using SEM, high resolution images of the catcher surface can be obtained, which can give valuable information about the (potential) ND impactors, as well as about the target-catcher interaction. Using metallic catchers, SEM requires no sputtering and is a quick method to scan catcher surfaces.

2.4.3. Transmission Electron Microscopy

TEM is another powerful technique using electrons to image samples with very high resolution. In contrast to SEM, in TEM the electrons are transmitted through the sample and registered by a detector. In Scanning Tunnelling Electron Microscopy (STEM) mode, the sample is scanned in a raster pattern analogous to SEM. STEM is capable of resolving structures down to the atomic level and can directly visualise crystal structures. Another operation mode of TEM is the Electron Energy Loss Spectroscopy (EELS) mode. Here, the electrons lose energy, depending on the excitation of electronic states and plasmon resonances, as they are transmitted through the sample.

The high resolution of STEM and the possibility to probe the chemical nature directly, make it a well suited tool to look for NDs in catchers. However, for TEM the electrons need to penetrate the sample. This requires very thin slices (<100 nm) of the sample. Because some of the catchers used in this work were metal plates, they needed to be prepared as thin cross sectional slices of such a thickness. This was done by using a FIB. A FIB uses a strongly focused ion beam (often gallium) for milling at high acceleration voltages or deposition at low voltages in combination with a deposition material like platinum. The process is very delicate and requires a lot of time and expertise to prepare a sufficiently thin lamella for further analysis in a TEM. An outline of the process to produce a TEM-lamella is given in Sec. A.8.

It is also possible to use TEM on liquid samples. For this, a TEM grid, consisting of a larger copper matrix filled with lacey carbon, is deposited with small drops of a suspension containing the nanoparticles of interest. To obtain good signal quality, contaminations of the suspension must be kept to a minimum. The advantage of TEM from liquids is that the tedious procedure of producing a TEM lamella is not required.

TEM is a highly sophisticated imaging technique able to produce atomic resolution images of cross sectional slices and nanoparticle suspensions. In this work TEM was both used to analyse the catcher surfaces via FIB-cut lamellae, as well as via a solution deposited on a TEM grid. For a thorough description of TEM and EELS the reader is referred to the references [188, 189].

2.4.4. Electron Energy Loss Spectroscopy

In EELS a sample is illuminated with an electron beam and the energy spectrum of the transmitted electrons is recorded. As the electrons are transmitted through the sample, they can be scattered inelastically and lose energy depending on the material they are transmitted through. Analogous to Raman spectroscopy the energy loss depends on the atom type and the bond structure. Key regions of EELS spectra are the zero-loss, low-loss and the core-loss region [190]. The zero-loss peak at 0 eV represents the unaltered electrons just passing through the sample without modification. The low-loss region up to 50 eV contains information about band structure and surface plasmons of the material. The core-loss region contains the peaks for the shell ionisations. The ionisation edges typically contain a sharp rise at the ionisation energy and decrease more subtly. The carbon K-edge starts at 285 eV [190]. However, the exact shape is determined by the bond nature of the material. Therefore, it is possible to distinguish e.g. diamond from graphite or amorphous structures through EELS. Especially the fine structure separation of the K-edge in π^* and σ^* peaks as well as shifts in the plasmon peak are distinct features for differentiating *sp*² from *sp*³ bond carbon [191, 1].

In general, the signal intensity scales with a power law of the form $I = AE^{-r}$, where E is the energy loss [192]. Therefore, at higher energy shifts, typically beyond the low-loss regime, the signal-to-noise ratio suffers notably and longer integration times might be required.

2.4.5. Energy-Dispersive X-Ray Spectroscopy

When using an electron beam to image a sample, be it either in SEM or TEM, some of the inner shell electrons of the atoms can be excited to the continuum. When this inner shell hole is filled by a higher energy electron within the atom, x-rays of an atom characteristic energy are emitted. In Energy-Dispersive X-Ray Spectroscopy (EDS) a detector registers the emission spectrum which is then associated with an atom type. In this way, it is possible to compose a spatially resolved atomic composition map. Overlaying this with the high resolution images of either TEM or SEM can be very helpful to determine potential ND candidates in the samples.

2.4.5.1. Confocal Microscope

Although it is not able to identify ND candidates directly, a confocal microscope can still be used to determine the effect of ND impacts into catcher materials indirectly via the crater morphology. A confocal microscope uses laser light in combination with a pinhole to reject out-of-focus light effectively. The sample is illuminated by a laser and a pinhole in front of the detection aperture (photomultiplier or Charge-Coupled Device (CCD)) which substantially reduces out-of-focus contributions. By changing the z -position of the focal plane a depth-dependent intensity map can be constructed to obtain a quasi three-dimensional scan of the studied object. A short introduction to the principles of a confocal microscope is given in [193].

In summary, the different techniques used in this work to determine the existence or possible impact of NDs into catchers rely on either 1) imaging (SEM, TEM, Confocal Microscopy) or probing of the bond structure or atomic composition of the material (Raman, EDS, EELS).

3. Experiments and Methods

This chapter presents the experimental setups and introduces and explains the simulation methods which are conducted in this work. In the context of ND recovery, different aspects play a role in determining the feasibility of synthesis via laser-driven shocks. Starting from a theoretical perspective, this chapter introduces the MD simulations carried out in the course of this work to understand the release of NDs from shock states. After that follows a description of the dynamic shock compression experiments, performed to gain knowledge about the formation and release dynamics of shock-produced NDs. Furthermore, the recovery experiments are introduced. Here, the term "recovery experiments" refers to setups, which are not solely focused on *in situ* diagnostics, but those which make use of a catcher material to actually determine, whether intact NDs were recovered during the shock compression experiments. Finally, this chapter will also introduce the diagnostic setups employed in this work to search for potential ND candidates in the catcher materials.

3.1. Molecular Dynamics Simulations

Many of the challenges described in Sec. 1.1.3 arise from the short-lived nature of the produced WDM state or the extremely short timescales of the involved processes. Two important processes relevant for this work are the expansion of NDs after the breakout of the shock wave, and the impact cratering when the NDs come in contact with the catcher material. Both processes occur on length and timescales which are experimentally inaccessible with current methods. Consequently, an understanding of these processes requires some form of modelling. As explained in Sec. 2.1.1, MD is an excellent tool for this goal. The following sections will explain the setup for the MD simulations performed in this work to understand the release (Sec. 3.1.1) and impact process (Sec. 3.1.2). Results are presented in Sec. 4.1 and 4.4.

3.1.1. Nanodiamond Release and Breakout

As described in Sec. 2.1.3, a rarefaction wave is travelling into the sample after the shock wave reaches the rear surface. The NDs are still at an elevated temperature and pressure, but as the expansion into vacuum progresses, the pressure is rapidly released. As the pressure is released and the volume expands, the system performs work against the surrounding material, causing the NDs to cool. Understanding how NDs respond to this expansion requires careful consideration of the cooling timescale relative to the expansion dynamics. The NDs form under conditions where diamond is the stable phase but ultimately reach ambient conditions, where diamond is only metastable. Therefore, the thermodynamic path during expansion is crucial for their stability and eventual recovery.

This expansion process is extremely fast and happens as the release wave is propagating backwards into the sample. The conditions across the entire sample are now vastly different, with parts of the materials still in compression, parts releasing and other parts already expanded. As mentioned in Sec. 1.1.3 this process is modelled by using MD. As explained, the exact result of an MD simulation can strongly depend on the chosen interaction potential. Although the interaction potential was chosen to best describe the disintegration of diamond along a large pressure range, the results are presented to provide qualitative estimates for ND-stability upon release from shock-compressed states and not to draw exact lines along different release paths.

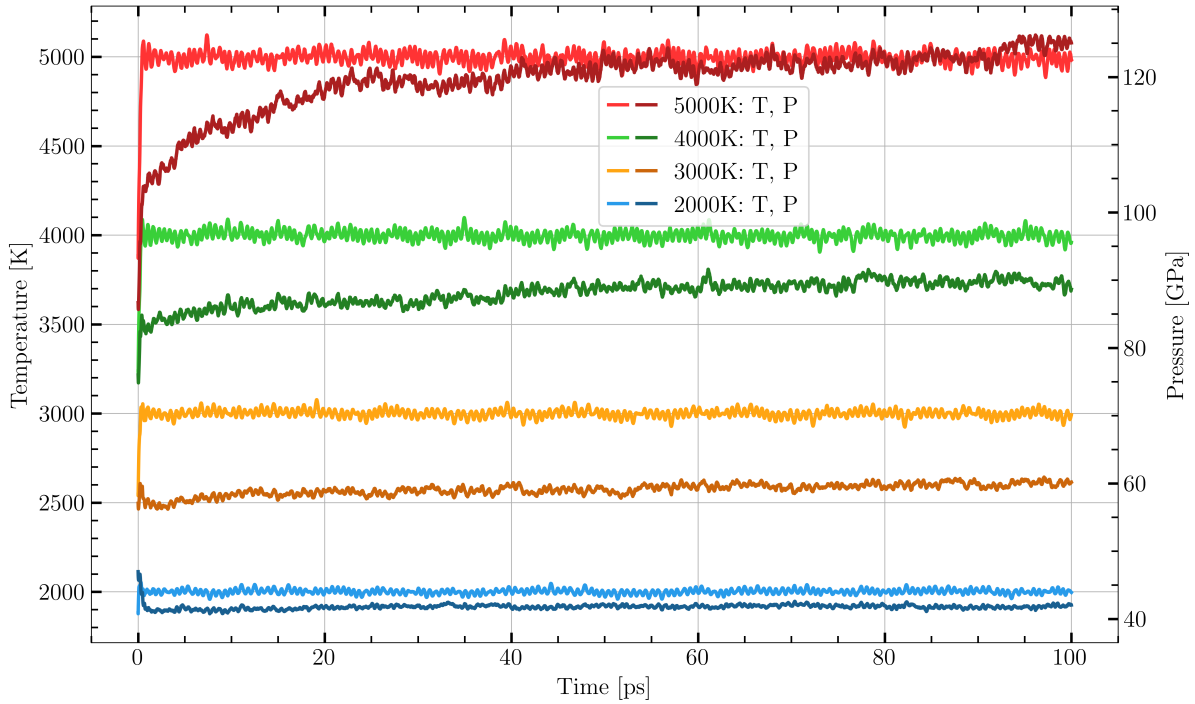


Figure 3.1.: Temperature and pressure evolution during the expansion phase. The four different states are displayed. The bright color represents the temperature, and the dark color the pressure.

All expansion simulations are performed using the EDIP potential, due to its superiority in describing such a process as outlined in Sec. 1.2.3 [117, 118].

The entire expansion process simulation is divided into four steps using the LAMMPS software [194] and is published in [195].

Step 1: Equilibration I

First, a physically meaningful system has to be obtained during an equilibration phase. To do so, a carbon atom cube in an ideal diamond lattice is initiated. To reduce the degrees of freedom, it was decided not to couple a barostat to the system, but rather to adjust the box volume for a fixed number of unit cells. This effective scaling of the unit cell mimics the compression in the shocked region. By coupling the system to a Nosé-Hover thermostat the temperature during the simulation is kept constant [196–199]. Using a Verlet style integrator on this NVT-ensemble, an equilibrium system at the required conditions is prepared by running the simulation for 10^6 timesteps with $\Delta t = 0.1\text{fs}$ [200]. This timestep proved sufficient for energy conservation. The four initial states are chosen on the PET Hugoniot curve at temperatures of $T_{\text{init}} = \{2000, 3000, 4000, 5000\}\text{K}$ [201].

Fig. 3.1 shows the entire equilibration phase. The different color schemes indicate the different temperatures of the thermostats. The bright shade is used for the temperature, while the dark shade is used for the respective pressure evolution.

After this step the system exists in an equilibrium state. Because the boundary conditions are non-periodic, the interaction of the ND cube with the walls can result in a disintegration of the ND at the surface. This disintegration increases with temperature, such that at the highest simulated temperature, only 30% of the carbon atoms remain in the diamond phase after the equilibration. Common Neighbour Analysis (CNA) is used to determine the carbon

phase [202, 203]. Whether a carbon atom is in the diamond phase or not is determined by its direct neighbouring atoms and their direct neighbours. Depending on the neighbouring graph, an atom can either be in a diamond grid, first or second neighbour of a diamond grid atom, or completely unrelated to a diamond lattice [204].

Step 2: Expansion

During the second step, the box walls are continuously expanded, increasing the volume that is available to the atoms. This is implemented by using LAMMPS "deform" command with remapping of the atomic coordinates. The rate of expansion is determined by the target expansion time:

$$\dot{\epsilon} = \frac{d_0 - d}{d} \frac{1}{t_{\text{exp}}}, \quad (3.1)$$

with the ambient and compressed diamond lattice constants d_0 , d and the target expansion time t_{exp} . This results in a linear increase of the unit cells along all dimensions that reach the ambient lattice constant of diamond after the target/nominal expansion time. The expansion times are varied to assess how different strain rates affect the expansion process. The expansion times are referred to as nominal expansion times, because in reality the system does not reach zero pressure at the ambient diamond lattice constant. The elevated temperatures and partial melting require the system to expand beyond the ambient diamond lattice to reach zero pressure.

The expansion phase is halted once the system's pressure drops below zero, well after the ambient diamond lattice constant had been reached. However, the nominal expansion times are still reported, as they provide a much more intuitive way than strain rates or real expansion times. For each initial P - T combination, five different nominal expansion times $t_{\text{exp}} = \{50, 100, 250, 500, 1000\}$ ps are tested. An overview of the corresponding strain rates can be found in Tab. A.1. These expansion times are chosen to be the same order of magnitude as the one studied by Ileri et al. in [119], which are mentioned in Sec. 1.2.3. The number of carbon atoms in the diamond phase and the thermodynamic path is recorded during this phase until the expansion phase is halted (negative pressure).

Step 3: Cooling

Until now, the effects of radiative cooling of the NDs have been completely neglected. All cooling they experience is purely related to the expansion process. However, the NDs have a very high temperature on the PET Hugoniot and consequently do emit radiation, which facilitates cooling. As a quantum mechanical process, radiative cooling is very difficult to incorporate into MD simulations explicitly, especially when phase transformations are involved. Under the assumption that the expansion process is much faster than radiative cooling of the ND, the two phases are treated consecutively. This assumption is based on the fact that in the shocked state, the NDs are expected to be in thermal equilibrium with the surrounding WDM; therefore, radiative cooling could only occur as soon as the release has sufficiently diluted the material. After the partial melting of the ND during the expansion, a fast cooling could result in the recrystallisation in parts of the simulations cell.

To assess how subsequent cooling after expansion will affect the ND evolution, an explicit cooling phase is implemented. This is done by keeping the simulation box size constant, after

the pressure dropped below zero, and coupling the system to a heat reservoir. The reservoir's temperature is then linearly reduced to 300 K over a timespan of $t_{\text{cooling}} = 250$ ps. This is chosen to replicate a cooling rate in the same order of magnitude as a similar study, which did not find a difference in the results of compressed carbon for cooling rates below $2.82 \times 10^{14} \text{ K s}^{-1}$ [119]. However, to assess how even slower cooling rates would affect the ND stability, additional simulations are performed on the intermediate $T_{\text{init}} = 3000$ K simulation over a cooling time of $t_{\text{cooling}} = \{2500, 25000\}$ ps.

Step 4: Equilibration II

After the system has cooled to ambient temperature, it is important to ensure again that the obtained state is indeed an equilibrium state. Post-cooling effects could occur that further modify the ND properties. To ensure this, a second equilibration phase is added in an NVT ensemble. Whether a remaining diamond core would be stable on the long term, is determined during this second equilibration phase, which lasted for 200 ps.

These four steps intend to model the expansion process from the beginning of the release wave progressing into the target, until the very end of the expansion back to an equilibrium state.

Sec. 1.2.1.7 explained that ND has previously been found to also form in off-Hugoniot states. This means the temperatures can significantly differ from the Hugoniot curves of the plastic. This could result in different expansion behaviour from such states. To qualitatively assess if such off-Hugoniot states could be preferable to achieve intact recovery, two such states are modelled. Those are initiated as one super-Hugoniot state, with an equilibration temperature exceeding the on-Hugoniot point ($T_{\text{init}} = 4000 \text{ K}, P_{\text{init}} = 113 \text{ GPa}$), and one sub-Hugoniot point ($T_{\text{init}} = 4000 \text{ K}, P_{\text{init}} = 75 \text{ GPa}$). Fig. 3.2 shows the initialised simulated states along with the diamond formation region from other shock compression experiments using PET and PS [36, 7], along with the theoretical diamond melting line from [205]. The PET Hugoniot curve is also displayed from reference [201].

3.1.1.1. Radiative Cooling Simulation

To put the chosen cooling rates into context, a simple radiative cooling simulation is performed. It is based on the Stefan-Boltzmann law [206, 207] of a radiating black body and the derivations can be found in Sec. A.2.1. This way an equation for the temperature development of a theoretical diamond particle with initial temperature T_0 is found. This can be modelled via Eq. 3.2. The factor k combines the surface area with the relevant physical and material constants (compare Sec. A.2.1).

$$T(t) = (3kt + T_0^{-3})^{-\frac{1}{3}}. \quad (3.2)$$

3.1.2. Hypervelocity Impact Simulations

In dynamic compression experiments, information about the presence of NDs is obtained by using XRD and looking at typical diffraction signals of diamond. However, this is constrained to the time when the material of interest is located within the focus of the probing XFEL beam. After breakout, this is not the case and the NDs are ejected at hypervelocities until they hit the catcher, which is placed behind the target. Another way to know if the diamond

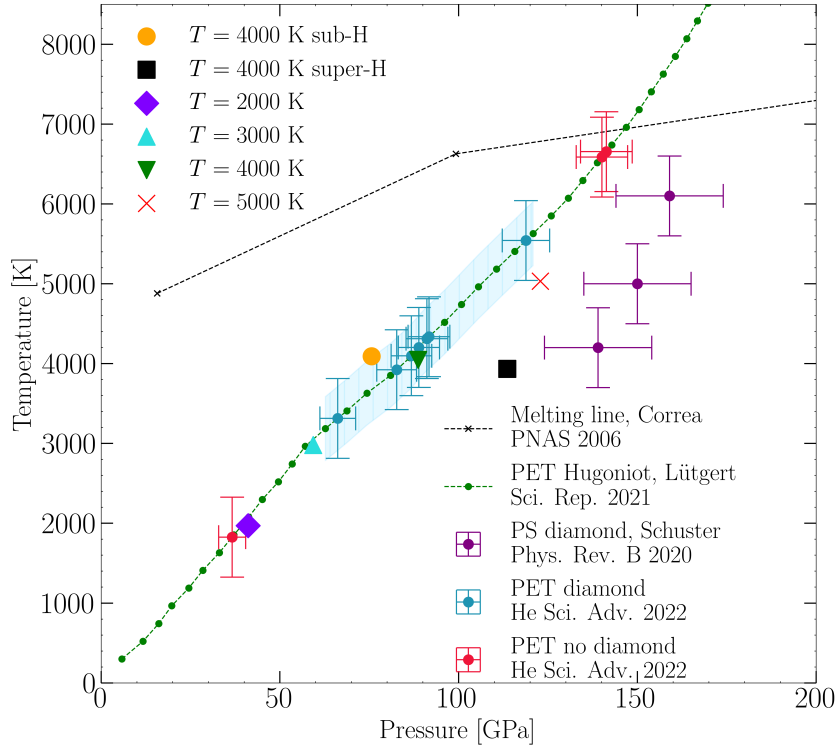


Figure 3.2.: PET Hugoniot curve from [201] with the four initiated on-Hugoniot states and the two sub- and super-Hugoniot states. The diamond melting line from [205] and the experimental diamond formation conditions in PET and PS are also indicated [36, 7].

survived breakout is to model the HVI using MD. The resulting crater morphologies can be compared to detailed AFM scans of the surface and be related to the impact morphologies of non-diamond impactors. This way it is also possible to get estimates for the maximal impact velocities which NDs can survive.

To gauge how an ND impacting a catcher would influence the catcher surface, a simulation is set up similar to reference [38] (see Sec. 1.2.3). However, here it was initialised with a spherical diamond with a diameter in the order of magnitude as measured in previous shock compression experiments [122]. Therefore, a spherical ND with a diameter of $r_{\text{ND}} = 2.5 \text{ nm}$ is initialised to impact an aluminium catcher at velocities of several km s^{-1} . The same simulation is set up using a non-diamond impactor for comparison of the crater morphologies.

The diamond sphere and the catcher are equilibrated in an NVT ensemble for $t_{\text{eq}} = 20 \text{ ps}$ at a temperature of $T_{\text{eq}} = 300 \text{ K}$, using a timestep of $\Delta t = 0.5 \text{ fs}$. To obtain a non-diamond impactor of a sensible composition, the diamond is melted in an NVT ensemble at $T_{\text{melt}} = 3000 \text{ K}$ for $t_{\text{melt}} = 25 \text{ ps}$. After that, the system is cooled to room temperature over $t_{\text{cool}} = 50 \text{ ps}$ and equilibrated for another $t_{\text{eq}} = 50 \text{ ps}$. The simulation box is set up with shrink-wrapped¹ boundary conditions in impact direction, and periodic boundary conditions perpendicular to the impact direction.

After the initialisation of the impactor and catcher, the impact velocity is added to the thermal velocity of the NDs. The simulation is carried out and continuously inspected to determine if the modification stage has ended (compare Sec. 2.3). If not, the simulation is continued. The studied impact velocities for the NDs are $v_{\text{impact}} = \{9, 11, 13, 15\} \text{ km s}^{-1}$, while, for comparison, annealed NDs are studied at $v_{\text{impact}} = \{9, 11\} \text{ km s}^{-1}$.

¹LAMMPS internal style for a finite box, that expands to incorporate escaping atoms.

The catcher morphologies after impact are analysed and parameterised for comparison with crater scans from experimental campaigns and values reported in the literature.

3.1.2.1. Cross-interaction Potential

The choice of potential for the cross-interaction between carbon and aluminium atoms can strongly influence the results. As explained in Sec. 2.1.1 these potentials determine whether bonded structures are possible and which bonds will be present or might be broken. In the case of the HVI simulations performed in this work, the bonding between impactor and target atoms are categorically excluded. Although such bonds are theoretically possible, their formation would require a breaking of the pre-existing bonds and could only occur during the time of contact of the two atomic species. Due to the nature of the extremely short-lived impact state, the assumption of non-interacting species will not greatly affect the results.

Therefore, a simple cross-interaction potential can be chosen in the form of an LJ potential (Eq. 2.1). The strongly repulsive core of the LJ potential is sufficient to avoid interpenetration of the colliding objects and mimic the impact. The chosen parameters are $\epsilon = 0.00284 \text{ eV}$, $\sigma = 3.4 \text{ \AA}$, and $r_{\text{cut}} = 2^{\frac{1}{6}}\sigma$, taken from a theoretical carbon-carbon repulsion potential [208]. These values showed no interpenetration between diamond and catcher.

3.1.2.2. Convergence Study

The subject of convergence is especially important in this simulation. If the aluminium catcher block is not sufficiently large, the lateral pressure waves expanding outwards from the impact point will reach the box walls. When they do, they will collide with the periodic image of the lateral pressure wave of the opposite site. This will essentially result in a merger of the two pressure waves. Such a scenario does not represent what happens in a singular ND impact. Therefore, the aluminium catcher has to be so large that the lateral pressure wave does not reach the simulation cell edge before the modification stage is completed.

To find the minimal required size, the simulation cells and catcher domain size are iteratively increased. Each time the aluminium lattices integrity is determined radially around the impact domain using CNA to identify where the aluminium-fcc lattice is broken [202, 203].

Nevertheless, the intermediate simulations with insufficient catcher size to reproduce a singular ND impact can still be of value. These simulations could be interpreted as cases in which multiple NDs impact the catcher over a small area. Although an impact scenario in which nine individual NDs impact the catcher in the same spot is highly unlikely, the number of produced diamonds in shock compression is immense. The un-converged simulations could give an idea about how important it is to disperse the NDs before they impact the catcher, and thus inform the catcher mounting point.

3.2. In-situ Diamond Formation

Multiple laser-driven shock compression experiments are performed in this work to understand diamond formation and ejection during and after the shock. The experimental setup for a laser-driven shock experiment is displayed in Fig. 3.3.

For *in situ* diagnostics of ND formation, an XFEL is required to determine the structural information within the shocked sample, both via XRD and SAXS. Two pump-probe experiments

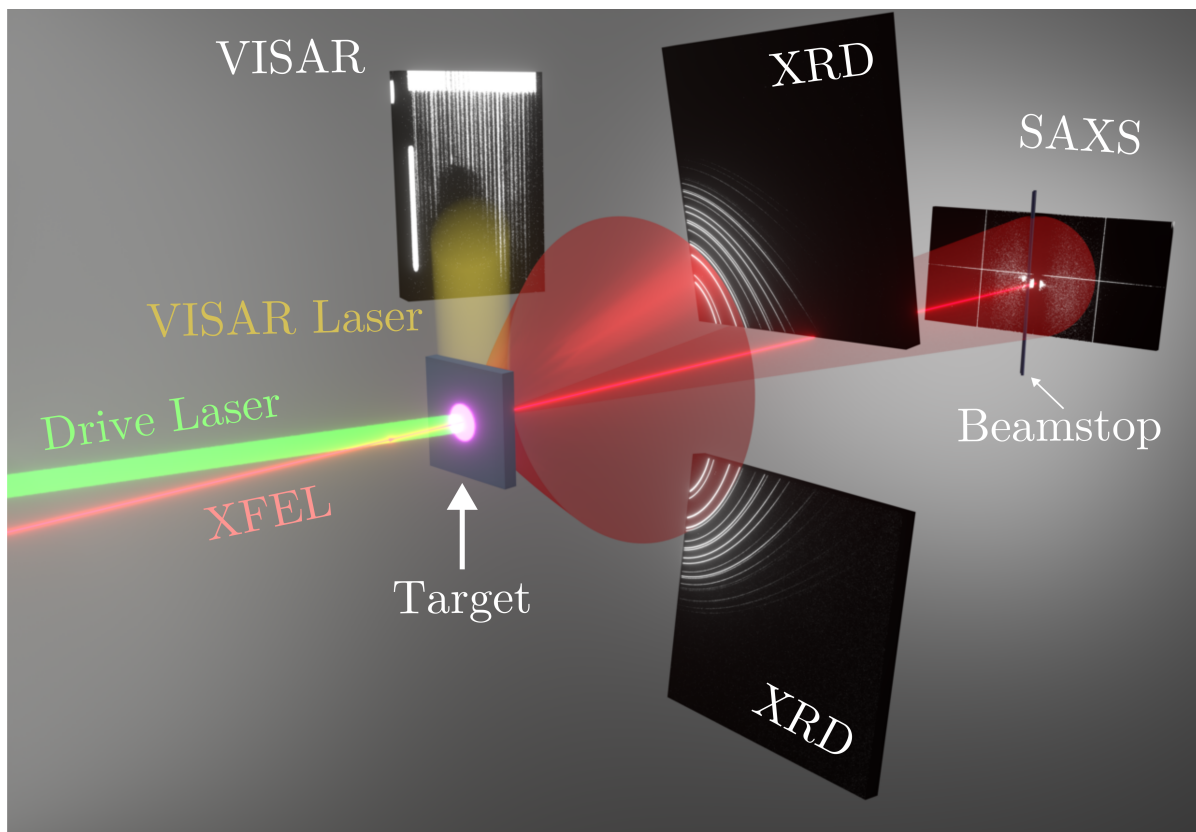


Figure 3.3.: Experimental setup of a pump-probe shock experiment at the European X-Ray Free Electron Laser (EU-XFEL). The drive laser is shown in green, the XFEL probe laser is shown in red, while the VISAR laser illuminating the backside is shown in yellow. The XRD and SAXS, and the VISAR detectors, show the actual collected data during an experiment.

with *in situ* x-ray probing are performed, one at the SPring-8 Angstrom Compact Free Electron Laser (SACLA), and the other at the EU-XFEL facility [209]. The XRD detectors used at SACLA are ePIX100 [210], a single pixel detector, while EU-XFEL uses two VAREX 4343 CT flat-panel detectors for XRD and, in addition, a JUNGFRU detector for SAXS [211]. Both facilities are equipped with a VISAR to determine breakout times and shock velocities.

At the experiment at SACLA, PET targets of a thickness of $75\text{ }\mu\text{m}$ are shot with an optical drive laser of $\approx 5\text{ J}$ after attenuation at an incident angle of 45° . This energy is delivered in a 5 ns square pulse over a spot size of $d = 170\text{ }\mu\text{m}$, resulting in an intensity of $\approx 4.4\text{ TW cm}^{-2}$. The SACLA XFEL is set to an energy of 9.996 eV . The experiment intends to analyse ND formation in PET in on-Hugoniot conditions, and especially the behaviour of the NDs after the shock has broken out of the rear surface.

At the EU-XFEL experiment, the drive laser is used in a step pulse mode to achieve a double shock and thus off-Hugoniot conditions. The targets consists of 75 and $100\text{ }\mu\text{m}$ PET foils. Different step profiles are tested to reach the off-Hugoniot diamond formation region in PET. The energy of the the drive laser is set to up to $\approx 33\text{ J}$ and the XFEL energy is 18 eV . Two different phase plates are used, which lead to spot sizes of 100 and $d = 250\text{ }\mu\text{m}$ respectively. The EU-XFEL experiment aims at determining the diamond formation region in double shock conditions and the after breakout behaviour of NDs. In addition to XRD, SAXS data is taken to determine information about the ND size distributions.

3.2.1. Diamond Formation in PET Targets

As Fig. 3.3 shows, the drive laser is used to pump the sample, creating the shock-compressed state. The XFEL is used to probe the shock state. Such pump-probe-experiments are common. By repeating the experiment while adjusting the pump-probe delay the time evolution of the system can be explored.

The experimental setup shows two area detectors with the actual diffraction data taken during a calibration shot at the p4463 experiment at EU-XFEL on CeO_2 . This sample has a well-known crystal structure. The detector pixels are mapped to diffraction angles with the softwares DIOPTAS and the library PyFAI [212, 213]. The uncertainties of the diffraction data is estimated from the azimuthal variance along the ring, a process outlined in Sec. A.6.1.

The pressure and density conditions are inferred by measuring the breakout times in single shocks and relating this the shock speed to HDS. The conditions are taken from HELIOS HDSs using the ProPacEOS EOS for $\text{C}_5\text{H}_4\text{O}_2$, which shares the PET C-H-O ratio. Here, the breakout times from the simulations are matched with the breakout times of the VISAR measurement by adjusting the laser intensity with a multiplier. The pulse shapes are taken as ideal square or step pulses with rise and fall times of 500 ps . During some shots at the experiment, the VISAR laser stopped functioning which makes determination of breakout times very difficult. At the EU-XFEL facility experiment, this is compensated by determining the required multiplier to match the HDS with those shots, where VISAR breakout times could be determined.

If the data quality obtained at the facility is sufficient, a full Rietveld refinement can be performed as explained in Sec. 2.2.1. To determine crystallite sizes and lattice constants accurately from XRD, the IRF of the system is determined from the reference diffraction sample. It is assumed that the crystallite sizes of the calibrant are sufficiently large as to not cause any size broadening. All broadening is attributed to the IRF. A convolution of the IRF with the ideal peak positions is fit to the data of the CeO_2 sample to determine the parameter values of the IRF as described in Sec. A.4.3. A plot of the resulting fit along with the data for

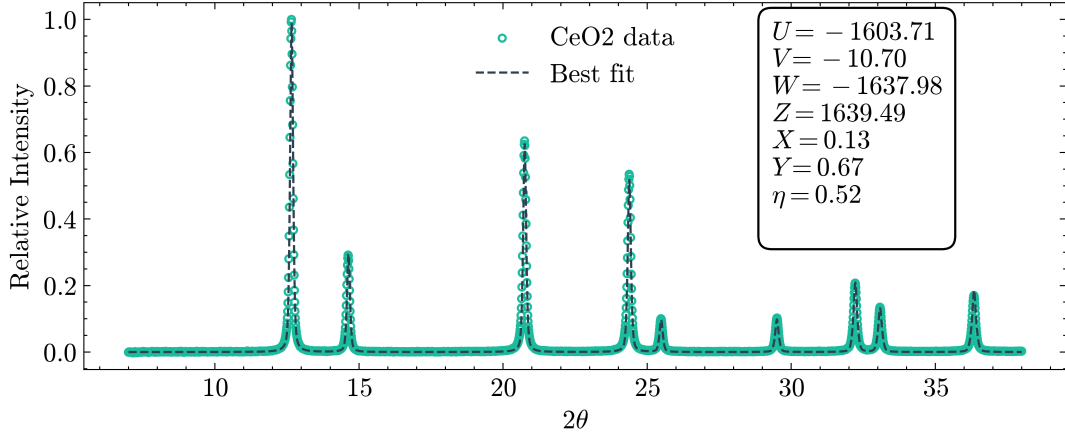


Figure 3.4.: Integrated XRD pattern of CeO_2 used as a calibrant in the EU-XFEL experiment. The best fit along with the fit parameters is also shown.

the calibrant during the EU-XFEL experiment is displayed in Fig. 3.4. The IRF convoluted with the ideal peak positions of CeO_2 can reproduce the data well. The convolution of the IRF with the fitted parameters is then applied to all further fitting procedures (see Sec. 2.2). To determine a good fit, the model described in Sec. A.4.2 is fit to the data. It consists of the diamond signal, the liquid diffraction taken from the two-dimensional DFT interpolation grid, as well as a partial cold shot in case the shock had not broken out of the rear sample. The DFT grid is used to interpolate the liquid diffraction signal of shock-compressed PET at different temperatures and pressures. The diamond peak positions and liquid diffraction peaks are used to determine breakout timings. After breakout, the rapid expansion results in a shift to lower angles.

Upon release the material expands rapidly and differences in electron density emerge on a scale relevant for SAXS. Therefore, this diagnostic can only be used while the material has not started releasing. As the WDM liquid expands, the Radial Distribution Function (RDF) peaks change, and the main liquid peak in the diffraction signal moves to lower angles. The DFT simulations are no longer valid after breakout due to the highly non-equilibrium state. Therefore, for shots after breakout, the liquid diffraction signal is modelled with a triple Gaussian plus a linear background.

From the fit of pre-breakout shots, the best fitting DFT based diffraction lineout, and thus density and temperature conditions, are extracted. Additionally, the sizes (peak broadening) and temperature (intensity reduction) of the ND crystallites are obtained. By choosing different time delays between pump and probe laser the evolution of ND size in shock-compressed PET and the time evolution of these quantities is determined. While the shock has not broken out of the rear surface, SAXS fits are performed for comparison.

DFT simulations for PET are available from 2000 to 10000 K, and 2.5 to 4.0 g cm^{-3} with steps of 1000 K and 0.5 g cm^{-3} respectively, which were provided by J. Vorberger from Helmholtz-Zentrum Dresden-Rossendorf (HZDR). The interpolation points on that grid are sampled with a resolution of 250 K and 0.05 g cm^{-3} respectively.

The uncertainty of the fit parameters are estimated by using an Monte Carlo Markov Chain (MCMC) algorithm [214]. The best fitting point in the T - ρ grid was chosen and the parameters crystallite size, lattice constant, and diamond signal amplitude sampled. The uncertainties presented in Ch. 4.2 refer to the upper and lower bounds of the 68% confidence interval, corresponding to the 16th and 84th percentiles of the posterior distribution.

For the experiment at the SACLA facility, the data quality was not sufficient to perform a full Rietveld refinement. Here, the values for lattice constant, diamond size and temperature are determined by fitting a background plus individual peak models. The uncertainties for this experiment's fit parameters (e.g. diamond (111) reflection center, width, and amplitude) are determined separately by using an MCMC algorithm. They are combined by using a χ^2 fit of the individual contributions and Ch. 4.2 reports the uncertainties as the standard deviation of Gaussian fits to the posterior distribution. The effects of the IRF could not be determined due to a failure to fit the calibrant data. However, assuming a perfect instrument would underestimate the ND sizes. The Scherrer formula gives an estimate for the lower crystallite size limit, which should be kept in mind when interpreting the results.

3.2.2. Nanodiamond Size Distribution and Growth

As explained in Sec. 2.2.2, SAXS can give important information about the size distributions of nanoparticles from *in-situ* experiments. Therefore, it has established itself as a powerful diagnostic in the context of ND nucleation during shock compression [7, 122, 120, 124]. A detailed analysis of the SAXS methodology in the context of ND nucleation in shock compression is published in [124].

He et al. [122] have shown that the size distribution can be obtained by making use of NNs. The authors used a feed forward NN with three hidden, fully connected layers with 512, 256 and 128 neurons. The intensity values, binned in 1000 q values, was fed along with the volume fraction and the network was trained to the radius distribution. The loss function used was the Mean Absolute Error (MAE). Using an NN for predicting the size distribution with SAXS is a very fast way to obtain results, once the integration and raw data cleaning procedure is completed, as inference only takes negligible time. However, the training of the NN can take a long time and the training data needs to be recalculated for each experiment.

To supplement the analysis of ND formation via SAXS from shock-compressed plastics discussed in [124], an NN is trained on synthetic data to predict the size distribution from the scattering signal. A detailed explanation of how the azimuthal lineouts are obtained from the raw data is given in [124]. To train the NN artificial data needs to be generated. The procedure is similar to what was implemented in [122].

First, an artificial size distribution of nanoparticles is sampled as part of this study. This is done by choosing one to three different mean radii and polydispersity values with a single, common volume fraction. The mean radii are sampled within given r_{min} and r_{max} values. Then, for linearly spaced r values, the probability densities for the one to three distributions are computed, by using a lognormal distribution of the form:

$$f(r) = \frac{1}{r\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\ln(r) - \mu}{\sigma}\right)^2\right), \quad (3.3)$$

with $\sigma = \sqrt{\log(1 + p^2)}$ and $\mu = \log(\bar{r}) - \sigma^2/2$, for a polydispersity p . The sum of the distributions is then normalised to integrate to unity. The lineout is computed as the sum of all radii, using the corresponding PY structure factor and the form factor from Eq. 2.24. Each radius contribution is scaled by the radius frequency. The maximum value for each lineout is set to one.

When trying to use the NN implementation from [122] to evaluate the SAXS data of the EU-XFEL experiment, the results were not sufficiently accurate due to the noisy data. Therefore, the NN is not trained on the synthetic data directly but artificial noise is added to the training data.

The noise on the data is calculated by using the number of pixels $n_P(q)$, which are averaged for each q value. This was determined by Lindqvist and is discussed in [124, Sec. 4.5] therein. The noise has a Gaussian form and was chosen to be inversely proportional to the square root of the number of pixels. To match the experimental noise, the value under the root was down-shifted by 1000 pixels and the entire noise scaled by a factor k . The final semi-empirical form was:

$$\Delta I(q) = k \cdot \mathcal{N}(0, 0.2) \cdot \frac{1}{\sqrt{n_P(q) - 1000}} \cdot I(q), \quad (3.4)$$

with $k = 10$ and the normal distribution $\mathcal{N}$ around a mean of 0 and standard variation $\sigma = \sqrt{0.2}$.

Using an efficient parallel implementation, a total of 200000 spectra could be generated within 260s on consumer hardware. The NN trained to predict the particle size distribution and volume fraction using a combined loss function. For the distribution a Kullback-Leibler (KL) divergence loss was chosen because it is a very good measure for the overlap between two probability distributions. The definition is given in Sec. A.7. This was combined with a Mean Squared Error (MSE) loss for the prediction of the volume fraction.

3.3. Recovery Experiments

To study how the recovery of NDs from the extreme states in which they nucleate can be achieved, different recovery experiments have been conducted in this work. The experiments had two main objectives. The first objective was to try to use different catchers in conjunction with the experimental techniques introduced in Sec. 2.4 to find evidence of NDs present after the experiment. Because absence of evidence is not evidence of absence - which is especially true when dealing with tiny particles in small quantities - this included the preparation of reference samples from commercial NDs and testing the diagnostic techniques in the expected concentrations. The second objective was the design of a high-repetition-rate platform with a suitable catcher module to increase the ND concentration in the catcher. Such a high-repetition recovery platform could be used in future experiments to explore the recovery of other metastable phases.

This section will explain the methods and experimental setups used to collect samples and find evidence for NDs therein, as well as the development of a high-repetition-rate platform.

3.3.1. TEM Lamellae Measurements

For analysing a cross-sectional view of crater impacts into aluminium and copper catchers with a TEM, such catchers are prepared during two different experiments. The ejecta from the shock compression experiments are collected at the LULI and ELI facilities in similar setups. This was essentially identical to the setup displayed in Fig. 1.3, despite no backlighter nor high-speed camera was used.

At the LULI facility, a PET target is compressed with a single shock and an aluminium plate catcher of dimensions $25 \times 25 \times 1 \text{ mm}^3$ is mounted at a distance behind the PET sample. The ejecta of a single shot is collected in the catcher, which was polished to have a smooth surface. At the ELI facility an aluminium plate of thickness 0.3 mm was used, collecting the ejecta of a total of 54 shots. An additional copper catcher was used at the ELI facility to collect the ejecta of 51 shots. The high repetition rate of the ELI facility (one shot in about three minutes) makes the collection of multiple shots on the same catcher possible. This increases the chances of finding ND candidates in the TEM lamella. The high repetition rate has been made possible by the recent development of a tape target [215].

For the LULI aluminium and the ELI aluminium catcher plates, one TEM lamella is prepared each. For the ELI copper catcher, two lamellae are cut. The lamella preparation process is outlined in Sec. A.8. The copper catcher was actually intended as a pinhole, used with a different catcher material, however, due to misalignment all ejecta is collected in the copper (see Fig. A.20). Tab. 3.1 shows the key parameters for ejecta collection with the two different catchers. All lamellae have been prepared with help by A. Worbs from HZDR.

Catcher	Laser Intensity (TW cm^{-2})	Pulse Duration (ns)	PET thickness (μm)	Catcher mounting distance (mm)	Number of Shots	Number of Lamellae
LULI-Al	6.35	5	100	60	1	1
ELI-Cu	3.0 ^a	5	75	30	51	2
ELI-Al	3.0 ^a	5	75	10	54	1

Table 3.1.: Parameters for collecting catcher samples at the LULI and ELI facilities from shock-compressed PET.

^aThe laser intensity is calculated from the target laser energy and the FWHM beam diameter. Because multiple shots are taken and the energy fluctuated, the target value is reported here.

After cutting the lamellae, they are analysed with a TEM in scanning and normal mode. To identify possible ND candidates, promising features are mapped in normal mode and later studied in detail using scanning mode, which offers higher resolutions. Here, two-dimensional Fast Fourier Transformations (FFTs) of the entire images, or the identified Region Of Interests (ROIs) are performed. The FFT is able to identify the frequency components most prominent in the image. A TEM is able to resolve individual atoms and the frequency components of the FFT are thus equivalent to lattice planes of the crystal. Therefore, the FFT images can be a very good measure for identifying diamond candidates. EDS is also performed on the cross-sectional slices to obtain an atomic mapping of the cross section.

The TEM images of the lamella from the LULI experiment are taken with the help of R. Hübner and A. Worbs at HZDR on a Titan 80-300 (FEI), while the ELI lamellae are recorded together with K. Oldenburg at the Center for Interdisciplinary Electron Microscopy Mecklenburg-Vorpommern (ELMI) on a Jeol JEM-ARM200F NeoARM.

3.3.2. TEM in Solution

The lamella preparation process is very delicate and time consuming. Simultaneously metallic catchers have a high density, decreasing the probability of ND survival upon impact. An ionic gel was used, to produce a catcher that has a low density and is simultaneously easy to dissolve.

Ionic liquids are liquids that consists of charged particles, essentially molten salts. Because the Coulomb forces in ionic liquids are strong compared to the forces in regular liquids, they have extremely low vapour pressures. This means, they do not evaporate in vacuum, making them ideal catcher candidates. However, a liquid is difficult to use in a horizontal beamline setup because it can not be mounted without spilling. Although attempts at mounting liquids horizontally with the use of self-healing membranes are made during this work, they remain unsuccessful.

Ionic gels are much easier to handle than ionic liquids. Ionic gels are essentially ionic liquids with a higher viscosity and can thus be mounted horizontally. They are made by adding a substance that can create a three-dimensional cross-linking network to an ionic liquid. Such ionic gels have been used in a context where water soluble, biocompatible films are required [216]. Because many application of NDs are in the field of biomedicine, a biocompatible catcher material would be a big advantage.

In this work, ionic gels are synthesised similar to Ref. [216] from $[\text{MTEOA}]^+[\text{MeOSO}_3]^{-2}$ and Polyvinyl Alcohol (PVA) in varying ratios. The synthesis procedure from [216] was adapted and different options for ionic gels synthesis were explored. This synthesis was conducted with P. Böhringer as part of a Bachelor thesis project [217]. A total of five different ionic gel samples are used as catchers at the ELI facility. The laser parameters are set to a square pulse of 5 ns with a nominal intensity of 3 TW cm^{-2} within the FWHM. The target is a PET tape of $75 \mu\text{m}$ thickness. The shock timings in conjunction with the PET Hugoniot, would place the samples at about 80 GPa and 3800 K [201]. The ejecta of between 35 and 133 total number of shots are collected in the catchers, which are mounted 2 cm behind the target. A picture of an ionic gel catcher just before mounting and after it was shot can be found in Fig. A.24a and A.24b.

After ejecta collection, the ionic gels contain the potential ND candidates. The ionic gel catchers are dissolved by repeatedly adding distilled water, sonicating to disaggregate ND clusters, centrifuging to sediment the NDs, and removing the supernatant to yield a clean, concentrated aqueous sample of potential NDs. During the process the centrifuge speed is changed to make sure all visible particles did sediment. For alter analysis of the suspension with the TEM grid, the impurities need to be minimised. Therefore, the suspension is cleaned with nitric acid which is washed out with isopropanol and distilled water. The laboratory protocol for the procedure can be found in Tab. A.6.

