

CHARACTERIZING THE PICOSECOND DYNAMICS OF LIQUID WATER
SUBJECT TO HARD X-RAY IRRADIATION

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Abstract

The interaction of ionizing radiation with liquid water is pervasive in science and engineering. When liquid water absorbs radiation, it initiates a complex sequence of electronic, structural, and chemical processes that underpin phenomena ranging from radiation damage in biological systems to energy deposition in accelerator environments and radioactive waste management in nuclear technology. Although the chemical motif of water radiolysis has been studied extensively, direct experimental observations of the structural dynamics occurring immediately after ionization remain limited. In particular, the onset of the chemical stage, which spans nanometer length scales and picosecond timescales, has remained largely inaccessible due to practical limitations in experimental methodologies. This thesis addresses this gap through a combination of ultrafast hard X-ray pump-probe scattering experiments enabled by recent advances in split-and-delay optics at two X-ray free electron laser facilities. The experiments are complemented by hydrodynamic modeling, with the chief objective of providing an interpretation of the transient structural response of liquid water following hard X-ray ionization.

Time-resolved small- and wide-angle X-ray scattering measurements were performed at the SPring-8 Angstrom Compact Free-Electron Laser and Linac Coherent Light Source facilities. Initial experiments conducted under high pressure conditions, with the water contained in a flow-cell geometry, revealed the emergence of a previously unobserved low-momentum-transfer scattering feature on sub-picosecond timescales, alongside a well-known high-momentum-transfer transient signature associated with ultrafast heating of approximately 13 K. The low-momentum-transfer feature evolved in time, developing a characteristic length scale of 3.7–3.9 nm within 0.6 ps, shifting toward lower momentum transfer with increasing pump-probe delay, and decaying after approximately 6 ps. Measurements performed independently at both facilities yielded consistent results across distinct beamline configurations, detector geometries, and pressure conditions, demonstrating the robustness of the observed phenomenon.

To extend the accessible reciprocal-space range and probe the long-time evolution of the signal, additional measurements were performed using a free-flowing liquid jet. These experiments demonstrated that the low-momentum-transfer response does not simply decay after a few picoseconds.

Instead, it progressively evolves toward lower momentum transfer while developing oscillatory features corresponding to long-range density correlations. Analysis of the scattering response further revealed a rarefaction–compression pattern propagating through the liquid at a speed of 1700–1800 m/s, comparable to the speed of sound in water. The scattering response was also found to be azimuthally symmetric, independent of pulse energy and temperature with respect to its characteristic length scales, and exhibited linear scaling with pump energy. Together, these observations established that the measured dynamics arise from a universal and reproducible structural response to hard X-ray ionization.

A physical interpretation of the observed dynamics was developed through consideration of radiation-induced energy deposition processes in liquid water. Estimates of the ionization fraction, radiation spur spacing, and electron thermalization timescales indicate that the experimental conditions correspond to weak ionization, with ionization fractions remaining below 1% even at the highest pulse energies investigated. Under these conditions, hard X-ray photoabsorption generates energetic photoelectrons that undergo secondary inelastic collisions and produce spatially isolated radiation spurs. Electron thermalization within these nanometer-scale regions deposits energy locally on sub-picosecond timescales, launching a transient density perturbation into the surrounding liquid. The experimentally observed length scales, propagation velocities, and pulse-energy scaling were all found to be consistent with this picture.

To quantitatively describe the experiments, a hydrodynamic framework based on the compressible Navier–Stokes equations was developed. Within this formulation, electron thermalization was represented as a localized temperature perturbation under isochoric conditions, generating an equivalent pressure rise that drives the density-wave propagation. Thermophysical properties were obtained from Helmholtz free-energy equations of state and constitutive relations. The model reproduced the experimentally observed SAXS response, including the emergence and propagation of oscillatory features, the evolution of the scattering signal in reciprocal and real space, and the apparent faster-than-sound velocities extracted from the experiments. Systematic variation of transport properties further demonstrated that the propagation velocity is governed by the speed of sound of the medium, whereas viscosity controls the attenuation of the response. Simulations performed for water, liquid carbon dioxide, and ethanol additionally revealed that the response is universal across liquids, predictable through the same continuum framework.

The results of this thesis illustrate that hard X-ray ionization of liquid water produces long-lived nanoscale density perturbations that evolve hydrodynamically on picosecond timescales. More broadly, the work established a connection between microscopic ionization processes and macroscopic transport phenomena and showed that continuum hydrodynamics remains remarkably effective at describing liquid dynamics on these spatiotemporal scales. These findings provide new insight into the earliest structural stages of water radiolysis and lay the groundwork for future investigations of radiation-induced dynamics in liquids using ultrafast X-ray scattering techniques.

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Dedication

This thesis is dedicated to my grandpa, Khalil, who instilled in me the value of hard work and resilience.

The larger the island of knowledge, the longer the shoreline of wonder.