After the final removal of the supernatant a concentrated suspension is obtained. This is sonicated for a few minutes and $3 \mu\text{L}$ of the suspension are placed on a lacey carbon film on a copper TEM grid. The preparation process is outlined in Tab. A.7.

Following the preparation of the TEM grid, the dissolved catchers are studied at the ELMI TEM, again in normal and scanning mode. Additional EDS mappings are performed where interesting structures are found on the grid. The EDS measurements yield spectra showing the characteristic elemental composition and relative abundances at each scanned spot. These spectra are analysed for elemental composition. While the procedure yields absolute detector counts, it primarily provides relative abundances. Peaks of little relevance (e.g., copper TEM grid) are excluded during analysis. The EDS analysis is performed with the Joel Analysis Station software. The TEM and STEM images are studied by identifying crystal reflections in the two dimensional FFT as described above. Finally EELS spot measurements and mappings (core- and low-loss regime) are performed, due to their ability to distinguish diamond and non-diamond carbon (compare Sec. 2.4.4).

²Tris(2-hydroxyethyl)methylammonium methylsulfate with sum formula $\text{C}_8\text{H}_{21}\text{NO}_7\text{S}$.

3.3.3. Raman Spectroscopy

To find ND candidates in the recovered catchers, the Raman setup at the University of Rostock is utilised. It uses an excitation laser of $\lambda = 532\text{ nm}$ with a maximal intensity of 100 W adjustable via a filter wheel with a spot size of $\approx 1\text{ }\mu\text{m}$. The scattered signal is collected in backscattering geometry on a triple grating spectrometer equipped with a CCD detector. The catcher samples are mounted on an xy -stage to probe different parts of the catcher. Two different catcher types are studied in the Raman setup with the help of A. Bergmann-Iwe and T. Korn. One catcher type are aluminium plates of a purity of 99.999%. The aluminium catcher was the same as studied in Sec. 3.3.1. The second type of catchers studied with Raman, are gel catchers which consisted of a glass tube filled with commercially available candle gel. It consists mainly of paraffin wax and has been used in previous recovery experiments due to its continuous structure that allows for a "soft landing" of the ejected material [218, 219]. Spikes in the spectra as a result of cosmic rays hitting the detector are removed in the process. The Raman spectra are analysed in regard to the presence of potential ND signatures according to the features outlined in Sec. 2.4.1.

3.3.4. High-Speed Camera Imaging

To determine the shock conditions in a material, a measurement of one of the quantities in the Hugoniot Eq. 2.4-2.6 is required. As mentioned, this is usually the shock or free surface velocity. Such a measurement, however, requires an unobstructed view on the rear side of the target. In a typical recovery experiment setup, such a line of sight is usually obstructed by the catcher. Therefore, this work explored the possibility to measure the free surface velocity not from the surface directly, but by using a ultra-high speed camera Shimadzu HPV-X2 in a perpendicular setup (compare Fig. 1.3). This is intended to image the released material's velocity to determine its impact velocity on the catcher. One shot is taken with the camera but without a catcher, allowing for a simultaneous VISAR measurement. Comparing the VISAR results with the ultra-high-speed camera data then indicates whether the optical camera alone can accurately determine the shock state.

Similar to the setup in Ref. [37], a laser backlighter is positioned on the opposite site of the camera to visualise particles, which do not emit light by themselves. The frequency of the backlighter is synced to the camera shutter. A sketch of the experimental setup can be found in Fig. 1.3. However, in this work, the catchers are placed at distances of several cm behind the sample, to have an unobstructed view of the release front.

The velocity is determined by measuring the position of the release front in each frame and fitting a linear function through the data points. Details for the experimental procedure can be found in Sec. A.10.

3.3.5. Cratering Landscape Measurements

After impacting a solid catcher, the ejecta will produce craters on the surface. The results by Price et al. suggest that by studying the morphology of the craters (given the impact velocity is known) conclusions about the impactor's density might be drawn (see Sec. 1.2.2).

To prove the sensitivity of the crater landscape to the presence of NDs in the ejecta, two shots on aluminium catchers are compared, using different target materials. One shot was on PET shocked to the diamond formation region, and the second was on PS at slightly higher pressures, where it does not form diamond [7, 6]. As mentioned in Sec. 1.2.2 the ratio of crater diameter to crater depth of single particles impacting the catcher can provide information

about the impactor's density. This can help differentiate between NDs and amorphous carbon or graphite impactors. In both cases the same type of highly polished aluminium sheets (compare Sec. 3.3.3) is used as catchers at the LULI facility, collecting the ejecta of a single shot.

The impact velocities are estimated from the shock state and the velocity doubling rule using HDS in HELIOS. The shocks are simulated using the ProPacEOS for $\text{C}_5\text{H}_4\text{O}_2$ for PET, and CH for PS, using a multiplier of 0.7, which agreed well with other samples of the same type shot during the experiment. The impact velocity is estimated by using the pressure of the HDS results combined with the particle velocity from published Hugoniot data of PET and PS [201, 220].

The catchers are analysed using an AFM to measure the catcher surface morphologies. The measurements are taken on a Park NX20 AFM with a PPP-NCHR cantilever in non-contact mode. This allows for an accurate measurement of crater diameters and depths. This analysis built upon work that has been conducted for a Bachelor thesis by J. Kuhlke [114].

Additionally, the catchers are analysed with a confocal microscope. Although a confocal microscope falls short of an AFM's resolution, it can be operated on a much larger area, scanning the entire catcher surface. Even though the confocal microscope's resolution is not capable of resolving the impacts produced by singular NDs, it could help to determine the average densities of impacting conglomerates. It is likely that the NDs will be impacting as part of conglomerates with other released material. Their presence (PET) or absence (PS) therein would change the densities and thus the observed crater shapes.

To analyse the large amount of craters, the confocal microscopy data is processed automatically. First a mean plane is subtracted to level the data. Secondly, to find craters in the images, the Segment Anything Model 2 (SAM2) by Meta AI is used, which has been proven to be effective in segmenting craters in satellite images [221, 222]. The model parameters used in this work can be found in table A.9. In contrast to satellite images, the confocal microscope is able to actually measure depth values of the catcher surface. Therefore, to segment the craters, each image is split into five different sub images equidistantly split in height between the lowest and highest point of the surface. Every pixel value outside the depth range is set to zero in the respective image. This proved to be better at differentiating craters, as it restricts the segmentation algorithm to a narrower depth range.

Thereafter, for each of the five images, the SAM2 model is used to determine distinct feature masks. Each mask is post-processed in regard to the depth information of the corresponding image, shape, and area to determine whether it is likely to be part of a crater. Because five layers of masks are obtained, the different layers are combined to merge potentially overlapping craters. Details of the entire procedure can be found in Sec. A.11. After segmenting the probable crater candidates, their crest diameters (under the assumption of spherical crater shape) and the maximal depths are calculated.

Using the phenomenological functions from Price et al., the theoretical crater diameter and depth values for the impact velocities are calculated. This is done for three different material densities: diamond (3.5 g cm^{-3}); amorphous carbon (2.0 g cm^{-3}); and graphite (2.25 g cm^{-3}). The obtained crater statistics can be found in Fig. 3.5. Using typical parameters for impact velocity and ND diameter, and assuming a Gaussian distribution for both quantities, the crater characteristics for these three densities are forward-calculated to be compared with the measurements (see Sec. A.11).

To summarize, two different samples are shocked into the diamond formation region (PET), and outside of it (PS). The ejecta of both is collected in the same type of highly polished Al

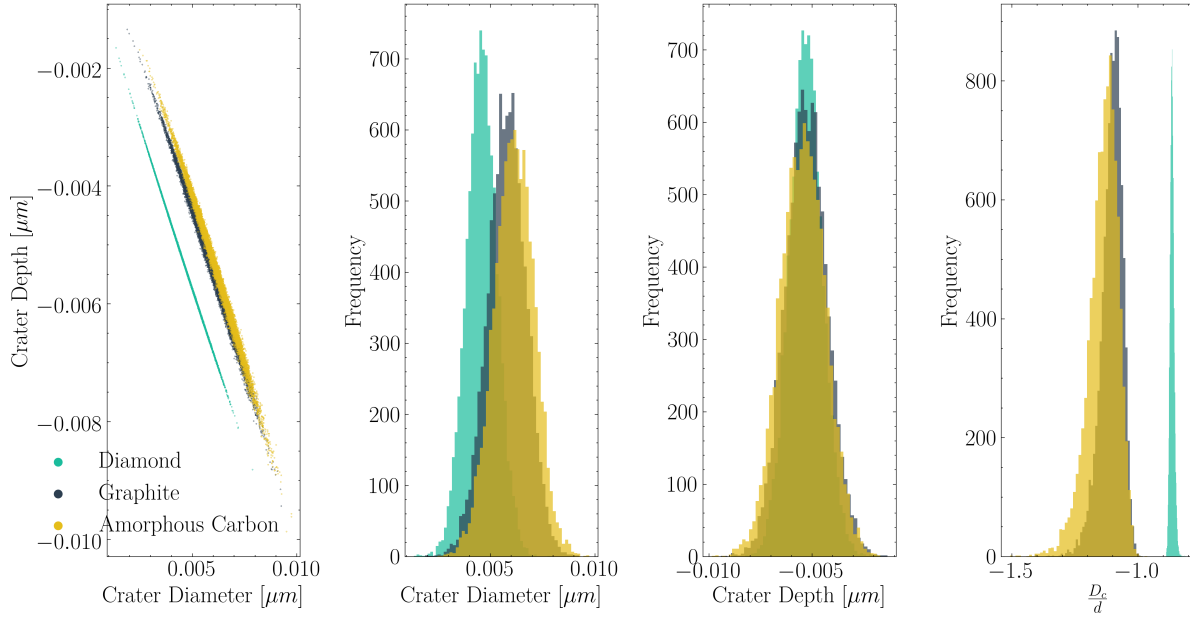


Figure 3.5.: Simulated crater statistics for diamond, graphite and amorphous carbon impactors from the phenomenological functions given in Ref. [113]. While the crater diameters and depths themselves make distinguishing impactors quite difficult, the dimensionless ratio is well separated. Details about the simulated velocity and size distributions can be found in Sec. A.11.

catcher. Those catchers are studied by a confocal microscope and with an AFM to determine the crater shapes. Additionally, forward calculations for crater shapes resulting from different impactor densities are performed. The experimental results can be compared to the theoretical predictions, to determine impactor characteristics.

3.3.6. High-Repetition Rate Design

Because the amount of NDs per shot is in the order of μg it is necessary to use high-repetition-rate lasers and targets. The requirements for such a target are that a new target can be mounted in vacuum without interfering with the catcher. The target is required to have an in-focus stability that is sufficient to achieve the laser intensities that are required for ND nucleation conditions in the target. The design developed in this work in conjunction with the University of Rostock workshop is essentially a simplified version of the design used by the ELI-Beamlines facility published in [215]. It is a tape target and was also used to obtain some of the catcher samples studied in this work. Sec. A.12 shows an image of the tape target drive.

To test the in-focus stability of this target, a Basler acA5472-17um camera with a zoom lens in perpendicular geometry is mounted. The tape is then moved via the attached step motor for a defined number of steps (10, 50, 100, 200). After each movement a snapshot of the tape is taken. A total of 100 motor-step-image sequences are taken for each number of steps to see if the step number affects the stability. In the design, the tape is not fixed in the horizontal direction. Therefore, when imaging it from the side, it can move in the direction-of-view. This can affect the measurement when using a method relying on optics and a narrow field of view. To see this effect, the measurements were repeated with a makeshift boundary that fixed the tape in horizontal direction.

The images have been automatically analysed by thresholding the image with a value of $0.7\max(\text{pixels})$, to only obtain those pixels that are part of the tape (for details see Sec. A.12). After the tape pixels were identified, the position of the laser-side edge of the tape was determined via a calibration image using a reference scale. This resulted in a distribution of laser-side edge positions of the tape target.

After detailing the simulations and experimental setups used to study the formation, release, and impact dynamics of NDs, the following chapter presents and interprets the results obtained through these methods.

4. Results and Discussion

This chapter presents and discusses the results of the simulations and experiments, following their order introduction in Ch. 3. It begins with the MD simulations and release experiments of NDs formed during shock compression, continues with the recovery experiments, and concludes with the high-repetition rate implementation attempt at the University of Rostock.

4.1. Molecular Dynamics Expansion Simulations

This section presents the results of the MD simulation of NDs releasing from compression states, as described in Sec. 3.1.1. After the equilibration at high pressures and temperatures, the NDs expand into the vacuum. The simulations are halted when zero pressure is reached in the simulation. This takes longer, the higher the initial pressure. The release times range from $t_{\text{release}} = 66.95$ ps to $t_{\text{release}} = 197.8$ ps.

4.1.0.1. On-Hugoniot States

As the density is decreasing, so do pressure and temperature of the diamond. Fig. 4.1 shows how the density, pressure, and temperature evolve as the spatial constraints are expanded. From Fig. 4.1a it is clear that with increasing initial pressure, the rate at which the pressure drops is also increasing. In the most extreme case ($P_{\text{init}} = 122$ GPa at 5000 K), the initial rate is as high as $dP/dT = 2.55$ GPa ps⁻¹ and decreases to a $dP/dT = 1.5$ GPa ps⁻¹ in the $P_{\text{init}} = 42$ GPa at 2000 K simulation.

The density decrease is simply determined by the box volume, strain rate, and initial conditions (compare Sec. A.2 for details on the strain rates). Due to the different release times to zero pressure, the final densities differ depending on the initial state. The higher the initial pressure, the more the box needs to expand to release to zero pressure. Because the pressure fluctuates, the equilibration pressure at the end of the expansion is not exactly zero immediately.

The temperature evolution in Fig. 4.1c, similar to the pressure show decreased reduction over time, with the highest cooling/pressure release just at the beginning. The cooling rates are substantial and range from 1.8×10^{12} K ps⁻¹ to 7.6×10^{12} K ps⁻¹ on average, consistent with sim-

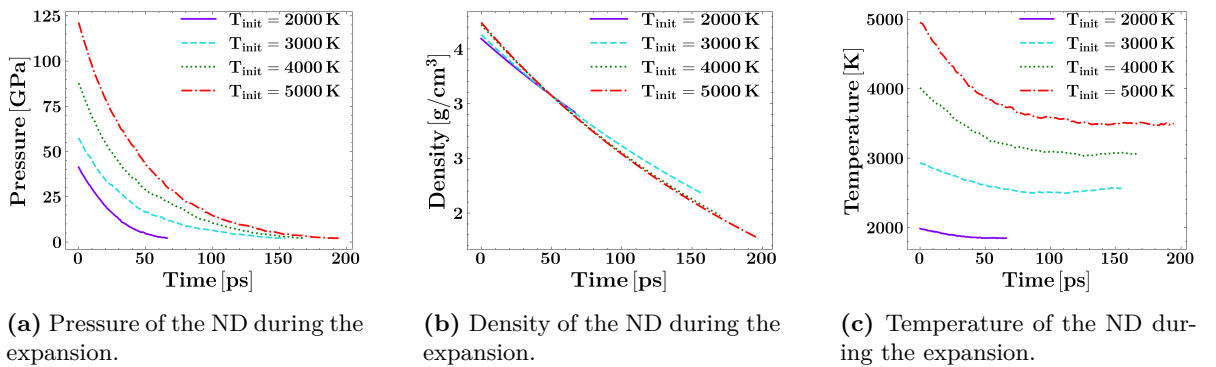
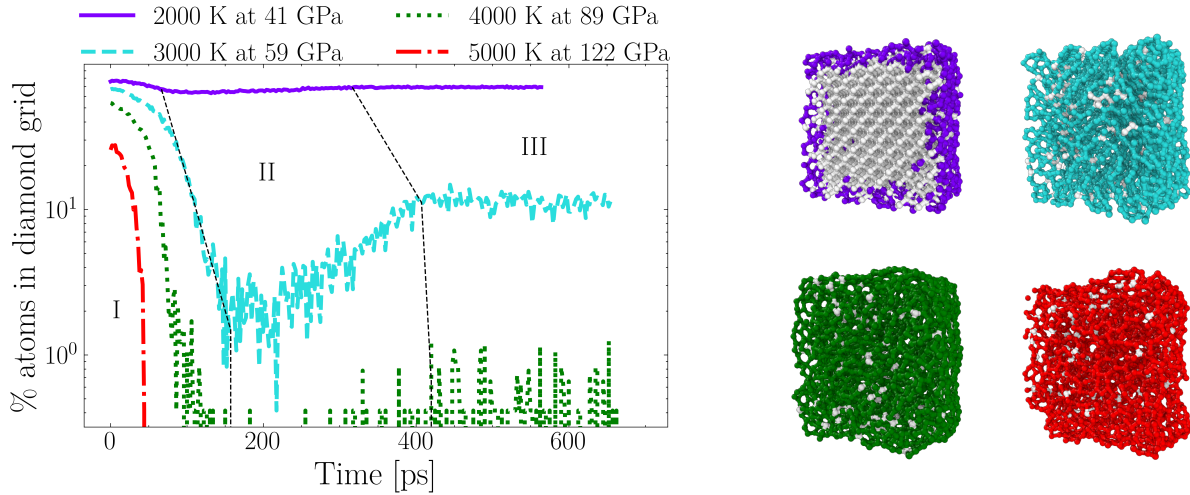


Figure 4.1.: Evolution of thermodynamic quantities in the ND during the expansion process. As the spatial constraints are expanded, more volume becomes accessible to ND and the pressure temperature and density decrease.



(a) Percentage of atoms in the diamond phase determined by CNA in logarithmic scale. The different phases of Expansion (I), Cooling (II) and Equilibration (III) as described in Sec. 3.1.1 are separated by dotted lines. Less compressed states result in more diamond atoms and significant recrystallisation during the Cooling phase can be seen in the 3000 K simulation.

(b) Snapshots after the Expansion phase (I). The atoms that are in the diamond lattice are coloured in grey. The other carbon atoms are coloured according to the initial simulation conditions.

Figure 4.2.: Results of the MD simulations for the release of ND from the different compressed states.

ilar MD studies on nanoparticles [223]. Higher initial temperatures result in higher cooling rates. Since higher initial temperatures also require longer release times, the expansion cooling is greater for more compressed states. While the least compressed state only drops about $\Delta T = 140$ K the most compressed state cools by $\Delta T = 1500$ K. This drop in temperature is attributed to the volume work that is done by the expanding system against the surrounding pressure. The higher the pressure, the more work is required to expand, leading to greater cooling.

An key property in terms of recovery is the effect of the initial state on the amount of diamond after expansion. Fig. 4.2a shows the percentage of atoms in the diamond phase as a function of time for all initial conditions. The three different phases are separated by dotted lines. The number of carbon atoms in the diamond phase drops sharply during the expansion phase (I) for all scenarios, except in the 2000 K simulation. Here, the diamond atoms remain almost constant around 70%. The NDs are disintegrating completely during the expansion starting at 5000 and 4000 K. Only a few percent remain intact for the 3000 K scenario. In the simulations, in which some atoms remain in the diamond phase, the cooling phase (II) shows substantial recrystallisation of atoms to the diamond phase. Such recrystallisation does not occur in cases where no diamond atoms remain. This is because the spontaneous formation of a new phase is highly unlikely, while recrystallisation in presence of a nucleus is not (compare Sec. 1.2.1).

The disintegration of the NDs during the expansion phase starts at the surface, which is visible in Fig. 4.2b. In the 2000 K simulation the atoms on the surface are not part of a diamond lattice, while the core remains in the diamond phase. According to the simulation results, almost the entire diamond should disintegrate quickly after breakout for shock states releasing from temperatures exceeding 2000 K.

The remaining carbon that is not part of the diamond phase after the expansion shows clear signs of graphitisation. This is directly visible in the form of hexagonal carbon rings on the surface of the cubes. This graphitisation starting at the outer walls and forming layers results

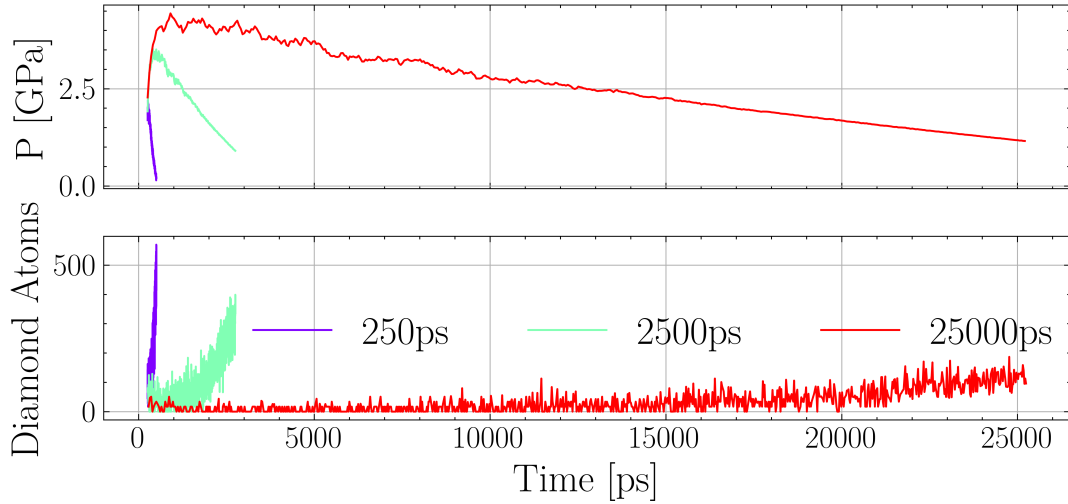


Figure 4.3.: Comparison of the different cooling times. Time evolution of the pressure as well as the number of atoms in the diamond phase. All simulations were performed on the 3000 K state because here the recrystallisation feature was most prominent. Each simulation was divided into 500 chunks for which the average values were computed. The graphs do not start at $t = 0$ because they start after the Expansion phase.

in an onion-like shell structure around the NDs. Such structures have also been the result of both, theoretical predictions and experimental campaigns [224, 116, 225].

During the Cooling phase (II) - given some diamond atoms remain - the elevated temperatures can result in partial recrystallisation of diamond. In the simulation, the system is cooled to room temperature over 250 ps. To assess the effect of the cooling rate on the recrystallisation, the 3000 K state after release is cooled over different times. A comparison of the different cooling rates is shown in Fig. 4.3. Compared to the reported cooling time of 250 ps, the slower cooling simulations show a reduction in the final amount of diamond atoms by a factor of 2 and 5 for cooling times of 2500 and 25000 ps respectively. For those slower times, the pressure also rises sharply, just after the cooling started. This rise does not occur with the fastest cooling simulation. In the fastest cooling rate, the dampening of particle movement is sufficiently fast, to compensate for the increase in pressure the system experiences by the box constraints. The faster the cooling, the faster the atoms get stuck in the local minimum of the ND lattice. The cooling rates corresponding to cooling over 250, 2500, and 25000 ps are $8.8[\times 10^{12}, \times 10^{11}, \times 10^{10}] \text{ K s}^{-1}$ respectively.

To put the cooling rates into context, a naive radiative cooling simulation is performed. The results for a constant heat capacity and the temperature dependent model are shown in Fig. 4.4. For a particle starting at 5000 K, cooling to 4000 K only takes about 500 ps. The average cooling rate over the first 2 ns is $3.6 \times 10^{11} \text{ K s}^{-1}$ and therefore close to the cooling simulation over 2500 ps.

The second Equilibration phase (III) in Fig. 4.2a shows the number of atoms in the diamond phase to be constant. This indicates that once the system has cooled and expanded, further modification of the remaining ND structure does not occur.

4.1.0.2. Off-Hugoniot States

The results for the expansion simulation of the two off-Hugoniot states at higher (super-Hugoniot) and lower (sub-Hugoniot) pressure are displayed in Fig. 4.5. The simulations show

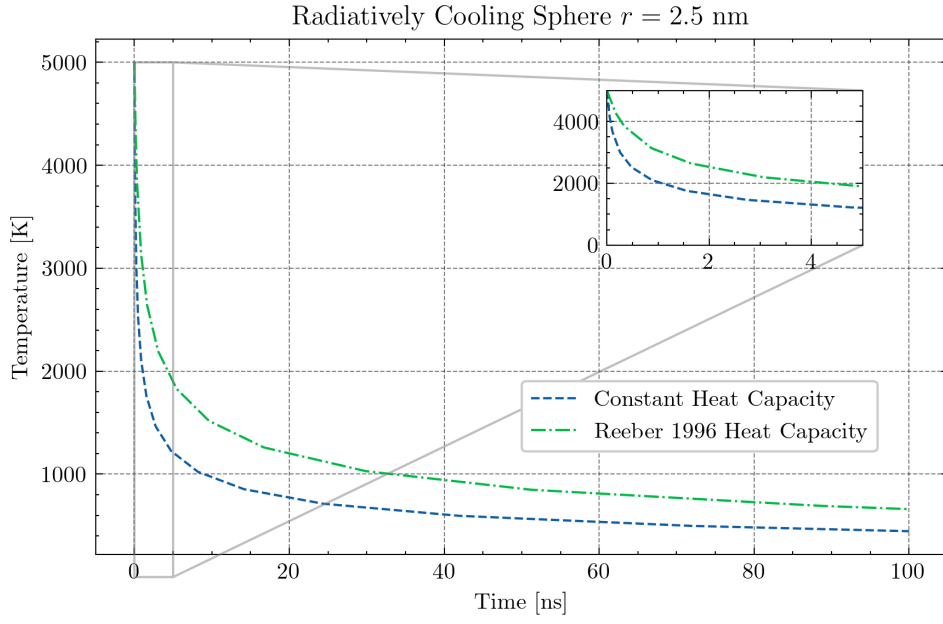


Figure 4.4.: Radiative cooling simulation of an ND sphere using a constant heat capacity of $c = 515.6 \text{ J g}^{-1} \text{ K}^{-1}$, as well as a model taking the temperature dependent heat capacity values from Ref. [226].

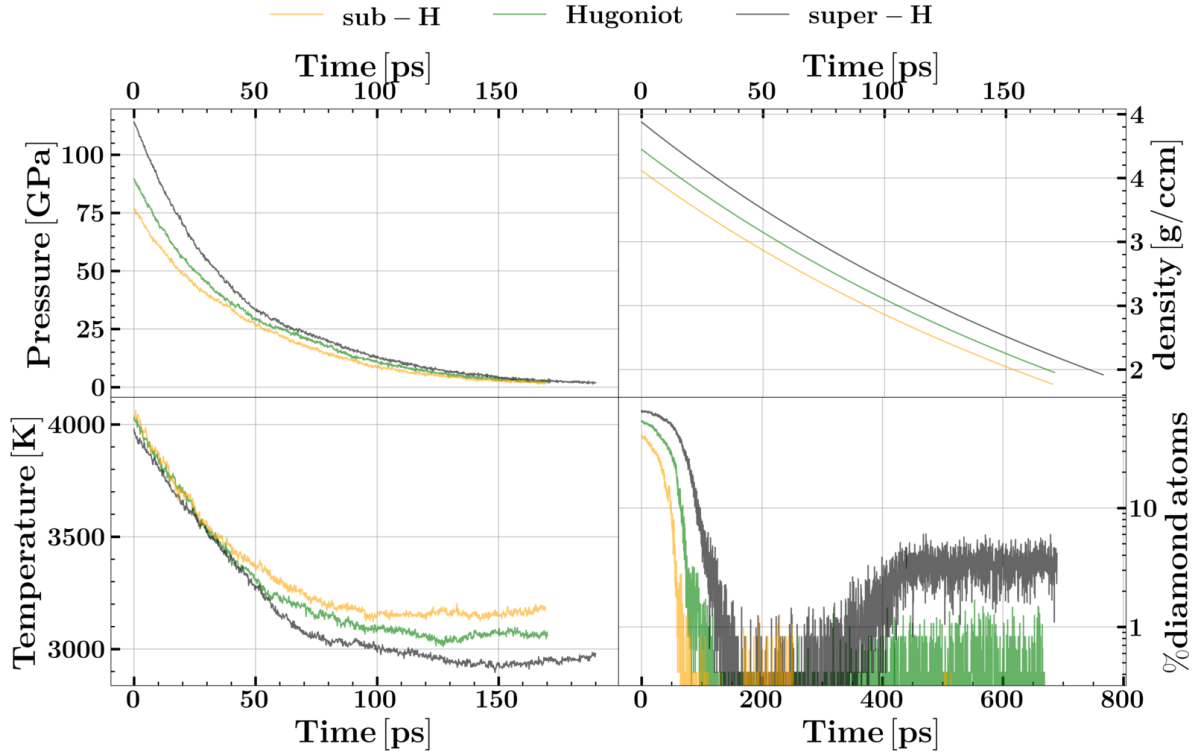


Figure 4.5.: Simulation of the expansion of an ND from the sub- and super-Hugoniot states compared to on-Hugoniot states. From the top right, counter clockwise, the density, pressure and temperature evolution are displayed during the expansion to zero pressure. The bottom right shows the percentage of atoms in the diamond lattice during the Expansion, Cooling and Equilibration phase. The y -scale in the last plot is logarithmic and the x -axis shows a longer timespan than the other plots to incorporate the additional two phases.

that the pressure releases notably faster from the super-Hugoniot state than from the sub-Hugoniot simulation. The final temperatures differ depending on the initial pressure. For the super-Hugoniot simulation, the system cools to a lower final temperature than the on-Hugoniot state. The opposite is true for the sub-Hugoniot state. The percentage of diamond atoms at the beginning increases with the initial pressure. This can be attributed to the stabilising effect of pressure on the diamond phase. For all three simulated states at 4000 K, the number of diamond atoms post-expansion effectively drops to zero. However, during the cooling simulation a much higher recrystallisation rate is observed for the super-Hugoniot state. The sub-Hugoniot state shows essentially no recrystallisation.

The super-Hugoniot state shows a higher recrystallisation rate than the Hugoniot state. This may result from faster cooling due to the higher initial pressure, which leads to less atomic disorder and atoms being closer to the ideal diamond lattice positions (quenching). A more ordered post-expansion state increases the likelihood of recrystallisation into diamond upon cooling. In contrast, the sub-Hugoniot simulation cools more slowly, giving the system more time to escape the local minimum of the metastable diamond phase (annealing).

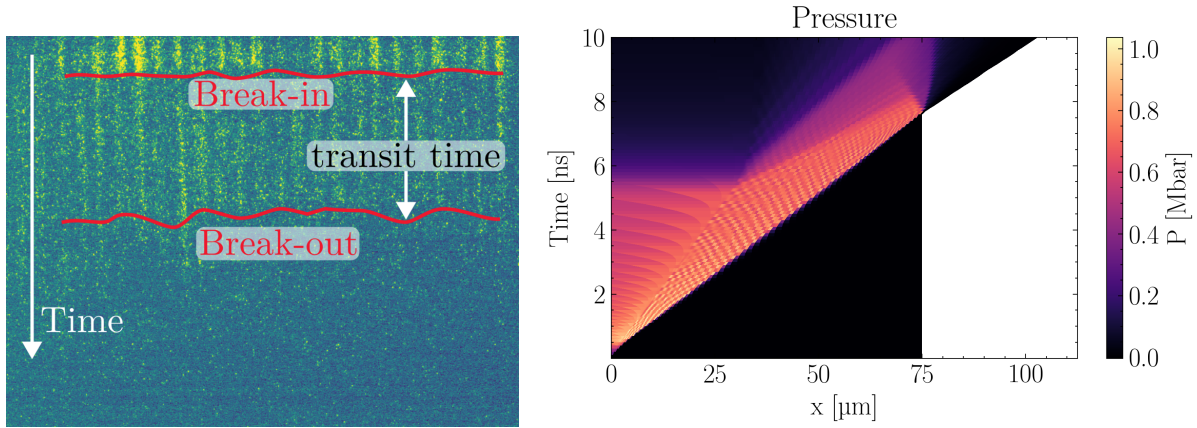
The Hugoniot states releasing from temperatures exceeding 3000 K show little to no diamond after the expansion. This is in clear contrast to the experimental results presented below (Sec. 4.2), where NDs could still be found even 10 ns after breakout, releasing from about 4000 K. A reason for this discrepancy might be the fact that in the actual experiment, the NDs are not released individually but are part of a plasma release cloud. The surrounding material could shield the ND core and mediate the expansion process such as to mitigate damage to the NDs. This could be evaluated by explicitly modelling the release cloud in the MD simulation, in the form of hot material surrounding a ND. Even though the WDM conditions could require a more accurate approach than standard MD potentials to model C-H-O interactions in the surrounding material, a qualitative estimate for the effect on ND stability during release could be obtained by conventional interaction potentials.

The chosen interaction potentials are another important reason for possible discrepancies to experimental results. The simulations cover a large thermodynamic regime from ambient conditions up to thousands of K and hundreds of GPa. Although the employed potentials are chosen with care for their properties as described above, they are likely unable to predict the interactions perfectly across the entire domain. However, due the reasons given in Sec. 2.1.1 they should still be sufficient to give a qualitative idea of which conditions might favour or inhibit ND recovery.

In summary, this section presented MD simulations of NDs releasing, cooling, and equilibrating from on- and off-Hugoniot states for temperatures from 2000 to 5000 K. It was found that in all cases, where the initial state exceeded 2000 K, the NDs are mostly melting upon pressure release, even though substantial expansion cooling of up to 1400 K is observed. Recrystallisation can occur and is favoured in above Hugoniot pressure states. Therefore, this work suggests that super-Hugoniot states achieved by, e.g. double shocks could increase the probability of ND recovery.

4.2. X-ray Diffraction of Releasing Nanodiamonds

The results for the analysis of the XRD data taken during the two shock compression experiments of PET at the SACLA and EU-XFEL facilities are discussed in this section. The experimental parameters for the respective experiment are found in tables A.3 and A.4. While the experiment at the SACLA facility used single shocks on PET, the one conducted at the



(a) VISAR image of a single shock travelling through the PET target shot at the SACLA facility. The initial drop in reflectivity is an indicator of the drive laser hitting the target. The final complete loss in reflectivity stems from the destruction of the rear surface. The transit time can be used to determine the shock conditions if the Hugoniot is well-known.

(b) HDS of the single shocked PET. The breakout time was matched to the VISAR data by applying a multiplier. The drive laser only lasts for 5 ns, thus front side release is visible before the shock has traversed the entire sample. The peak pressures in the PET reach about 70 GPa.

Figure 4.6.: Experiment and HDS of the PET target shot at the SACLA facility. The signal quality of the VISAR image is poor and results in large error bars in transit time.

EU-XFEL focussed on double shock compression of PET. Both aimed at determining the after-breakout behaviour of NDs and determine the ND sizes.

SACLA Experiment

The SACLA experiment aimed at analysing the properties of NDs forming and releasing in PET targets at on-Hugoniot conditions. To determine the shock conditions, transit times of the single shocks are measured with a VISAR. Fig. 4.6a shows the image of a single shock and how the transit time is determined. This transit time is used to determine the shock conditions in the sample using the well-known PET Hugoniot [201].

Additionally, the results are compared to HDSs performed with HELIOS. The SESAME EOS 07550 with opacity data PrOpacEOS data for $C_5H_4O_2$ is used. The ion and electron temperature in the simulation is forced to be equal and the multiplier was set to 0.35 to match the VISAR breakout time. The pressures from the shock speed and the HDS are 90 and 70 GPa depending on the shot, which corresponds to temperatures of 4300 and 3500 K from the Hugoniot. The VISAR quality is poor, thus determining breakout time is challenging, therefore yielding substantial uncertainties in pressure. However, the conditions on the PET Hugoniot are at the lower end of the diamond formation region according to [7].

The XRD signal after azimuthal integration is fit using the models described in Sec. 3.2.1. This includes a fourth order polynomial background, a Gaussian liquid peak, and three individual peaks for the diamond reflections. Fig. 4.7 shows the best fit to the diffraction signal. The pump-probe delay is set to 6 ns and the shock has not yet broken out. Therefore, the PET cold peak is still visible at $2\theta = 42^\circ$ and is included with another Gaussian peak. The three peak centres are used to determine the diamond density using the volume of the unit cell. The widths of the peaks are used to determine the crystallite sizes according to Eq. 2.17.

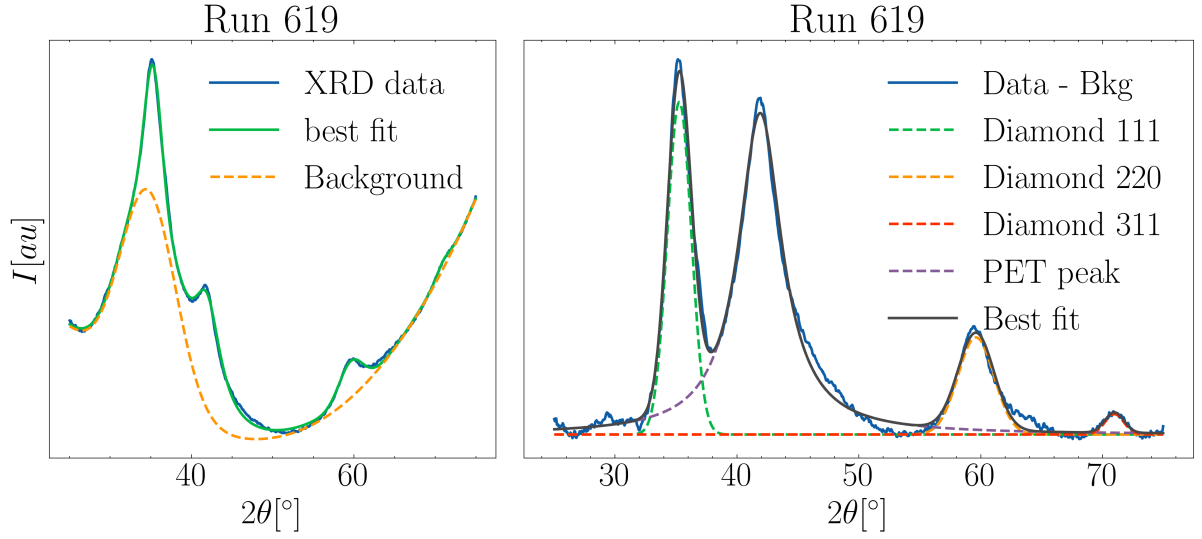


Figure 4.7.: Best fit of run 619 of shock-compressed PET during the SACLA experiment. The model contains a fourth order polynomial, a liquid Gaussian background and a Gaussian peak for each diamond reflection. The shot was not broken out and therefore the PET peak was still visible. The right plot shows the background subtracted data with the individual contributions.

A waterfall plot of the lineouts for different pump-probe delays is displayed in Fig. 4.8. The sample pressures are estimated from the breakout times to 70-90 GPa. The PET peak at the shortest delay is clearly visible. As the shock progresses, this peak disappears and the diamond peaks shift to lower q . This is because both the rear and front side of the sample are releasing, and the NDs expanding. This pressure release is accommodated by a decrease in density. At 6 ns delay, the diamond peaks are slightly broader and narrow down at 8 and 9 ns. At longer delays, the peaks are substantially wider and shift to lower q . The intensities of the higher order peaks are also decreasing with time. For all shots the (311) peak had a very low intensity and yielded large uncertainties.

The density and ND sizes determined from the peak centres and widths can be found in Fig. 4.9. The density before shock breakout is $3.59 \pm 0.01 \text{ g cm}^{-3}$, which is slightly above the ambient diamond density of about 3.52 g cm^{-3} , so only minimally compressed. This might be because the drive pulse only has a duration of 5 ns and the front side is already releasing. The probing beam passes through the entire shocked material, therefore the measured density is integrated over the partially released material. At later probing times the diamond density decreases to $3.35 \pm 0.01 \text{ g cm}^{-3}$ at 19 ns. This is a result of the elevated temperatures, and even at a pump-probe delay of 19 ns, about 11.6 ns after breakout, the thermal expansion is substantial. Overall, the densities after breakout show some fluctuations. This can be attributed to the difference in drive laser intensity, which showed substantial variations (compare Fig. A.12).

The estimated ND sizes in Fig. 4.9b show a growth of the ND up to 9 ns to diameters of $\approx 3 \text{ nm}$. After that, the size rapidly decreases to about $\approx 2 \text{ nm}$ and remains almost constant until the latest probing time at 19 ns. Comparing the growth to the shock dynamics obtained from the HDS (Fig. 4.6b), the time until the NDs are growing corresponds to the time when the two release waves are merging within the sample. Therefore, this could suggest that the NDs are growing as long as there is shocked material in the sample. However, the peak width is a superposition of all present diffraction domains. Thus, the width is dominated by the smallest crystallite domain in the probed volume. This suggests that even after the onset of front side release (5 ns), there is no immediate reduction in average ND size. To make accurate statements about the growth and shrinking dynamics, the average ND size is not enough and

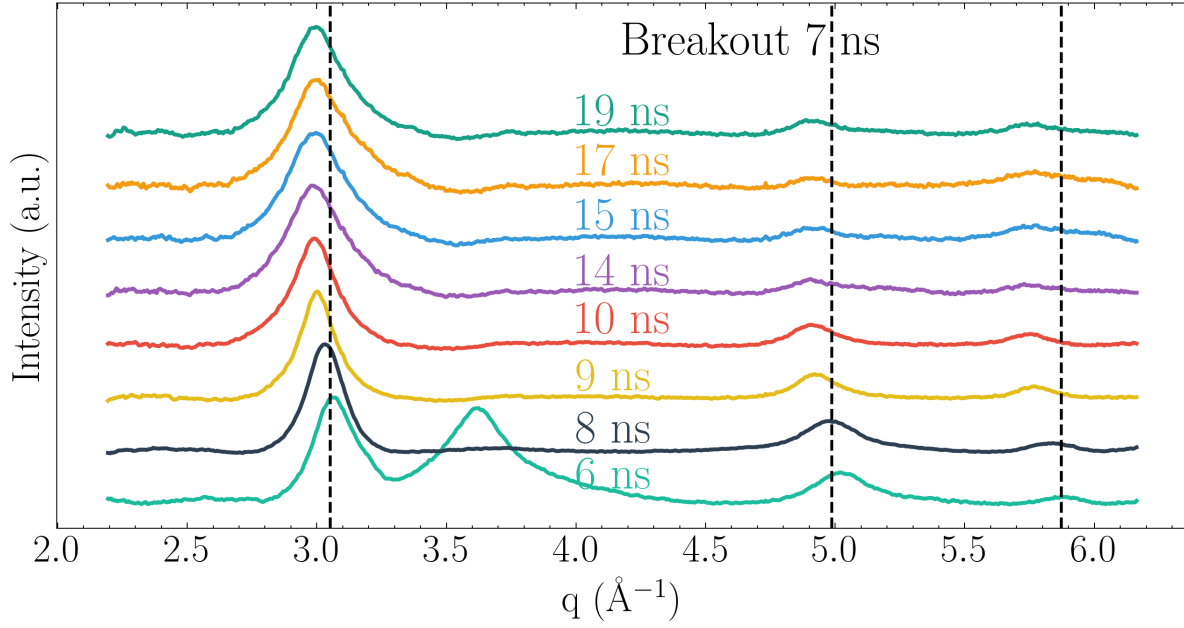
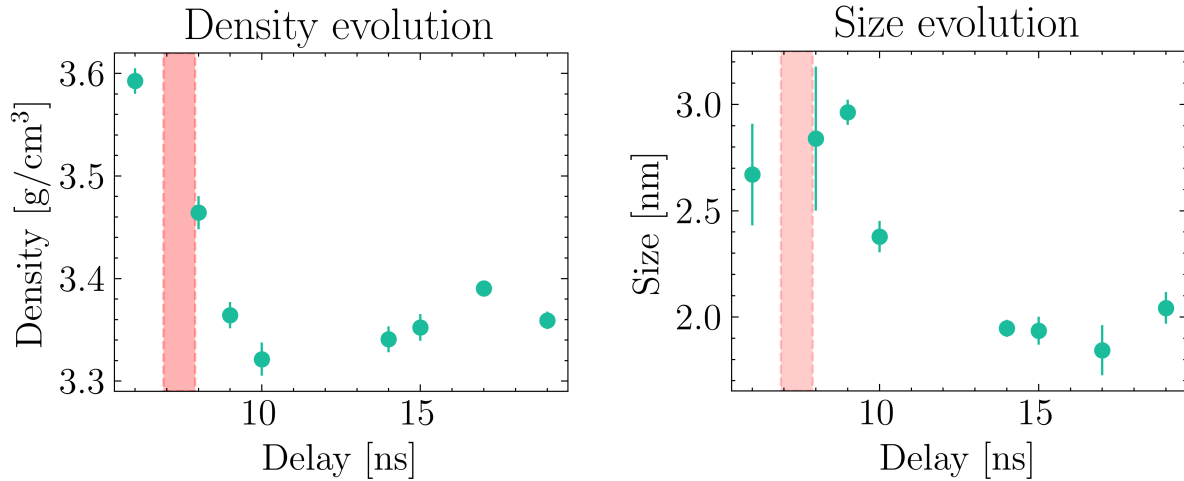


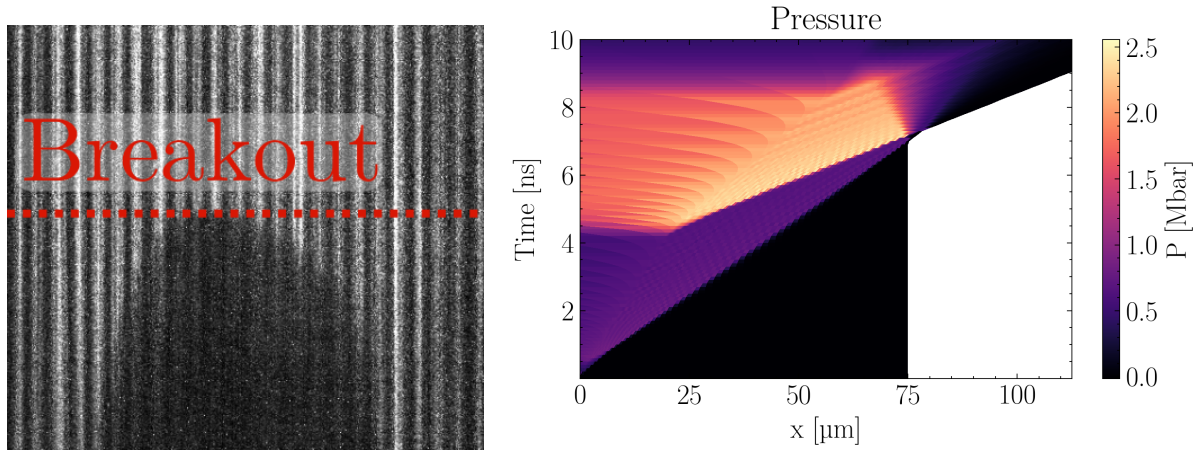
Figure 4.8.: Waterfall plot of the background subtracted (liquid and polynomial) at different pump-probe delays as a function of $q = 4\pi/(\lambda \cdot \sin(\theta))$. The measured breakout time for the different shots varied between 6.9 and 7.9 ns, placing the target at pressures between 70 and 90 GPa. The PET peak around $3 \text{ \AA}^{-1}$ is clearly visible in the shot at 6 ns pump-probe delay. The dashed lines show the ideal diamond diffraction signals for the (111), (220), and (311) peaks.