— Ralph W. Sockman

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Chapter 1

Introduction

Water is essential to life on Earth and is widely considered to be a key ingredient for life elsewhere in the universe [7]. Despite decades of intensive research, water continues to exhibit rich and sometimes anomalous behavior. Recently, a growing body of literature [5, 8, 9] has provided evidence for the existence of a liquid–liquid critical point in supercooled water. This suggests that ambient water may already exist in a supercritical state and highlights that even its phase behavior is not yet fully understood.

Beyond its scientific interest, water is ubiquitous in both natural and engineered systems. In nature, water is a major constituent of all living organisms [10] and a universal solvent capable of dissolving more solutes than any other liquid [11]. In engineering, it serves as the primary coolant in nuclear power plants [12], as a means of power generation [13], as a medium through which chemical reactions take place [14], and as the solvent environment in which the structure of proteins is determined [15]. In many of these settings, a common challenge arises: water is exposed to high-energy radiation. Unlike low-energy radiation, ionizing radiation—such as that from X-rays, γ -rays, and fast-moving charged or neutral particles—possesses sufficient energy to liberate electrons from water molecules, including from inner-shell orbitals. This, in turn, initiates a cascade of processes collectively known as radiolysis.

Radiolysis plays a fundamental role across a wide range of applications. In radiotherapy [16], high-energy proton and electron beams are employed to destroy cancerous cells, which are predominantly composed of water [10]. In nuclear technology [17], radiolysis accelerates corrosion and material degradation. In X-ray crystallography [18], radiation-induced effects in the hydration environment must be accounted for to accurately resolve the structure of macromolecules. Radiolysis has also been proposed as a central mechanism for oxygen formation in cometary ice [19] and hydrogen production in deep geological environments [20]. Besides its importance on Earth, understanding radiolysis is a critical component of mitigating radiation damage during extended human spaceflight [21].

1.1 Water Under Ionizing Radiation

Radiolysis is conventionally described as a sequence of stages (physical, physico-chemical, chemical, and biological) that immediately follow the deposition of energy by ionizing radiation. These stages span a large temporal domain [22]: the physical stage concludes within a few femtoseconds, the physico-chemical stage by approximately 1 ps, and the chemical stage extends from 1 ps to 1 μ s; processes occurring on longer timescales are typically grouped into the biological stage, which can last up to days or sometimes years.

At photon energies below 15 keV and for light elements such as oxygen and hydrogen, the photon absorption cross-section far exceeds that of elastic scattering [23]. As such, photoionization is the primary interaction mechanism, and it initiates the physical stage. In water, this process is dominated by ionization of the oxygen atom, as its photon absorption cross-section is significantly larger than that of hydrogen. A key threshold in this regard is the K-shell binding energy of oxygen, 538.2 eV [24]. Radiation with photon energies exceeding this threshold ejects core-shell electrons, leaving behind highly unstable water cations. Core ionization takes place on a femtosecond timescale and is typically associated with the physical stage of radiolysis [25].

During the physico-chemical stage, the water cations decay primarily via local Auger decay [26, 27], in which an electron from the same atom, but a higher-energy orbital, fills the core vacancy and a valence electron is released. This is not the only relaxation pathway, however. In pure liquid and aqueous environments, additional non-local pathways become available, including intermolecular Coulombic decay (ICD) [28], where an inner-shell electron fills the core hole and excess energy is transferred to a neighboring molecule, leading to electron emission, and electron transfer mediated decay (ETMD) [29], in which the core vacancy is refilled by a valence electron from a nearby molecule, resulting in ionization of that neighbor. These decay processes occur on ultrafast timescales (≤ 10 –50 fs, depending on the mechanism and local environment) [30–33] and result in the generation of energetic secondary electrons, water dications (H_2O^{2+}), and water cations with an inner-shell vacancy ($\text{H}_2\text{O}^{\bullet+}$). Both species (H_2O^{2+} and $\text{H}_2\text{O}^{\bullet+}$) are short-lived, with lifetimes not exceeding 52 fs [34, 35], and undergo rapid proton transfer reactions with neighboring water molecules to produce hydronium cations (H_3O^+) and hydroxyl radicals (OH).

Within ~ 1 ps [36, 37], at the onset of the chemical stage, the secondary electrons thermalize, become trapped, and eventually hydrated, i.e., their energy drops below the excitation threshold of liquid water, 7.3 eV [38]. In the process, they can be captured by nearby water cations in geminate recombination [39], resulting in excited water molecules (H_2O^*). The excited water molecules can then decompose into hydrogen (H) and hydroxyl radicals, or into molecular hydrogen (H_2) and excited oxygen atoms (singlet $\text{O}(^1D)$ or triplet $\text{O}(^3P)$ states). In addition, they can autoionize to produce hydrated electrons (e_{aq}^-) and water cations or relax back to the ground state by releasing energy [40]. Although the exact de-excitation pathways remain poorly understood, it is generally accepted that e_{aq}^- , H_3O^+ , and OH are present, among other species such as H, H_2 , and excited

oxygen atoms, near each core ionization site.