(a) Time evolution of the diamond density estimated from the diamond peak centres. The breakout time varied between 6.9 and 7.9 ns.

(b) Time evolution of the ND crystallite size estimated from the peak width according to the Scherrer formula in Eq. 2.17.

Figure 4.9.: Density and ND size estimates as a function of the pump-probe delay. The uncertainties were estimated from the MCMC modelling explained in Sec. 2.2.1. The corresponding posterior distributions can be found in Sec. A.6.1. The red region in the plots visualise the range of breakout times.



(a) ROI of the VISAR image of the double-shocked PET during shot 137. The field of view is much larger than the laser spot, therefore the transit time was determined by the earliest breakout time.

(b) HELIOS HDS of the double-shocked PET target. The breakout time was matched to the VISAR data by applying a multiplier of 0.75 to the laser intensity. The simulation used the ProPacEOS $C_5H_4O_2$ table.

Figure 4.10.: VISAR raw data and HELIOS HDS of shot 137 during the p4463 experiment at EU-XFEL. The shock breakout was at 6.9 ns.

a method is required to actually determine the size distribution during the shock like SAXS (see Sec. 2.2.2).

Nevertheless, the XRD results provide valuable information about the presence of ND up to 11.6 ns after breakout. Furthermore, they suggest that although some shrinking is observed after the shock release, the ND sizes remain stable at about 2 nm in diameter after release. The 3 nm ND diameter value in PET during the shock is slightly below values of ND sizes in PS [36], but compares well to previous SAXS studies on ND sizes in PET determined with SAXS [7]. The authors therein found the NDs to also grow after breakout up to sizes of about 4 nm. However, in that study, the actual size distribution was determined via SAXS and there are smaller NDs present after breakout, which would broaden the XRD peaks.

In summary, *in situ* probing of shock-compressed PET has confirmed the formation of NDs at on-Hugoniot conditions of 80 ± 10 GPa at 3900 ± 400 K. Although some decrease of the ND sizes after breakout was observed, the NDs remain stable long after shock release, making single shocked PET a promising material for laser-driven synthesis of NDs of single digit nm diameters. The presence of NDs long after release from the described Hugoniot states is in clear contrast to the complete melting of NDs, which the MD simulations described in Sec. 4.1.

EU-XFEL Experiment p4463

During the p4463 experiment at the EU-XFEL, PET targets were double-shocked to the diamond formation region. The properties of the NDs after shock breakout are determined. Fig. 4.10a shows a ROI of the VISAR image from which the breakout time is measured. This time is matched with the results of the HDS. The simulated pressures in the sample are presented in Fig. 4.10b. It is clear that the second shock reaches the rear surface shortly after the first shock. This means that, at the time just before breakout, almost the complete sample persists in the double-shocked state.

As the XRD data quality was very good, the full Rietveld refinement procedure was possible. Therefore, the shots are categorised into before and after breakout shots. The shots before

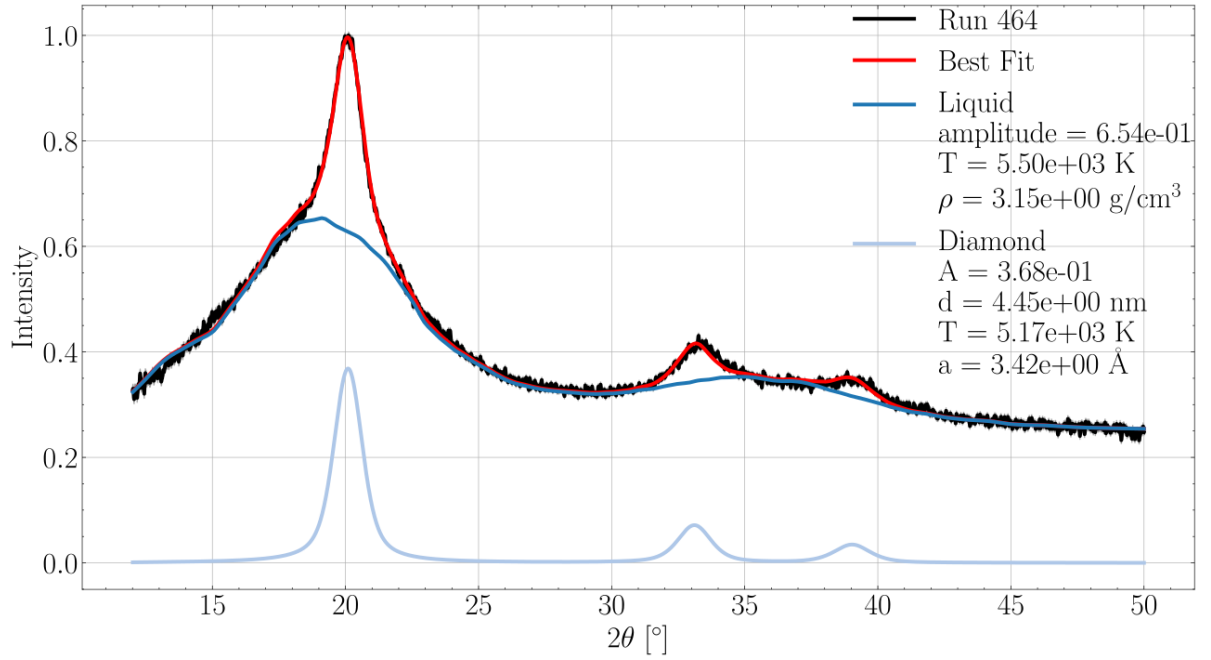
breakout are fit with the DFT liquid model, as described in Sec. 3.2.1 and in more detail in Ref. [125]. The after breakout shots are fit using the after breakout model described in Sec. 3.2.1.

Shots numbered 464 to 469 were aimed at investigating the diamond release dynamics. During these shots, the VISAR diagnostic failed, making it difficult to determine the shock state. However, the XRD lineouts still offer valuable insight into the conditions, both through comparison with liquid diffraction patterns (from the DFT simulations) and through analysis of the diamond lattice parameters. Shot 464 had a pump-probe delay of 10 ns. From the XRD data (Fig. 4.11a), it is clear that compressed material is still present, both from the shape of the liquid diffraction, as well as the positions of the diamond peaks. Even though the probing time is about 1.5 ns after the drive lasers stopped, the released material present in the sample is not dominating the XRD lineout. The shock conditions estimated from the liquid diffraction suggest a liquid temperature of $T = 5500$ K at a density of 3.15 g cm^{-3} . All background removed waterfall plots are shown in Fig. A.13

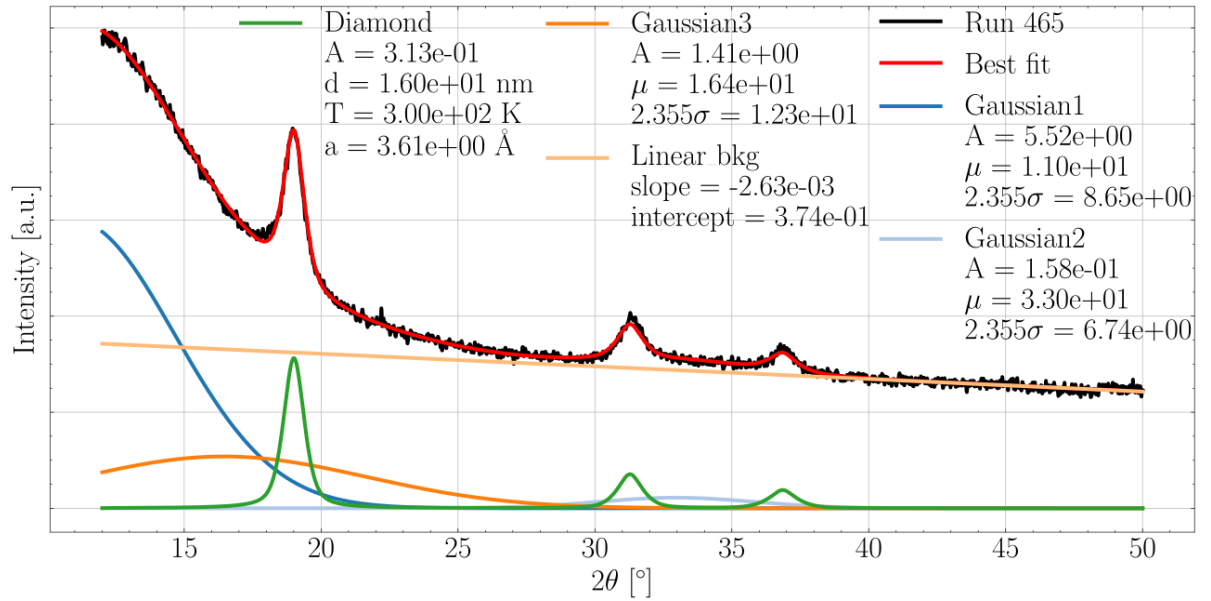
For an HDS to match these experimental conditions, the laser intensity multiplier was modified, until the breakout time was close to 9 ns and the density and pressure conditions were approximately those obtained from the DFT fit. This was achieved for a value of 0.6, which is similar to those multipliers required, to achieve good agreement of HDS and VISAR breakout times in shots where VISAR was available. Fig. A.15 shows the output of the HDS for the laser pulse, which facilitated diamond formation. Importantly, that the uncertainties in the EOS accumulate in a double shock. Therefore, the results of the HDS are simply presented to provide an idea of the double shock dynamics and to roughly compare them to the results from the DFT liquid fit. The uncertainties in pressure and temperature are estimated by changing the laser multiplier ± 0.1 . According to the HDS, the double-shocked state in PET would reach a peak pressure of about 150 ± 15 GPa at about 4000 ± 1000 K, 1500 K below the fit result. Since pressure and temperature gradients in the sample could smear out the liquids RDF, this could broaden the diffraction peaks. Such broadening can lead to an overestimation of the temperature via the XRD method. In any case, it is safe to say that in the double-shocked state, temperatures are comparable to those probed during the single shock experiments at SACLA but at substantially higher pressures.

The estimated densities and diamond sizes are shown in Fig. 4.12a and 4.12b. It is clear that at 10 ns the material is still highly compressed to a density of $3.995 \pm 0.001 \text{ g cm}^{-3}$, significantly higher than during the single shock at SACLA, and rapidly decreases to 3.38 g cm^{-3} . The final density in the double shock experiments is even higher than what was observed in the PET releasing from single shock conditions, suggesting lower density and less thermal expansion. The density after 15 ns is essentially constant, which means almost no cooling during that time.

ND sizes start at a diameter of $4.45^{+0.03}_{-0.03}$ nm at 10 ns. After breakout they rise significantly and reach values as high as $21.8^{+2.6}_{-2.0}$ nm at a pump-probe delay of 30 ns before dropping back to $11.5^{+0.8}_{-0.6}$ nm at 35 ns. Compared to the single shock experiment, it is clear that the ND sizes are substantially larger in the double-shocked PET. Even more, after breakout from the double-shocked state, the NDs seem to grow in diameter, while the NDs releasing from the single shock state were shrinking. Such increased recrystallisation for a double-shocked state is exactly what the MD simulations from Sec. 4.1 suggested. The temperature estimates of the NDs from the peak intensity reduction after breakout all show a temperature of about 300 K, which is unphysically low. This is because the higher angle liquid diffraction peak is strongly correlated to the ND temperature. Any intensity reduction in the 200 and 311 reflections, caused by elevated temperatures, would be compensated by an increase in the

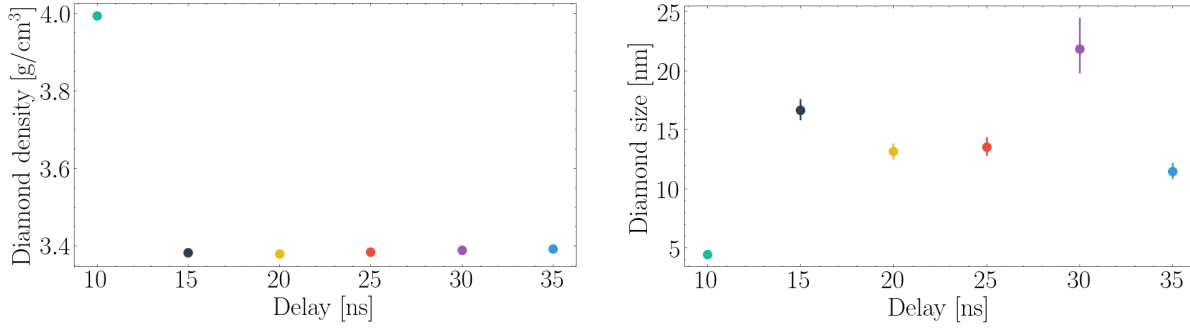


(a) Run 464 during the p4463 campaign at the EU-XFEL. Double-shocked PET is probed at 10 ns, shortly after shock breakout. The sample is still mainly liquid, and therefore the liquid DFT model is used to fit the XRD lineout.



(b) Run 465, which is essentially shot with the same parameters as 464. However, the probing delay is 15 ns in respect to the rising edge of the drive laser. Therefore, the release wave has traversed the sample and the liquid peaks are shifted to low angles as the density is decreasing.

Figure 4.11.: XRD lineouts with the best fitting parameters for shots 464 and 465. Both use a double pulse of durations 4 and 4 ns with an intensity ratio of 1:2.5. The entire energy in the pulse was 33 J delivered over a laser spot with diameter 250 ns.



(a) Development of the diamond density, estimated from the peak positions with increasing probing delay.

(b) ND sizes as a function of the probing delay.

Figure 4.12.: Evolution of the density and diamond size for increasing pump-probe delay. The uncertainty bars in the density plot is negligible, as the determination of the peak centres was extremely accurate.

liquid diffraction peak. Therefore, the model fits the reduction in intensity by reducing the liquid diffraction part instead of the ND temperature dependent part. This hypothesis was confirmed by forcing a high ND temperature, which yielded essentially the same quality of fit. Hence, in the absence of an accurate description of the liquid structure factor after breakout, the ND temperature estimate from the peak reduction is not trustworthy.

However, from the HDS and the MD simulations it is to be expected that the material at both the SACLA and EU-XFEL facilities, has completely released to zero pressure. This is certainly expected for probing times more than 5 ns after breakout. Under this assumption, the diamond temperature can also be estimated from the determined lattice constant [226]. The results show that, except for one outlier, the NDs resulting from a single shock persist at temperatures a few hundred K above the double-shocked values (see Fig. A.16). This further supports the hypothesis proposed in Sec. 4.1, namely that a release from a double-shocked state provides stronger cooling than from a single shock. Nevertheless, the uncertainty in the temperature of the shocked state is still considerable. Therefore, this phenomenon should be explored with *in situ* temperature diagnostic such as SOP.

In summary, this work observed ND formation in shock-compressed PET targets from single and double-shocked states at conditions of 80 ± 10 GPa at 3900 ± 400 K, and 150 ± 15 GPa at 4000 ± 1000 K respectively. The NDs forming in the single shocked PET reach up to $d = 3$ nm just after breakout and shrink to values about $d = 2$ nm at later pump-probe delays. The double-shocked ND diameters are much larger and reach $d = 5$ nm during the shock, even growing after breakout to values as high as $d = 22$ nm. This could enable the tailoring of ND sizes in recovery experiments via pulse shaping.

Using DFT-MD simulations, the liquid diffraction at different temperatures and densities is estimated, leading to decent agreement of the model and the data. The estimated diamond temperature from DFT-MD fits agrees well with the HDS. The after breakout temperatures for both experiments were estimated from the peak positions and yielded results of 2900 to 4000 K for the single shock and 2900 to 3000 K for the double shock. Overall, the experimental comparison between single and double shocks supports the MD simulation results - indicating both that double shocks tend to recover a higher percentage of the NDs and that release from a double-shocked state leads to enhanced cooling after breakout. However, because of the large uncertainty in temperature, a comparative experiment with dedicated *in situ* temperature diagnostic to compare the expansion cooling of single and double-shocked states would provide valuable information regarding ND recovery.

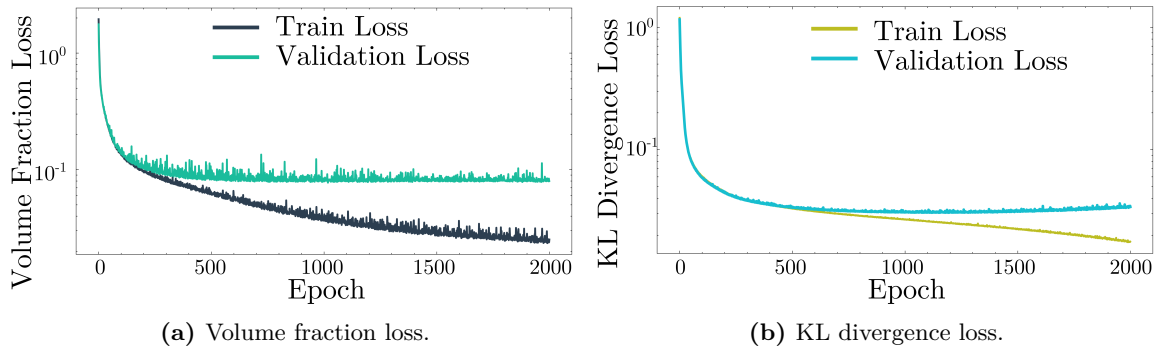


Figure 4.13.: Evolution of the loss functions during the training. Each epoch the entire training dataset is processed by the NN to minimize the loss functions.

4.3. Nanodiamond Size Estimation via Neural Network

This section presents the results for the NN based predictions of ND size distributions from SAXS data. This includes the results obtained from the training procedure of the NN and the results that were obtained with the NN from the SAXS data of shock-compressed PET during the p4463 experiment at the EU-XFEL. The results for the shock states of single and double-shocked PET are provided above (see Sec. 4.2). The obtained distributions are compared to an analytical SAXS model, as well as distributions obtained with McSAS, both of which were provided by B. Lindqvist and published in [124].

4.3.1. Neural Network Performance

The evolutions of the KL divergence loss and the volume fraction loss over the training procedure are displayed in Fig. 4.13. Here, the validation loss is computed on the portion of the data, which has not been utilised in the training procedure. While the validation loss for the volume fraction is almost constant after 600 epochs, the KL loss starts to rise around that time. Therefore, the training was stopped after 600 epochs to achieve the best results for the predictions and avoid over-fitting.

NNs are a black box, and when trained on sensible data, the NN output will always predict a reasonable radii distribution. Therefore, it is crucial to determine how noise would affect the predictions. Fig. 4.14 shows the NN predictions for a single radii distribution chosen at random. Two different times, random noise was added to the ideal SAXS lineout and the noisy data fed to the NN. The two different predictions are shown at the bottom (left and right). In both cases, the NN's prediction is very close to the input distribution. The incorporation of noise into the training data results in a robust NN prediction.

4.3.2. Polyethylene Terephthalate Double Shock Results

The trained NN is used to obtain size distributions for the particle radii from the shock compression p4463 experiment (experimental parameters are given in Tab. A.4). Fig. 4.15 shows the estimated size distributions for pump probe delays of 7,8,9, and 10 ns for a double shock laser profile with ratio 1:4.5 and an intensity of 26 J.

The NN results - which are rescaled to a maximum of 1 - show a clear trend of particle growth with increasing delay. The volume fraction increases up to 9 ns to a value of 0.2 after which it sharply falls to 0.009. This would mean that at a maximum about 20% of the volume is

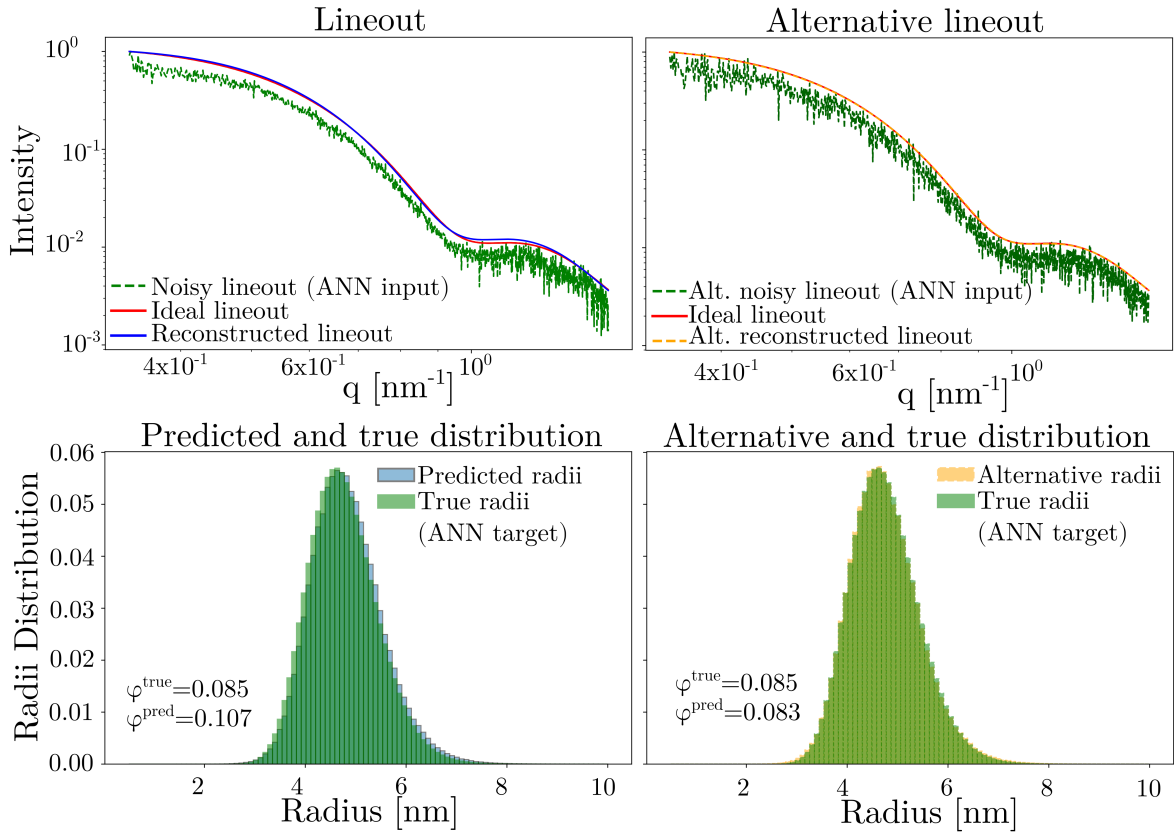


Figure 4.14.: Example predictions of a random radius distribution (bottom green). The noisy lineout (top left, green) is used to predict the radii (bottom left, blue) using the NN. An alternative lineout with the same noise level was sampled (top right, green) and the radii distribution reconstructed again with the NN (bottom right, yellow). The predicted and true volume fraction values are printed in the bottom plots.

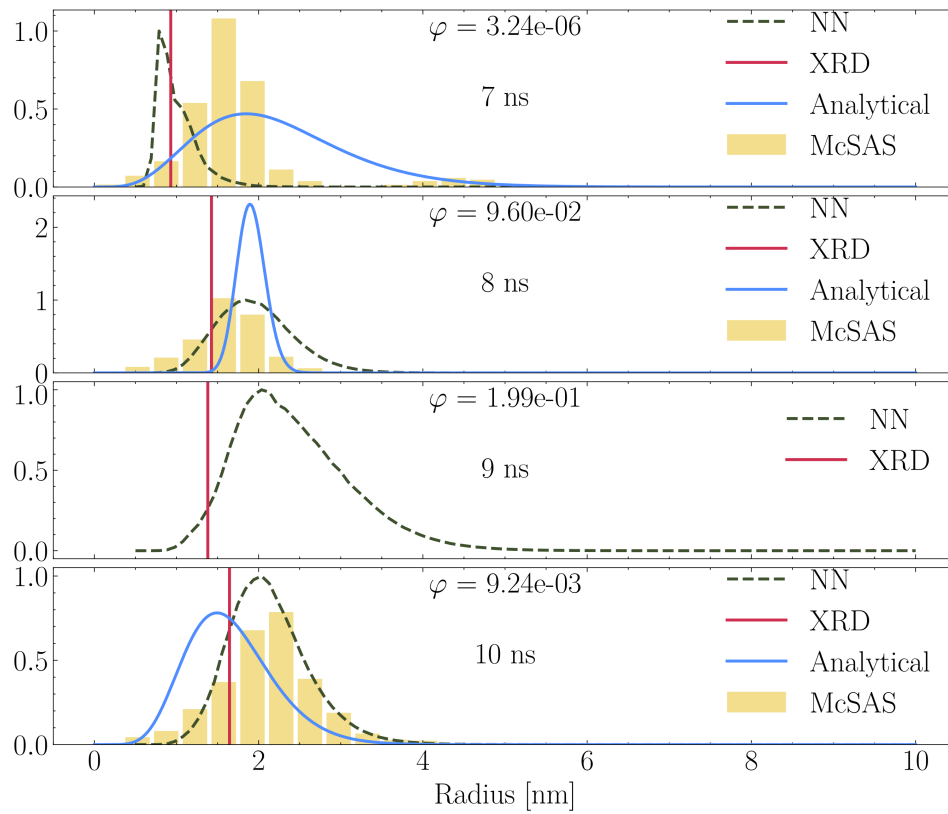


Figure 4.15.: Particle radii distributions of double-shocked PET estimated with different methods. The mean value from the XRD is obtained with the method described in Sec. 3.2.1. The analytical and McSAS results were provided by B. Lindqvist and published in [124]. Sometimes the analytical and McSAS fits failed (see 9 ns). The predicted volume fractions are printed to the plots.

covered by diamond. He et al. determined, that a maximum of about 18% of the carbon atoms in PET did transform to diamond [7]. Therefore, the results here are comparatively high. However, the volume fraction was only determined by the NN and should be measured using a more robust method including XRD for comparison. The XRD results agree well with the NN predictions, but suggest smaller particles for the earliest probing time. For the earliest probing the McSAS and analytical model yield larger particle sizes but agree well in the 8 ns delay. For the latest probing, the analytical model provides slightly smaller particles while the McSAS and NN results agree excellently. The results for the same target and pulse shape but slightly lower pulse energy (Fig. A.18) show very similar results. Overall, the different methods do show slight variations in the particle distributions, but generally agree that the NDs have sizes of up to 3 nm.

It is important to mention the up- and downsides of the different methods to determine the ND size. While the XRD method is sensitive to mean ND sizes, the analytical method is currently limited to the Schulz-Zimm distribution. McSAS is capable of providing arbitrary distribution matching via a Monte Carlo implementation. However, there are problems with convergence of the algorithm. The NN will always predict a sensible distribution, being limited by the training data, even though it might not be physically meaningful. Future studies should utilise a combination of guessing an initial distribution via a NN, combined with refining this in a Bayesian manner (McSAS). Such an approach seems most promising to determine accurate results.

In the p4463 experiment the SAXS data quality was suboptimal due to issues with melting and secondary scattering from the beam stop. It also lacked a precise normalisation of the probe laser intensity, which would usually provide valuable information about the number of scatterers in the probed volume. Additional possible improvements are discussed in Ref. [124].

The results presented here might show a slight ND growth over timespans of several ns. However, the agreement of the different methods is not sufficiently good to determine substantial growth. Additionally, the NDs only persist for about 3 ns in the shocked state, before releasing. Longer shock durations would enable a determination of whether there is a maximal ND size, or if the particles would grow further. This is a highly relevant question in the planetary context (compare Sec. 1.2.1.4).

An accurate knowledge of the time evolution of the size distributions could prove to be extremely valuable for benchmarking of ND nucleation models. These could strongly influence the ND sizes present in ice giant planets and, through thus, help to develop more accurate planetary models. Therefore, it is strongly recommended to perform a dedicated size distribution experiment focusing on SAXS diagnostic of shock-compressed plastics in the future. Furthermore, a shock compression experiment in which the NDs would have substantially longer times to grow could inform on a possible maximal ND size. It could also help to better understand ND nucleation processes in planets, in which the WDM conditions persists for a much longer time.

4.4. Molecular Dynamics Impact Simulations

This section presents the results of the MD impact simulations of the ND and annealed ND impactors. The lateral dimensions of the aluminium catchers were continuously increased until the spherical shock waves launching from the ND impact did not converge at the periodic boundary conditions before the excavation stage. The required dimensions are 500 Å in impact

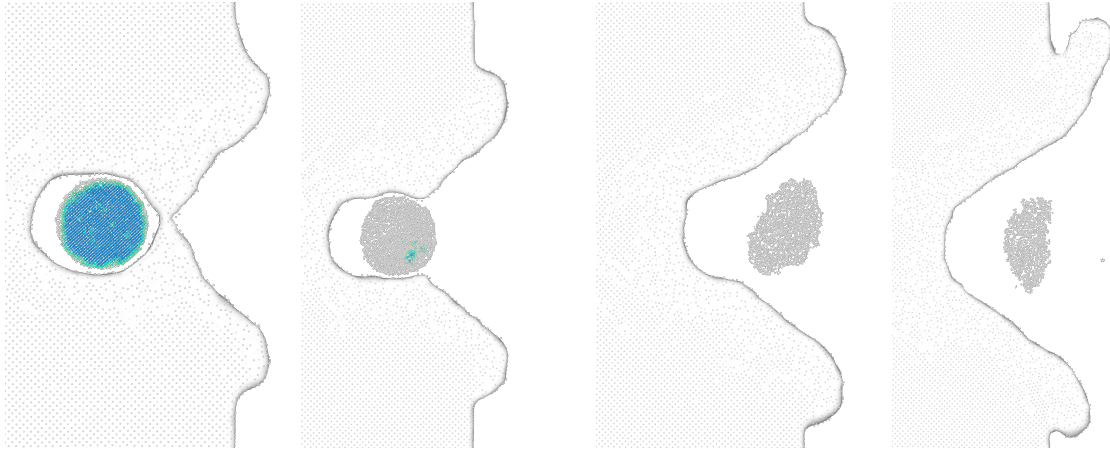


Figure 4.16.: Side view of Al-catcher at the end of the modification stage after the ND impact. From left to right, the impact velocities are 9, 11, 13, and 15 km s⁻¹. The carbon atoms are coloured as: **blue**: diamond, **turquoise**: diamond 1st neighbour, **green**: diamond 2nd neighbour, **grey**: other.

direction and 600 Å in the lateral dimensions. An example image of how the shock fronts during the excavation stage are progressing outwards from the impact site is shown in Fig. A.4.

After convergence was assured, the impact simulations were performed for a total of 21 ps. After that time the crater morphology did not change further. Fig. 4.16 shows cross sectional side views of the impact crater at the end of the simulation. The carbon atoms are coloured according to their structure type. It is clear that the ND only remains intact for the lowest impact velocity of 9 km s⁻¹. For all higher impact velocities the ND is completely destroyed after the impact into the catcher. However, in the actual experiment, the ND might be surrounded by a plasma cloud that could provide some protection during the impact. Future studies could include such material explicitly. While at 11 km s⁻¹ the impactor remains its initial spherical shape and is simply transformed to amorphous carbon, at higher impact velocities, the impactor is completely deformed. Compared to the ND cubes studied by Schuster et al., which could survive impacts up to 10 km s⁻¹, the spherical impactors show similar results. However, a spherical impactor is much more realistic.

For the 9 km s⁻¹ simulation, in which the ND remains intact, it is embedded into the catcher and the surface is closing behind it. In all other simulations the impactor is ejected out of the catcher. The crater morphologies have been measured using the Ovito software [227] and the diameters and depth values are given in Tab. 4.1. There is a clear relationship between the impact velocity and the crater diameter. However, the depth to impact velocity relation is not clear. The simulations of 9 and 11 km s⁻¹ results in substantially deeper penetrations. When analysing the impact process of these two velocities, it becomes clear, that the ND impactor remains intact during the entire/a large part of the excavation stage. An intermediate view of the 11 km s⁻¹ simulation after 1.1 ps shows that a large part of the ND is still in the diamond lattice after the end of the contact and compression stage (see Fig. A.5a). However, the elevated temperature leads to complete melting of the ND later on. In both cases where the ND impactor survives the contact and compression stage, the penetration depth into the catcher is significantly higher than in the cases with higher impact velocities. There, the NDs disintegrate immediately upon impact (Fig. A.5b). It is therefore plausible, that at impact velocities, which leave the ND intact during the contact and compression stage, the increased density and hardness of the impactor would result in a deeper and more narrow crater compared to velocities, which result in melting of the ND upon impact. This could explain the large difference in crater depth.

Impactor type	Impact velocity [km s^{-1}]	Diameter [nm]	Depth [nm]
ND	9	15.5 (6.3)	3.3/11.2 ^a (6.6)
ND	11	20.7 (7.2)	10.3 (7.6)
ND	13	22.9 (8.14)	8.1 (8.5)
ND	15	29.6 (9.0)	8.3 (9.4)
annealed ND	9	14.9 (7.2)	6.3 (5.9)
annealed ND	11	19.0 (8.3)	6.3 (6.8)

Table 4.1.: Crater shapes after the end of the modification stage measured from the MD simulations. The values in parenthesis are the predictions from Price et al. discussed in Sec. 1.2.2 using the densities determined in the MD simulation 3.51 and 2.37 g cm^{-3} , corresponding radii and simulated impact velocities.

^aDepending on whether the penetration depth, or depth of the surface crater is measured.

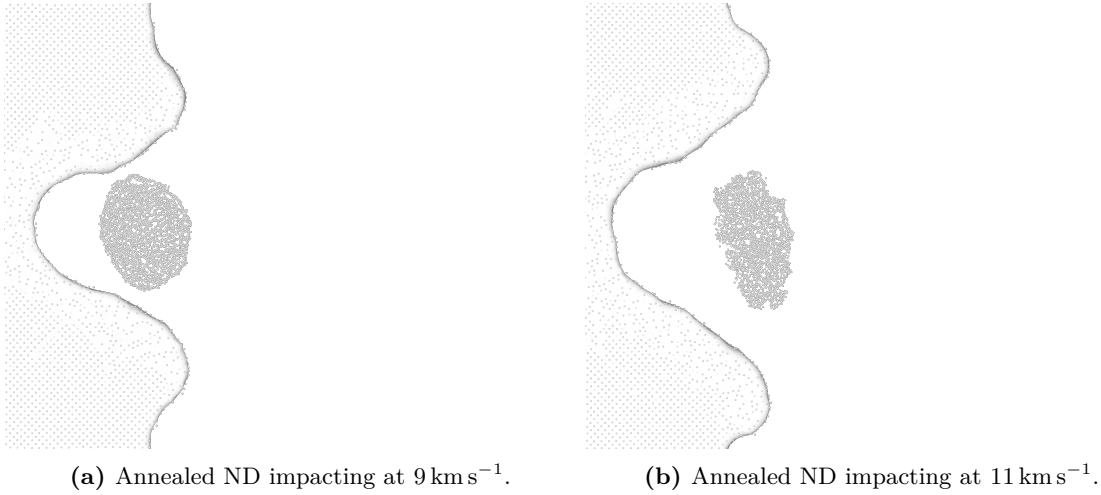


Figure 4.17.: Cross sectional view of the craters caused by annealed ND impactors.

The annealed ND impactor craters are displayed in Fig. 4.17 and the corresponding crater parameters in Tab. 4.1. The crater depths are much lower compared to the ND impacts at the same velocity, and the diameters are slightly smaller. This is, even though the impactor size of the annealed ND is increased to $d \approx 5.7 \text{ nm}$ due to its reduced density. The decreased depth, compared to ND impactors supports the theory that a softer projectile would not penetrate as deeply as a hard one.

The overall agreement with the predictions of the phenomenological functions from Price et.al (compare Sec. 1.2.2), is very poor. Here, the MD simulations lead to crater diameters which are at least double to what is predicted. The depth values however do agree much better between the two methods. It is important to mention, that Price et al. have only studied impactor diameters exceeding 100 nm . In any case, this work suggests, that at the same impact velocity and similar size, a ND impact crater would penetrate substantially deeper into an aluminium catcher.

In summary, the MD simulations show different results from the predicted crater shapes according to the phenomenological functions presented in Price et al. [113], which have only been fit to impactors of sizes exceeding 100 nm . The results presented here can provide additional data points for these fits. Furthermore this work suggest, that NDs will only survive an

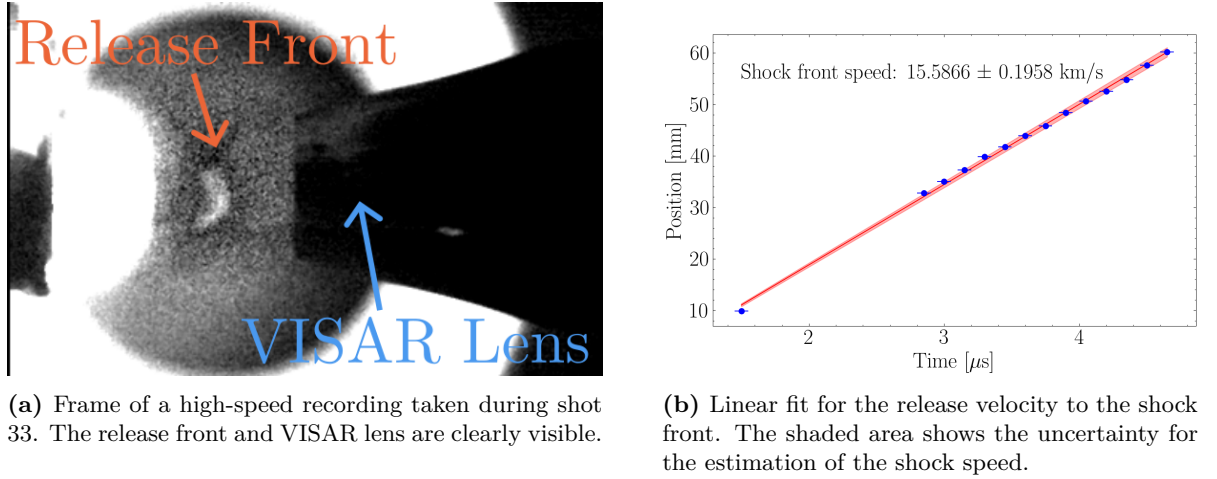


Figure 4.18.: High-speed recording of the quartz calibration shot 33 with the fit to the release front.

impact into aluminium at velocities below 11 km s^{-1} . They also show that it is possible for the NDs to be embedded just underneath the surface of an aluminium catcher. The MD results indicate that if aluminium catchers are used for ND recovery, shock states should be targeted that release with free surface velocities below 11 km s^{-1} . Additionally, the embedding into the surface would require the dissolution of the aluminium surface to obtain the NDs in solution for further processing.

4.5. High-Speed Imaging

To gauge whether a high-speed camera is useful as a shock state diagnostic, the recordings of a total of ten shots with different laser intensities are analysed. The shot parameters can be found in Tab. A.8. Shot 33 was performed with both diagnostics, VISAR and the high-speed camera. The combined velocity from the two VISARs is about $13.2 \pm 0.9 \text{ km s}^{-1}$, which corresponds to a particle velocity of 7.2 km s^{-1} [228]. The free surface velocity would thus amount to 14.4 km s^{-1} . This compares reasonably well to the velocity of the front of the shock release determined by the high-speed camera of $15.6 \pm 0.2 \text{ km s}^{-1}$. The uncertainties are determined from the size of a pixel and the integration time per frame. Fig. 4.18 shows the image of the shock wave during release, as well as the linear fit to the data. The corresponding pressure estimates from the quartz Hugoniot to $P_{\text{high-speed}} \approx 291$ and $P_{\text{VISAR}} \approx 253 \text{ GPa}$.

The determination of the shock state via transversal high-speed imaging suffers mainly from the low resolution of the optical camera, and the difficulty to determine the front of the release wave exactly. However, in a recovery setup, in which a catcher mounted behind the target prohibits the use of a VISAR system, high-speed cameras could be a valuable *in situ* diagnostic to roughly estimate the shock state.

4.6. Cratering Landscape Measurements

This section presents the results of the cratering surface measurements for the two different targets. The HDS with the experimental laser parameters places the PET sample at around 150 GPa , just in the diamond formation region [7] and the PS sample at around 190 GPa , i.e. outside the diamond formation region [6]. The release velocities of the two different targets are estimated from the linear u_s - u_p relationship and the velocity doubling rule as

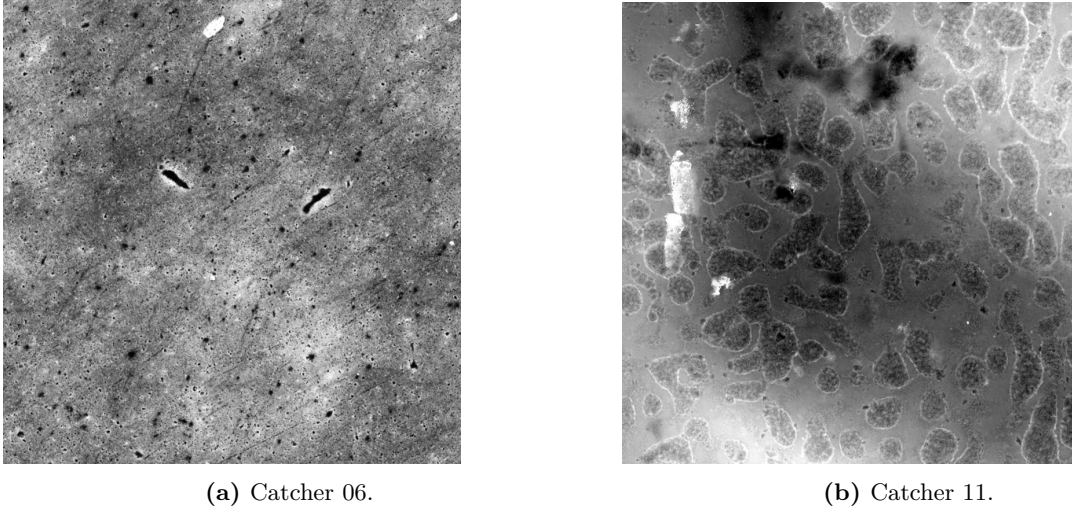


Figure 4.19.: Confocal microscope images for the catcher from PET (left) and the PS sample (right). Both images show an area of 600 by 600 μm .

$v_{\text{impact}}^{\text{PET}} \approx 16 \text{ km s}^{-1}$ and $v_{\text{impact}}^{\text{PS}} \approx 22 \text{ km s}^{-1}$. The impact velocity determination comes with large uncertainties. However, the simulation of impact craters showed that the ratio of crater diameter to depth can still be meaningful in differentiating impactor densities even with large variations of the impact velocity (compare Fig. 3.5).

Fig. 4.19 shows confocal microscope images of the two catchers for PET (Catcher 06) and PS (Catcher 11) covering an area of $0.6 \times 0.6 \text{ mm}^2$ each. Even from the overview it is evident that the impact landscapes differ substantially. While Catcher 06 contains many individual small craters with a few larger ones, the surface of Catcher 11 is largely dominated by bigger craters with smaller craters inside of them and in between. The scratches from the polishing process can still be identified in Catcher 06, while they are completely obscured in Catcher 11.

The segmented masks for parts of the catchers are shown in Fig. 4.20. Most craters are well segmented by the algorithm. The cratering statistics are displayed in Fig. 4.21. The diameter of the craters is estimated from the mask area under the assumption of a perfectly spherical crater, while the depth of the crater was calculated as the difference between the deepest point in each crater and the average depth of the unmasked surface.

The most prominent difference between the two catchers is the number of craters. In Catcher 06, a total of 6013 craters were segmented and analysed, while Catcher 11 had 3929. The area covered by craters is 7.1 % and 24.5 % in Catchers 06 and 11, respectively. For both catchers a total area of 1.08 mm^2 was analysed. This confirms what the example images in Fig. 4.19 suggest, namely, Catcher 06 containing many small craters, while the Catcher 11 surface is covered by large craters.

When comparing the dimensionless D_c/d ratio, the simulations suggest that for diamond impactors, the distribution should peak at around a value of -0.9 . The peaks of the distributions for both catchers are vastly different from this value. The last two columns in Fig. 4.21 also show the distribution with a log-normal fit. The ratio peaks at about -2.05 in Catcher 06, and at -2.41 in Catcher 11. Both values are much smaller than the ones predicted from any of the simulated impactors. There could be a systematic overestimation of the crater diameters, because the diameters in Price et al. were measured from crest maximum to crest maximum [113]. The segmentation, however, includes the entire crater with the crater edges beyond the maxima.