On nanosecond to microsecond timescales, radiolytic species formed at the onset of the chemical stage begin to diffuse away from their parent ionization sites and undergo bimolecular reactions, including radical recombination and scavenging reactions [41]. This transition marks the crossover to homogeneous chemistry and the production of longer-lived molecular species such as hydrogen peroxide (H_2O_2) [22]. For timescales beyond a few microseconds, radiolysis is well described by established chemical kinetics frameworks [6, 42, 43]. Figure 1.1 shows a pictorial representation of the various radiolysis stages along with the timescales at which they evolve.

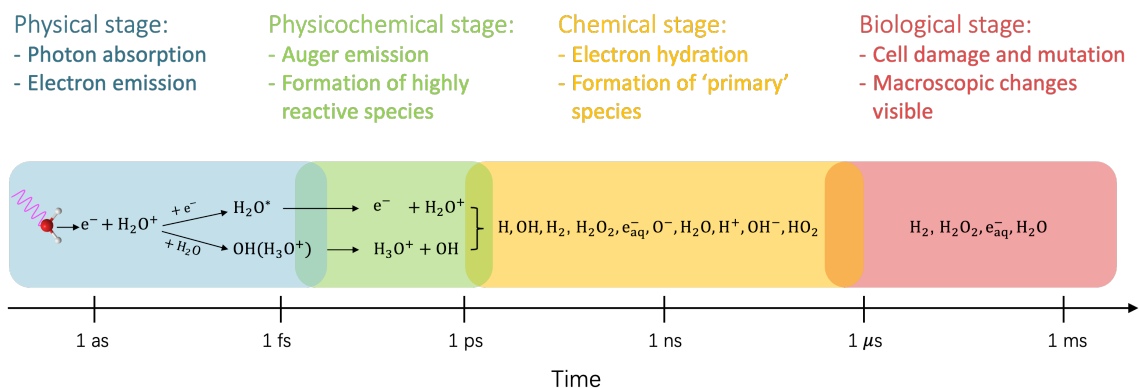


Figure 1.1: **Summary of ionization events and primary species in radiolysis.** Ionization by high-energy radiation occurs in the physical stage, producing highly reactive water cations and secondary electrons. The water cations react during the physico-chemical stage with nearby water molecules to generate hydronium cations and hydroxyl radicals, and undergo local or non-local decay that produces additional cations. Longer-lived, primary radiolysis species are formed in the chemical stage that contribute to radiation damage on longer than microsecond timescales.

1.2 The Structural Motif of Radiolysis

While the foregoing discussion has focused on radiation chemistry, radiolysis is inherently a spatially heterogeneous process, and its structural motif is equally important. This is because at the onset of the chemical stage, radiolytic species (e_{aq}^- , H_3O^+ , OH , etc.) form and are distributed in distinct geometric patterns known as radiation track structures [1, 44–47]. The structures arise from local energy deposition by secondary electrons [48] and define the initial conditions for subsequent diffusion-controlled chemical reactions [49]. Ultimately, it is these reactions, along with inelastic collisions between hydrated electrons and surrounding molecules, that mediate radiation damage in biological contexts [10, 50, 51].

The spatial extent and morphology of radiation track structures are complex and strongly depend on the ionizing energy. In the low linear energy transfer (LET) regime, isolated “Magee” spurs [45, 46]

are expected. The spurs manifest as nearly spherical clusters with characteristic radii in the range of 2–5 nm [52,53]. In the high LET regime, however, a picture of overlapping spurs emerges, resulting in a geometry referred to as a short track [46] with characteristic dimensions on the order of the inelastic mean free path of the ionizing electrons. Figure 1.2 highlights a typical radiation track structure under high-LET radiation.

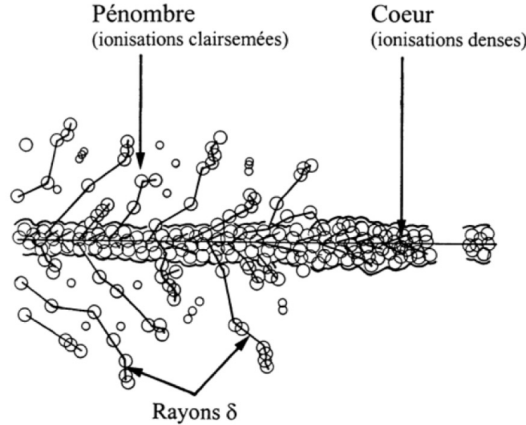


Figure 1.2: **Radiation track structure under high-LET radiation.** A short track is formed along the primary ionization path. In addition, secondary ionization events involving energetic electrons produce a surrounding penumbra and lead to δ -ray branches that propagate into adjacent regions. Figure from [1].

In addition to the spatial distribution of radiolytic species, an important aspect of radiation track structures is the local energy deposition by secondary electrons, which has long been theorized to produce a transient temperature increase within the structures, a so-called “thermal spike” [54–58]. Estimates of the temperature rise vary widely, from a few tens of degrees for low-LET radiation [59,60] to as high as 10^4 K in the tracks of high-LET fission fragments [61]. Although the magnitude of the thermal spike has not been experimentally established in water, such localized heating is predicted to give rise to a thermomechanical response in the vicinity of the track structures [62–64], potentially influencing long-term radiolytic yields [47,65] and radical diffusion kinetics. As a result, radiation track structures not only serve as the starting point from which radiation-induced damage develops [66], but they also modulate their local environment. Despite their significance, a direct characterization of the dynamics of radiation track structures and their local environment has remained elusive.