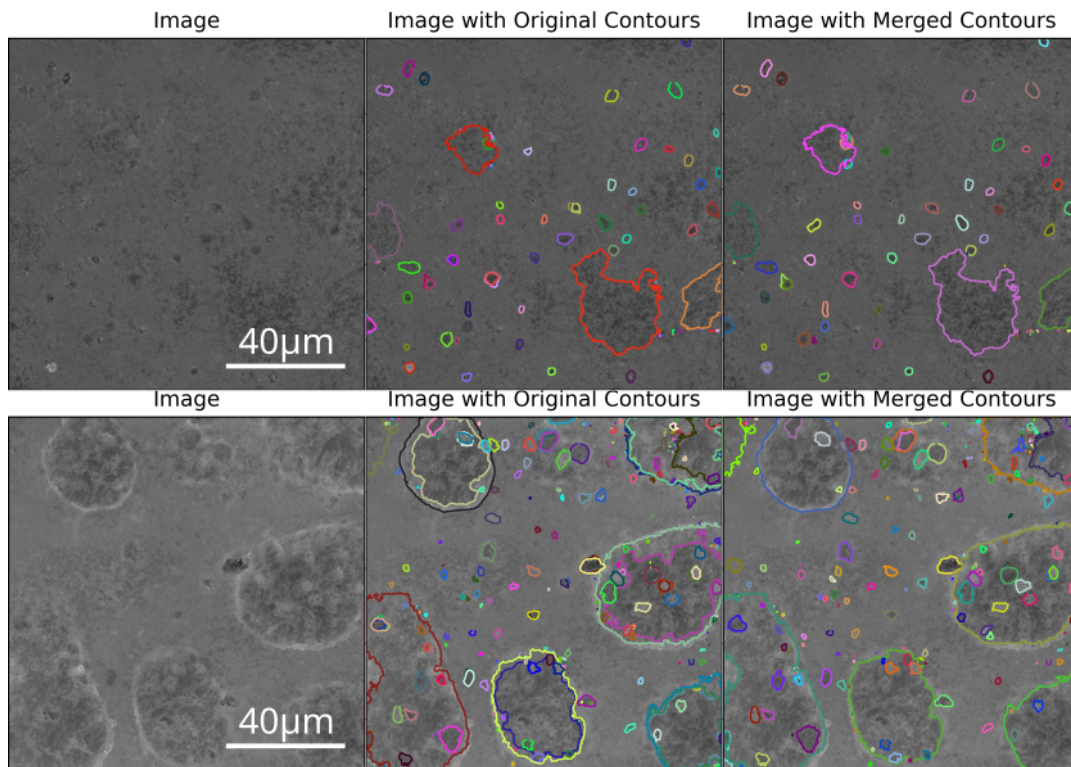


Figure 4.20.: Confocal microscope images of the two catchers. The top row shows Catcher 06 (PET in diamond forming region) and the bottom row Catcher 11 (PS outside diamond forming region). In each row, the raw image, the segmented craters and the merged segmented craters according to Sec. A.11 are shown. The segmented craters for all five height slices were merged.

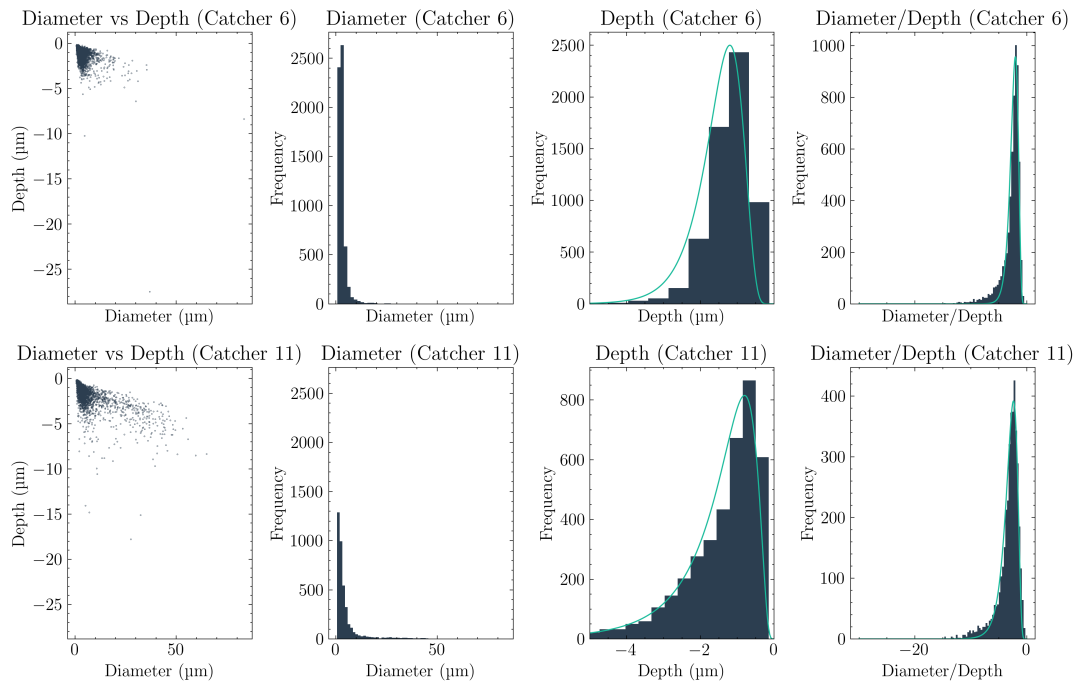


Figure 4.21.: Statistical analysis of the crater parameters found in the two catchers. The upper row shows the Catcher 06 results (PET in diamond formation region). The lower row shows Catcher 11 results (PS outside diamond formation region).

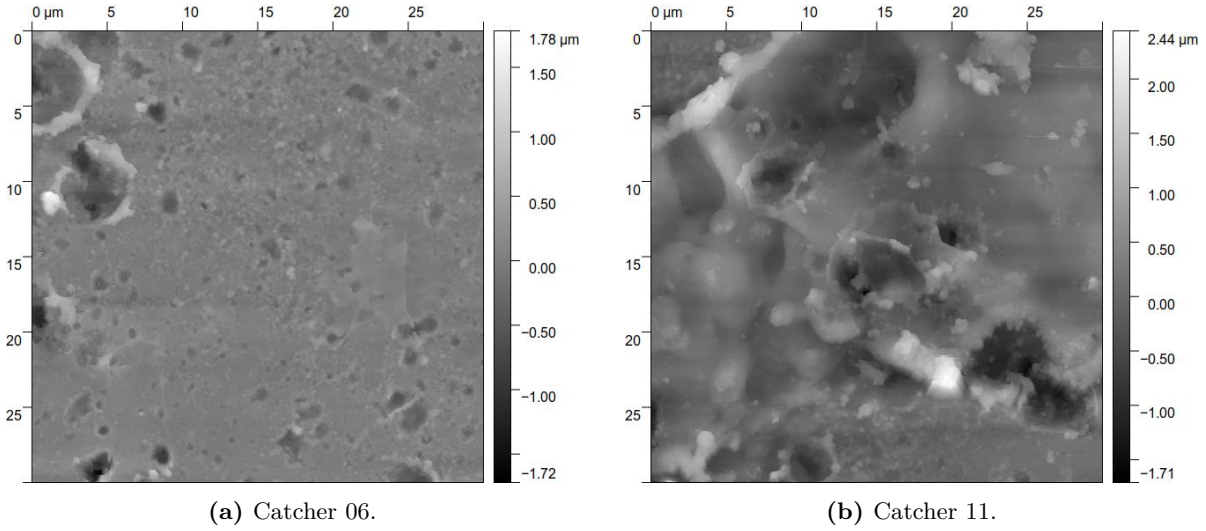


Figure 4.22.: AFM measurements of the two catchers each covering an area of 30 by 30 μm .

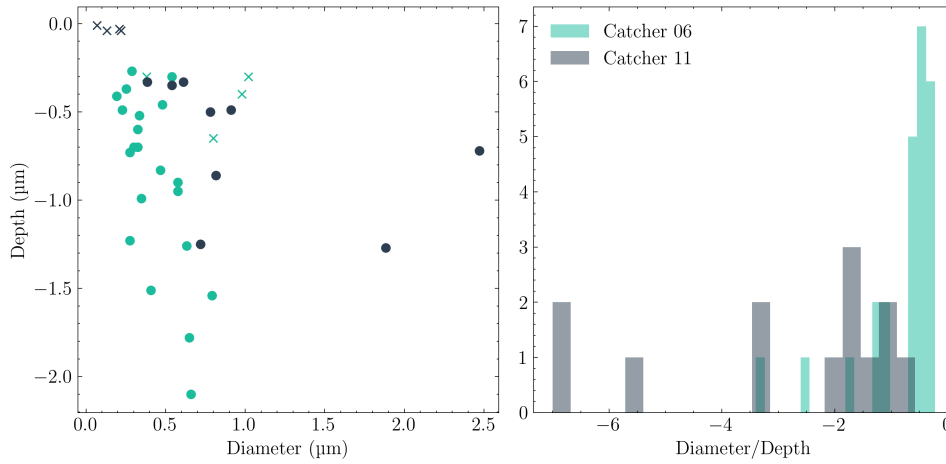


Figure 4.23.: Crater depth and diameters determined from the AFM measurement. Two different AFM scans with different spatial resolutions were analysed. The measurements taken from the higher resolution scans are plotted with an "x" symbol.

The depths histograms have maxima at -1.23 and $-0.78 \mu\text{m}$ for Catcher 06 and 11, respectively. In other words, Catcher 06 is covered by craters which are much deeper than Catcher 11. The diameter distributions have maxima at 3.07 , for Catcher 06, and $1.34 \mu\text{m}$ for Catcher 11.

Furthermore, the crater diameters and depths are substantially larger than what is expected from singular ND impactors. Therefore, the simulations are adapted to chose an impactor size resulting in similar values for diameter and depth. The matching distributions are obtained for an impactor size of 600 nm and are displayed in Fig. A.35. Although the obtained diameter values for the larger impactors of diamond density are centred around $2.79 \mu\text{m}$, in better agreement to the experimental values of Catcher 06, the experimental values for Catcher 11 do not match any of the simulated distributions. Additionally, there is a large discrepancy for the simulated crater depths and ratio values.

Generally, the analysis of the confocal microscope data does not indicate the presence of impactors with diamond density nor any other of the simulated forms of carbon. It is possible that

the impact landscape of the catchers are a result of highly non-homogeneous impactors due to other phases (e.g. graphite or amorphous carbon) forming within a release cloud. Therefore, a simple cratering model cannot reproduce these values. Additionally, the methodology includes systematic errors, such as overestimating the crater diameters.

The AFM scans of the same two catchers are shown in Fig. 4.22. Some of the measured crater profiles can be found in Fig. A.33 and A.34. The AFM measurements agree with the suggestions of the confocal microscope, at a much higher spatial resolution. Catcher 06 contains many individual small craters while the Catcher 11 surface is covered by larger particles and craters. A plot of the measured crater diameters and depths for the two different catchers is displayed in Fig. 4.23. The crater measurements are performed on two different scans with different spatial resolutions (compare Sec. A.11). The higher spatial resolution values are displayed as "x" symbols. It is clear that for a given depth, the craters found in Catcher 11 are much larger in diameter. The D_c/d ratio for Catcher 06 peaks at ≈ -0.5 , below the theoretical prediction for diamond density impactors. The ratio for Catcher 11 is much smaller but suffers from low statistics.

Overall, the AFM measurements offer a much higher spatial resolution enabling to resolve smaller craters. Despite the high spatial resolution, neither of the studied catchers shows craters as small as the ones predicted from single ND impactors. Even the AFM, which could resolve these craters spatially, shows much larger diameters. Catcher 06, which is expected to be exposed to ND impactors, contains many individual craters with a tendency to deeper craters for a given diameter which could be a sign for a higher impactor density. However, despite the qualitatively very different cratering landscape no clear findings were obtained from the analysis. Both catcher surfaces show landscapes that suggest impactors that vastly exceed the few nm expected from the ND sizes. This could be a sign for the agglomeration of NDs after breakout into clusters.

To summarise, the analysis of the catcher surfaces by the confocal and AFM show a clear qualitative difference. While the catcher exposed to the ND containing ejecta shows many individual craters, the catcher exposed to the plasma release without NDs shows large craters at less depth. However, none of the found craters is consistent with singular ND impact. This raises the question of post breakout agglomeration of NDs and the underlying mechanism.

4.7. Raman Measurements

In total, Raman spectra of five different catchers of two types are recorded: 1) The polished aluminium plates, and 2) the candle gel catchers. To get an overview of all spectra present in the scanned area, Fig. 4.24 shows a collection of representative spectra taken of four catchers. The spectra for one candle gel and three aluminium catchers are displayed. All spectra show a double peak feature with a broad first and a narrower second peak. The first peak shows a large upwards tail, while the second peak is skewed to the right.

The candle gel catcher (Fig. 4.24 **a**) shows the first broad peak at 1390 cm^{-1} before rising to a small pre-peak at 1620 cm^{-1} close to the main second peak at 1642 cm^{-1} . At some positions in the catcher, a small broad post-peak at 1940 cm^{-1} is visible.

The spectra from the positions scanned in the aluminium catchers (Fig. 4.24 **c-d**) look very similar. However, the position of the first broad band peaks is slightly up-shifted to 1405 cm^{-1} and the pre-peak before the second broad feature at 1620 cm^{-1} is more prominent. The second

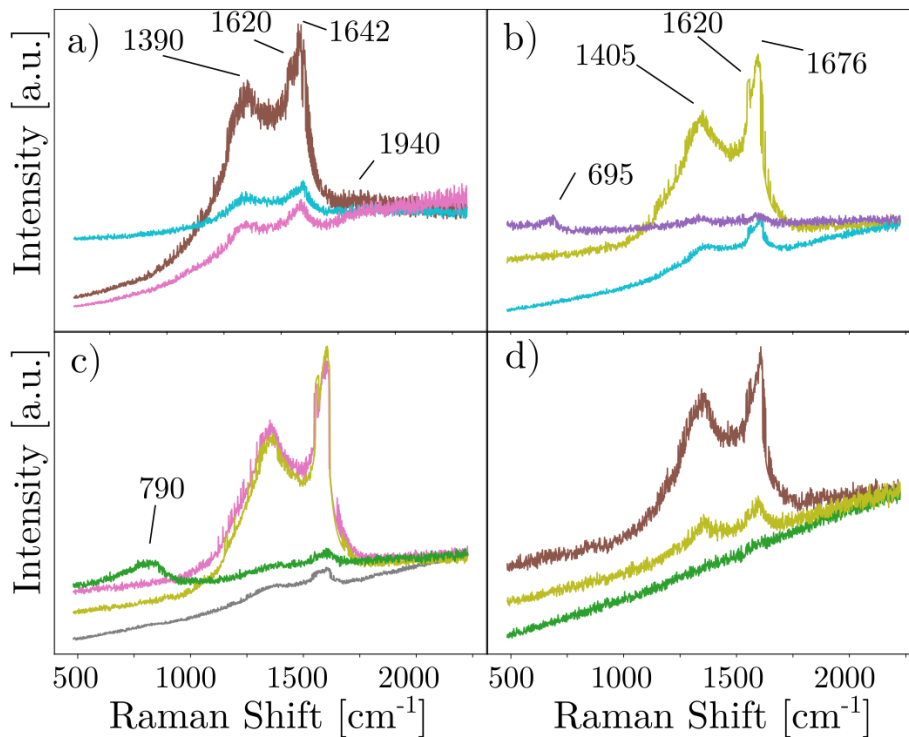


Figure 4.24.: Spectra taken of four different catchers. The spectra are normalised and the catchers are **a**, a candle gel catcher and **b-d** polished Al plates.

main peak is also up-shifted to 1676 cm^{-1} in respect to the gel catcher. Additional peaks at low wavenumbers are also present in some scan positions.

The location of the lower broad peak, present in both catchers is close to the *D*-band value introduced by defects in graphite (1350 cm^{-1}). However, they are up-shifted by up to 55 cm^{-1} . Such an up-shift was described in the literature as an effect of an increased excitation wavelength [229]. For an excitation wavelength of 532 nm , the *D*-band is located at around 1380 cm^{-1} . The second main feature is close to the *G*-band, but also appears at higher wavenumbers compared to the literature. Such a shift has been observed in nano-crystalline graphite [182]. However, such an up-shift was only found up to 1620 cm^{-1} .

In both catcher types, the spectra show features similar to the *D*- and *G*-bands but at higher wavenumbers. An upwards shift is known from nano-crystalline samples, but cannot completely explain the results found in this work. At none of the scanned positions the typical ND peak at 1332 cm^{-1} was found. The laser spot in the Raman experiments conducted in this work had a size of about $1\text{ }\mu\text{m}$. Therefore, the signal was collected over a very large area compared to the expected sizes of the NDs. It is possible that the NDs only comprise a fraction of the scanned area or might have been destroyed during the impact. To determine which is the case, future experiments could employ micro Raman techniques, which would strongly increase the relative contribution of possible ND candidates.

4.8. TEM Lamellae Measurements

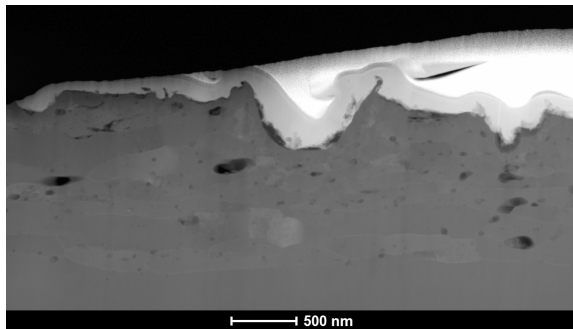
This section presents the results for the analysis of the four different TEM lamellae. In total, four cross sectional lamellae were cut from three different catchers: One for each catcher and an additional lamella for the copper catcher (compare Tab. 3.1).

Single-Shot Aluminium Catcher

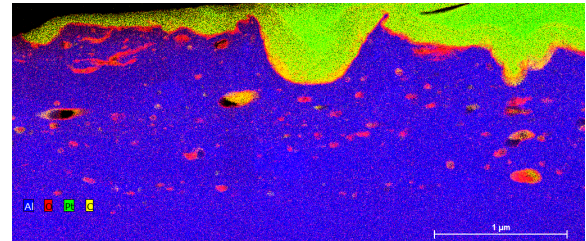
The first lamella was cut from the polished aluminium plate, which collected the ejecta of a single PET shot. A cross sectional view of the lamella and the corresponding EDS mapping is shown in Fig. 4.25. The top side, which was hit by the ejecta, is coated with platinum for protection.

Clearly, the impacts resulted in the typical cratering landscape. The entire surface region, up to 1.5 μm inwards, shows inclusions with particles consisting mainly of oxygen and carbon. The impacted material shows a clear difference in grain size to the bulk material beneath. The impacted area has substantially smaller grains compared to the bulk, which shows not a single grain boundary in the observed area. Such a grain refinement is a well-described effect of shock compression of pure aluminium [230]. It is probably a result of the ejecta compressing the catcher surface.

Zooming into one of the inclusions containing a large amount of carbon, no crystal structure can be observed (compare Fig. A.21). The inclusion in the catcher is comprised of amorphous carbon. Although no crystalline carbon is found, the presence of embedded carbon material within the catcher - especially in areas without craters - suggests that some carbon ejecta impacted the aluminium while it was already molten. If the ejecta is spatially sufficiently dispersed, the ejecta front could impact the solid aluminium, resulting in shock melting of the catcher. The rest of the ejecta would then impact a partially liquid catcher. This would explain embedded carbon also without craters. None of the embedded particles show signs of diamond crystal structure.



(a) Cross-sectional view of the cut lamella from the aluminium catcher plater shot at LULI during the 2021 campaign.

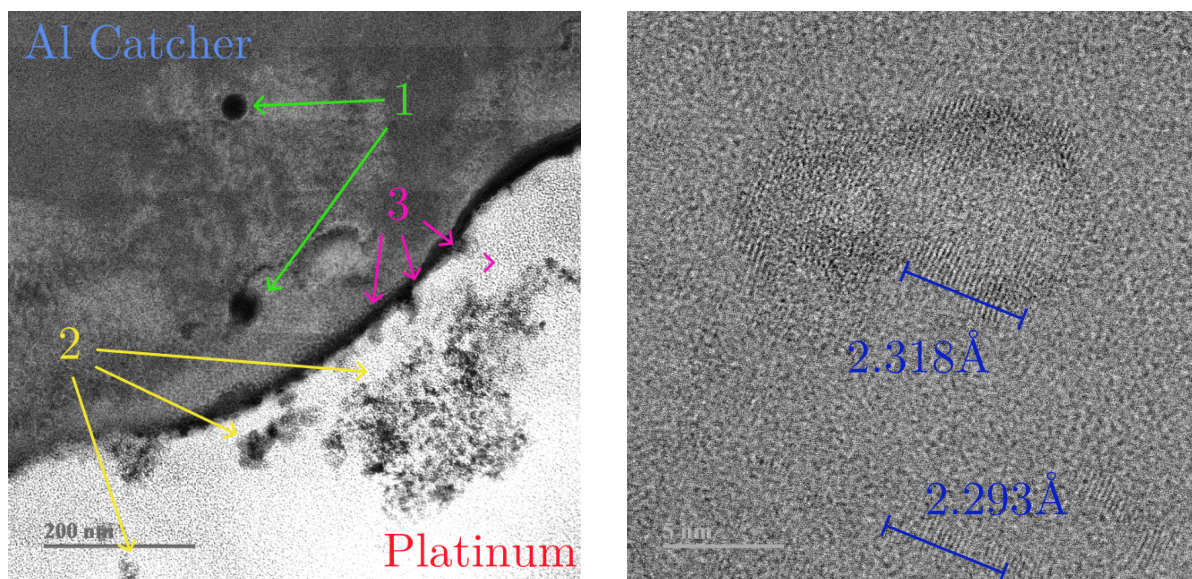


(b) EDS atom type mapping of the cross-sectional slice.

Figure 4.25.: View of the cross-sectional slice of the aluminium catcher cut with the FIB. The cratering landscape is clearly visible, as are inclusions in the top layer of the sample. The top side was exposed to the ejected material.

Multi-Shot Aluminium Catcher

The second lamella was cut from the aluminium catcher used at ELI, which collected the ejecta of 54 shots (see Tab. 3.1). Fig. 4.26 shows the surface of the Al catcher as well as some nanoparticles found in the material. The catcher shows visible signs of surface cratering, surface deposits, and particles embedded into the bulk (Fig. 4.26a). The overall cross-sectional view of the lamella is very similar to the one hit by only a single shot (compare Fig. A.22a). A closer look at some of the particles (Fig. 4.26b) exposes the lattice as aluminium. These particles are probably just in-focus grains of the bulk aluminium material. No sign of crystallite ND impactors is visible in the lamella.



(a) Impact sites on the aluminium surface. The impact direction was from the bottom right. Prominent features are: 1) large spherical inclusions, 2) surface deposits, and 3) crater crests. The horizontal lines are an artefact of the locally enhanced contrast.

(b) Example of one of the particles found buried in the catcher. The inter-planar distances of the particles are close to 2.3 Å, which is very close to the aluminium (111) value of 2.33 Å. The displayed values show the lattice d -spacing.

Figure 4.26.: Examples of a TEM scan of the aluminium catcher shot during the campaign at the ELI facility.

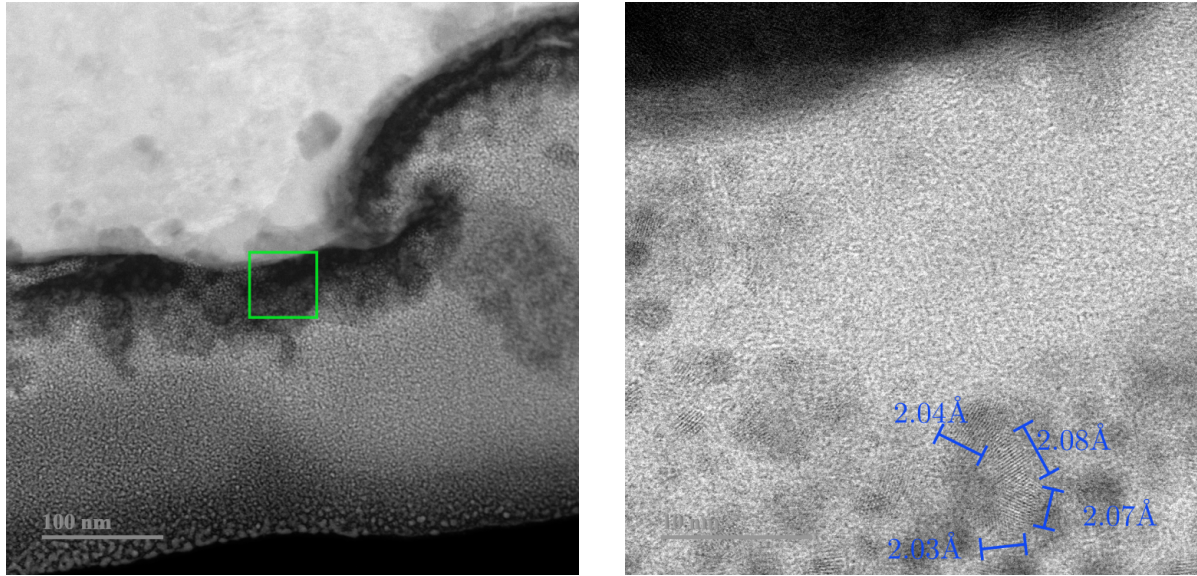
Multi-Shot Copper Catchers

Two lamellae were cut from the copper catcher shot at ELI, which accumulated the ejecta of 51 shots. Fig. 4.27 shows the surface of the catcher. There are several nano-particles visible in the carbon containing surface layer. However, the EDS measurement showed similar amounts of carbon and copper in that surface layer (44% to 34% C:Cu by mass per cent). Therefore, it is possible that the particles with a lattice spacing of 2.04 – 2.08 Å could be either the diamond (111) reflection at 2.06 Å or copper (111) reflection at 2.09 Å. Without a high resolution EDS mapping this is difficult to differentiate. The second lamella from the same catcher shows the similar features. Particles are embedded and a cover layer (Cu and C) is present.

In summary, no ND particle are found in any of the catcher materials. However, several spherical particles are identified which were embedded into the catcher surface in both materials. The copper catcher shows nano-particles embedded within the C-Cu layer. The d -spacings of these particle's planes are consistent with either NDs or copper nanoparticles. In general, fabricating TEM lamellae is very tedious and can suffer from low contrast between carbon and the surrounding material. Therefore, it is preferable to collect the ejected material in a soluble material to make use of simpler TEM techniques, such as using TEM grids.

4.9. TEM Measurements in Solution

This section presents the results of the analysis of the TEM scans taken of the dissolved ionic gel catchers. Fig. 4.28 shows three distinct features that were found on the TEM grid in bright field mode. The images are taken at different magnifications and show different species of structures. Fig. 4.28a shows two clusters of sizes ten to hundreds of nm that seem to be comprised of smaller particles. Fig. 4.28b shows a fibre-like structure of about 300 nm located



(a) Surface of the copper catcher in dark field mode. The platinum coating is well visible along with the carbon layer covering the surface (dark layer). The rectangle shows the ROI displayed on the right.

(b) Zoomed image into the ROI taken in bright field mode. The measured d -spacings are printed alongside the particles.

Figure 4.27.: Examples of a TEM scan of the copper catcher shot during the campaign at the ELI facility.

on the carbon mesh. Fig. 4.28c shows another cluster comprised of particles along with a large rod-like particle, about $3\mu\text{m}$ in diameter. A higher magnification shows that the rod-like particle seems to be comprised of smaller pill-shaped particles of width 30 and length 70 nm.

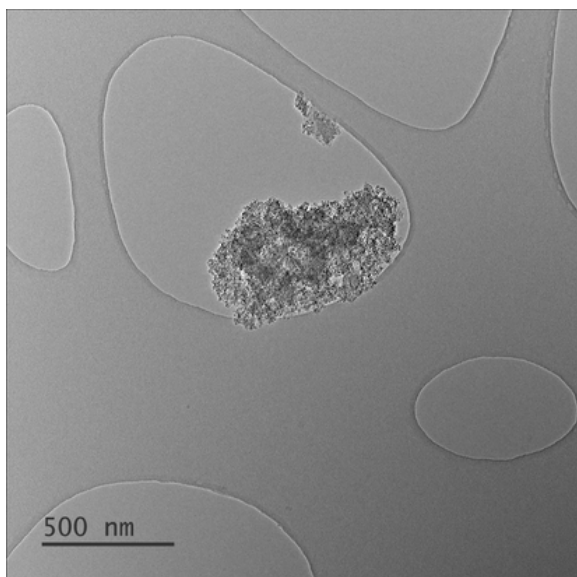
4.9.1. Rod-Like Particle

To understand what the rod-like particle is made of, EDS measurements were taken at different points and an elemental analysis was performed. Fig. 4.29a shows the points for the rod-like structure, where an EDS measurement was taken, along with an exemplary EDS spectrum. The elemental composition for each point is shown in Tab. 4.2. Each spectrum was collected over two minutes.

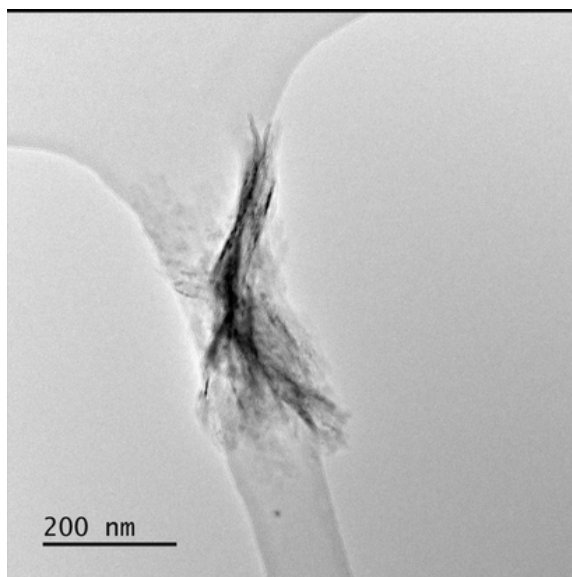
Position	5	6	7	8 (vacuum)	9
C mass %	90.22	99.61	99.17	96.00	96.58
C counts	17752.4	30426.0	14299.9	2779.5	10448.9
O mass %	4.58	0.22	0.60	3.12	2.31
O counts	1867.2	133.6	168.9	177.0	488.4
Si mass %	4.93	0.17	0.23	0.88	1.11
Si counts	2025.0	107.15	68.9	52.9	250.5

Table 4.2.: Results of the EDS analysis of the rod-like particle found in the ionic gel catcher which was shot at the ELI facility.

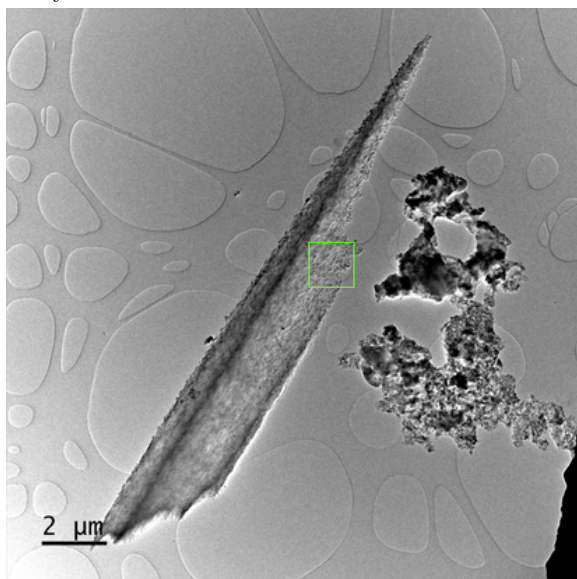
From the EDS results it is clear that spots 6 and 7 are almost exclusively comprised of carbon. Only traces of oxygen and silicon are present at these spots, and their counts are comparable



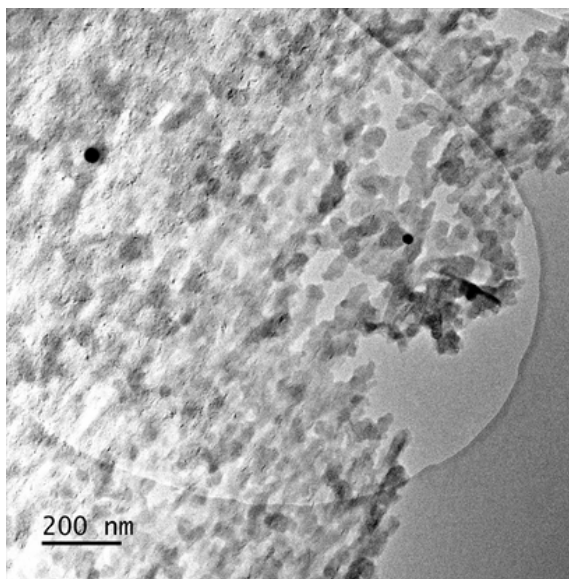
(a) A big cluster of smaller particles at the bottom and a smaller cluster at the top. They are located well inside the pore, providing a good opportunity to study them in STEM mode.



(b) A fibre-like structure was identified on the mesh.



(c) A very large rod-like particle can be seen on the left overlaying multiple pores. On the right, there is a big cluster containing many small individual particles.



(d) TEM image of the rod-like particle in the pore.

Figure 4.28.: Bright field images taken in TEM mode of particles found in the dissolved ionic gel catcher.

to the vacuum reference. It is thus safe to assume that the small pill-shaped particles are a carbon allotrope. The dark particle at spot 5 has a comparatively high silicon and carbon content. It is probably a silicon particle. Such particles have been found on other grids of the same type and probably stem from the manufacturing process of the TEM grid. Overall the abundance of oxygen is low. Nearly no traces of the ionic liquid (like sulphur or nitrogen) are present in the spectrum.

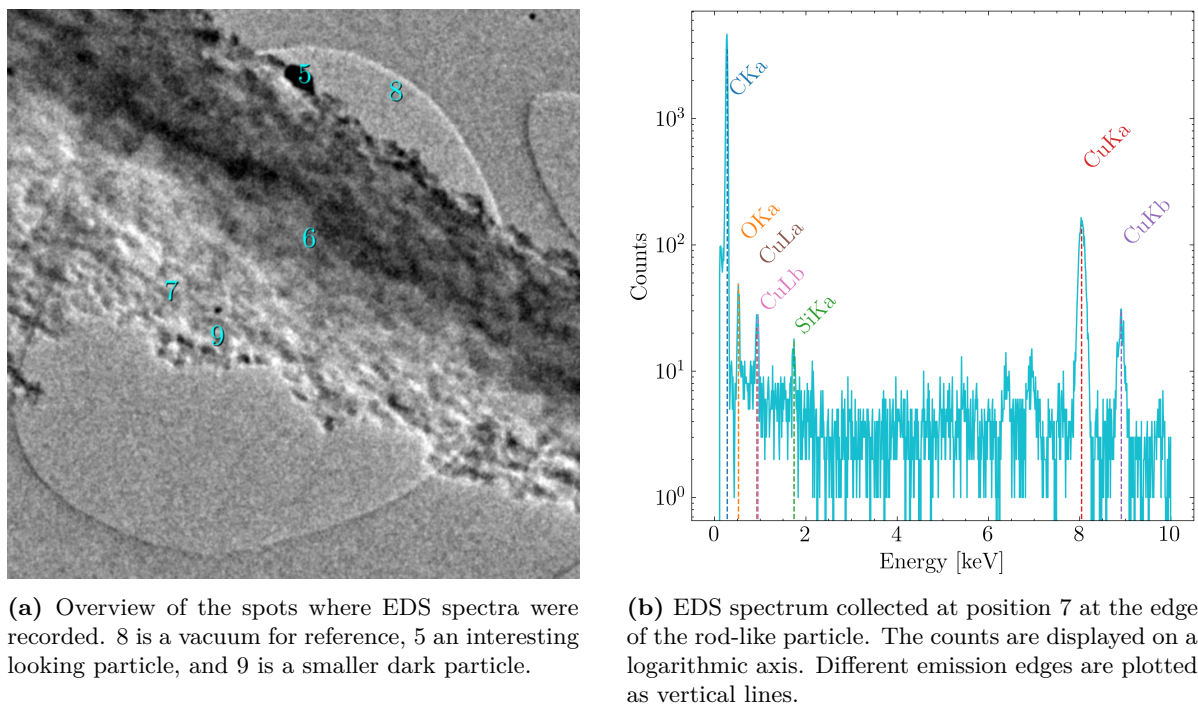
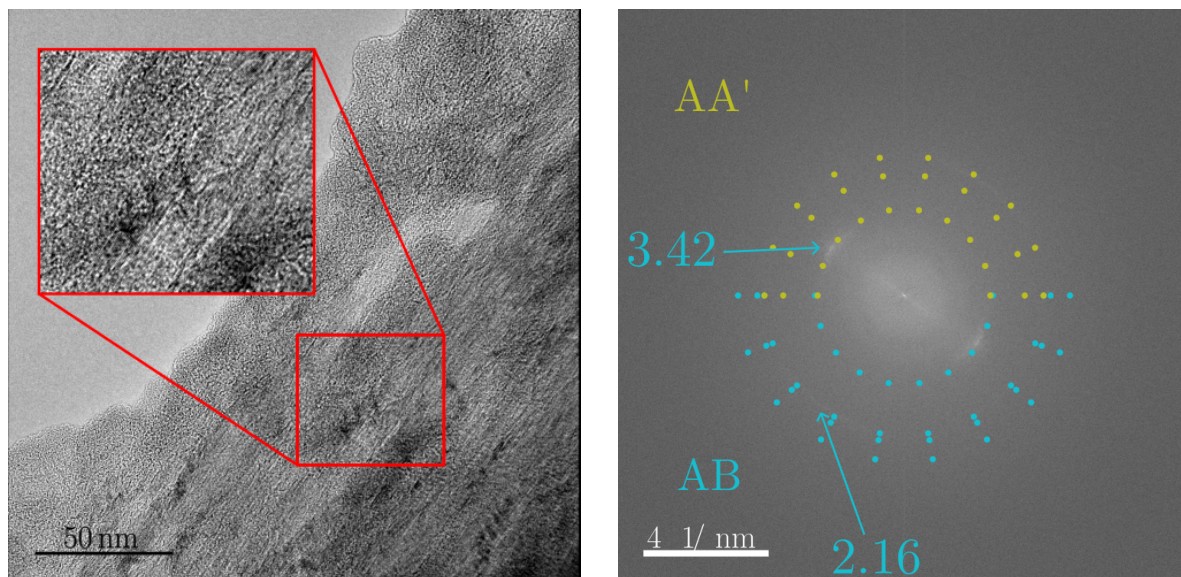


Figure 4.29.: EDS spectra and their location taken from the rod-like structure found in the ionic gel catcher.

Zooming further into the pill-shaped particles exposes lattice planes with an orientation from the lower left to the upper right diagonal (compare Fig. 4.30a). The FFT of the ROI is displayed in Fig. 4.30b and shows two clear spots in frequency space in the corresponding direction ($3.42 \text{ \AA}$ d -spacing). The frequencies of regular AB-stacked graphite peaks are plotted as rings on top of the data. The (002) reflection fits with the frequency present in the image, but the lattice distance was measured to $3.42 \text{ \AA}$ compared to the literature value of $3.35 \text{ \AA}$ [231]. The two visible reflections are in good agreement with the (002) and (020) reflections of AA' graphite [232]. This is a form of graphite, in which the layers are shifted compared to the common AB-stacking. The most prominent peak (002) describes the inter-layer distance, which is measured to $3.42 \text{ \AA}$ and compares well to the literature value of $3.44 \text{ \AA}$ [232].

AA' graphite is a metastable structure which requires the system to overcome the energy barrier. The AA'-stacked graphite in [232] was synthesised by thermally treating graphite nanopowders (5 nm at 1500 K). In the case of ND impacting an ionic gel, the energy to form this material can be provided by the high impact speed resulting in a similar process to this synthesis. Upon impact the NDs heat up and graphitise into the AA'-stacking. The graphite domains extended over up to 50 nm along the (001)-plane direction and up to 10 nm perpendicular to that. Other regions of the rod-like particle show clear signs of AB-stacked graphite as well as carbon onions (compare Sec. A.9.3. These carbon onions have been described as products of annealing NDs at temperatures of $1000 - 1500 \text{ K}$ [116].

The presence of AA'-stacked, AB-stacked graphite, and carbon onions could be a product of NDs impacting and annealing at high temperatures provided by the HVI. However, the XRD studies of NDs formed in the specific precursor material (PET) at comparable laser intensities suggest ND sizes of only a few nm in diameter (compare Sec. 4.2). While the carbon onion sizes are in good agreement with this, the graphite domains extend up to 50 nm in some directions, far exceeding expectations. They also show a clear preferred orientation such that the entire rod particle and its smaller constituents are elongated along the (001)-plane. Due



(a) Zoomed ROI of the rod-like particles. The red rectangle shows the region which was chosen for the FFT. Lattice planes are clearly identified and seem to have a preferred orientation from the lower left to the upper right diagonal.

(b) FFT of the ROI marked in the left image. The reflection rings of AB-stacked (turquoise) and AA'-stacked (gold) graphite are displayed on top of the data. From centre to edge, they are: AB: ((002), (020), (111), (022)) and AA': ((002), (200), (020)). Only two frequencies are visible in the experiment at 3.42 Å and 2.16 Å in real space.

Figure 4.30.: TEM scan of the rod-like particle and the FFT of the marked region.

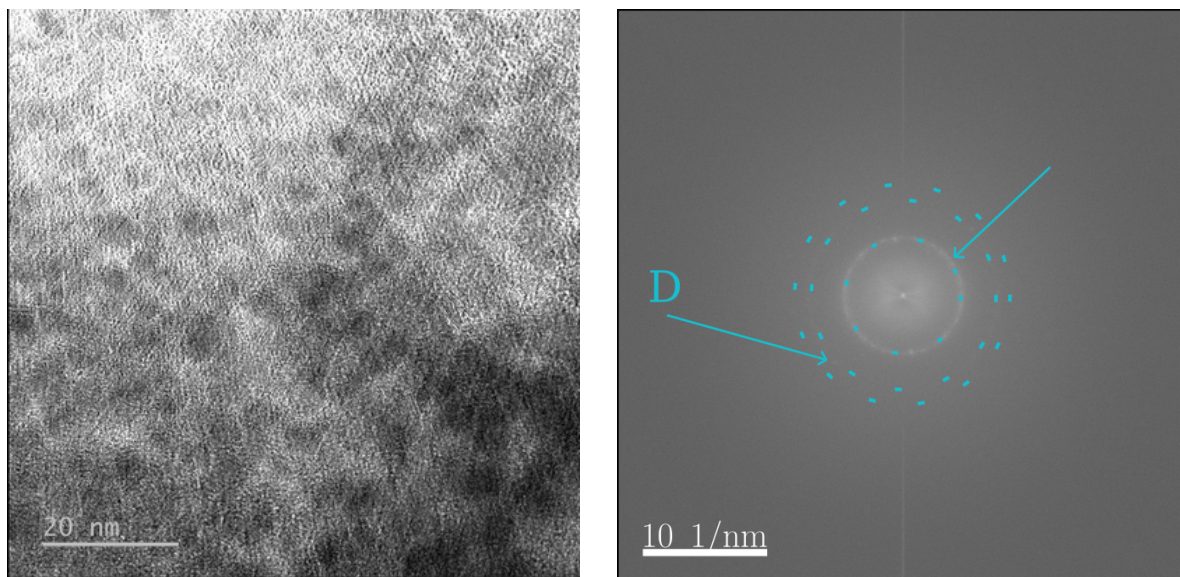
to the intensive cleaning process, it is impossible to know whether this orientation is a result of the chemical and mechanical treatment or not.

As noted in [232], the final stacking form of graphite resulting from annealing graphite nanopowders is largely governed by kinetics. This effect becomes significant below temperatures of $T < 2600$ K, potentially leading to AB, AA, or AA'-stacked graphite. The NDs impact the ionic gel at several km s^{-1} and remain hot after release (see Sec. 4.1). These elevated temperatures could explain the presence of various graphite forms in the catcher, possibly formed via annealing of the nanoparticles. A single hot ND might transform into graphite and act as a seed for local phase growth within the catcher. Since not all carbon transforms into diamond, NDs are likely surrounded by a carbon containing plasma cloud, which may supply additional material for growth. The observed elongation of these graphite domains may result from the directional strain and impact dynamics of the HVI. Future MD simulations could test this hypothesis in more detail.

The presence of carbon onions can be explained by the exact same principle. NDs impacting at elevated temperatures, or heated during the HVI, are annealing and forming carbon onions. They were only present in sizes compatible with the predicted ND size. The annealing of NDs to carbon onions was already observed experimentally [116]. According to [116] they form by an exfoliation process and it is less likely to capture additional free carbon atoms during this process. Therefore, it is reasonable for them to occur in the sizes of the NDs.

4.9.2. Fibre-Like Structure

Only a single of the fibre-like structures was found in the catcher. Unfortunately, this particle was almost entirely located on the TEM grid, so the thickness of the material prohibited an



(a) TEM scan of one of the larger particle clusters. It is clear that the cluster consists of smaller particles of the sizes from 3 to 5 nm.

(b) Two-dimensional FFT of the particle cluster. The theoretical reflections from a diamond lattice are also shown (inside to outside: (111), (022), (311) reflections). Some prominent reflections are marked.

Figure 4.31.: TEM scan of one of the particle clusters found in the ionic gel and the corresponding two-dimensional FFT.

accurate examination of its structure and composition. However, from the TEM image the appear several hundreds of nm long and span single digit nm in diameter. Although these dimensions could be consistent with carbon nanotubes, further studies would be required to determine the nature of these structures accurately.

4.9.3. Particle Clusters

A zoomed-in image of a large particle cluster is shown in Fig. 4.31a. The cluster consists of smaller particles of sizes 3 to 5 nm which are visible as darker spots. They show a clear sign of a crystal lattice. Fig. 4.31b shows the FFT of the TEM image, along with the theoretical diamond rings. At a d -spacing of 2.02 Å, there is an almost perfect ring in the FFT, close to the theoretical diamond value of $d_{111} = 2.06$ Å. A faint spot is found at 1.29 Å, where the diamond literature value is $d_{002} = 1.26$ Å. No other reflections are present and the excellent alignment with the theoretical diamond FFT is a strong indicator that the particles are NDs with sizes from 3 to 5 nm.