1.3 Need for High-Energy Ultrafast Probes

The complex nature of radiation track structures, along with their formation on picosecond timescales and nanometer length scales, poses significant challenges for existing experimental techniques. On

the one hand, advances in modern X-ray free electron lasers (XFELs) [67–69], with the capability of generating ultrashort energy pulses on the order of femtoseconds, have allowed real-time tracking of the femtosecond dynamics in liquid water following strong-field ionization [35], optical excitation [70], and extreme ultraviolet laser absorption [36, 71]. These developments have improved the understanding of the physical stage by establishing lifetimes of early radiolytic species, such as H_3O^+ and OH . At the same time, hydrated electrons (e_{aq}^-) have been extensively studied using absorption spectroscopy [37, 72, 73]. Most recently, the generation of attosecond pulses [74] has opened the door to tracking electron dynamics immediately following photoionization. Yet, these techniques fall short in that they do not directly probe radiolysis initiated by high-energy ionizing radiation.

Pulse radiolysis [59, 75–77], on the other hand, using sources such as γ -rays or high-energy electron beams, overcomes this limitation and has traditionally been used to study the formation and decay kinetics of transient species in the chemical stage, on nanosecond-to-microsecond timescales. However, even the fastest implementation of pulse radiolysis is limited to a time resolution of 10 ps [77], which is still insufficient to directly observe the dynamics of radiation track structures during the early part of the chemical stage.

Latest developments in high-energy split-and-delay optics (SDO) [78–80] at two XFEL facilities, SPring-8 Angstrom Compact Free-Electron Laser (SACLA) [81] and the Linac Coherent Light Source (LCLS) [82] at the Stanford Linear Accelerator Center (SLAC), bridge this gap. In particular, by generating two coherent X-ray pulses with tunable femtosecond-to-picosecond time delays, these instruments combine the ultrafast temporal resolution of XFEL sources with the ability to initiate radiolysis through high-energy photon absorption. This unique capability provides a direct pathway to probe the picosecond dynamics of liquid water during the chemical stage of radiolysis.

1.4 Research Objectives

The primary objective of this thesis is therefore to investigate how ultrafast energy deposition within radiation track structures impacts their local environment. To this end, the thesis presents results from three separate experimental campaigns, conducted at both SACLA and LCLS, with the aim of providing a comprehensive characterization of the picosecond dynamics of liquid water radiolysis. The specific objectives of the thesis are as follows:

- Identify the spatial and temporal length scales over which the response of liquid water to ultrafast energy deposition evolves, from the initial sub-picosecond regime up to 100 ps. This includes explaining how local energy deposition is converted into detectable structural features.
- Understand how this response is affected by thermodynamic conditions, specifically high pressure and elevated temperature. Special attention is given to how changes in transport properties influence the resulting dynamics.

- Elucidate the physical mechanism underlying the observed response within the picosecond measurement window and analyze its dependence on the deposited energy.
- Develop a reduced-order analytical model that captures the experimentally observed dynamics while remaining both physically and computationally tractable. The model should reproduce key observables and provide insight into the parameters governing the structural dynamics.

1.5 Thesis Outline

The remainder of the thesis is organized as follows:

- Chapter 2 describes the experimental methods employed at SACLA and LCLS to probe ultrafast structural dynamics in liquid water, including the theoretical background of X-ray scattering, the experimental geometries, and the data analysis procedure.
- Chapter 3 presents the first set of experimental results obtained using a high-pressure flow-cell geometry. The chapter focuses on the long-term response of liquid water at elevated pressure and the early-time response following ultrafast energy deposition. These results establish the emergence of nanometer-scale structural dynamics on sub-picosecond timescales.
- Chapter 4 extends these results in momentum space using a liquid jet geometry. The chapter investigates the evolution of the observed low- Q response at larger length scales, its dependence on pulse energy and temperature, and the scaling behavior of the scattering signal under different fluence conditions. These results reveal reproducible structural features associated with liquid water radiolysis initiated by hard X-ray ionization.
- Chapter 5 develops an interpretation of the observed dynamics. The chapter discusses the characteristic spatiotemporal scales of the response and motivates the physical framework used to describe the results.
- Chapter 6 introduces a computational framework to model the experimental observations. The model is used to connect local energy deposition to macroscopic variables.
- Chapter 7 summarizes the main findings of the thesis, discusses their implications for radiolysis, and outlines possible directions for future research.

1.6 Accomplishments

The work presented in this thesis advances the understanding of the chemical stage of radiolysis, and, more broadly, radiation-induced damage in aqueous systems by providing insight into the ultrafast structural dynamics. The major contributions of this work are summarized below:

- Leveraged an experimental framework based on X-ray free-electron laser split-and-delay optics to enable femtosecond-resolution pump–probe measurements of liquid water following X-ray absorption. This approach bridged the gap between conventional pulse radiolysis and ultrafast spectroscopy by combining X-ray ionization with ultrafast temporal resolution.
- Resolved the dynamics in the chemical stage of radiolysis from the sub-picosecond regime up to 100 ps. In doing so, we established characteristic timescales associated with the onset of the structural evolution and the early development of radiation track structures.
- Demonstrated how the structural dynamics are influenced by thermodynamic conditions, including elevated pressures and temperature. This highlighted the role of transport properties in shaping the early dynamics of radiation-induced changes.
- Developed a reduced-order analytical model that reproduces the experimentally observed dynamics. The model connected local energy deposition to measurable structural observables and provided a physically interpretable description of the evolution of X-ray irradiated liquid water on nanometer length scales.

Chapter 2

Background and Methods

This chapter provides an overview of X-ray scattering principles employed in this thesis. It establishes the theoretical framework required to interpret the measured signals and describes the experimental methods used to probe ultrafast structural dynamics in liquid water. Two complementary hard X-ray pump-probe approaches are introduced. Together, they enable measurements of radiolysis on picosecond timescales and nanometer length scales.

2.1 Fundamentals of X-ray Scattering

In a typical X-ray scattering experiment, an incident X-ray pulse with wavelength in the range $\sim 0.01\text{--}10$ nm [83], corresponding to photon energies of 100–0.1 keV, impinges on a sample. As it propagates through the sample, the pulse is attenuated due to interactions with the electronic structure of the atoms and molecules. Three main interactions channels dominate [84]:

1. **Elastic (Rayleigh) scattering**, in which photons are deflected without energy loss;
2. **Inelastic (Compton) scattering**, in which photons are deflected, lose part of their energy to electrons, and may ionize them in the process;
3. **Photoabsorption**, in which photons are absorbed, leading to electronic excitation or ionization.

At higher photon energies, additional processes such as nuclear interactions or electron-positron pair production may occur, although these are negligible in the energy regime considered in this work [85]. These interaction channels are probabilistic in nature, governed by quantum electrodynamics (QED). However, their averaged cross-sections are well established and readily tabulated [23, 86]. In this work, unless otherwise stated, tabulated cross-sections are used.

A detector placed downstream of the sample collects the transmitted and scattered photons. The measured detector intensity can be expressed as [87]:

$$I(\mathbf{Q}) = I_{th}|F(\mathbf{Q})|^2, \quad (2.1)$$

where $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ is the scattering vector defined by the scattered and incident wavevectors, $\mathbf{k}'$ and $\mathbf{k}$, respectively. For elastic scattering, its magnitude is given by:

$$Q = |\mathbf{Q}| = \frac{4\pi}{\lambda}\sin(\theta), \quad (2.2)$$

where θ is half the scattering angle and λ is the X-ray wavelength. The prefactor I_{th} is the Thomson scattering cross-section of a single electron, while $F(\mathbf{Q})$ is the molecular form factor.

The molecular form factor is the Fourier transform of the electron density for a single molecule. Thus, it encodes information about the instantaneous spatial distribution of electrons, and, by extension, the atomic positions and molecular orientation. Since the detector measures only the scattered intensity, i.e., $|F(\mathbf{Q})|^2$, the phase information is lost and the complex form factor cannot, in general, be reconstructed directly. This limitation is known as the phase problem in X-ray scattering [88]. For a system consisting of a discrete number of atoms or molecules, the electron density can be recast as [87]:

$$\rho(\mathbf{r}) = \sum_a \rho_a(\mathbf{r} - \mathbf{r}_a), \quad (2.3)$$

where $\mathbf{r}$ is the spatial coordinate and $\mathbf{r}_a$ denotes the position of atom a . Substituting this expression into the Fourier transform yields:

$$F(\mathbf{Q}) = \sum_a f_a(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{r}_a}, \quad (2.4)$$

where $f_a(\mathbf{Q})$ is the atomic form factor. Equation (2.4) is valid within the single-scattering (kinematic) approximation, in which the X-rays scatter only once throughout the sample. In turn, such an approximation is well satisfied for thin liquid samples and gases [87]. Moreover, in liquid water, the scattering signal is dominated by oxygen atoms due to their substantially larger electron density relative to hydrogen (oxygen has eight times more electrons than hydrogen). As a result, Equation (2.4) can be approximated as:

$$F(\mathbf{Q}) \approx f_O(\mathbf{Q}) \sum_{j=1}^{N_O} e^{i\mathbf{Q}\cdot\mathbf{r}_{O_j}}, \quad (2.5)$$

where N_O is the total number of oxygen atoms in the scattering volume. In Equation (2.5), the atomic form factor describes the scattering strength of an individual oxygen atom, whereas the exponential term contains the spatial arrangement through interference between the scattered waves. The atomic form factor for a myriad of atoms, including oxygen, is tabulated in [89].