A TEM scan at lower magnification is shown in Fig. 4.32, with an EELS mapping of the ROI (centre image). Four points of interest were integrated and background-subtracted. Their summed EELS spectrum (right plot) shows a clear diamond peak at 302 eV, matching excellently with the DND reference spectrum [233]. These results confirm the presence of NDs within the recovered material. However, the presence of a more pronounced graphite pre-peak at 285 eV in the particle cluster suggests a higher graphite content in the recovered NDs. The probed volume per pixel is also large, probing many NDs and their graphitic surfaces and might contain additional non-diamond carbon, thus increasing the graphite peak. A comparative study of differently produced NDs EELS spectra showed that the core-loss spectra can have graphitic pre-peaks of different intensities, most prominent in DNDs [233]. The NDs found in this work have even higher pre-peak intensities than those DNDs.

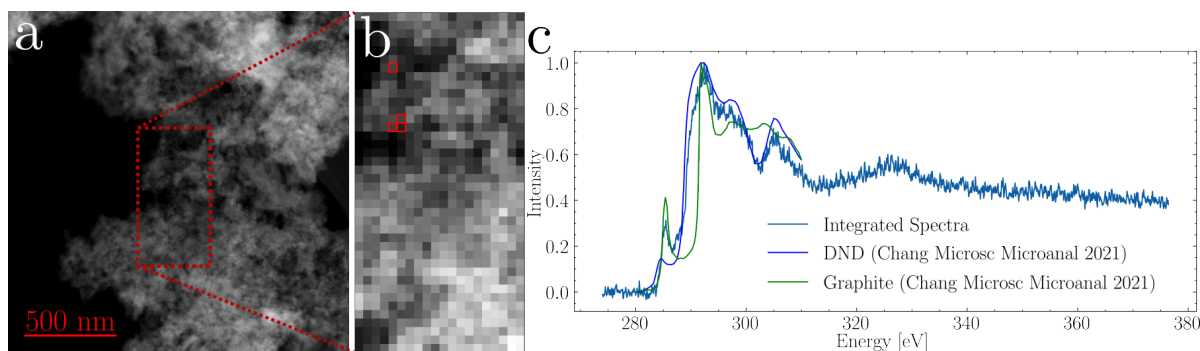
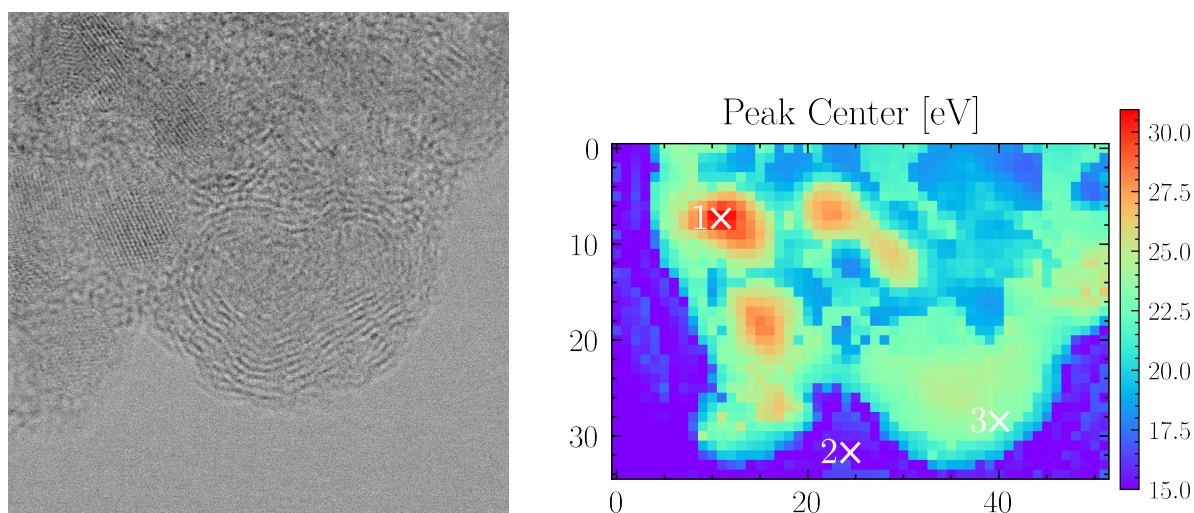


Figure 4.32.: (a): TEM scan of a particle cluster found in the ionic gel catcher. The marked rectangle shows where an EELS mapping was taken. (b): ROI of the EELS mapping. The pixel values represent the integrated intensity of the spectra. The marked pixels are chosen for integration. (c): Background-removed EELS spectrum of the integrated pixels. Literature values of EELS spectra for DNDs and graphite are also displayed [233].



(a) TEM scan of a carbon onion and multiple ND candidates seen as darker spots found in the ionic catcher.

(b) Low-loss EELS map of the left TEM scan. The pixels show the centre position of a skewed Voigt + exponential background model which can help differentiate between vacuum, graphite and diamond. The white crosses indicate the positions 1, 2, and 3, where the EELS spectra are plotted in Fig. 4.34.

Figure 4.33.: TEM scan and low-loss EELS map of a twin carbon onion and multiple ND candidates.

As explained in Sec. 2.4.4, the low-loss spectrum can be especially useful for differentiating diamond from graphite. An interesting region with a feature looking like a carbon onion and multiple ND candidates is mapped in the low-loss EELS. Fig. 4.33 shows the low-loss EELS scan along with the TEM image. The EELS spectra of three distinct points are displayed in Fig. 4.34. The pixel map (Fig. 4.33b) was created by fitting a skewed Voigt profile plus an exponential background to each spectrum. The graphite peak is centred around 28 eV, the diamond peak at 32 eV, and amorphous carbon at around 23 eV [1]. The mapping clearly shows that in the centre of the NDs, the EELS peak exceeds 30 eV, while it is about 23 eV in the surface of the carbon onion. In the space between the NDs it reaches values as low as 20 eV. The values do not exactly correspond to the literature values, which can be attributed to the fact that a single peak model was used to incorporate all three features. However, the

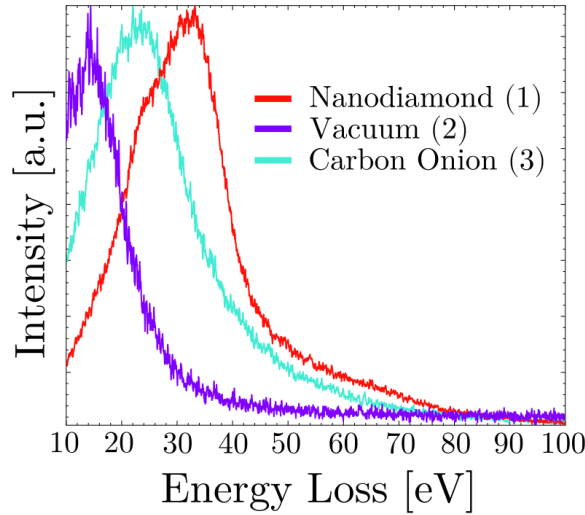


Figure 4.34.: Low-loss EELS spectra of three distinct points in the map marked in Fig. 4.33b. The carbon onion shows a single peak structure centred at 23 eV, while the ND clearly contains a double peak feature. It has a pre-peak, close to the carbon onion position and a main peak feature at 32 eV.

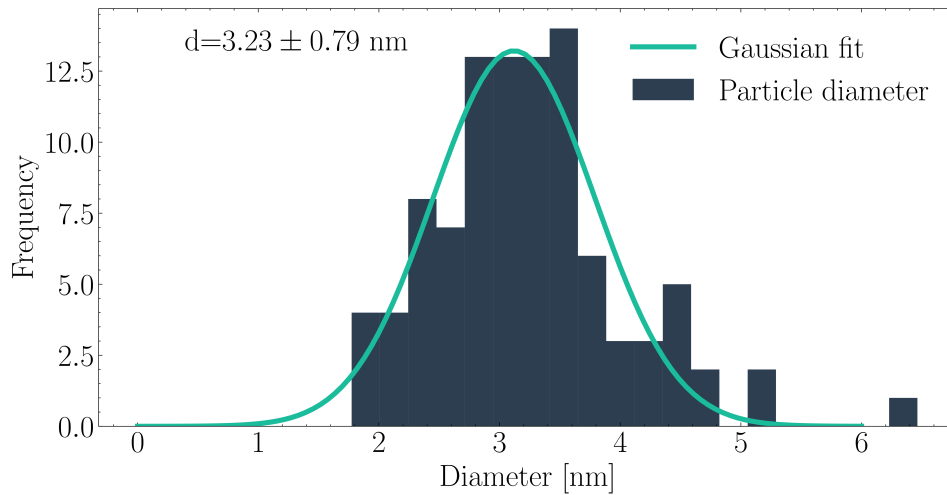


Figure 4.35.: Measured particle sizes of the NDs found in the ionic gel catcher. A Gaussian function was fit to the distributions.

EELS spectra further substantiate the presence of NDs and carbon onions in the ionic gel catcher.

To determine the sizes of the recovered NDs in the catcher, 98 NDs found in another particle cluster are measured by hand using the software ImageJ [234]. Fig. 4.35 shows a histogram of the measured particle diameters. A Gaussian function is fit to the data and the particle diameter determined to $d = 3.23 \pm 0.79$ nm. The corresponding STEM scans are shown in Fig. A.28. The sizes were measured by choosing the visible lattice domains.

To summarise, by using an ionic gel catcher, this work, for the first time, was able to recover NDs produced in laser-driven shock compression. The NDs are slightly larger than what was found for the after-breakout probing times during the SACLA campaign. In addition to ND, carbon onions and amorphous carbon were found in the catcher. The former might be a result of NDs transforming due to elevated temperatures. The amorphous carbon could be a product of untransformed carbon during the shock. Additionally, a single, fibre-like structure was found

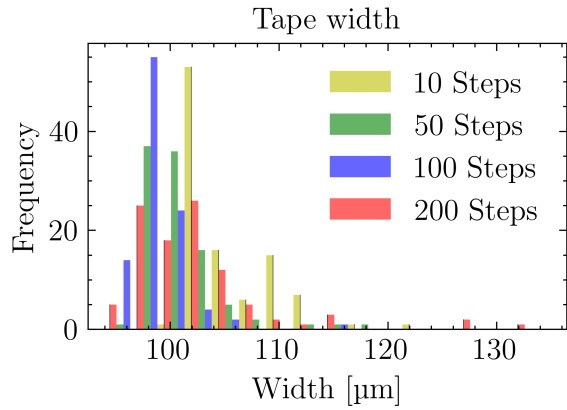
on the TEM grid, but could not be investigated further. Therefore, future studies should determine, whether such structures are systematically found and what they are composed of. Furthermore, this work found that the recovered NDs' core-loss EELS spectra show a very prominent graphitic pre-peak. It was confirmed that ionic gels are an excellent catcher material due to their vacuum compatibility, the possibility for horizontal mounting, and the fact that they are water soluble and biocompatible. Due to the high repetition rate of the experiments conducted, much more material than in a single shock was collected in the same catcher. TEM was proven to be an exceptional diagnostic for future experiments, because it enables access to the most interesting quantities, such as ND sizes and the possibility to determine doping of the NDs via EELS measurement. These pioneering experiments open the door to future synthesis paths of many different metastable phases forming at WDM conditions. One such phase are the carbon BC8 phase, proposed to form under high compression [235]. It could also enable the synthesis of doped NDs by modifying the precursor material.

4.10. Tape Target In-Focus Stability

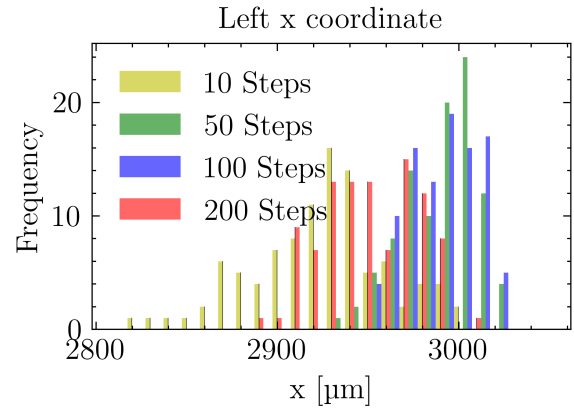
The stability measurements for the tape target design are obtained using an optical camera with the process outlined in Sec. 3.3.6 and A.12. To first determine that the process produces accurate results, the thickness of the tape was measured from the thresholded images. For each stepsize (10, 50, 100, 200 motor steps) the thickness was calculated. Fig. 4.36a shows the measurements for the case without horizontal fixing (compare Sec.3.3.6). It is clear that the width is in very good agreement with the nominal width of 100 μm . Special attention should be paid to the absence of a clear cut-off at high thickness. This implies that the highest intensity pixel is well centred within the tape and that the thresholding with cut-off method is well suited.

To determine whether the tape stability is sufficient for high-repetition-rate operation, the tape's positional variation is determined. The right column in Fig. 4.36 shows the measured tape positions. In the unfixed case (Fig. 4.36b), the 10 and 200 step results seem to be skewed to lower x -values. It seems arbitrary that specifically these two stepnumbers should result in a large deviation. When looking at the result for the fixed setup (Fig. 4.36d) it becomes clear that the number of steps indeed has no effect on the tape targets stability. When fixing the tape in horizontal direction there seems to be no correlation between the step size and the tape stability. This suggests that this is an artefact of the tape moving out of focus, which would affect how the tape position is determined. Combining measurements of the four different stepnumbers to a singular histogram, a Gaussian distribution can be fit to the left-most position and the tape width to determine the in-focus stability of the tape target design. Fig. 4.37a shows the combined width measurement of the tape target which has an uncertainty of $\sigma = 2.4 \mu\text{m}$ and is in good agreement with nominal tape width. The combined in-focus stability is shown in Fig. 4.37b and is accurate up to a standard deviation of $\sigma = 22.17 \mu\text{m}$. As a comparison, the original design by ELI Beamlines achieved a focal plane stability of $\sigma = 8.6 \mu\text{m}$ [215]. However, that was on a copper tape which is significantly more rigid and allows for stronger holding currents in the stepper motor. Due to the optical method to determine the stability in this work, the values given here should be taken as a worst case scenario.

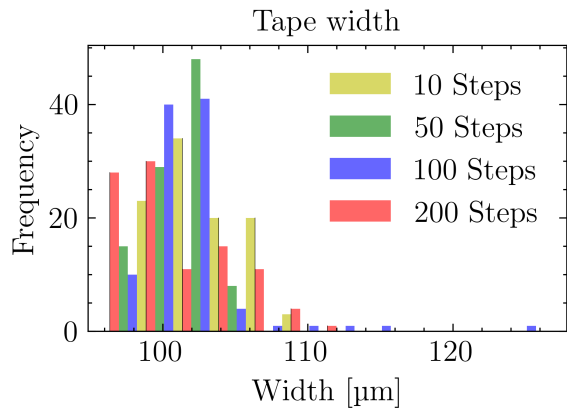
The current setup at the University of Rostock uses lenses of 400 mm for focusing the drive laser on the target [236]. With these lenses the optimal lens position was determined within an accuracy of 0.2 mm. Because the tape targets stability is an order of magnitude more precise, it is sufficient for high-repetition-rate experiments, even when employing shorter focal lengths.



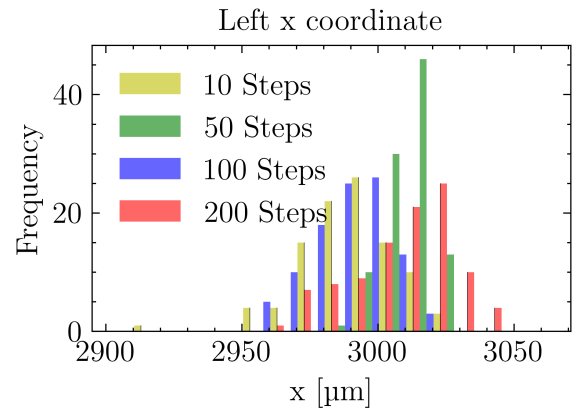
(a) Measured width of the tape target from the automatically processed image in the horizontally unfixed setup.



(b) Laser side position of the edge of the tape target from the automatically processed image in the horizontally unfixed setup.

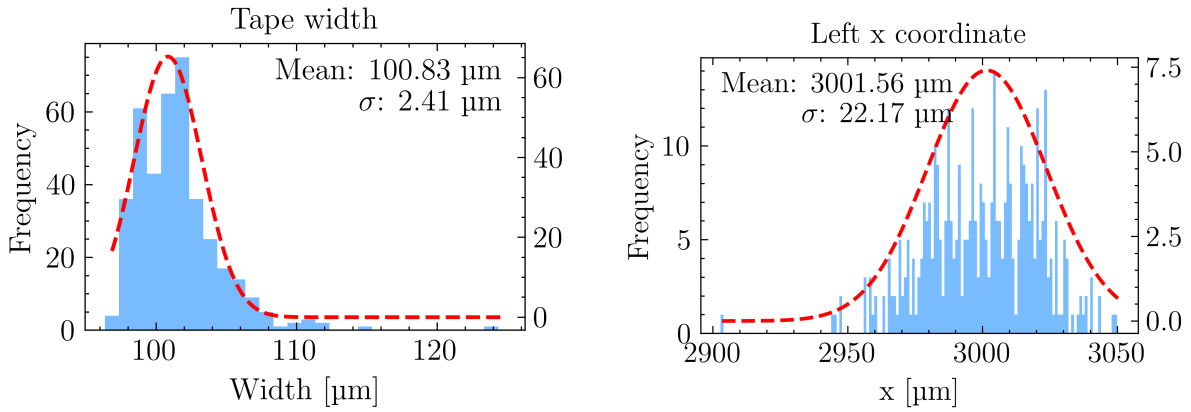


(c) Measured width of the tape target from the automatically processed image in the horizontally fixed setup.



(d) Laser side position of the edge of the tape target from the automatically processed image in the horizontally fixed setup.

Figure 4.36.: Tape target stability measurements for the unfixed and fixed setups.



(a) Measured width of the tape target from the automatically processed image in the horizontally fixed setup.

(b) Laser side position of the edge of the tape target from the automatically processed image in the horizontally fixed setup.

Figure 4.37.: Histogram for all different steps combined with a Gaussian fit through the data point. The mean and standard deviation are displayed in the figure.

To summarise, the developed tape target was able to achieve a focal plane stability of $\sigma = 22.17 \mu\text{m}$, which suffices for high-repetition-rate experiments. This will enable a feasible path for producing ND-containing catchers at the University of Rostock. In combination with the advanced presented on recovery, many of the proposed experiments can be conducted directly at the University of Rostock.

5. Conclusion and Outlook

This work set out to deepen the understanding of ND formation in planetary interiors and to assess whether laser-driven shock compression offers a viable synthesis pathway for NDs.

In the context of planetary interiors, this study observed NDs with diameters around 3 nm in single-shocked PET at conditions of 80 ± 10 GPa and 3900 ± 400 K, which shrink to about 2 nm 12 ns after breakout. Double-shocking PET to 150 ± 15 GPa at 4000 ± 1000 K yielded larger NDs, approximately 4.5 nm in size during the shock, with signs of substantial post-breakout growth to values up to 22 nm. Furthermore, this work suggests that dynamic compression of plastics, combined with SAXS diagnostics, is a promising approach to experimentally benchmark ND growth dynamics. Such a combination can be a powerful tool to determine nucleation and growth dynamics for NDs at WDM conditions.

This work also demonstrated that NNs trained with physically realistic noise outperform those trained on ideal data, making them suitable to provide priors for probabilistic modeling of size distributions using MCMC approaches such as McSAS. However, the size distribution results presented here are limited by poor data quality and high method-dependent variability. Future experiments explicitly targeting ND size distributions under compression are therefore strongly recommended. When combined with theoretical models such as those by Pontin et al., such data could significantly improve our understanding of planetary evolution [90].

The MD simulations conducted in this work show that NDs experience significant release cooling - reaching from hundreds to above 1000 K - increasing with the degree of compression. However, MD studies of NDs releasing from PET Hugoniot states exceeding 2000 K predict an almost complete loss of diamond structure. This finding is contrasted by the experimental results, which confirm the presence of ND releasing from single-shocked PET up to 12 ns after breakout. A possible explanation for this discrepancy is the presence of a protective plasma cloud around the NDs, which is not implemented in the simulations.

Additionally, MD simulations at above-Hugoniot pressures predict enhanced recrystallisation into diamond. This prediction is supported by experimental observations of substantial post-breakout growth of the NDs up to 22 nm, in double-shocked PET. To investigate the potential shielding effect of a surrounding plasma cloud on NDs, future MD simulations should explicitly include such material. Experimentally, extending the release studies to more extreme states, e.g. via triple-shock compression, could help determine whether such conditions further enhance post-breakout ND growth.

Furthermore this work has investigated NDs impacting aluminium catchers at hypervelocities via MD. The simulations showed that NDs can only survive an impact velocity below 11 km s^{-1} . However, if they do survive they can be embedded into the catcher surface. These simulations are again lacking any surrounding material of the NDs. A comparative study with simulated amorphous carbon impactors showed that the crater shapes caused by NDs will result in substantially deeper craters. Importantly, high impact velocities which result in immediate destruction of the ND during the contact and compression stage, yield much shallower craters compared to impact velocities in which a large part of the NDs survived this stage. In general, the crater morphologies found in these simulations are largely inconsistent with the descriptions found by Price et al. [113]. This is attributed to the fact that Price et al. only considered impactors of a minimal size of 100 nm. The results obtained in this work could extend the data to smaller impactors.

An experimental comparison of VISAR diagnostic and a high-speed camera has shown that such cameras can be a valuable tool to estimate shock states in recovery experiments.

Another part of this work examined the crater landscapes formed by NDs impacting an aluminium catcher and compared them to those created by non-diamond impactors, using confocal microscopy. In this work, qualitatively, NDs produced smaller, better differentiated, and deeper craters, while non-diamond impactors left larger ones. Notably, NDs created significantly more craters, with an area density about 1.5 times higher. However, even with the high resolution capability of an AFM, the observed crater diameters far exceeded expectations based on ND sizes of a few nm. This suggests that NDs are not fully separated after breakout but instead form larger conglomerates. Their presence within a hot carbon cloud may explain the post-breakout growth observed in this work.

Different catcher materials were tested in this thesis for their ability to successfully recover NDs to ambient conditions, serving as a foundation for laser-driven shock synthesis of NDs. The catcher materials were investigated using Raman spectroscopy and TEM measurements. The materials studied in this work are candle gel, aluminium and copper plates, and newly developed ionic gels, comprised of the ionic liquid Tris-(2-hydroxyethyl)-methylammonium-methanesulfate and PVA. This work has shown that the ionic gel catchers are vacuum compatible and can easily be mounted in any recovery setup due to their high viscosity.

Different lamellae were cut from the aluminium and copper catchers and analysed in a TEM, but no evidence of NDs was found. Given the time-consuming lamella preparation process and high densities of these materials - which would decrease the chances of ND survival upon impact - this work advises against their use in future catcher experiments.

The dissolved ionic gel catcher yielded suspensions that could be readily analysed in the TEM, using standard grids. While in this study nitric acid was used for cleaning to reduce contamination, the water solubility of these gels allows for gentler cleaning methods to be considered in future studies.

Within these catchers different carbon containing structures were identified. Along with AA' and AB stacked graphite - as part of a long (tens of μm) rod-like particle - a fibre-like structure was found. Unfortunately, this structure was ill-positioned on the TEM grid, so further analysis thereof was impossible. Consequently, future recovery studies should determine whether such particles are routinely found and what they are. Carbon onions were also found in the catcher, which could be a result of NDs annealing at elevated temperatures.

Clear signs of recovered NDs were found in this research, both through TEM and EELS analysis of the ionic gel catcher. The catcher collected the ejecta of 133 shots on PET shocked to about 80 GPa at 3800 K. The size of the NDs were measured to $d = 3.23 \pm 0.79$ nm, which is slightly larger than what this study measured via *in situ* probing 12 ns after breakout. This further supports the hypothesis that the NDs do grow after release. The EELS signal of the recovered NDs is very similar to the literature values of DNDs but does contain an increased graphitic pre-peak at 285 eV. This points towards a higher degree of graphitisation of the NDs, although more thorough examinations are required to determine this in detail.

During the course of this work, it was shown that low-loss EELS can be a powerful technique to find NDs in TEM samples. Due to the increased signal in the low-loss regime, the integration times for these spectra are much shorter than in the core-loss.

Finally, as part of this thesis, a new design for an in-house tape target was developed for implementation at the University of Rostock. By using a step motor and custom made parts

it was possible to develop a vacuum compatible holder with an in-focus stability of $22.17\text{ }\mu\text{m}$. This is sufficiently stable for use with the lasers in the laboratory setup.

In sum, this thesis advances both planetary and material science by contributing to the understanding of formation and recovery of NDs from plastic targets via laser-driven shock compression. Using an ionic gel catcher, it successfully recovered NDs from a laser-compressed state for the first time, marking a key step toward the controlled synthesis of metastable materials. The development of a high-repetition-rate target platform opens the door to such recovery experiments for many research groups around the globe. Beyond a potential scalable synthesis path for NDs, this research lays the groundwork for systematic production of doped NDs by tailoring the precursor composition. More broadly, the approaches developed here could enable novel synthesis pathways for a wide range of previously inaccessible materials.

A. Appendix

This appendix contains additional derivations, plots and information on sample preparation. It is structured as follows: First, Sec. A.1 contains additional information on the ND nucleation and growth model developed by Pontin et al. After that Sec. A.2 details about the MD expansion simulations. Thereafter, Sec. A.3 presents the fit parameters of the phenomenological functions by Price et al. This chapter continues with Sec. A.4 which will present the diffraction models used in the analysis of the XRD data, along with some general derivations and definitions. Following this, Sec. A.6 will present the experimental parameters used in the shock experiments at SACLA and EU-XFEL along with a brief discussion of uncertainties in diffraction experiments. Sec. A.7 follows, which contains information on the implementation of the NN used to analyse the SAXS data. Furthermore, the TEM lamella preparation process will be outlined in Sec. A.8 followed by the detailed description of the dissolution of the ionic gel catchers in Sec. A.9 these sections also contain additional images of features found on the catchers. Sec. A.10 presents additional information about how the high-speed camera was used to determine release velocities. Then, Sec. A.11 details how the crater measurements were performed. Finally, Sec. A.12 concludes this appendix, by a description of how the stability of the tape target was determined.

A.1. Nanodiamond Nucleation Model

This section contains information of the ND nucleation and growth model developed by Pontin et al. The authors have constructed a nucleation and growth model for diamond, which can forward simulate size distributions of NDs [90] . With this, it is possible to simulate a shock-compressed sample in multiple slices, each reaching the nucleation conditions at different times and obtain size distributions of the NDs as a function of time. Fig. A.1 shows the poster presented at the 18th Conference of Physics of Non-Ideal Plasmas.

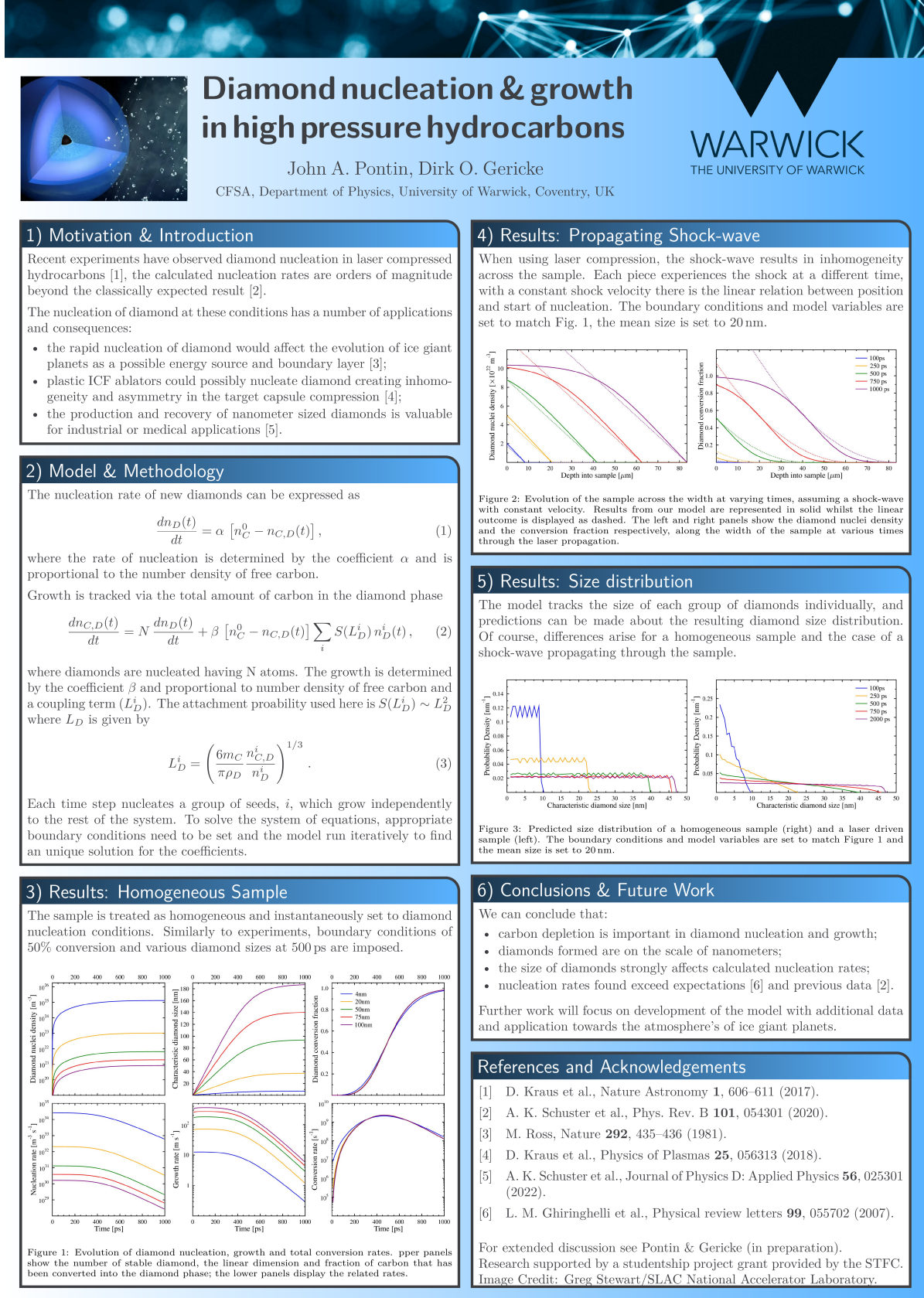


Figure A.1.: Poster of the nucleation and growth model presented by D. Gericke at the 18th Conference of Physics of Non-Ideal Plasmas. Reprinted with permission.

A.2. Release and Expansion: Molecular Dynamics Simulation of Nanodiamonds after Breakout

This section contains additional information on the release and expansion simulations conducted in this work as they are described in Sec. 3.1.1.

Sec. 3.1.1 reports the nominal expansion times for the simulations, which can be related to the strain rate via Equation 3.1:

T_{init} [K]	d_{init} [Å]	Strain rate $\dot{\epsilon}$ [ps ⁻¹]				
		$\dot{\epsilon}(50 \text{ ps})$	$\dot{\epsilon}(100 \text{ ps})$	$\dot{\epsilon}(250 \text{ ps})$	$\dot{\epsilon}(500 \text{ ps})$	$\dot{\epsilon}(1000 \text{ ps})$
5000	3.35	30.18×10^{-3}	15.01×10^{-3}	6.04×10^{-3}	3.02×10^{-3}	1.51×10^{-3}
4000	3.355	30.12×10^{-3}	15.06×10^{-3}	6.03×10^{-3}	3.01×10^{-3}	1.51×10^{-3}
3000	3.38	29.81×10^{-3}	14.90×10^{-3}	5.96×10^{-3}	2.98×10^{-3}	1.49×10^{-3}
2000	3.39	29.68×10^{-3}	14.84×10^{-3}	5.94×10^{-3}	2.97×10^{-3}	1.48×10^{-3}

Table A.1.: Strain rates for each initial temperature and nominal expansion time. The initial diamond lattice constant d_{init} required to reach the target pressure is also shown for each simulation.

After the equilibration phase, the non-periodic boundary conditions result in partial disintegration of the diamond cubes. Depending on the temperature and pressure, a smaller or larger diamond core remains. The images of the final snapshot in the equilibration phase are displayed in Fig. A.2.

The higher the equilibration temperature, the less carbon atoms remain in the diamond phase after the equilibration. For $T_{\text{init}} > 2000 \text{ K}$ the diamond does not fill the entire simulation box. A layer of non-diamond atoms seems to be covering the simulation box walls at these temperatures. When looking at a cutout of a surface layer for the $T_{\text{init}} = 3000 \text{ K}$ simulation (Fig. A.3), it becomes clear that here the surface is partially graphitised or rather "fullerene-nated". This is evident from the large portion of hexagonal or pentagonal carbon rings, which are characteristic for fullerene structures. Such a formation of a carbon onion from ND is well-known in the literature [116].

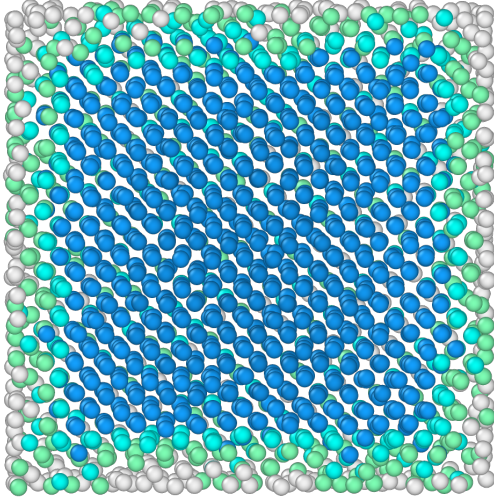
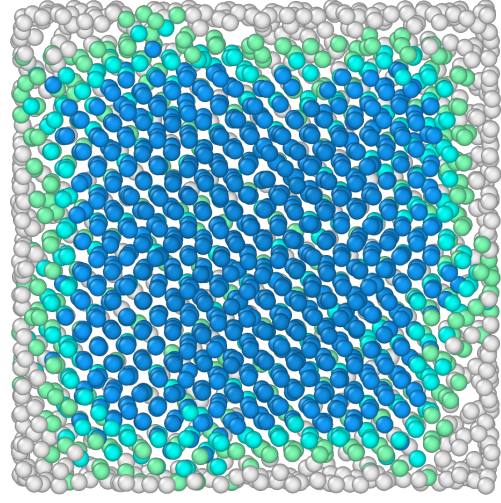
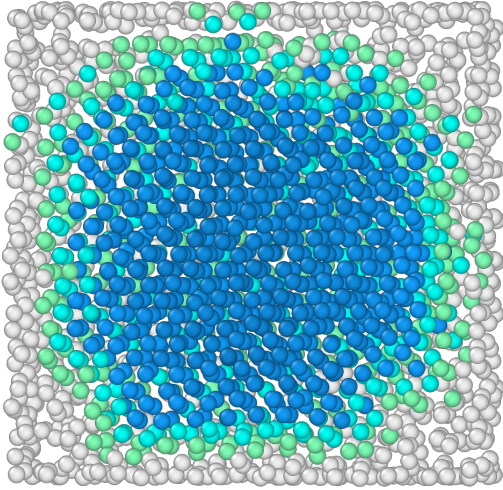
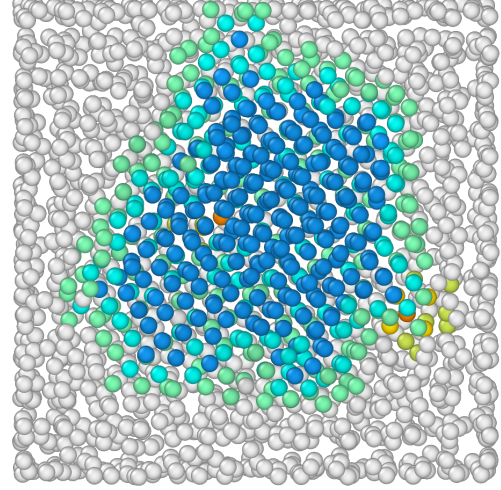
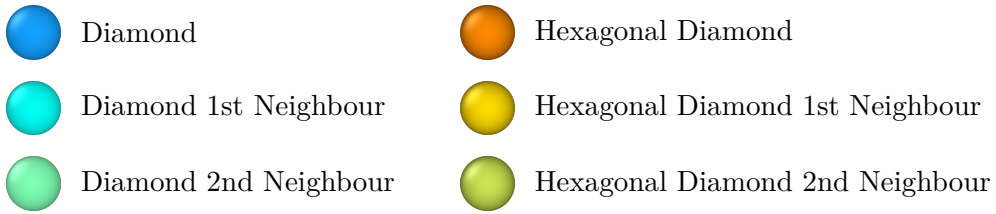
A.2.1. Radiative Cooling Model

The modelling of a cooling sphere was facilitated by the simplistic assumptions of a spherical particle as a black body. Here the Stefan-Boltzmann law [206, 207] describes the radiated power P from a surface A :

$$P = \epsilon \sigma A T^4, \quad (\text{A.1})$$

ϵ is the emission constant (1 for a black body) and the Stefan-Boltzmann constant σ . Separating this and inserting $k = \epsilon \sigma A / mc$, with mass of the sphere m and heat capacity of the material c leads to:

$$T^{-4} dT = -k dt, \quad (\text{A.2})$$

(a) 2000K, $d_{\text{init}} = 3.39 \text{ \AA}$ (b) 3000K, $d_{\text{init}} = 3.38 \text{ \AA}$ (c) 4000K, $d_{\text{init}} = 3.355 \text{ \AA}$ (d) 5000K, $d_{\text{init}} = 3.35 \text{ \AA}$ 

(e) Legend for atom types.

Figure A.2.: Remaining diamond core after the equilibration phase for all initial temperatures and pressures. The images show a cross-sectional view of the cubic simulation cell. The atoms are coloured by their neighbouring structure in the diamond grid according to [204].

which can be integrated to:

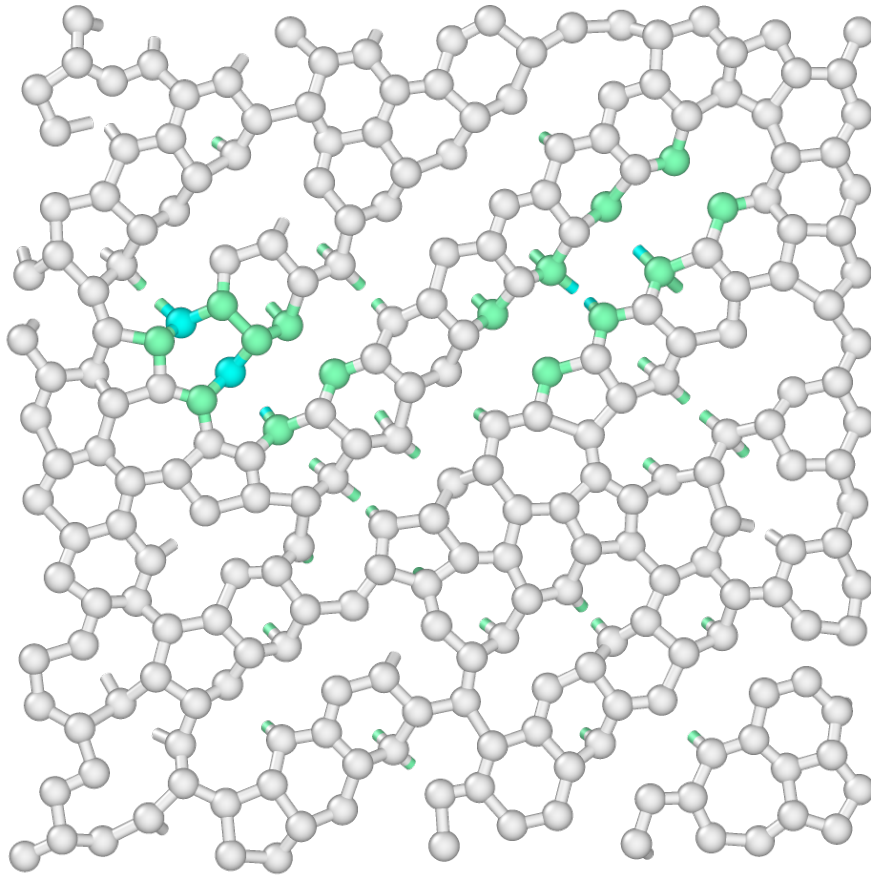


Figure A.3.: Surface layer of the $T_{\text{init}} = 3000 \text{ K}$ simulation. The bonds are created by the interatomic distances with a uniform cut-off of $d_{\text{cut}} = 1.8 \text{ \AA}$. The hexagonal and pentagonal rings are clearly visible in large portions of the surface. This surface "fullerenation" is a well-known feature in ND disintegration [116].

$$-\frac{1}{3}T^{-3} = -kt + C. \quad (\text{A.3})$$

When inserting the boundary conditions for $t = 0$ the time dependence of the temperature is determined to:

$$T(t) = (3kt + T_0^{-3})^{-\frac{1}{3}}. \quad (\text{A.4})$$

By using this equation the temperature evolution of a ND sphere of radius 2.5 nm was computed using a constant heat capacity of $516 \text{ J g}^{-1} \text{ K}$ and a temperature dependent model [237, 226]. Outside the range of available data, the closest data point was chosen as the heat capacity.

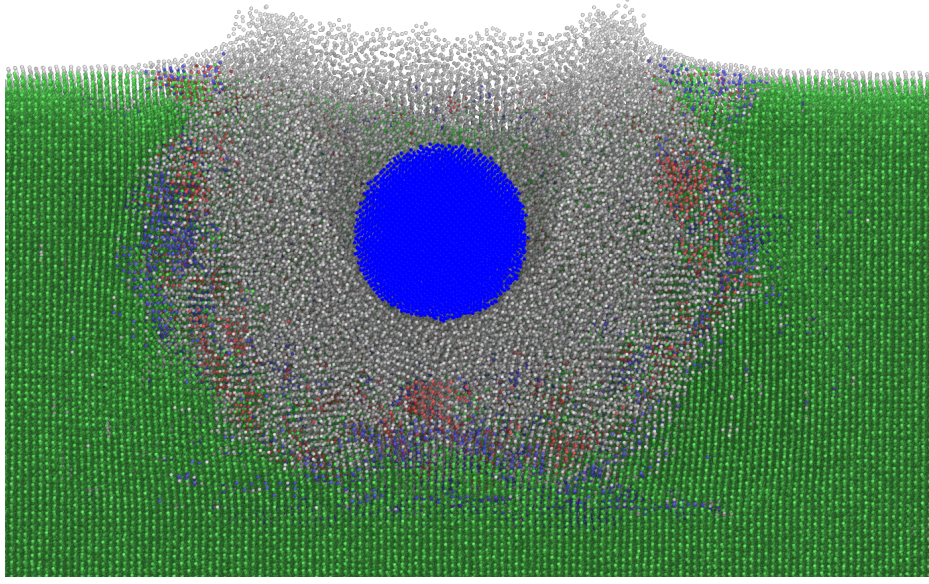


Figure A.4.: Side view of a ND impacting an Al catcher at 9 km s^{-1} . Half of the atoms were removed for better visibility. The carbon atoms are coloured bright blue. The structure of the Al atoms was determined by a common neighbour analysis [202]. The atoms colouring is as follows: **green:** fcc, **red:** hcp, **blue:** bcc, **yellow:** ico .

A.3. Molecular Dynamics Impact Simulation

This section contains the fit parameters for the phenomenological functions to describe crater shapes according to Price et al. [113]. It also presents images of the NDs impacting the catcher to illustrate how convergence was determined.

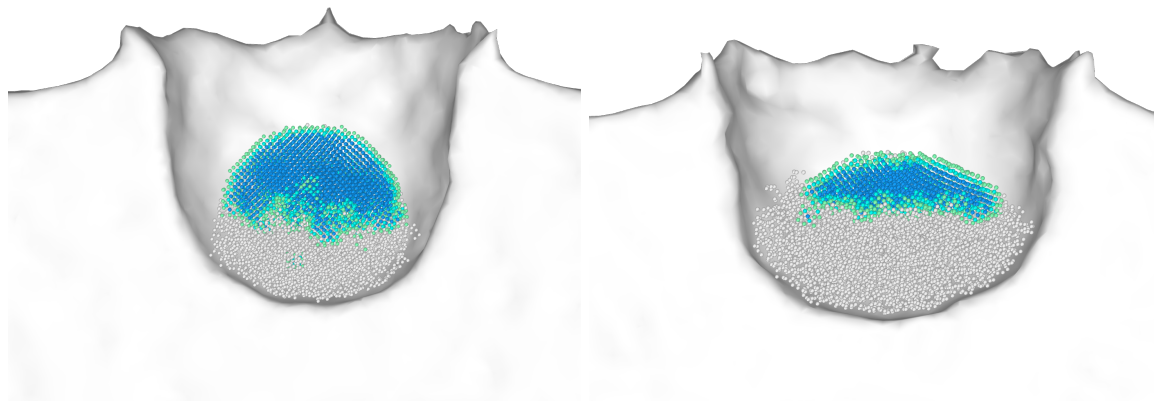
The best fit parameter values for the fit functions are given in the Eq. 1.2 and 1.3.

Constant	Value	Constant	Value
A	0.295	A_2	6.95×10^{-2}
α	0.556	χ	1.52
B	0.939	B_2	1.04
β	0.164	ψ	2.39×10^{-2}
C	0.734	C_2	1.42
γ	8.77×10^{-3}	ω	-0.611

Table A.2.: Values for the best fit for the phenomenological function describing the crater and diameter of a hyper-velocity impact (Eq. 1.2 and 1.3). The functions and the values are taken from Ref. [113].