In Equation (2.1), Thomson scattering from a single electron accounts for experimental parameters such as the incident photon fluence, X-ray polarization, and detector geometry. It can be written as [87]:

$$I_{th} = \Phi \langle |\mathcal{P}|^2 \rangle r_e^2 d\Omega, \quad (2.6)$$

where Φ is the incident photon fluence, $\langle |\mathcal{P}|^2 \rangle = \langle |\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'|^2 \rangle$ is the polarization factor, with $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}'$ denoting the polarization vectors of the incident and scattered X-rays, respectively, $r_e = 2.82 \times 10^{-15}$ m is the classical electron radius, and $d\Omega$ is the solid angle subtended by a detector pixel. For a total X-ray pulse of energy E_{tot} , the photon fluence is:

$$\Phi = \frac{E_{tot}}{h\nu A_{beam}}, \quad (2.7)$$

where $h\nu$ is the photon energy and A_{beam} is the beam cross-sectional area.

For structural analysis, particularly for isotropic liquids such as water, it is often convenient to perform an azimuthal average over all detector angles. This reduces the dependence on the full scattering vector, $\mathbf{Q}$, and retains only its magnitude, Q (Equation 2.2), yielding a one-dimensional scattering profile, $I(Q)$. In addition, the structure factor, $S(Q)$, is commonly defined to remove the instrumental dependence (X-ray polarization, fluence, beam size, etc.) and isolate the spatial correlations between scattering centers in the sample. The structure factor is defined as [87]:

$$S(Q) = \frac{I(Q)}{NI_{th} \sum_O |f_O(Q)|^2}, \quad (2.8)$$

where N is the number of molecules within the X-ray illumination volume, determined by the mass density ρ , sample thickness L , beam cross-section A_{beam} , Avogadro's number $N_A = 6.022 \times 10^{23}$ mol⁻¹, and the molecular weight $M = 18.015$ g/mol, i.e., $N = \rho L A_{beam} N_A / M$. In the remainder of this work, the normalized scattering intensity is used:

$$\tilde{S}(Q) = \frac{I(Q)}{NI_{th}}, \quad (2.9)$$

which retains the atomic form factor weighting. This formulation is adopted because the oxygen form factor varies smoothly [89] over the momentum-transfer range studied herein and hence does not alter the dynamics of the measured response.

2.2 Time-resolved Pump–Probe Scattering

Equation (2.9) describes a static scattering measurement. To probe time-dependent structural dynamics initiated by X-ray ionization, two X-ray sub-pulses are needed, commonly referred to as a pump and a probe. Not any two sub-pulses can be used, however. In practice, the sub-pulses must

originate from the same parent X-ray pulse in order to ensure identical spectral properties and precise temporal synchronization. This is the primary role of a split-and-delay optical (SDO) system.

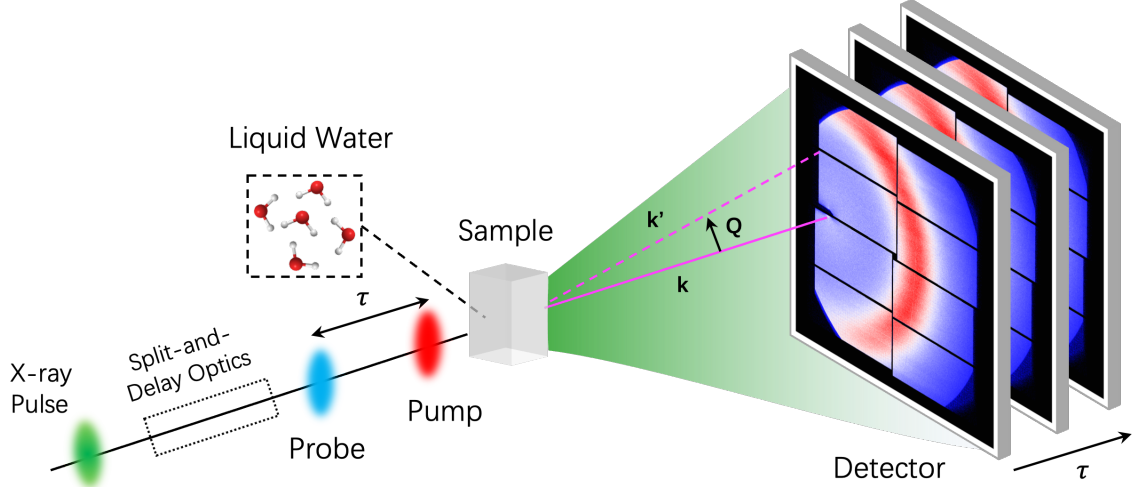


Figure 2.1: **Time-resolved X-ray scattering setup.** An X-ray pulse from an XFEL source is split by split-and-delay optics into two coherent sub-pulses: a pump pulse (red) and a probe pulse (blue). The pump pulse initiates the structural dynamics in the liquid water sample, while the probe pulse scatters from the evolving structure after a controlled time delay, τ . By varying the delay between the two pulses on femtosecond-to-picosecond timescales, ultrafast structural changes can be monitored in the chemical stage of radiolysis. A detector placed downstream of the sample collects the scattered and transmitted photons from both pulses.