A.3.1. Nanodiamond Impact

When the NDs are impacting the catcher surface, a spherical shock wave is launched into the catcher material. Fig. A.4 shows a side view of a ND impacting at 9 km s^{-1} into the aluminium catcher. The spherical shock waves is clearly visible progressing outwards from the impact site. The catcher dimensions in the simulations were adjusted such that it was sufficiently large to avoid the merging of such shock waves at the periodic boundary conditions.



(a) ND impacting with 11 km s^{-1} during the excavation stage at 1.1 ps. (b) ND impacting with 13 km s^{-1} during the excavation stage at 0.8 ps.

Figure A.5.: Side view of a NDs impacting the Al catcher. C atoms are coloured as in Fig. 4.16.

An intermediate cross-sectional view of a ND impacting an aluminium catcher at 11 km s^{-1} after 1.1 ps is shown in Fig. A.5a. It is clear, that the ND remains largely intact during this phase. However, the temperature of the ND rises substantially due the impact, which leads to subsequent melting of the ND. For comparison, the same view for an impact velocity of 13 km s^{-1} at 0.8 ps is shown in Fig. A.5b. In there, most of the ND is already destroyed directly upon impact, leaving a flat amorphous impactor front.

A.4. X-Ray Diffraction

This section contains details about the XRD analysis performed in this work. It starts briefly iterating over the general description of a scattering process and continues by presenting the XRD model function used to fit the XRD data. After that details about the IRF are presented. It finally the Scherrer Equation and Debye-Waller factor are outlined.

A.4.1. Scattering Process

A brief construction of the description of a coherent scattering process most relevant to this work is given in this appendix. For detailed derivations the reader is referred to [238, 239, 165, 240].

In a coherent scattering process, the detector intensity can be derived by assuming a plane wave assumption for the incoming radiation. Each electron hit by an incoming x-ray itself emits an electromagnetic wave of amplitude:

$$A_m(\mathbf{q}) = f_m(\mathbf{q}) \exp(-i\mathbf{q}\mathbf{r}), \quad (\text{A.5})$$

with form factor $f_m(\mathbf{q})$. The vector $\mathbf{r}$ is the position vector of the electron relative to a defined origin. Therefore, the total amplitude of a plane wave that is scattered by a collection of N atoms as a function of the momentum transfer $\mathbf{q}$, is calculated as:

$$A(\mathbf{q}) = \sum_{m=1}^N f_m(\mathbf{q}) \exp(-i\mathbf{q}\mathbf{r}_m). \quad (\text{A.6})$$

The observable quantity of the amplitude is the intensity, which is:

$$I(\mathbf{q}) = A(\mathbf{q})A^*(\mathbf{q}), \quad (\text{A.7})$$

and which combines to:

$$I(\mathbf{q}) = \sum_{m=1}^N \sum_{n=1}^N f_m(\mathbf{q})f_n(\mathbf{q}) \exp(-i\mathbf{q}(\mathbf{r}_{mn})), \quad (\text{A.8})$$

where $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$. For a sufficiently large collection of scatterers that are randomly oriented the intensity can be integrated over all solid angles yielding an average:

$$I(\mathbf{q}) = \frac{1}{4\pi} \sum_{m=1}^N \sum_{n=1}^N f_m(\mathbf{q})f_n(\mathbf{q}) \int_{\Omega} \exp[-i\mathbf{q}(\mathbf{r}_{mn})] d\Omega. \quad (\text{A.9})$$

Using the projection of $\mathbf{q}$ on $\mathbf{r}_{mn}$, $\mathbf{q} \cdot \mathbf{r}_{mn} = qr_{mn} \cos(\theta)$, the integral over all solid angles $d\Omega$ becomes:

$$\int_{\Omega} \exp[-i\mathbf{q}(\mathbf{r}_{mn})] d\Omega = \int_0^{2\pi} \int_0^{\pi} \exp[-iqr_{mn}\cos(\theta)] \sin(\theta) d\theta d\phi, \quad (\text{A.10})$$

substituting $x = \cos(\theta)$ and $dx = -\sin(\theta)d\theta$ and the integral limits alike, becomes:

$$\int_{\Omega} \exp[-i\mathbf{q}(\mathbf{r}_{mn})] d\Omega = 2\pi \int_{-1}^1 \exp[-iqr_{mn}x] dx, \quad (\text{A.11})$$

which is solved by the spherical Bessel function of the zeroth order [241] to yield:

$$I(\mathbf{q}) = \sum_{m=1}^N \sum_{n=1}^N f_m(\mathbf{q}) f_n(\mathbf{q}) \frac{\sin(qr_{mn})}{r_{mn}}. \quad (\text{A.12})$$

This is the Debye scattering Eq. 2.13. An illustration of an elastic, coherent scattering process can be found in Fig. A.6. In general, every electron that is illuminated by an incoming x-ray is the source of a new electromagnetic wave. Therefore, all electrons would have to be summed up to obtain the scattering signal. However, in XRD, only the scattering from atoms is considered and the electronic structure of the atoms is absorbed into the atomic form factor. The atoms are expected to only occur at the crystal positions.

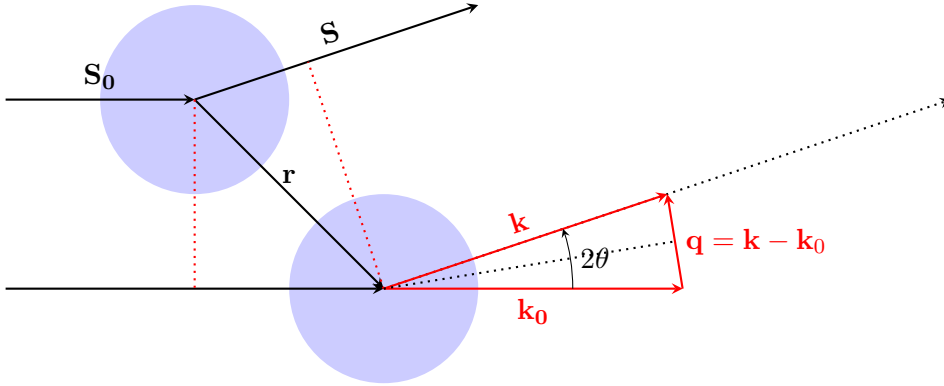


Figure A.6.: Illustration of the involved vectors and quantities in a coherent elastic scattering process. The incoming radiation $\mathbf{S}_0$ is scattered and an outgoing wave $\mathbf{S}$ is emitted.

A.4.2. Diffraction Model in Shock-Compressed PET

The complete signal on the detector in an XRD experiment is a superposition of all contributions within the sample convoluted with the IRF. An excellent overview of the different contributions in a Rietveld refinement is given in Ref. [239]. In this, only the contributions that were included in this work are outlined briefly. All described effects are restricted to the isotropic case. This was based on the assumption of a homogeneously shocked sample.

First, the IRF is determined with the shape given in Sec. A.4.3 and fitted to a well-known reference sample or calibrant. In the shock-compressed states with ND nucleation, the sample consists of a liquid in which the NDs form. Therefore, the two most prominent contributors are the ND crystallites and the liquid.

To obtain the scattering signal of the crystal part, all reflections need to be multiplied with their respective multiplicity (representing symmetry equivalent hkl reflections) and the summed up to:

$$I(2\theta) = \sum_{hkl} M_{hkl} |F_{hkl}(2\theta)|^2, \quad (\text{A.13})$$

with the structure factor $F_{hkl}(2\theta)$.

The crystallite temperature can affect the diffraction peak intensity. The intensities are reduced in according to the Debye-Waller factor (Eq. 2.20). This results in an intensity:

$$I(2\theta) = DW \cdot \sum_{hkl} M_{hkl} |F_{hkl}(2\theta)|^2. \quad (\text{A.14})$$

Other factors affecting the diffraction intensity are the Lorentz and Polarization factors. The first is a geometrical factor accounting for the probability of the reciprocal lattice intersecting with the Ewald sphere and is given as [239]:

$$L = \frac{1}{\cos(\theta) \sin^2(2\theta)}. \quad (\text{A.15})$$

The second scaling factor is the polarisation factor which describes the intensity reduction due to the polarisation of the x-ray beam with the use of a monochromator . It can be written as [239]:

$$P = \frac{1 - K + K \cos^2(2\theta) \cos^2(2\theta_m)}{2}, \quad (\text{A.16})$$

with θ_m as the Bragg reflection angle of the monochromator and K , a factor determined by the polarisation degree. In this work, the experiments were conducted on synchrotron sources. Therefore, θ_m can be set to 90° and $K = 0.05$ [239]. Combined into a single Lorentz-Polarisation factor LP , the intensity becomes:

$$I(2\theta) = LP \cdot DW \cdot \sum_{hkl} M_{hkl} |F_{hkl}(2\theta)|^2. \quad (\text{A.17})$$

To determine the diffraction signal of the crystallite, its size has to be known. Finite sizes cause a broadening of the diffraction peaks as explained in Sec. A.4.4. This finite size broadening needs to be convolved with the entire signal to obtain the intensity. Here the size broadening function was chosen to also be a Pseudo-Voigt function with the $FWHM_G = FWHH_L$ taken from Eq. 2.17. The entire intensity becomes:

$$I(2\theta) = \left(LP \cdot DW \cdot \sum_{hkl} M_{hkl} |F_{hkl}(2\theta)|^2 \right) \otimes (SB). \quad (\text{A.18})$$

This entire signal is then convolved with the IRF to obtain the intensity. Then the model is fit using a least-squared algorithm to obtain the model parameters, such as crystallite size and sample temperature.

Besides the crystallites, the remaining liquid also contributes to the diffraction intensity. To model the liquid, an accurate description of the structure factor of the remaining C-H-O mixture at the WDM conditions is required. For this, DFT-MD simulations can be used to determine the per-species RDF at different densities and temperatures. The partial structure factors for all C-H-O combinations can be obtained from the DFT-MD simulations. From this, the structure factors and the scattering intensity of the liquid can be determined.

However, this requires knowledge of the WDM conditions within the target, to perform the DFT-MD simulations at the correct point in the WDM regime. In case the exact conditions are not known, many different DFT-MD simulations can be performed in a density-temperature grid and an interpolation scheme can be used to determine the point in density and temperature to best reproduce the scattering intensity. This process is described in Ref. [125] for the cases of PET and CA, Therein the DFT-MD simulations were performed by Jan Vorberger from the HZDR, which are also used for this work.

Together with Rips et al., a software package was developed that is capable to perform a Rietveld-like fitting routine for whole-pattern matching of in-situ probed WDM states. It uses a two-dimensional interpolation scheme to match the liquid signal based on DFT-MD simulations. A detailed outline of the procedure is given in [125].

A.4.3. Instrument Resolution Function

The IRF is obtained by using a well defined standard material which is assumed to produced perfect delta peaks on the detector. These standards are also used to determine the exact detector geometry. In case of areal detectors the individual pixels have to be mapped to the corresponding diffraction angle by geometric transformation. After azimuthal integration, a one dimensional diffraction pattern as a function of the diffraction angle 2θ can be obtained. To get the IRF the delta peaks are convolved with the proposed IRF parameters to minimize the residuals. It is common practice to use an IRF in the shape of a Pseudo Voigt, a combination of a Gaussian and a Lorentzian shape [239]:

$$PV(x) = (1 - \eta)G(x) + \eta L(x), \quad (\text{A.19})$$

with the Gaussian and Lorentzian:

$$G(x - x_0) = \frac{1}{\sigma\sqrt{2\pi}} \exp^{-\frac{1}{2}\left(\frac{x-x_0}{\sigma}\right)^2}, \quad (\text{A.20})$$

$$L(x - x_0) = \frac{\frac{2}{\pi\text{FWHM}_L}}{1 + 4\left(\frac{x-x_0}{\text{FWHM}}\right)^2}. \quad (\text{A.21})$$

The FWHM values themselves have an angular dependence and using the Thompson-Cox-Hastings parametrization for the FWHM values [242, 243], they can be written as:

$$\text{FWHM}_G = \sqrt{U \tan^2(\theta) + V \tan(\theta) + W + \frac{Z}{\cos^2(\theta)}} = 2\sqrt{2 \ln(2)}\sigma, \quad (\text{A.22})$$

$$\text{FWHM}_L = X \tan(\theta) + \frac{Y}{\cos(\theta)}. \quad (\text{A.23})$$

The U , V , W , X , Y and Z values can then be optimised to match the pattern of the reference sample. Any peak broadening, asymmetry or peak intensity reduction for the calibrant is attributed to the instrument. The reference sample is assumed to produce perfect delta peaks at the correct relative intensities.

A.4.4. Scherrer Equation

Using the Scherrer Eq. 2.17, the coherently scattering domain size of a crystal reflection can be related to the FWHM of the angular diffraction. A thorough derivation can be found in [244]. A visualisation of the compensation of varying x-ray beams by a stack of lattice plains is displayed in Fig. A.7.

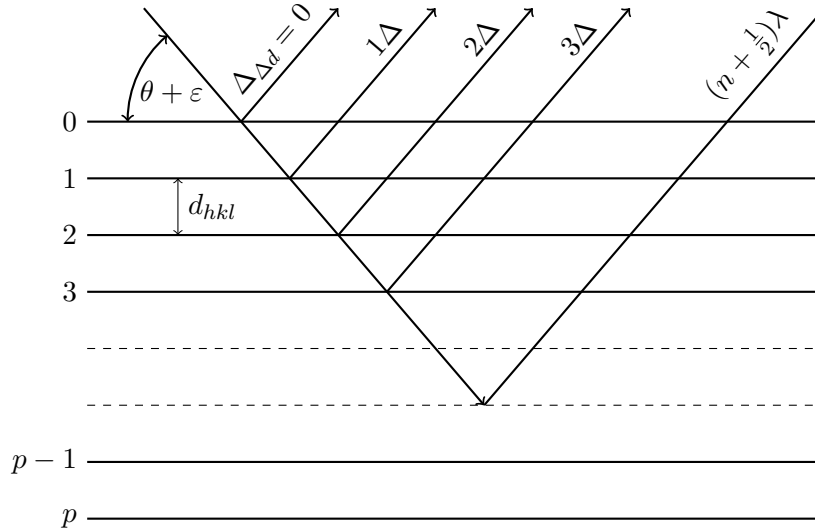


Figure A.7.: Geometrical visualisation for the reflection of x-rays from lattice planes. An additional path length difference Δ_d is accumulated at each plane. If a quasi infinite number of planes is present, there will be one, satisfying the condition, of destructive interference. Because of this Bragg peaks are sharp for large crystals and well defined light sources. The figure was reproduced from [239].

A.4.5. Debye-Waller Factor

The Debye-Waller factor is used to quantify the temperature induced peak reduction of crystal diffraction peaks. In the common expression of the Debye-Waller factor from Eq. 2.18 and 2.19, the $\phi(y)$ can be Taylor-expanded for $T \gg \Theta$. Using the series expression for:

$$\frac{x}{e^x - 1} \approx 1 - \frac{x}{2} + \frac{x^2}{12} - \frac{x^4}{720} + \mathcal{O}(x^6). \quad (\text{A.24})$$

Expanding the integral leads to:

$$\int_0^y \frac{x}{e^x - 1} dx \approx \left[x - \frac{x^2}{2} + \frac{x^3}{6} - \frac{x^5}{600} + \mathcal{O}(x^7) \right]_0^y. \quad (\text{A.25})$$

Inserting the integral boundaries and combining with $\frac{1}{y}$ term from Eq. 2.19 yields:

$$\phi(y) = \frac{1}{y} \int_0^y \frac{x}{e^x - 1} dx \approx \left[1 - \frac{y}{2} + \frac{y^2}{6} - \frac{y^4}{600} + \mathcal{O}(y^6) \right]. \quad (\text{A.26})$$

Finally, ignoring terms of $\mathcal{O}(y^2)$, and inserting this into Eq. 2.18 results in:

$$2W = \frac{3\hbar^2|k|^2}{Mk_b\Theta} \left[\frac{T}{\Theta} \phi\left(\frac{\Theta}{T}\right) + \frac{1}{4} \right] \approx \frac{3\hbar^2|k|^2}{Mk_b\Theta} \left[\frac{T}{\Theta} \right]. \quad (\text{A.27})$$

A.5. Small Angle X-Ray Scattering

This section discussed the basics of SAXS. It starts with the general description of the scattering oh spherical particles, before considering how the scattering is observed from the PY closure relation. Finally the Schulz-Zimm distribution is explicitly introduced.

Using Eq. 2.23 the theoretical intensity distribution of a single spherical nanoparticle of radius r can be calculated using the form factor from Eq. 2.24. Fig. A.8 illustrates how such a signal depends on the radius of the nanoparticle.

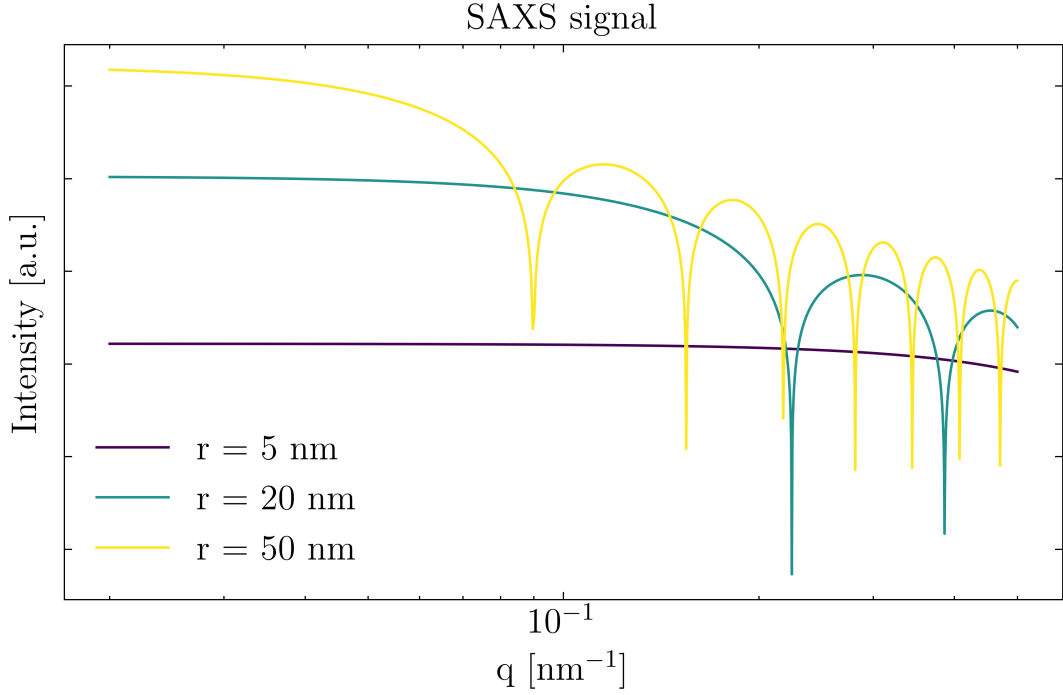


Figure A.8.: Simulated SAXS signal for a single nanoparticle of different radii. The plot is double logarithmic to enable a clear differentiation of the particle radii. The high frequency oscillations are typical for nanoparticles in the order of several tens/hundreds of nanometres.

A.5.1. Structure Factor of Hard-Spheres in the Percus-Yevick Closure

Assuming a hard-sphere model, in which the spherical particles interact via a binary potential (either zero or infinite), the structure factor becomes a function of only the sphere radius R and the volume fraction η . A thorough derivation was published by Wertheim in 1963 [168]. The structure factor is given as [245]:

$$S_{PY}(q) = \frac{1}{1 + 24\eta \frac{G(Rq)}{Rq}} \quad (\text{A.28})$$

where $G(A)$ is expressed as:

$$\begin{aligned} G(A) = & \frac{\alpha}{A^2} (\sin(A) - A \cos(A)) \\ & + \frac{\beta}{A^3} (2A \sin(A) + (2 - A^2) \cos(A) - 2) \\ & + \frac{\gamma}{A^5} (-A^4 \cos(A) + 4 [(3A^2 - 6) \cos(A) + A(A^2 - 6) \sin(A) + 6]) \end{aligned} \quad (\text{A.29})$$

with:

$$\alpha = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad (\text{A.30})$$

$$\beta = \frac{-6\eta(1 + \eta/2)^2}{(1 - \eta)^4}, \quad (\text{A.31})$$

$$\gamma = \frac{\eta}{2} \frac{(1 + 2\eta)^2}{(1 - \eta)^4}. \quad (\text{A.32})$$

A.5.2. The Schulz-Zimm Distribution

The Schulz-Zimm distribution is a commonly used distribution in the context of SAXS, due to its exhaustive analytical treatment. It is suitable to describe the frequencies of the length of a growing polymeric chain [246, 247]. The frequency distribution for a given length/radius r is given as:

$$n(r) = \frac{1}{\Gamma(z+1)} \left(\frac{z+1}{\langle r \rangle} \right)^{(z+1)} r^z \exp \left(-(z+1) \frac{r}{\langle r \rangle} \right), \quad (\text{A.33})$$

with the mean radius $\langle r \rangle$. The parameter z is related to the polydispersity value p via $z = \frac{1}{p^2} - 1$ and describes how broad the distribution is. The mean form factor, averaged over all orientations, for a Schulz-Zimm distribution can be calculated to [248]:

$$\langle |F(q)|^2 \rangle = 8\pi^2 \left(\frac{\langle r \rangle}{z+6} \right)^6 \alpha^{(z+7)} G_{FF}(q), \quad (\text{A.34})$$

with the factors:

$$\alpha(q) = \frac{z+1}{q\langle r \rangle}, \quad (\text{A.35})$$

$$\begin{aligned} G_{FF} = & \alpha^{-(z+1)} - (4 + \alpha^2)^{-(z+1)/2} \cos \left[(z+1) \tan^{-1} \left(\frac{2}{\alpha} \right) \right] \\ & + (z+2)(z+1) \left\{ \alpha^{-(z+3)} + (4 + \alpha^2)^{-(z+3)/2} \cos \left[(z+3) \tan^{-1} \left(\frac{2}{\alpha} \right) \right] \right\} \\ & - 2(z+1)(4 + \alpha^2)^{-(z+2)/2} \sin \left[(z+2) \tan^{-1} \left(\frac{2}{\alpha} \right) \right]. \end{aligned} \quad (\text{A.36})$$

The difference of electron density between liquid and particles is sometimes included in the form factor but is explicitly left out here. Using this in conjunction with the PY structure factor from Eq. A.28 the intensity is given as [165]:

$$I(q) = \varphi(1 - \varphi) \cdot (\Delta\rho)^2 \cdot V \cdot |F(q)|^2 \cdot S(q), \quad (\text{A.37})$$

with the volume fraction φ occupied by the particles.

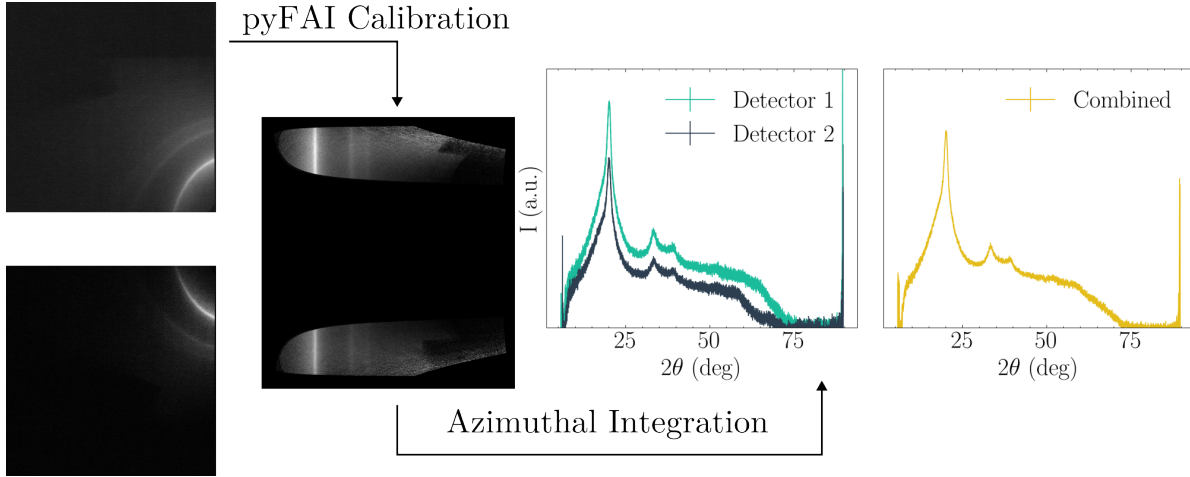


Figure A.9.: Outline of the procedure to obtain an azimuthal lineout of the XRD signal via multiple detectors. The raw image pixels are mapped to 2θ values using pyFAI, and integrated to a one-dimensional pattern. Those patterns are combined to a single lineout.

A.6. *In situ* X-Ray Diffraction of Releasing Nanodiamonds

This section reports the experimental details for the SACLA and EU-XFEL experiments, before considering the uncertainty contributions in azimuthal XRD lineouts. After that supportive plots, which help illustrate the findings and fitting procedure are presented.

The experimental parameters for the two different experiments conducted at the SACLA and EU-XFEL facilities are given in Tab. A.3 and A.4. Both experiments had the same setup and diagnostics, with the addition of the SAXS detector JUNGFRU at the EU-XFEL.

run	target	E [J]	spot [μm]	duration [ns]	delay [ns]	pulse shape
414	PET 75	8.12	170	5	9	square
420	PET 75	5.12	170	5	15	square
422	PET 75	6.23	170	5	17	square
424	PET 75	5.90	170	5	19	square
426	PET 75	5.54	170	5	10	square
432	PET 75	4.41	170	5	14	square
617	PET 75	7.38	170	5	8	square
619	PET 75	6.46	170	5	6	square

Table A.3.: Experimental parameters for the different runs at the SACLA 2022A4048 experiment. The energy values given are the energies delivered to the target. The spot size refers to the diameter of the laser spot. The delay refers to the time between the rising edge of the drive laser pulse and the timing of the probing XFEL. The target type is given as material and thickness in μm .

A.6.1. Uncertainty Estimation

The XRD signal is obtained by azimuthally integrating over the flat detector images using the pyFAI package [212]. Fig. A.9 shows how the lineout is obtained from the raw data. To estimate the uncertainty, the variance of each 2θ value is calculated over all pixels i , which contribute to it as:

run	target	E [J]	spot [μm]	duration [ns]	delay [ns]	pulse shape
320	PET 75 ^a	24.8	100	4&4	7	9V3
321	PET 75 ^a	26.0	100	4&4	8	9V3
322	PET 75 ^a	26.2	100	4&4	9	9V3
323	PET 75 ^a	26.0	100	4&4	10	9V3
324	PET 75 ^a	25.9	100	4&4	6	9V3
325	PET 75 ^a	22.8	100	4&4	8	9V3
326	PET 75 ^a	22.4	100	4&4	9	9V3
327	PET 75 ^a	22.6	100	4&4	7	9V3
328	PET 75 ^a	34.7	100	4&4	6	9V3
329	PET 75 ^a	34.8	100	4&4	7	9V3
464	PET 100	33.4	250	4&4	10	8V3
465	PET 100	33.5	250	4&4	15	8V3
466	PET 100	33.3	250	4&4	20	8V3
467	PET 100	33.3	250	4&4	25	8V3
468	PET 100	33.5	250	4&4	30	8V3
469	PET 100	33.4	250	4&4	35	8V3

Table A.4.: Experimental parameters for the different runs at the EU-XFEL 4463 experiment. The target type is given as material and thickness in μm . The energy values given are the energies delivered to the target and the spot size refers to the diameter of the laser spot. The delay refers to the time between the rising edge of the drive laser pulse and the timing of the probing XFEL.

^aThese targets had a reflective Al coating on the laser side of a thickness of about 100 nm.

$$\sigma^2(2\theta) = \frac{1}{n} \sum_{i=1}^n (I_i(2\theta) - \langle I(2\theta) \rangle)^2. \quad (\text{A.38})$$

By using this azimuthal variance, an estimate of the uncertainty of the XRD lineout is computed. All fits have been performed with the azimuthal variance as an estimation for the uncertainty.

A.6.2. SACLA Experiment 2022A8048

The 2022A8048 was conducted at the SACLA facility in 2022 by the principal investigator Michael Stevenson. The (partial) goal of this experiment was to understand the after-breakout behaviour of ND formed in on-Hugoniot compressed PET foils. The experimental parameters for the relevant shots can be found in Tab. A.3. The results for the best fit for run number 422 is displayed in Fig. A.10. The posterior distributions for the peak centres and widths for that fit can be found in Fig. A.11. Gaussian functions were fitted to the posterior distributions to determine the uncertainties.

The fluctuations in the after breakout ND size can be attributed to fluctuations in the drive laser energy. Fig. A.12 shows the estimated densities from the ND peak positions as a function

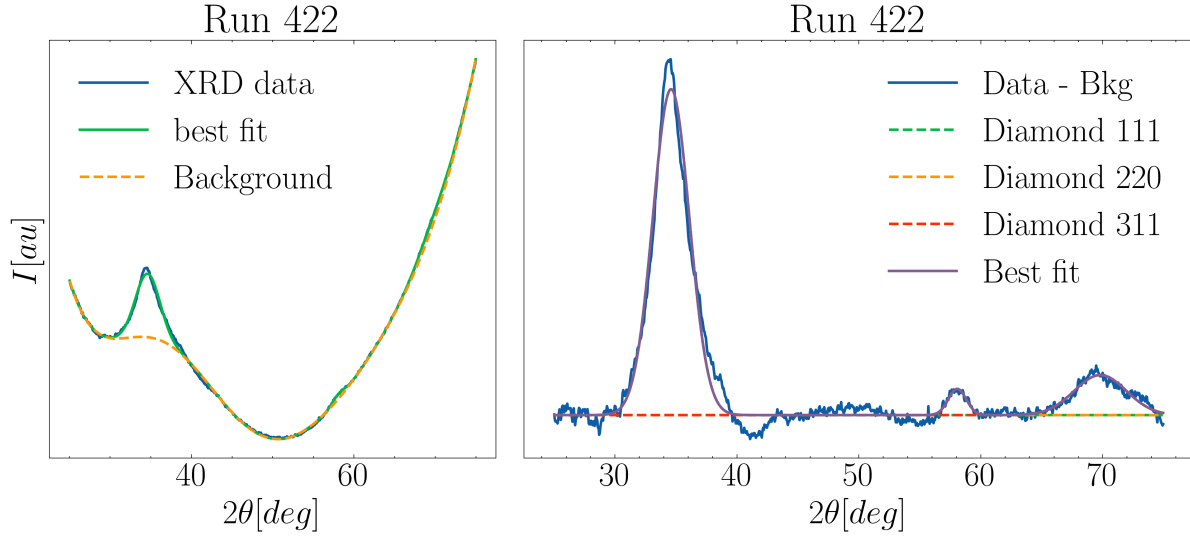


Figure A.10.: Best fit of run 422 of shock-compressed PET during the SACLA experiment. The left shows the entire azimuthal integration and the right shows the background subtracted data along with the model contributions.

of the drive laser intensity. Unfortunately, the number data points and uncertainties do not warrant a statement about the correlation of drive laser intensity and ND density.

A.6.3. EU-XFEL Experiment 4463

The 4463 experiment at the EU-XFEL facility was one of the first experiments ever to use the DIPOLE drive laser. It was conducted in October 2023.

The experimental parameters for the double-shocked PET targets are listed in Tab. A.4. The main focus of this work was on the after-release ND signal. Therefore, a special focus was on runs 464 to 469 with very late probing times. The pulse profiles all consisted of step pulses with different intensity ratios. The ratio for profile 9V3 was 1:5 and 1:2.5 for profile 8V3. These are the nominal profiles from the DIPOLE laser system. The actual pulses were measured with a photodiode for temporal resolution, and a calibrated calorimeter for the entire energy in the pulse. This way, the intensity profile was calculated.

Fig. A.14 displays the measured pulse profiles for runs 320 (9V3 with 24.8 J over phase plate 100 μm) and 464 (8V3 with 33.43 J over phase plate 250 μm). The plot also shows a simplified fit, which used a thresholding method to determine the pulse estimates to be fed into the HDS software HELIOS for comparison. For both runs, the ratio for the fit agrees well with the nominal pulses.

A waterfall plot of shots 464 through 469, in which the original and background-subtracted model is shown, is displayed in Fig. A.13. The shift of the liquid diffraction peak to low angles is clearly visible for those shots, which were probed way after breakout (≈ 9 ns). The same is visible for the diamond peaks, which start out highly compressed and shift to lower angles as the material is releasing and the thermal expansion of the NDs results in densities even below ambient density.

Determining the shock conditions in the double-shocked PET targets was done by using the ProPacEOS table and adjusting the laser intensity multiplier, such that the breakout time in the simulation is congruent with the experimental results. Fig. A.15 shows the results for an

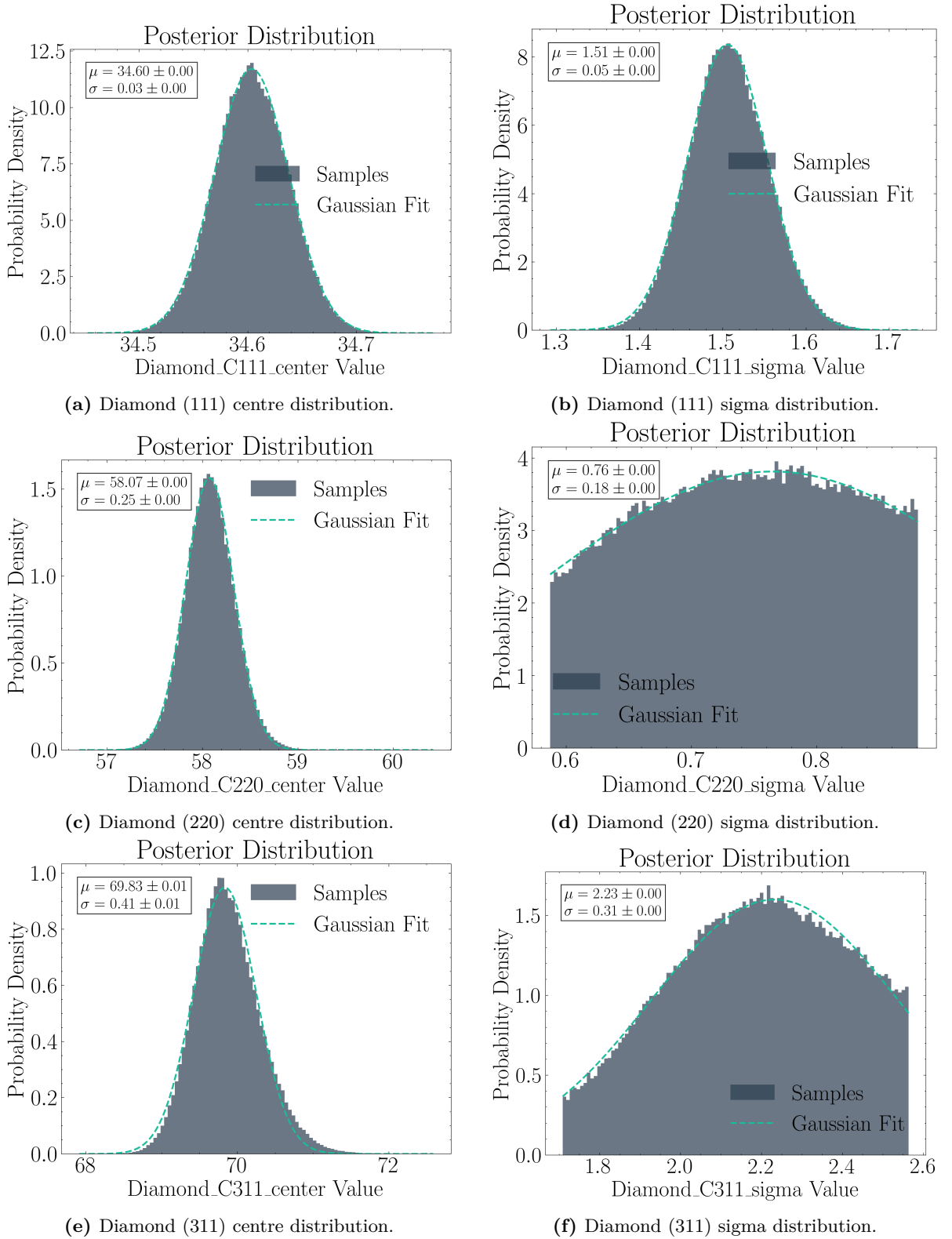


Figure A.11.: Posterior distribution for the diamond peak fits for run 422 at the SACLA experiment. Gaussian distributions were fit to all posterior distributions to determine the uncertainties. The fit results are written in the plots.

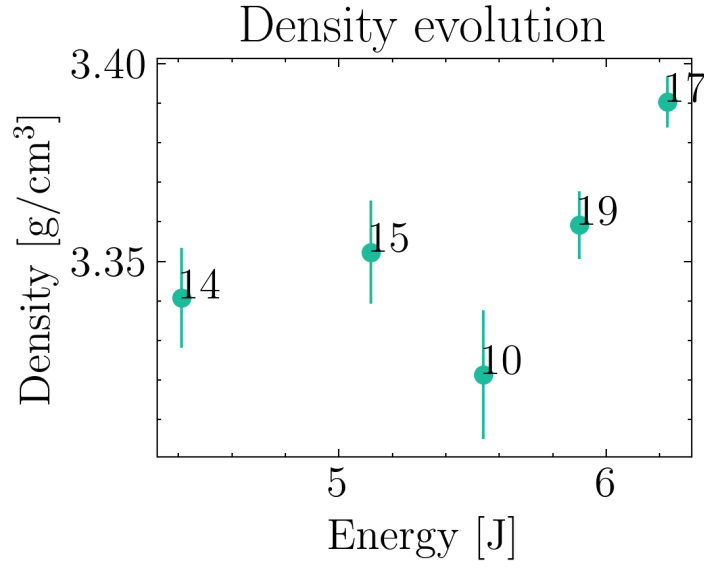


Figure A.12.: The diamond density estimates, plotted against the drive laser intensity. The pump-probe delay is added as an annotation to the plot.

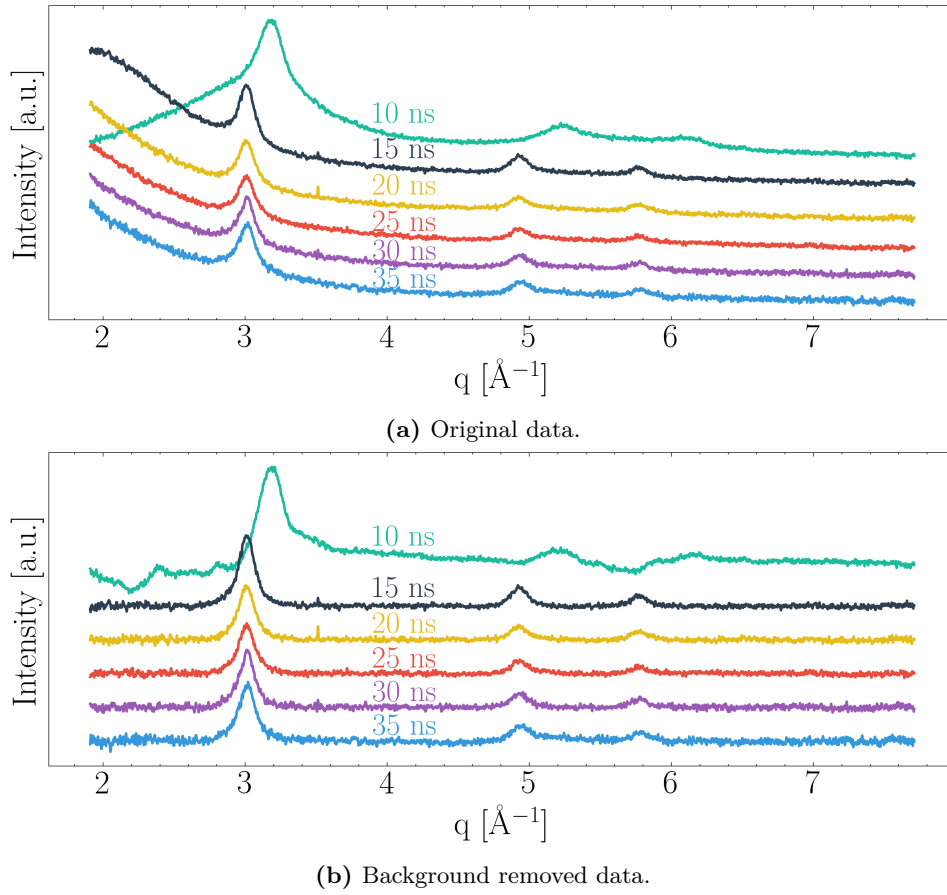
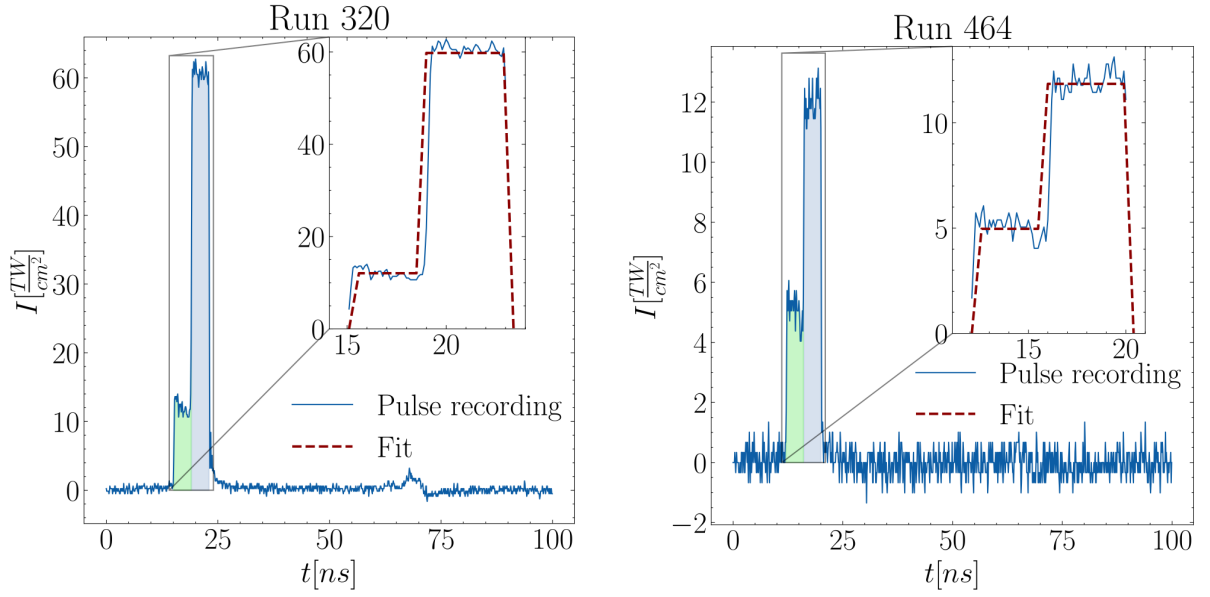


Figure A.13.: Waterfall plot of the original as well as background removed data for the double-shocked PET targets at different delays.



(a) DIPOLE pulse profile for run 320. The thresholding fit estimate yielded an intensity ratio of 1:4.96.

(b) DIPOLE pulse profile for run 464. The thresholding fit estimate yielded an intensity ratio of 1:2.39.

Figure A.14.: Recorded pulse shapes of two runs at the EU-XFEL 4463 experiment. The intensity was scaled so that the entire energy in the pulse was equal to the estimate from the calorimeter measurement.

HDS using a multiplier of 0.6 which resulted in a shock breakout at about 10 ns, which was consistent with the diffraction data. The simulation results show a peak pressure of 150 GPa at a density of 3 g cm^{-3} and 4000 K. At 10 ns the sample is already releasing from the front and rear side, but a large portion of the PET is still in a compressed state.

The temperature estimates from the diamond lattice constant are obtained by assuming a fully released state of the NDs. The lattice constants from [226] are used to estimate the corresponding temperatures. Fig. A.16a shows the results for the after-breakout shots of the single and double shock-compressed PET targets. Here, the shots with a pump-probe delay exceeding 9 (SACLA) or 10 (EU-XFEL) ns are used.

The time evolution of the ND temperatures is shown in Fig. A.16b. A very clear cooling trend is visible. Attempts were made at matching the cooling with the radiatively cooling spheres model described in Sec. 3.1.1.1. However, the required ND size for an initial temperature of 3500 K that would match the cooling curve, would exceed $d = 160 \text{ K}$. Nevertheless, the model of a single, radiatively cooling diamond for an ND within a plasma release cloud is also inaccurate. Therefore, more thorough temperature diagnostics and cooling models are required.

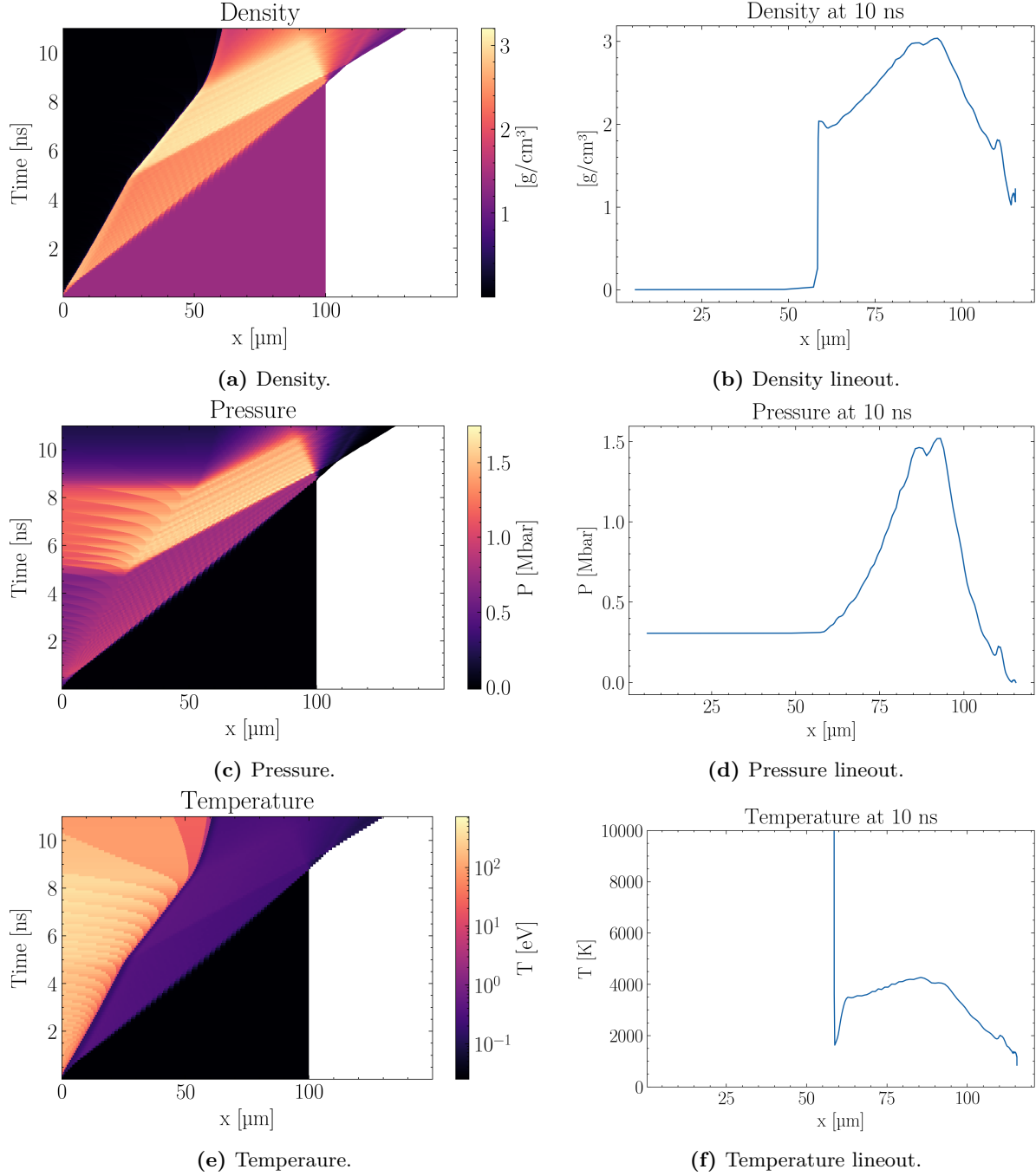
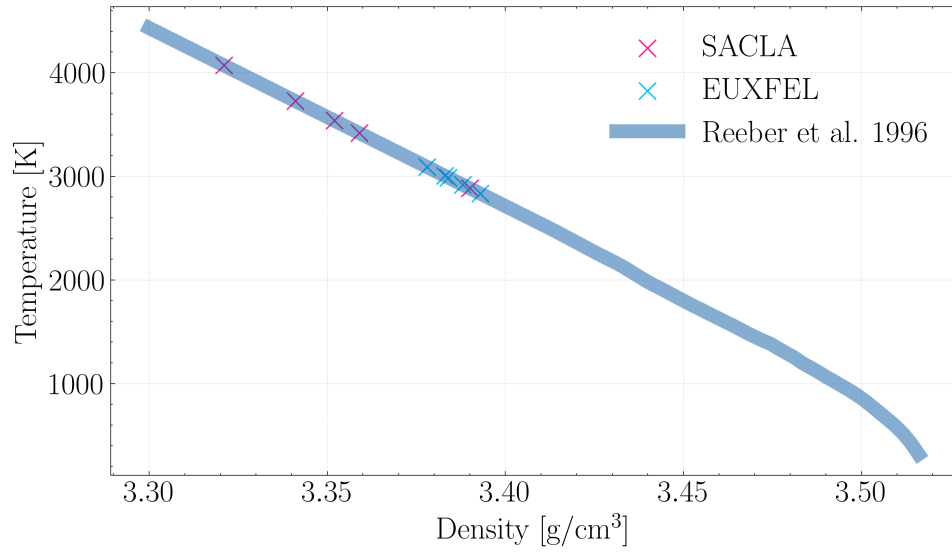
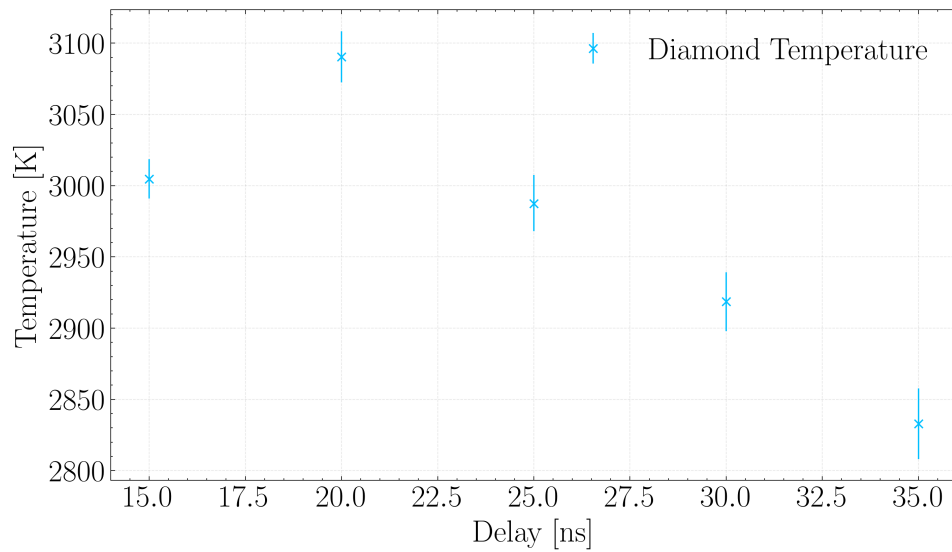


Figure A.15.: Results of the HDS of the double-shocked PET for the shots 464 through 469, during the p4463 experiment. The left column shows the two-dimensional results, while the right column shows the lineout at a probing time of 10 ns.



(a) Temperature estimates for the EU-XFEL (double shock) and SACLA (single shock) experiments for the measured densities.



(b) Temperature estimates for the EU-XFEL double shocks as a function of time. A clear cooling trend over the course of tens of ns is visible.

Figure A.16.: Estimates for the after-breakout temperature of the released ND. The estimates were taken from the thermal expansion coefficients given in [226].

A.7. Obtaining Nanodiamond Size Distributions via Small-Angle X-ray Scattering

This section will provide the additional information required to implement and train the NN on simulated SAXS data, as discussed in Se. 3.2.2. The KL divergence loss in the discrete case (essentially bins of a probability distribution) is a measure for how similar a given distribution P_{true} is to a test or predicted distribution P_{pred} [249]. In machine learning, the distribution vectors are commonly generalised to tensors y_{true} , y_{pred} and the KL divergence loss is mathematically formulated as:

$$L(y_{pred}, y_{true}) = \sum y_{true} \cdot \log \left(\frac{y_{true}}{y_{pred}} \right). \quad (\text{A.39})$$

The KL loss is a non-negative, asymmetric loss function and stems from information theory. It is well-suited for determining the overlap for the predicted radii distributions but not for the prediction of the volume fraction. Therefore, an MSE loss was used for the prediction of the volume fraction. As this is only a singular value, it simplifies to:

$$MSE(\varphi_{pred}, \varphi_{true}) = (\varphi_{pred} - \varphi_{true})^2. \quad (\text{A.40})$$

An artificial NN is essentially an optimisation problem, that tries to minimise the loss between the target (true values) and the prediction for a given input. If this loss was simply calculated over a singular sample (one theoretical SAXS pattern and volume fraction for a given radii distribution) the generalisation potential of the NN would be very poor. Therefore, NNs are usually trained over so-called batches. These batches contain multiple samples and the loss function is calculated over the entire batch. The batchsize is an important hyperparameter of NNs and has a strong influence on the training progress and generalisation potential of an NN. It is an active part of research [250, 251]. Simplified, a smaller batchsize increases the noise on the gradient which might be beneficial for escaping local minima, but takes a very long time to converge. A larger batchsize improves the generalisation of the NN but requires more memory and is prone to get stuck in a local minimum.

In this work, a batchsize of 4096 spectra was chosen for training. The two separate loss functions were added with a scaling of 1 and 10 for the KL divergence and volume fraction loss, respectively. This loss is calculated across the entire batch. Then an optimisation step is taken. The entire NN consisted of one input, three hidden, and one output layer. The hidden layers had a total of 512, 256, and 128 neurons respectively. The network was implemented using PyTorch [252].

A.7.1. Particle Size Distributions in Double-Shocked Polyethylene Terephthalate

The size distributions of double-shocked PET, obtained from the p4463 experiment using a step pulse with a ratio of 1:4.5 over 4 and 4 ns and a total pulse energy of 26 J, are shown in Fig. 4.15. Results for the same pulse shape, but with a slightly lower total pulse energy of 21 J, are shown in Fig. A.18.

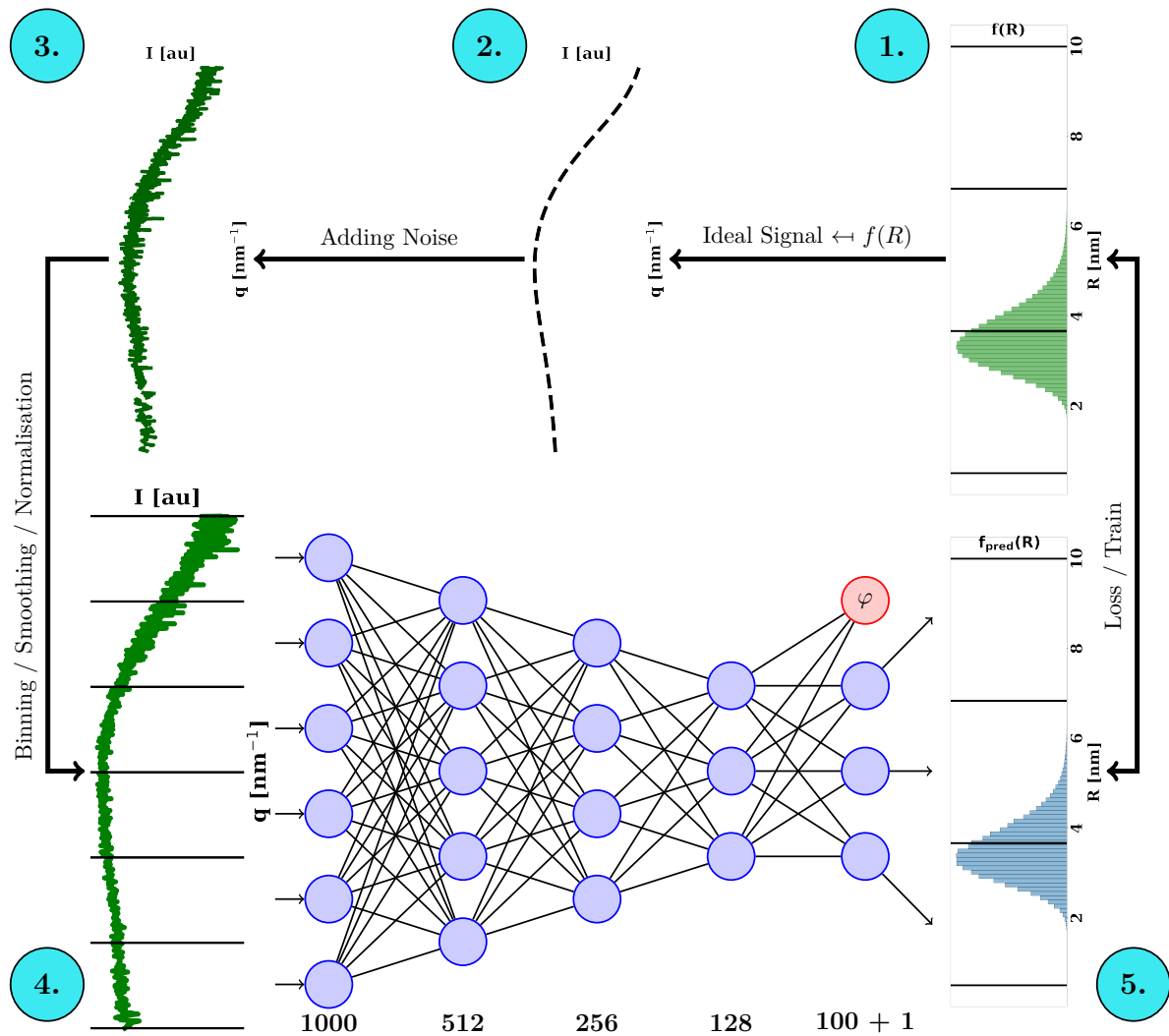


Figure A.17.: Visualisation of the NN architecture used to predict the radii distribution function and volume fraction by the SAXS lineout signal. The process starts in the upper right corner by: choosing a radius distribution function (1), going counter-clockwise, the ideal scattering signal is then computed (2). After noise is added (3) and the signal normalised, the artificially noisy signal is smoothed and binned (4). This noisy signal is then fed to the NN and the loss function of the NN output and the predicted radius distribution computed (5). Based on that loss, a training (optimisation) step is taken.

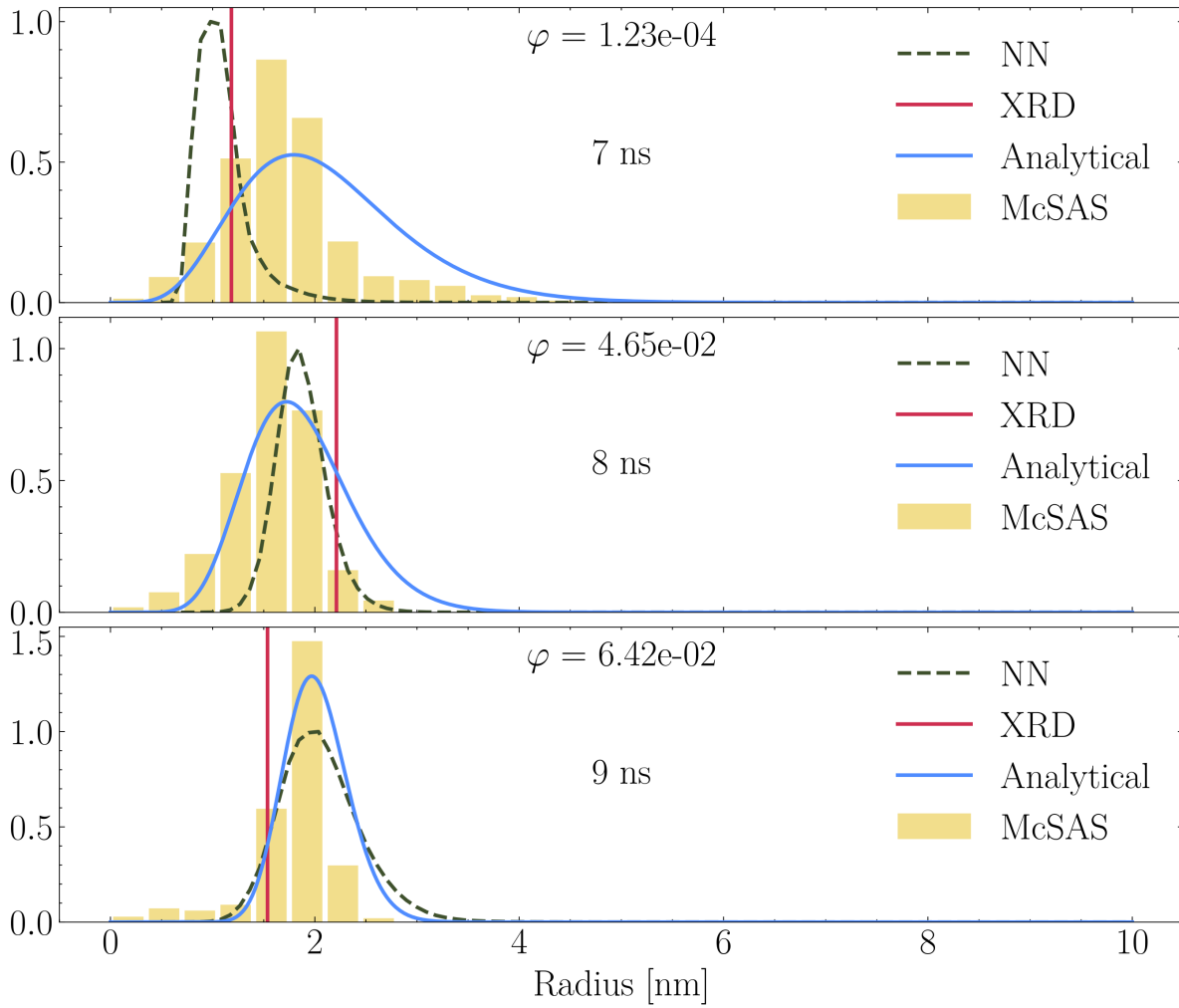


Figure A.18.: Particle radii distributions of double-shocked PET estimated with different methods. The mean value from the XRD was obtained with the method described in Sec. 3.2.1. The analytical and McSAS results were provided by B. Lindqvist and published in [124]. The predicted volume fractions are printed in the plots.

A.8. Transmission Electron Microscopy - Lamella Preparation

The following section will outline and illustrate how a TEM-lamella is cut from a metal catcher using a FIB. It also presents additional images of the TEM scans.

The required thickness for good imaging with the TEM is about 100 nm. To obtain such a thin cross-sectional slice through the catcher surface, the ion beam is guided to mill a trench around the area of interest. To minimise the alternations of the sample, it needs to be protected by a coating before the milling is done.

The entire process can be separated into 5 steps which are illustrated in figures. First, a surface scan is performed to identify a ROI, of which a slice is cut (see Fig. A.19a). Secondly, to protect the sample from damage, the ROI is coated with a layer of platinum using the deposition mode of the FIB. An image of the surface with the coated area is shown in Figures A.19b and A.19c. Third, after the surface is protected by a platinum coating, a U-shaped crater is milled around the ROI to produce a cross-section of the catcher. Depending on the catcher material, this process can take several hours and needs to be monitored constantly to insure that possible drift in the positioning does not result in damaging of the lamella. A side view of the U-shaped trench is shown in Fig. A.19d. It can be clearly seen, that material also slides down into the trenches. Thus far, the entire milling process is performed with the ion beam perpendicular to the catcher surface. Fifth, to remove the lamella at the bottom, the ion beam is now tilted to an angle of 52° and the ion beam is set to remove the bottom of the lamella. A side view after bottom milling is shown in Fig. A.19e. In the fourth step, the lamella needs to be removed from the catcher. To do this a micromanipulator is inserted into the trench. It consists of a rigid needle, which can be controlled extremely precisely with a very thin tip only few micro metres across. This tip is attached to one side of the sample via platinum deposition. An image after attachment of the micromanipulator to the lamella is shown in Fig. A.19f.

The copper catcher mentioned in Sec. 3.3.1 was originally intended as a pinhole to be used with an ionic liquid catcher. However, the catcher was misaligned and the ejecta was cantered on this pinhole instead.

A.8.1. Aluminium Lamella Catcher LULI 2021

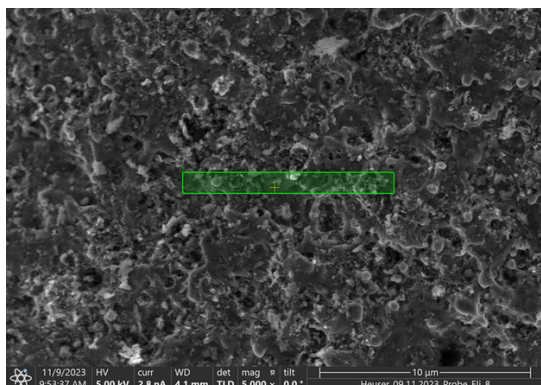
An EDS scan of a copper containing inclusion within the high purity aluminium plate catcher is shown in Fig. A.21. On the left side the EDS mapping is displayed and on the right side a zoomed in TEM image in conventional TEM mode is shown. No crystal structure is visible in the carbon material.

A.8.2. Aluminium Lamella Catcher ELI 2023

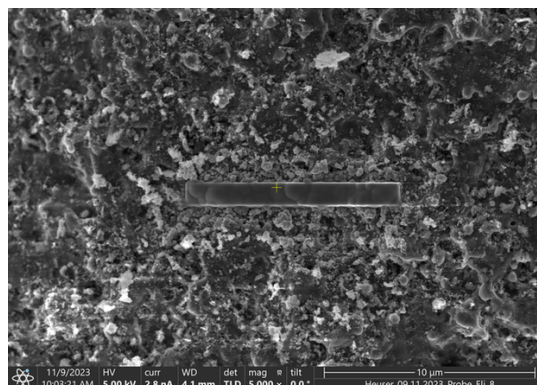
Fig. A.22a shows the cross sectional slice of the TEM lamella from the aluminium catcher, which was shot 54 times.

A.8.3. Copper Lamella Catcher ELI 2023

Fig. A.22b and A.22c show the two cross-sectional slices of the TEM lamellae from the copper catcher, which was shot 51 times.



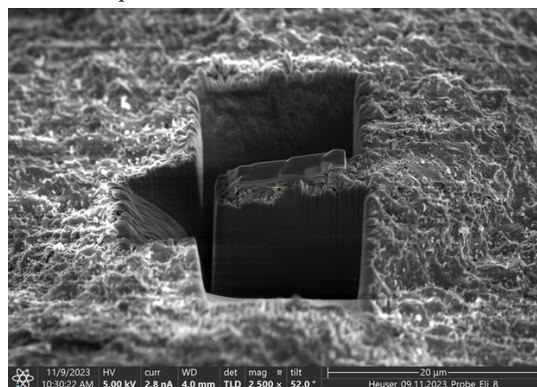
(a) Surface scan of the catcher with the selected lamella region marked with a green box.



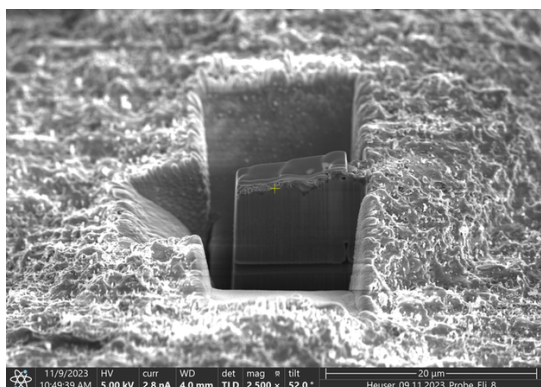
(b) Surface scan of the catcher after coating of the ROI with platinum.



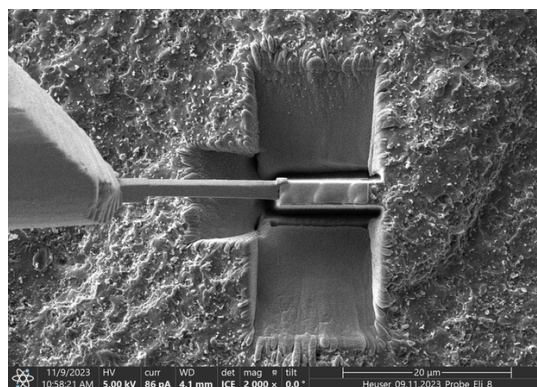
(c) Side view of the ROI coated with platinum.



(d) Side view of the the ROI after the trenches have been milled.



(e) Side view of the lamella after the bottom material has been removed by milling. The lamella has also been thinned by milling from the side.



(f) Top view of the lamella with the micromanipulator attached via platinum deposition. At the bottom of the lamella, the cut where the FIB has cut the bottom of the lamella can be seen.

Figure A.19.: Overview of the lamella preparation process.

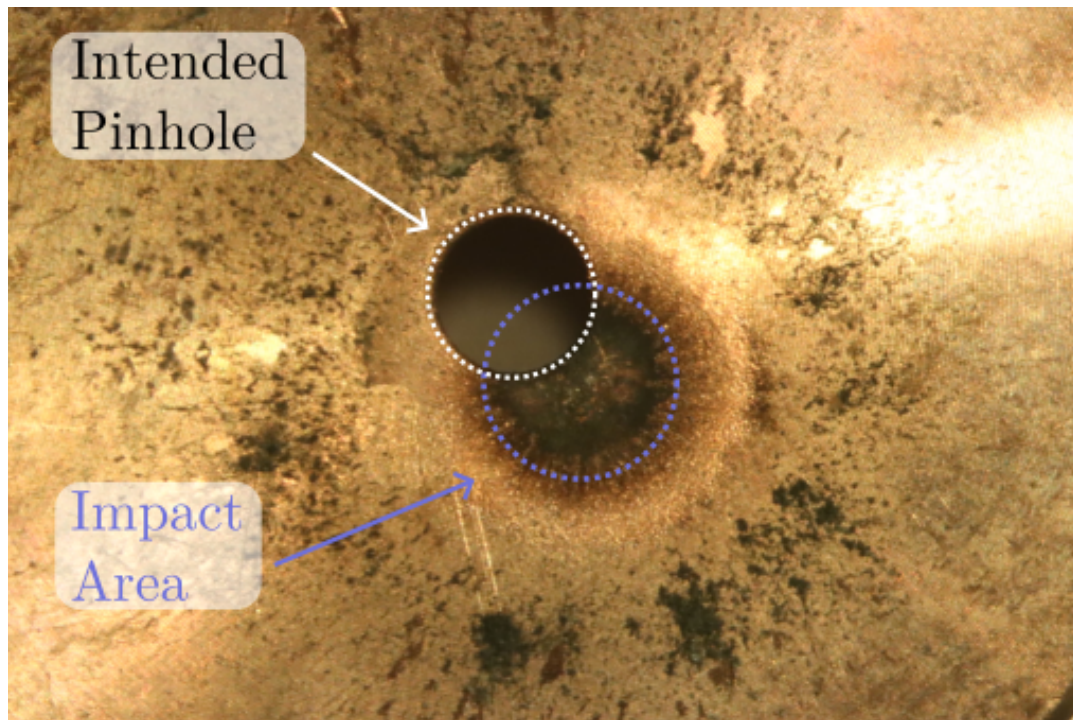


Figure A.20.: Microscope image of the copper pinhole. Due to misalignment, the impact region was not well-centred in the pinhole and most impactors hit the copper material instead. This region was later used for cutting TEM lamella to study the impact into copper.

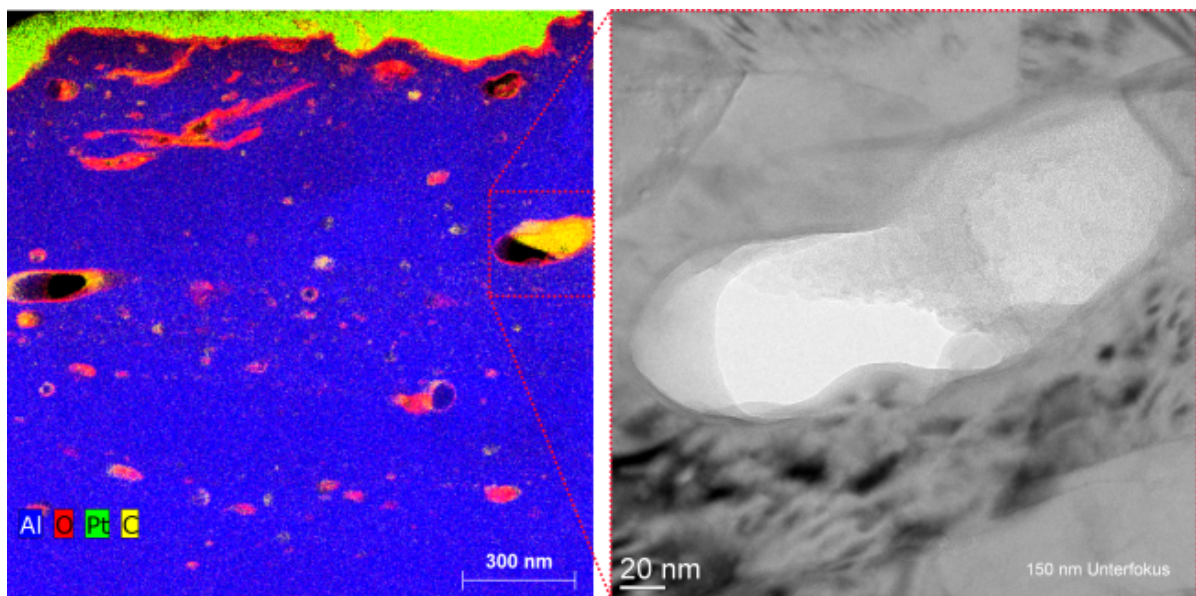
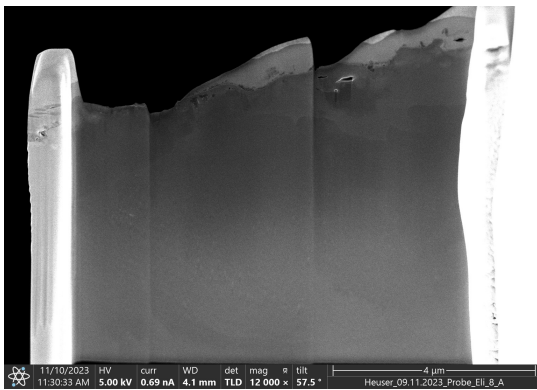
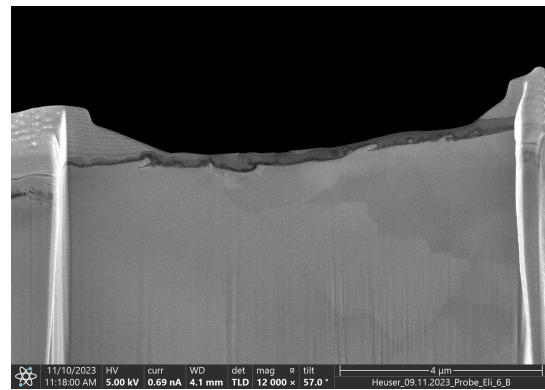


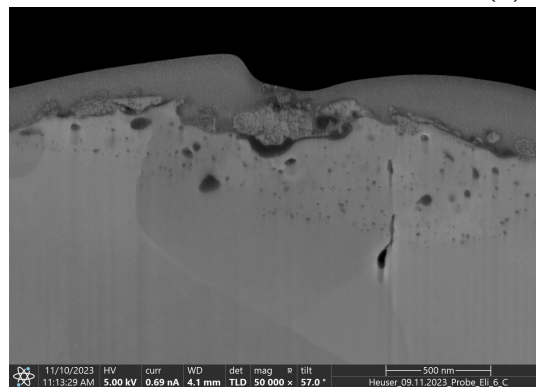
Figure A.21.: EDS scan and zoomed in TEM image of the aluminium lamella used as catcher material during the 2021 experiment at the LULI facility.



(a) Aluminium lamella.



(b) Copper lamella 1.



(c) Copper lamella 2.

Figure A.22.: Cross-sectional views of the different lamellae cut from the catchers shot at the ELI facility.

A.9. Transmission Electron Microscopy Analysis

This section presents the preparation process for the TEM samples obtained from the ionic gel catcher as well as the commercial ND references. Additionally, supporting images of the TEM scans obtained during this work are displayed.

A.9.1. Commercial Nanodiamond Reference

To test the capabilities and best settings of the TEM and to get an idea of the expected signal, a commercial ND reference suspension was prepared. The NDs were obtained from PlasmaChem and had sizes from 4 to 6 nm. A suspension was prepared by the process outlined in Tab. A.5. The TEM images of the reference solution are shown in Fig. A.23a and the corresponding FFT of the ROI can be seen in Fig. A.23b. The diamond reflections are clearly visible, and the (111) spacing of $d_{111} = 2.067 \text{ \AA}$ relates to a lattice constant of $a = 3.61 \text{ \AA}$. This is slightly above the literature value for diamond $a = 3.567 \text{ \AA}$ [253].

As mentioned in Sec. 2.4.4, diamond can be clearly identified by an EELS measurement. To have a reference spectrum for comparison, an EELS scan of the commercial NDs was performed. Fig. A.25 shows the EELS spectrum of the ND sample. The spectrum is very similar to literature values, as given in [1]. However, the π^* peak is more prominent in the PlasmaChem sample, suggesting a higher graphitisation. It is important to note, that the EELS spectra of NDs can depend on their synthesis method [233]. Therefore, DND EELS spectra differ from CVD NDs. It is not clear how exactly NDs produced in laser-compressed plastics would look like. However, all NDs EELS spectra share the 302 eV dip.

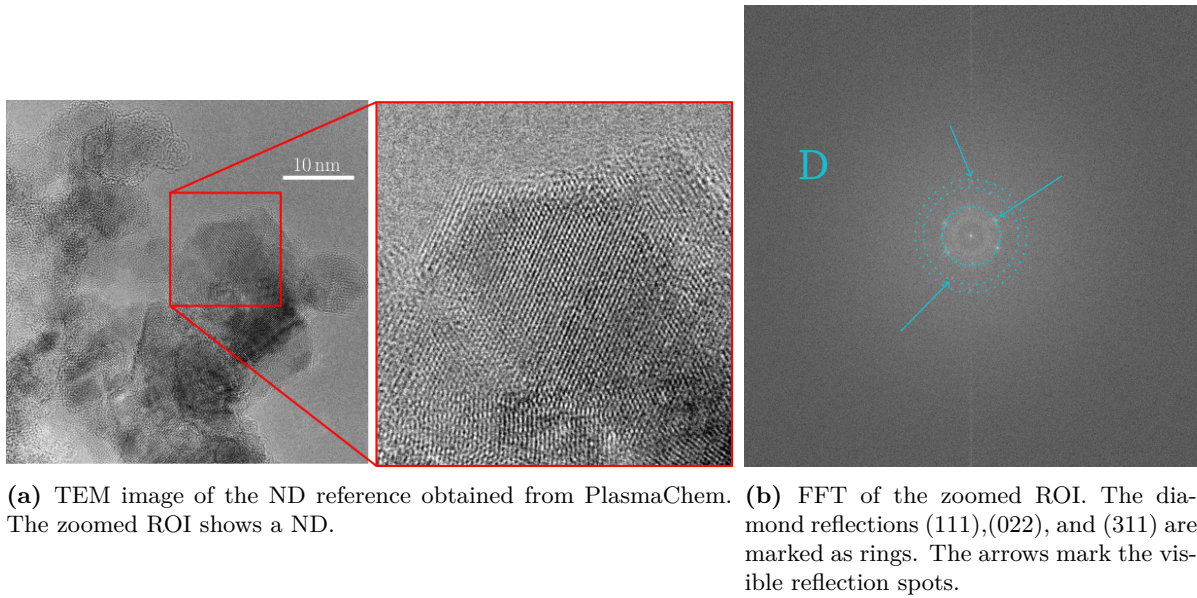


Figure A.23.: TEM image and FFT analysis of a commercial ND reference prepared for comparison.

A.9.2. Image of an Ionic Gel Catcher

The ionic gel was scooped into a glass tube, which was fixed inside a catcher mount using a circlip. A photo of the ionic gel catcher before mounting can be found in Fig. A.24a. After it was shot, the black soot is clearly visible in the target side part of the catcher, where the

Step	Description
1	Weighed 0.0027 g of PlasmaChem NDs (purity >97%, powder grade G01).
2	Dispersed in 2000 μL of ethanol.
3	Sonicated for 5 min at 40 °C.
4	Placed a TEM grid in a Petri dish.
5	Deposited 10 μL of suspension onto the grid.
6	Allowed to dry at room temperature.

Table A.5.: Preparation of commercial ND reference.

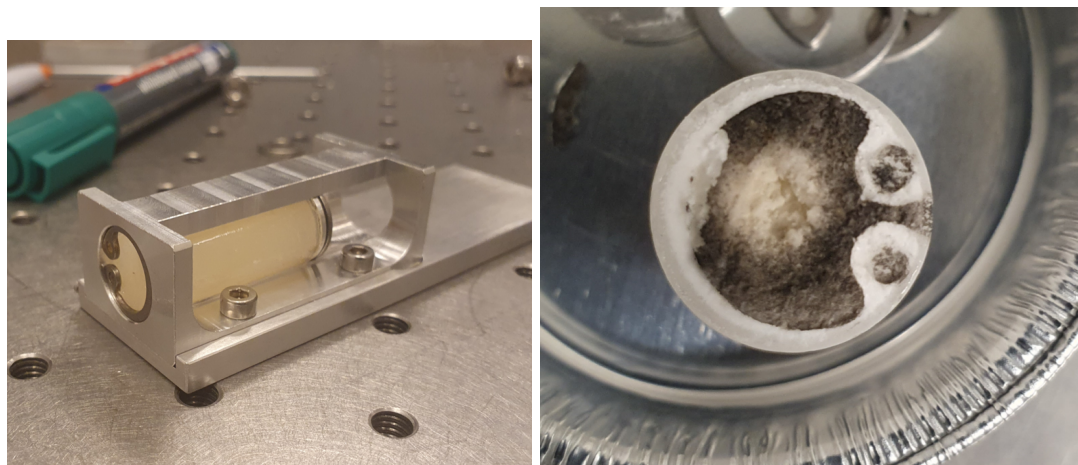
Step	Description
1	Placed catcher components over centrifuge tube and filled with distilled water.
2	Scooped IL with soot and filled up to 30 mL with distilled water.
3	Shook and sonicated at 50 °C for 3 min.
4	Centrifuged at 4000 min^{-1} for 3 min, then 5 min.
5	Removed supernatant, refilled with 30 mL distilled water.
6	Repeated shaking, sonication 50 °C for 3 min, and centrifugation 4000 min^{-1} for 3 min (twice).
7	Replaced liquid with ethanol and repeated step 6.
8	Washed with distilled water and centrifuged at 4000 min^{-1} for 3 min.
9	Final removal of supernatant.
10	Sonicated for 1 min.
11	Deposited $2 \times 7 \mu\text{L}$ onto the grid.
12	Heated grid at 100 °C.
13	Captured TEM images.
14	Cleaned with HNO_3 due to contamination.
15	Dissolved residue in 45 mL isopropanol, evaporated at 100 °C.
16	Treated dried residue with 65 % nitric acid overnight.
17	Neutralised with isopropanol.

Table A.6.: Preparation of the actual catcher from ELI 5.

ejecta has impacted the surface (see Fig. A.24b). Interestingly, the central region of the catcher, although it looks strongly impacted, contains no black soot.

A.9.3. Transmission Electron Microscopy of Dissolved Ionic Gel Catcher

A zoomed-in region of the rod-like particle mentioned in Sec. 4.9 can be seen in Fig. A.26. The zoomed-in region shows an onion-like particle and graphite domains. Fig. A.27b shows another region of the TEM scan in which multiple onion-like particles are clearly visibly. The onion-like particles range from 4.2 to 8.7 nm. The graphite domains extend up to 33 nm along the graphite (001)-plane and 10 nm in orthogonal direction. Fig. A.27a shows the two-dimensional FFT of the red ROI in Fig. A.26 along with the theoretical reflections for AA'-stacked and



(a) Ionic gel catcher just before mounting at the ELI facility.

(b) Ionic gel catcher after it was shot.

Figure A.24.: Ionic gel catcher as it was used at the ELI facility during a recovery campaign.

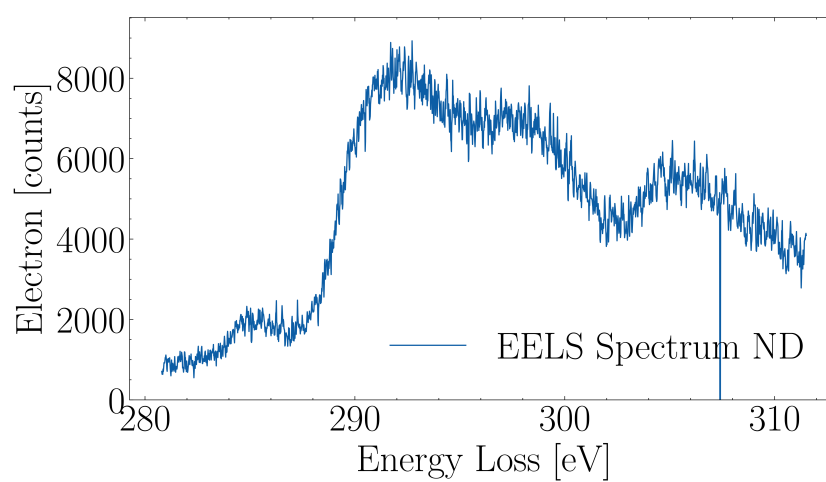


Figure A.25.: EELS spectrum of the ND reference. The characteristic diamond dip at 302 eV is prominent.

Step	Description
1	Added 20 mL of distilled water for a total of 40 mL.
2	Centrifuged at 210 min^{-1} for 1 min (brake 1/0). No visible sediment.
3	Centrifuged at 210 min^{-1} for 1 min (brake 1/0). No visible sediment.
4	Centrifuged at 1000 min^{-1} for 1 min (brake 2/2). No visible sediment.
5	Centrifuged at 2000 min^{-1} for 1 min (brake 4/4). No visible sediment.
6	Centrifuged at 3000 min^{-1} for 1 min (brake 9/9). No visible sediment.
7	Centrifuged at 5000 min^{-1} for 1 min (brake 9/9). No visible sediment.
8	Centrifuged at 6000 min^{-1} for 4 min (brake 9/9). No visible sediment.
9	Centrifuged at 8000 min^{-1} for 4 min (brake 1/1). No visible sediment.
10	Centrifuged at 5000 min^{-1} for 4 min (brake 1/0). No visible sediment.
11	Centrifuged at 7000 min^{-1} for 5 min (brake 1/0). Some big fibres started to sediment.
12	Removed supernatant except 10 mL, refilled with 30 mL distilled water.
13	Centrifuged at 7000 min^{-1} for 5 min (brake 1/0), removed 30 mL supernatant.
14	Refilled with 30 mL distilled water, centrifuged at 8000 min^{-1} for 5 min (brake 1/0).
15	Removed 37 mL supernatant, refilled to 40 mL with distilled water.
16	Replaced broken counterweight and sample containers.
17	Centrifuged at 7000 min^{-1} for 5 min (brake 1/0), removed supernatant to 3 mL.
18	Refilled with 40 mL distilled water, centrifuged at 7000 min^{-1} for 3 min (brake 1/0).
19	Removed supernatant to 3 mL.
20	Sonicated for 1 min.
21	Deposited $3 \times 7 \text{ }\mu\text{L}$ of sample onto the grid.
22	Placed the grid on a heating plate at 100°C .

Table A.7.: Cleaning of the suspension.

AB-stacked graphite. The presence of both the (002) and (004) reflections at the predicted distances provides strong evidence for the presence of AB-stacked graphite in the sample.

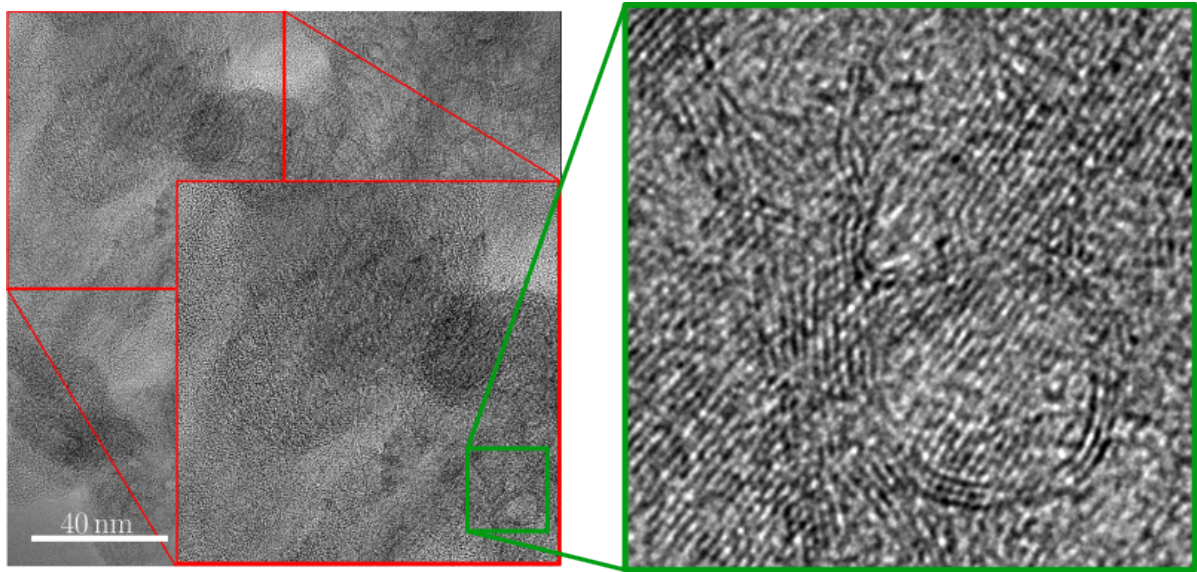
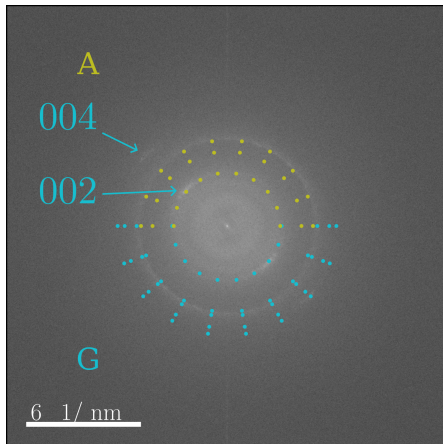
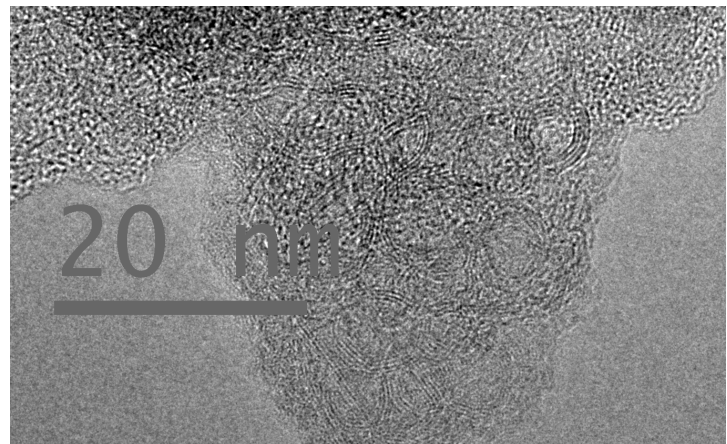


Figure A.26.: TEM scan of the rod-like particle found in the dissolved ionic gel catcher shot at the ELI facility. The red region marks the ROI of which an FFT was calculated. The green region shows a graphitic shell and different graphitic domains.