A schematic of a representative time-resolved X-ray scattering experiment is shown in Figure 2.1. By controlling the temporal separation between the pump and probe pulses, denoted by the time delay τ , a series of detector images can be collected. The normalized scattering intensity can then be generalized as:

$$\tilde{S}(Q, \tau) = \frac{I(Q, \tau)}{NI_{th}}, \quad (2.10)$$

where we now explicitly specify the dependence on the pump-probe time delay. In addition, the energies of the individual sub-pulses, E_{pump} and E_{probe} , may vary on a shot-to-shot basis. Since the Thomson scattering term depends on the incident photon fluence (Equation 2.6), the measured scattering intensity acquires an additional dependence on the total incident pulse energy, E_{tot} :

$$E_{tot} = E_{pump} + E_{probe}. \quad (2.11)$$

The normalized scattering intensity can therefore be written as:

$$\tilde{S}(Q, \tau, E_{tot}) = \frac{I(Q, \tau, E_{tot})}{N\Phi(E_{tot})\langle|\mathcal{P}|^2\rangle r_e^2 d\Omega}. \quad (2.12)$$

The pulse energy dependence is investigated further in Chapter 4.

2.3 Facilities and Instrumentation

Time-resolved hard X-ray (photon energies in the 5–20 keV range) scattering experiments were performed at two XFEL facilities: beamline 3 (BL3) [90] of SACLA and the X-ray Pump Probe (XPP) instrument [91] at LCLS of SLAC. Both facilities employed SDO systems to generate X-ray pulse pairs with tunable femtosecond-to-picosecond time delays for pump–probe measurements, and the SDO was optimized before each delay condition to ensure that the pump and probe pulses had the same spatial overlap at the sample.

2.3.1 SACLA

At SACLA, the XFEL operated in self-seeded mode with a central photon energy of 10 keV, a pulse duration of 10 fs, and a repetition rate of 30 Hz. Each incident X-ray pulse was split into a coherent pulse pair using a wavefront-division SDO based on channel-cut (CC) silicon crystals [79]. The SDO, depicted in Figure 2.2(a), controlled the relative temporal separation between the pump and probe pulses over delays up to 100 ps while preserving their coherence and spatial properties.

Within the SDO, photodiodes independently recorded the energies of the pump pulse, E_{pump} , and the total incident pulse, E_{tot} . The probe pulse energy was then obtained by Equation (2.11). The pump pulse was monitored using a silicon photodiode that detected X-rays scattered from a Kapton foil, while the total pulse energy from both branches was recorded using a chemical vapor deposition (CVD) diamond diode [92, 93]. Downstream of the SDO, the pulse pair was focused onto the sample using a set of Kirkpatrick–Baez (KB) mirrors [94]. The X-ray focal spot was characterized using an X-ray beam profile monitor (HAMAMATSU, ORCA flash) with a spatial resolution of 325 nm [93] and measured to have a full width at half maximum (FWHM) diameter of 3 μm .

Scattered X-ray photons from both pulses were recorded using octal-sensor multiport charge-coupled device (MPCCD) detectors with a pixel size of 50 μm [95]. Two experimental configurations were studied at SACLA in this work: a high-pressure cell geometry and a liquid jet geometry. Each configuration utilized a distinct detector arrangement and sample environment; configuration-specific details are discussed in Chapters 3 and 4, respectively.

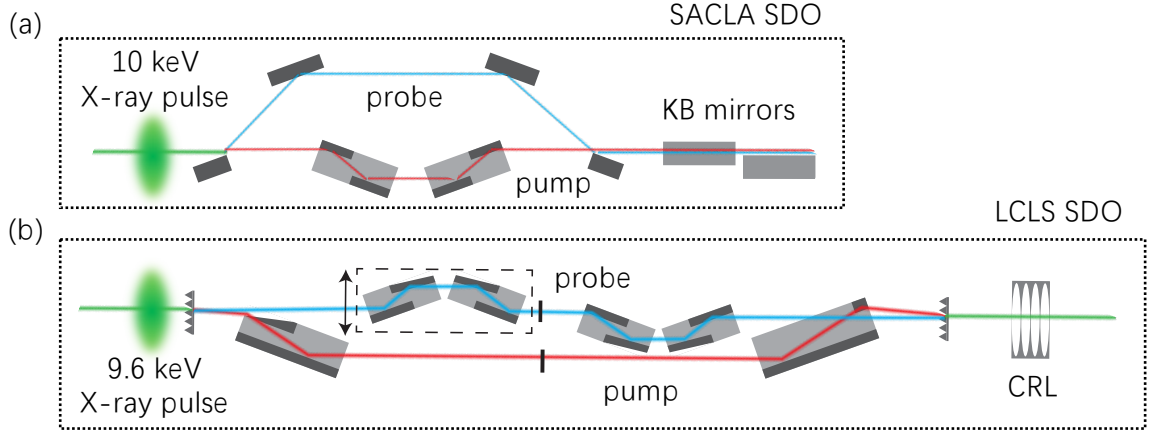


Figure 2.2: **Hard X-ray split-and-delay optics.** (a) Wavefront-division SDO configuration at SACLA used to generate coherent pump–probe pulse pairs focused by Kirkpatrick–Baez (KB) mirrors; (b) Amplitude-splitting SDO configuration at LCLS with a compound refractive lens (CRL) for focusing.