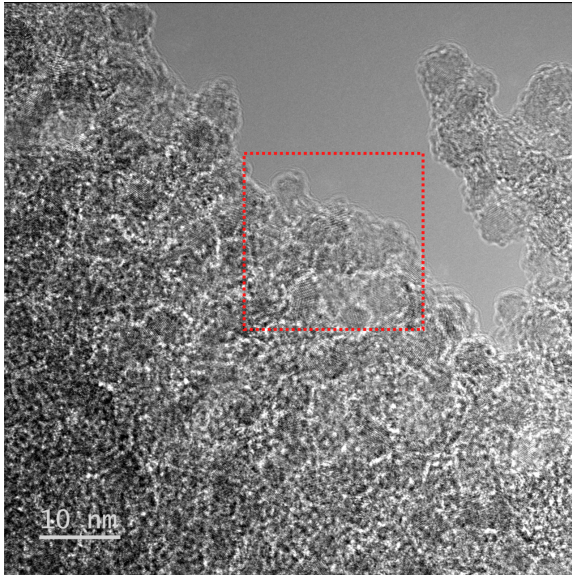
(a) FFT of the red ROI in Fig. A.26. The reflections of AB-stacked (turquoise) and AA'-stacked (gold) graphite are shown. Two reflection spots are marked.



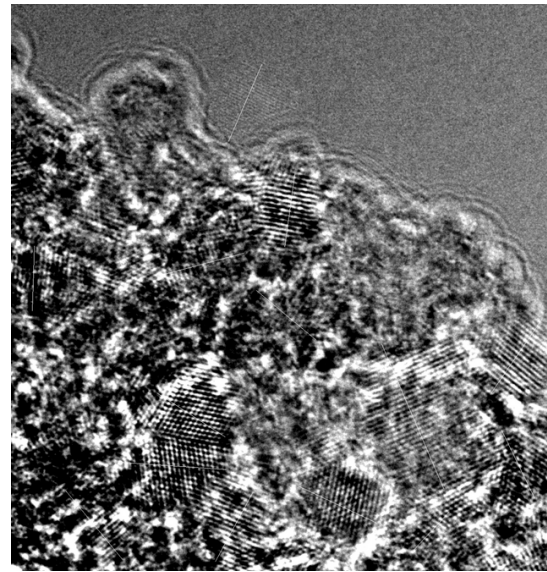
(b) Zoomed in ROI of the rod-like particle. Many of the small onion-like particles are present in the catcher. The catcher also showed larger domains of graphite layers.

Figure A.27.: TEM image of the carbon onions found in the ionic gel catcher and FFT of the TEM scan. The reflections are from inside to outside AB: ((002), (020),(111),(022),(004)) and AA': ((002), (020),(200)). The present reflections agree well with AB-stacked graphite.

The sizes of the NDs were measured manually with the software ImageJ [234]. The STEM scan and some of the measured particles are displayed in Fig. A.28.



(a) STEM scan of the particle cluster. The NDs are clearly visible as dark spots and via their lattice planes.



(b) Zoomed-in region of the particle cluster. The ND lattice planes are clearly visible. Some measured particles are marked by their diameters.

Figure A.28.: STEM image of the NDs that were measured to determine the size distribution.

A.10. High-Speed Imaging

The high-speed camera images were processed by removing a static recording taken before the actual shock to remove the noise. Fig. A.29 shows the resulting image for run 42 at the LULI facility during the recovery experiment in 2021. The relevant shot parameters for all shots taken with the high-speed camera can be found in Tab. A.8. Shot number 33 was taken on a layered target intended for shot characterisation. Therefore, a Kapton pusher, an aluminium heat shield, and a quartz sample were combined to a layered target. Quartz is a well-characterised material and thus often used in calibrating diagnostics. Here, it was used to compare the free-surface velocity estimated from the shock state via the velocity doubling rule to the measurements of the high-speed camera.

To compare the free-surface velocity of the releasing material to the measurement of the high-speed camera, the shock state of the sample needs to be determined.

The shot was a very high intensity shot delivered over 2 ns. Therefore, the drive laser stops before the shock breaks out at the rear surface, leading to front side release as well as a decrease in shock intensity over time. Two separate VISAR systems were used with two different wavelengths 532 and 1064 nm with sensitivities of 12.81 and 4.96 km s⁻¹ VPF. The raw data and the obtained velocity profiles are shown in Fig. A.30. The decaying velocity profiles are clearly visible. After the aluminium surface has started to move, the shock is travelling in the quartz, which becomes reflective at high pressures [254]. Therefore, the shock speed measured with the VISAR is the speed of the shock front in the quartz. A small re-shock is visible at about 5 ns. This can be attributed to the shock being reflected at the aluminium-quartz interface, travelling back into the aluminium before being reflected again at the Kapton-aluminium interface and finally arriving at the quartz as a second shock. This means that the shock state is also slightly off the quartz Hugoniot. However, this is only a small effect and was neglected in the further analysis.

To determine the free-surface velocity, the velocity doubling rule is used, which describes the surface velocity as roughly double of the particle velocity. The material is releasing from the final shock state. Therefore, the shock velocity at breakout time was used in conjunction with the quartz Hugoniot to determine the particle velocity of the shock. The free-surface velocity was then determined by using the velocity doubling rule estimate. All determined release velocities and their uncertainties are shown in Tab. A.8.

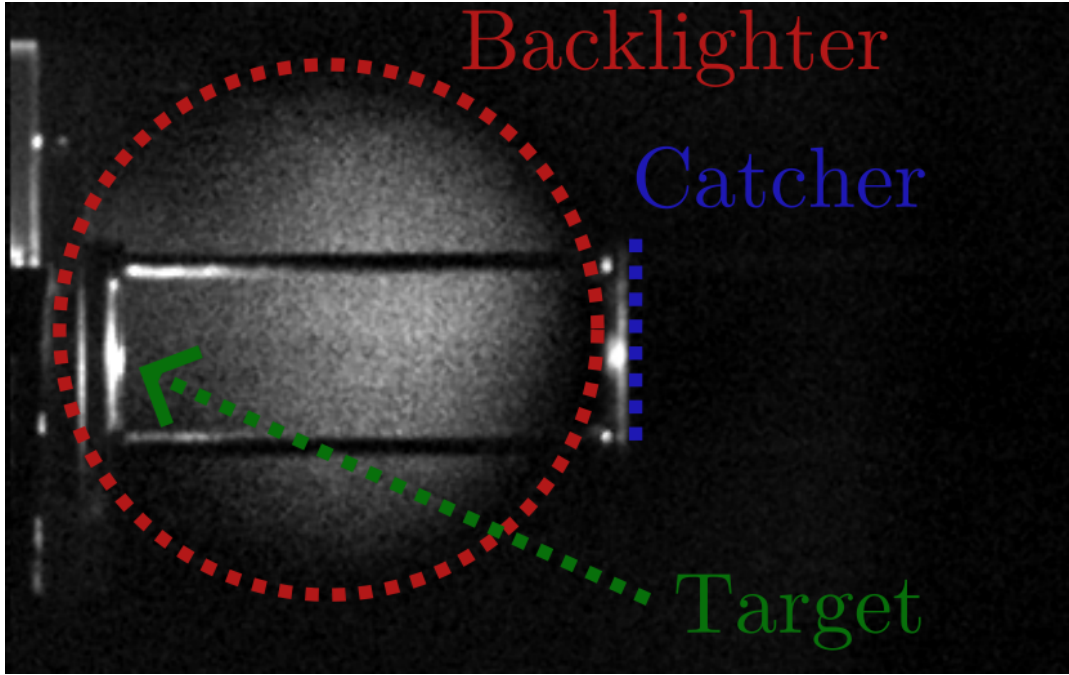
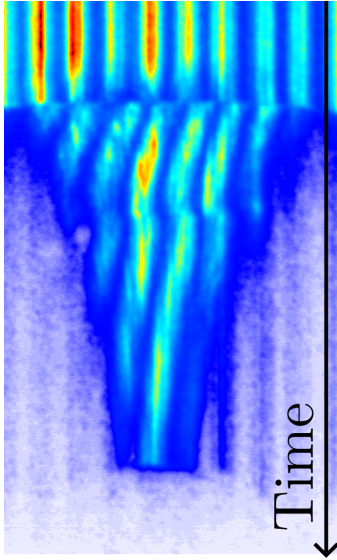
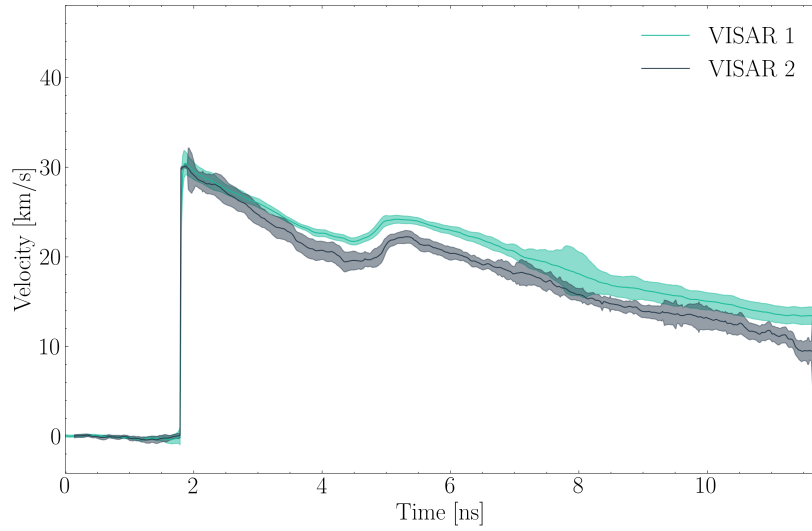


Figure A.29.: High-speed camera image at the moment the drive laser hits the target. The catcher - an Al plate - is mounted behind the target. The bright round spot is the laser backscatterer.



(a) VISAR image of shot 33, shot at LULI during the 2021 campaign.



(b) Velocity lineouts obtained with the Neutrino software [255]. The shaded area shows the uncertainty. Both VISARs are displayed. The VISARs were matched with an integer fringe shift to agree in the velocity.

Figure A.30.: VISAR results for the calibration shot 33 at the LULI facility. This shot was chosen as it had both a VISAR setup and a simultaneous measurement with the high-speed camera.

run	target	E [J]	spot [μm]	duration [ns]	v_{releases} [km s^{-1}]
33	CH/Al/SiO ₂	1025	500	2	15.6 ± 0.2
36	PET 75	108	500	5	9.8 ± 0.2
38	PET 50	124	500	5	13.8 ± 0.3
40	PET 75	62	500	5	7.8 ± 0.3
41	PET 75	208	500	10	13.4 ± 0.3
42	PET 75	375	500	10	15.8 ± 1.6
43	Al/CA	79	500	10	2.97 ± 0.01
46	PET 75	353	800	5	10.8 ± 0.5
50	PET 75	282	800	10	11.0 ± 0.1
58	CA	304	500	10	13.0 ± 0.2

Table A.8.: Parameters for the shots taken during the 2021 experiment at the LULI facility, during which a simultaneous measurement with the high-speed camera was performed. Kapton (CH) was used as an ablator in some shots and cellulose acetate (CA) as a target for Hugoniot characterisation.

A.11. Crater Landscape Measurement

This section presents additional information about how the crater morphologies were measured from the confocal microscope images explained in Sec. 3.3.5. It introduces the model used to segment the craters, as well as the forward modelling of the crater morphologies depending on the impactor parameters.

The SAM2 model used to segment the craters in the confocal microscope scans use the parameters given in Tab. A.9. To determine likely craters, those segmentation masks, which were not sufficiently circular, were excluded. For a circularity measure, the roundness was used:

$$R = \frac{4\pi \cdot \text{area}}{\text{perimeter}^2}. \quad (\text{A.41})$$

The threshold value was set to exclude $R < 0.8$. The confocal microscope height data was split into four layers, and masks were determined for each layer. Sometimes, the crater crests extended through multiple layers and were recognised as individual craters in separate layers. Therefore, a merging criterion was defined to combine the masks from each layer. Two craters from different layers were merged if the area of the union of their masks exceeded 60 percent of the area of the larger mask:

$$A(M_1 \cup M_2) > 0.6 \cdot \max(A(M_1), A(M_2)), \quad (\text{A.42})$$

where M_1 and M_2 are the masks of the two craters, and $A(M)$ represents the area of a mask M . Another filter was applied to determine if the masked object was indeed a crater and not a particle on top of the surface. Therefore, the mean height of the mask edge (crest) was compared to the mean height of the masked object. Those objects were excluded, in which the mean height of the edge was above the mean height of the object. Fig. A.31 and A.32 show three example images taken with the confocal microscope and analysed automatically using the SAM2 model for each catcher. It is clear from the images that most of the craters are well segmented. However, there are still some unrecognised craters present in the image. In general, it is not possible to determine all craters by eye. Thus, the results using the SAM2 model are acceptable within the margins of errors made by human crater segmentation. In some cases, the entire image seems to be falsely recognised as an object. To exclude this, any crater covering more than 50 percent of the image was not considered in the statistical analysis.

The six example images were taken because they represent the two different catchers well. The PET catcher shows an overall smooth surface with small craters, while the PS catcher displays large craters and small craters. These larger craters are not always perfectly recognised by the algorithm. This contributes to systematic uncertainties toward larger craters.

points_per_side	pred_iou_thresh
64	0.1
stability_score_thresh	stability_score_offset
0.1	0.1

Table A.9.: Parameters for analysing the crater landscape confocal microscope images with SAM2.

A.11.1. Crater Forward Modelling

The forward modelled craters were simulated using the crater shape fits from Price et al. [113]. The impact velocity was $19 \pm 4 \text{ km s}^{-1}$, with a ND diameter of $2.50 \pm 0.13 \text{ nm}$, both sampled from a Gaussian distribution to obtain crater parameter distributions. The large uncertainty in the impact velocity was used to account for the uncertainty of the velocity during the experiment. The two ejecta velocities also vary because the PS is shocked above the diamond formation region. Therefore, the width of the Gaussian distribution in the forward modelling of the craters was also used to cover both catcher experiments.

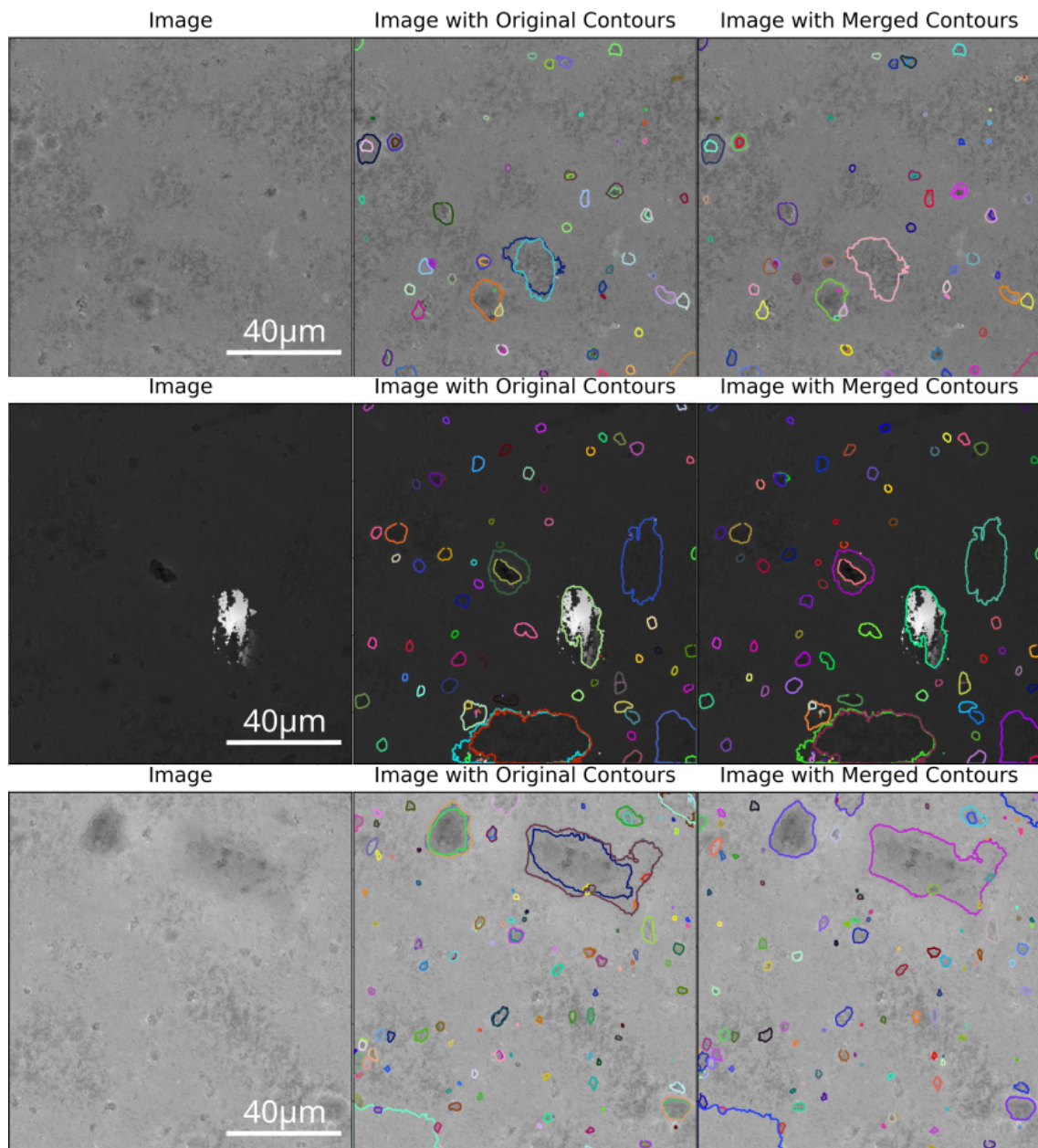


Figure A.31.: Three different cratering landscape images of the Al catcher shocked to the PET diamond formation region. The left column shows the original images, the middle column the masks before merging, and the last column the segmentation masks after the merging algorithm.

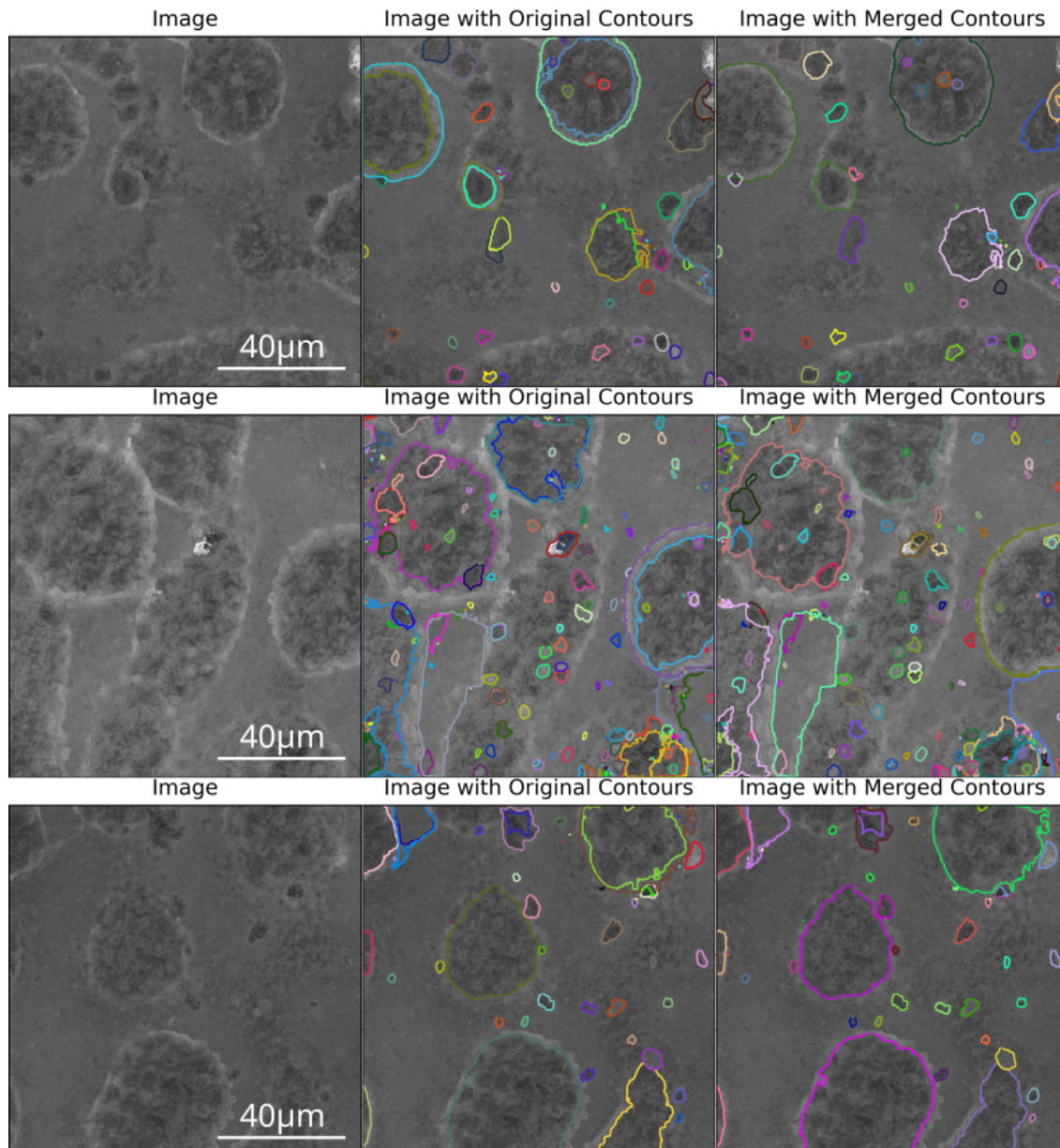


Figure A.32.: Three different cratering landscape images of the Al catcher from shocked PS outside the diamond formation region. The left column shows the original images, the middle column the masks before merging, and the last column the segmentation masks after the merging algorithm.

A.11.2. AFM Crater Measurements

The measurements of the catchers conducted with the AFM were performed using ImageJ [234]. Some of the crater profiles are displayed in Fig. A.33 and A.33. They show the scans from two different AFM measurements, with different resolutions. The low resolution measurements were taken on an AFM scan of an area of $30 \times 30 \mu\text{m}^2$ and the high resolution ones on an area of $5 \times 5 \mu\text{m}^2$, each with an image size of 256×256 pixels. The spatial resolution is therefore much higher in the smaller scan area.

To match the significantly larger craters found experimentally in the catchers, simulations were conducted with an increased impactor size. The histograms for the different materials are shown in Fig. A.35.

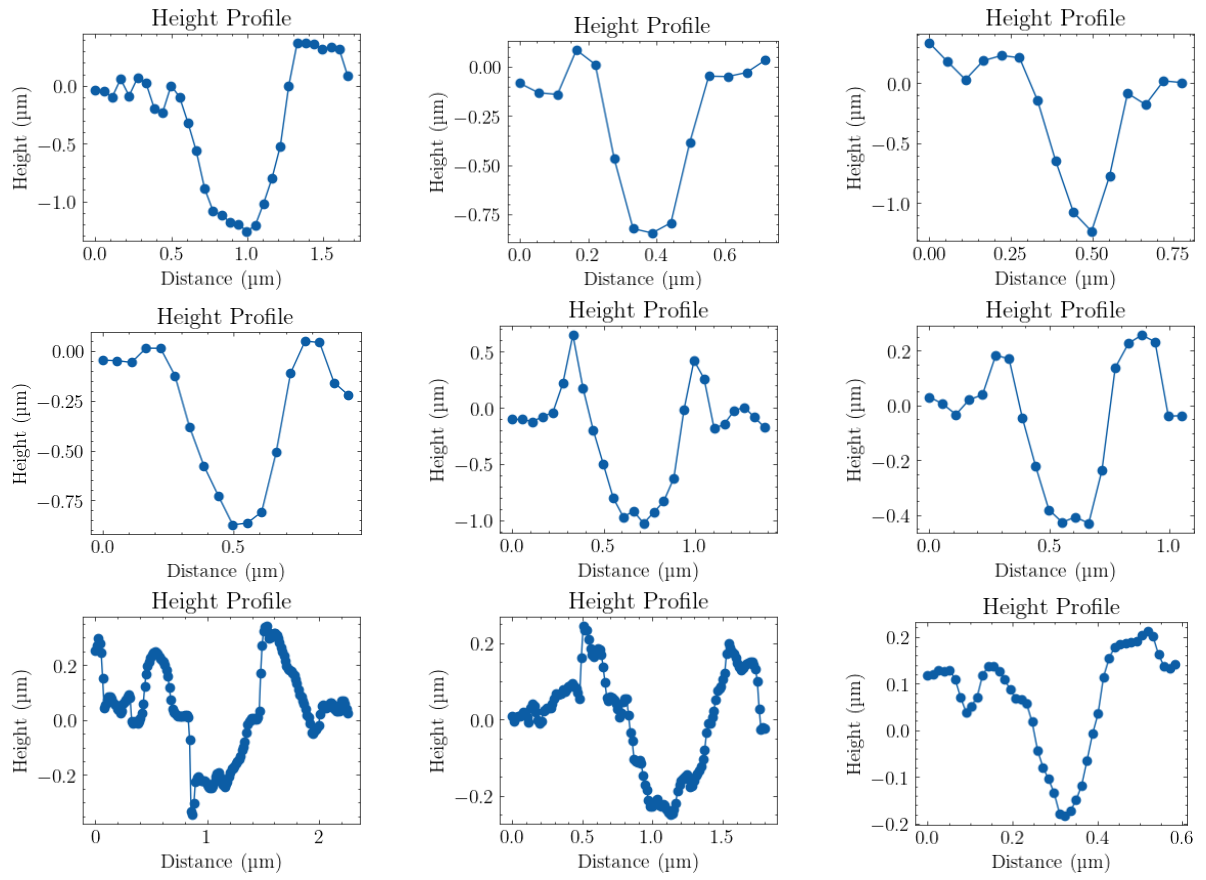


Figure A.33.: AFM crater profiles of Catcher 06. The first and second row was measured from a large scan area and the last row from a smaller area. The depth and diameter parameters of the craters were extracted from these profiles.

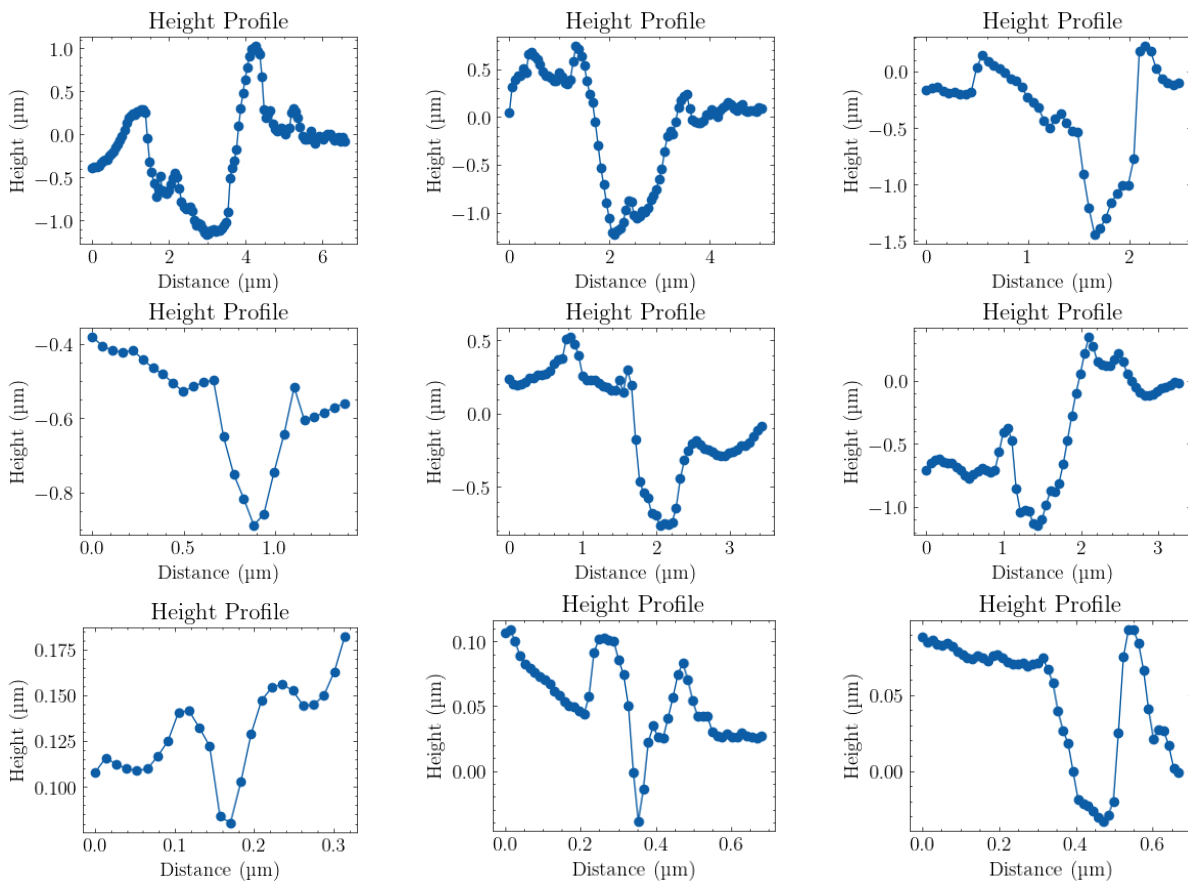


Figure A.34.: AFM crater profiles of Catcher 11. The first and second row was measured from a large scan area and the last row from a smaller area. The depth and diameter parameters of the craters were extracted from these profiles.

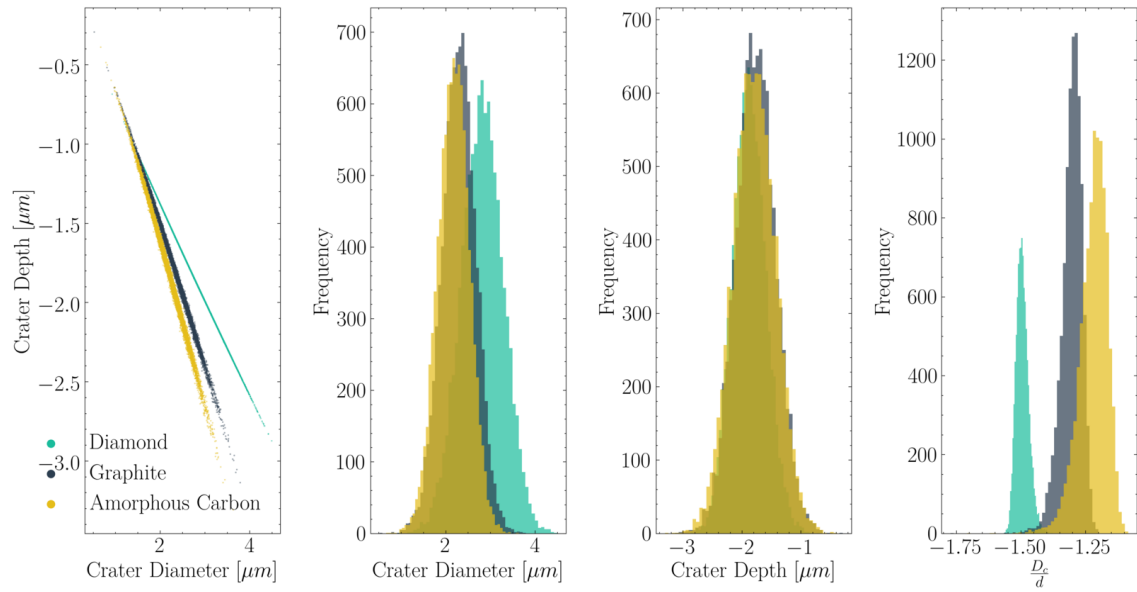


Figure A.35.: Simulated cratering statistics according to the phenomenological functions from Price et al. [113] for an impactor size of $600 \pm 30 \text{ nm}$ at an impact velocity of $19 \pm 4 \text{ km s}^{-1}$.

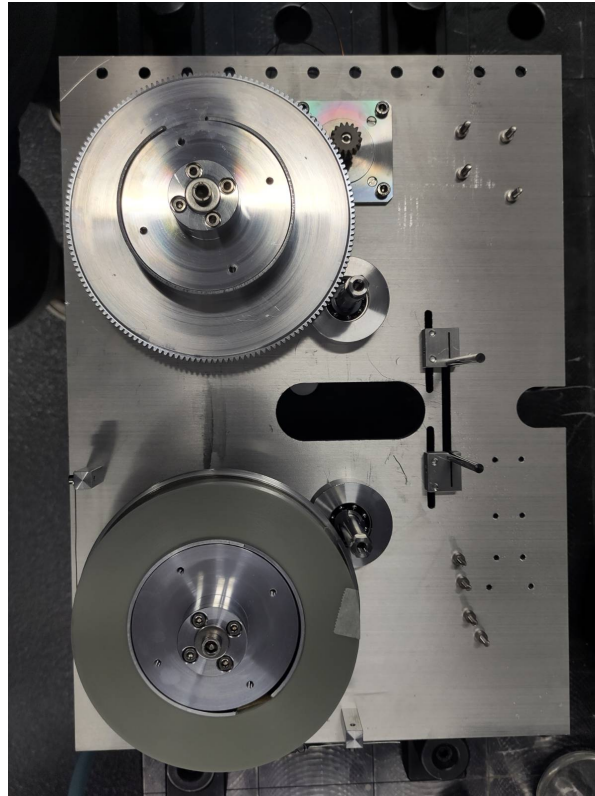
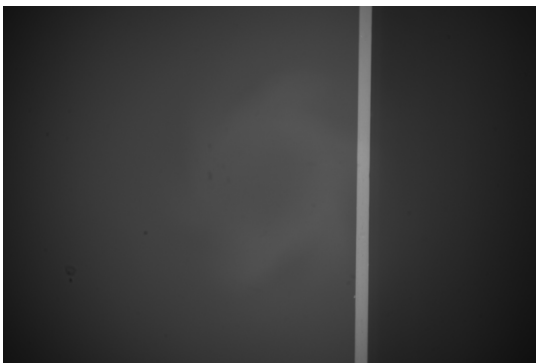


Figure A.36.: Picture of the tape target developed with the workshop at the University of Rostock.

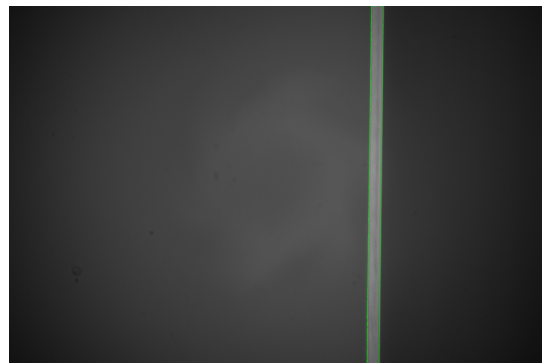
A.12. Tape Target Stability Measurement

This section provides additional details on how the tape target position was determined automatically.

To determine the spatial in-focus stability of the tape target design, the images that were taken with the Basler camera were automatically processed. The goal was to determine the laser-side position of the tape target and assess whether the stability is sufficiently high to assure that the laser can create the required shock conditions.



(a) Reference image of the tape target before moving it with the step motor.



(b) Tape target overlayed with the contours after thresholding.

Figure A.37.: Image of the tape target and the tape contour calculated after the automatic thresholding technique.

Fig. A.37a shows the tape target imaged from the side. The brightly lit tape is clearly visible and well distinguished from the background. The image processing pipeline started with determining the maximum pixel value, which is assumed to be part of the tape. After that the image was thresholded to binary values by using a threshold of $0.7 \cdot \max(\text{pixels})$. In the camera setup, one pixel corresponded to about $0.82 \mu\text{m}$, which was determined by using the tape thickness as a reference. The tape had a nominal thickness of $100 \mu\text{m}$ which was confirmed with a micrometer to be accurate within the uncertainty of $\pm 1 \mu\text{m}$. To remove the effect of faulty pixels and noise, all thresholded pixels that were $> 82 \mu\text{m}$ away from the maximal pixel value in laser beam direction were removed. This value was experimentally determined to provide good results. Such a cut-off might result in wrong thickness measurements, if the maximal pixel location is not well centred within the tape. Other ways to separate tape pixels from background pixels included k-means clustering, a step model to fit the image integrated over the y-coordinate, and several models including edge detection. However, the simple thresholding was significantly faster than these more advanced methods and in most cases even produced better results for the images that were inspected. A contour plot of the thresholded image is overlayed over the original in Fig. A.37b.

Acronyms

AFM Atomic Force Microscopy. ix, 8, 11, 16, 45, 55, 56, 80, 81, 96, 142–144

CA Cellulose Acetate. 18, 110

CC Coupled Cluster. 22

CCD Charge-Coupled Device. 39, 54

CNA Common Neighbour Analysis. 42, 46, 60

CNT Classical Nucleation Theory. 10, 11, 17

CVD Chemical Vapour Deposition. 6, 13, 14, 131

DAC Diamond Anvil Cell. 4, 13

DFT Density Functional Theory. 7–11, 16, 18, 21–24, 49, 68–70, 110

DND Detonation Nanodiamond. 6, 13–15, 37, 89, 90, 96, 131

EDIP Environment Dependent Interaction Potential. 17, 42

EDS Energy-Dispersive X-Ray Spectroscopy. 39, 52, 53, 83–85, 87, 127, 129

EELS Electron Energy Loss Spectroscopy. 38, 39, 53, 89–92, 96, 131, 133

ELI Extreme Light Infrastructure. ix, 51–53, 83–85, 127, 130, 133, 135

ELMI Center for Interdisciplinary Electron Microscopy Mecklenburg-Vorpommern. 52, 53

EOS Equation of State. 4, 24, 26, 29, 31, 48, 64, 68

EU-XFEL European X-Ray Free Electron Laser. 47–49, 51, 63, 64, 67, 69–71, 99, 116–118, 121, 123

FFT Fast Fourier Transformation. 52, 53, 87–89, 131, 132, 135

FIB Focused Ion Beam. 16, 38, 83, 127, 128

FWHM Full Width Half Maximum. 32, 52, 53, 111

HDS Hydrodynamics Simulation. 24, 25, 48, 55, 64, 65, 67, 68, 70, 77, 118, 121, 122

HPHT High-Pressure High-Temperature. 4–6, 13, 14, 37

HVI Hyper Velocity Impact. 9, 15, 19, 21, 35, 45, 46, 87, 88

HZDR Helmholtz-Zentrum Dresden-Rossendorf. 49, 52, 110

- ICF** Inertial Confinement Fusion. 5
- IRF** Instrument Resolution Function. 31, 48–50, 107, 108, 110
- KL** Kullback-Leibler. 51, 71, 124
- LJ** Lennard-Jones. 22, 46
- LULI** Laboratoire pour l’Utilisation des Lasers Intenses. ix, 51, 52, 55, 83, 127, 129, 137–139
- MAE** Mean Absolute Error. 50
- MC** Monte Carlo. 18, 35
- MCMC** Monte Carlo Markov Chain. 49, 50, 66, 95
- MD** Molecular Dynamics. 7, 11, 16–19, 21–24, 41, 43, 45, 59, 60, 63, 67, 68, 70, 74, 76, 77, 88, 95, 99, 110
- ML** Machine Learning. 11, 23
- MSE** Mean Squared Error. 51, 124
- NASA** National Aeronautics and Space Administration. 15, 16
- ND** Nanodiamond. 3–19, 21, 23, 24, 31, 33, 35–39, 41–46, 48–57, 59–68, 70, 71, 74–77, 80–84, 87–92, 94–97, 99, 101, 103–106, 108, 117, 118, 121, 123, 131–133, 135, 136, 141
- NN** Neural Network. 18, 19, 23, 50, 51, 71, 72, 74, 95, 99, 124, 125
- NVT** Canonical Ensemble - Fixed Particle Number, Volume, and Temperature. 23, 42, 44, 45
- PE** Polyethylene. 5
- PEL** Potential Energy Landscape. 22
- PET** Polyethylene Terephthalate. 11, 14–16, 18, 19, 24, 25, 42–45, 48, 49, 52–55, 63–71, 73, 74, 77–79, 83, 87, 95, 96, 110, 116–118, 120–122, 124, 126, 139–141
- PS** Polystyrene. 11–13, 15, 18, 44, 45, 54, 55, 67, 77–79, 140–142
- PVA** Polyvinyl Alcohol. 53, 96
- PY** Percus-Yevick. 34, 35, 50, 112, 114
- QMC** Quantum Monte Carlo. 22
- RDF** Radial Distribution Function. 49, 68, 110
- ROI** Region Of Interest. 52, 67, 85, 87–90, 127, 128, 131, 132, 135

- SACLA** SPring-8 Angstrom Compact Free Electron Laser. 48, 50, 63–65, 68, 70, 91, 99, 116–119, 121, 123
- SAM2** Segment Anything Model 2. 55, 140
- SAXS** Small-Angle X-Ray Scattering. 11, 13, 14, 18, 19, 30, 33–35, 46–51, 67, 71, 74, 95, 99, 112–114, 116, 124, 125
- SEM** Scanning Electron Microscope. 8, 16, 38, 39
- SOP** Streaked Optical Pyrometry. 30, 70
- STEM** Scanning Tunnelling Electron Microscopy. 38, 53, 86, 91, 135, 136
- TEM** Transmission Electron Microscopy. 8, 11, 13, 16, 19, 38, 39, 51–53, 82, 84–86, 88–90, 92, 96, 99, 127, 129, 131, 132, 135
- TNT** Trinitrotoluene. 14
- VISAR** Velocity Interferometer System for Any Reflector. 29, 30, 47, 48, 54, 64, 67, 68, 77, 96, 137, 138
- VPF** Velocity Per Fringe-shift. 29, 137
- WDM** Warm Dense Matter. 4–11, 15, 17–19, 21, 24, 30, 33, 41, 43, 49, 63, 74, 92, 95, 110
- XFEL** X-Ray Free Electron Laser. 5, 8, 30, 33, 44, 46–48, 116, 117
- XRD** X-Ray Diffraction. 6, 11, 13, 15, 18, 19, 30, 32, 33, 35, 44, 46–49, 63, 64, 67–69, 73, 74, 87, 99, 107, 108, 116, 117, 126

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Education

Curriculum Vitae

Since 02/2021 PhD student at Universität Rostock

2018 - 2020 Master of Science in Physics at University of Copenhagen:

Master's thesis:

Folding Carbon, Computational Study of the Auto-Assembly of Existing Fullerene Precursor Molecules, Towards Fast Automated Quality Assessment of Precursors for Arbitrary Fullerene Structures

2013 - 2017 Bachelor of Science in Physics at Technische Universität München:

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2005 - 2013 Gymnasium Kirchheim, Germany university entrance diploma (German: Abitur)

Acknowledgement

During the course of the past years, I have embarked on this scientific mission with the guidance and support of numerous people, whom I would like to mention here. First and foremost, I would like to thank my supervisor Prof. Dr. Dominik Kraus, who provided the initial idea for this exciting project along with a never wavering optimism. The positive atmosphere and spirit of collaboration in the interest of science in his group are truly inspiring. During our work, we were supported by scientists at SACLA, EU-XFEL, LULI, and ELI, and I would like to extend my gratitude to all the staff who made this project possible. My special thanks go to Dr. Alessandra Ravasio, Dr. Alessandra Benuzzi-Mounaix, and Dr. Tommaso Vinci who have made every visit to LULI a particular pleasure, even without electricity.

I would further like to thank Prof. Dr. Tobias Korn and Annika Bergmann-Iwe for their patient help with the Raman measurements, Andreas Worbs and Dr. René Hübner for their support with the preparation and analysis of TEM lamellae, and Dr. Ingo Barke for introducing me to the AFM. My gratitude extends to the workshops at HZDR and the University of Rostock - especially to Manfred Sobiella and Paul Voss - for their help in designing various catchers and targets. My thanks also extend to Dr. Bratislav Lukic for the provision and operation of the high-speed camera.

I would like to thank Julian Lütgert for our fruitful scientific discussions and his honest opinions and Divyanshu Ranjan for his calming presence and friendship. Special thanks go out to Chongbing Qu for our wonderful conversations. I am also grateful to all the members of the Institute of Physics at the University of Rostock who have brightened my day: Dr. Michael Stevenson, Samuel Schumacher, Johannes Rips, Björn Lindqvist, Jonas Kuhlke, Marie-Luise Herbert, Philipp Thomas May, and Rike Klauck for always providing me with excellent coffee. I would like to thank Dr. Martin Preising for helping me to take care of my physical well-being and Dr. Anna-Julia Poser for her advice and humour.

Finally, I would like to extend my deepest gratitude to all my friends and family. The friends I have made in Rostock made the past years a most enjoyable and educational experience. Special thanks go to my parents Karin

and Andreas, whose unwavering support always made me feel that I could achieve anything I set my mind to. Last but not least, I want to thank Stella for sharing her life with me and making our time on earth a most precious adventure.

None of this could I have done alone.

Selbstständigkeitserklärung

Ich versichere hiermit, dass ich die vorliegende Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Rostock, den 15. Mai 2025