2.3.2 LCLS

At LCLS, the XFEL operated in self-amplified spontaneous emission (SASE) mode with a photon energy of 9.6 keV, a pulse duration of 30 fs, and a repetition rate of 120 Hz. Pulse pairs were generated using an amplitude-splitting SDO [80] based on CC crystals, which controlled the relative delay between the pump and probe pulses. Upstream of the SDO, the incident XFEL beam passed through a diamond transmission grating. A second grating was positioned downstream to recombine and steer the split beams before focusing onto the sample. The pulse pair was subsequently focused onto the sample interaction region using a beryllium compound refractive lens (CRL) [80]. The SDO is shown in Figure 2.2(b), where pump–probe delays up to 3.6 ps were scanned continuously on a run-by-run basis.

Unlike the SACLA configuration, separate pulse-energy measurements for the pump and probe pulses were not available at LCLS. Instead, the average pulse-energy branching ratio was determined from dedicated pump-only and pump–probe measurements acquired at identical time delays. The X-ray focal spot size was measured to be $1\text{ }\mu\text{m}$ at FWHM. Scattering patterns were collected using hybrid silicon JUNGFRAU detectors with a pixel size of $75\text{ }\mu\text{m}$ [96].

2.4 Sample Environments

Two sample environments were studied in this work. Early measurements at SACLA and LCLS utilized a high-pressure flow cell [97] to contain liquid water at elevated pressures, while later experiments employed a free-flowing liquid water jet with heating capability to investigate temperature-dependent dynamics.

2.4.1 High-Pressure Flow Cell

A sample of ultrapure type-I deionized water (Milli-Q, Sigma-Aldrich) was contained within a titanium pressure flow cell [97]. The cell was enclosed by two single-crystal, type IIa, diamond windows and sealed to prevent leakage. At SACLA, 200 μm -thick diamond windows were used, resulting in an effective sample thickness of $\sim 800 \mu\text{m}$. At LCLS, 100 μm -thick diamond windows were used with an effective sample thickness of $\sim 1000 \mu\text{m}$.

Pressure was maintained and the sample continuously refreshed using an *Air Valve Continuous Flow Systems* pump from Teledyne Labs. Measurements at SACLA were performed at pressures of 50 bar and 150 bar, while measurements at LCLS were conducted at 2 bar. The average flow rate was approximately 0.26 mL/min. The sample temperature was maintained near room temperature, specifically at 30°C and 22°C at SACLA and LCLS, respectively.

Empty-cell measurements were collected at time-zero ($\tau = 0$) at SACLA and at pump-probe delays up to 2 ps at LCLS in order to characterize scattering contributions from the diamond windows and isolate the structural response of the liquid water sample.

2.4.2 Liquid Jet Geometry

For the liquid jet measurements, ultrapure type-I deionized water (Milli-Q, Sigma-Aldrich) was injected into a helium chamber to minimize background scattering. The liquid was delivered through a piezoelectric nozzle at room temperature (20°C). The sample was supplied at atmospheric pressure (~ 1 bar) using the same *Air Valve Continuous Flow Systems* pump from Teledyne Labs. The average flow rate was monitored by the pump and measured to be ~ 50 mL/min.

The jet diameter, i.e., sample thickness along the beam path, was estimated from Gaussian fits to the measured jet profile and determined to be $391 \pm 49 \mu\text{m}$. Additional measurements were performed under elevated temperature conditions of 80°C, detailed in Chapter 4. Table 2.1 summarizes the sample conditions investigated at both facilities.

2.5 Data Reduction and Analysis Workflow

The raw detector images collected at SACLA and LCLS were post-processed to obtain time-dependent azimuthally averaged scattering profiles as a function of momentum transfer, pump-probe delay, and

Facility / Geometry	Pressure (bar)	Temperature ($^{\circ}\text{C}$)	Sample Thickness (μm)
SACLA, cell	50, 150	30	800
LCLS, cell	2	22	1000
SACLA, jet	~ 1	20, 80	391 ± 49

Table 2.1: **Summary of sample environments considered in this work.** The table compares pressure, temperature, and effective sample thickness for the high-pressure flow cell and liquid jet geometries at SACLA and LCLS.

pulse energy. Although the experimental configurations differed between the two facilities and sample environments, the overall workflow remained similar. The analysis consisted of detector filtering and masking, background subtraction, normalization to the Thomson scattering, azimuthal averaging, pulse-energy and/or time-delay binning, and uncertainty propagation.

2.5.1 Pressure Cell Measurements

SACLA

For the high-pressure flow-cell measurements, the detector images were first corrected prior to azimuthal averaging. At SACLA, the pressure cell was rotated by 7° relative to the incident X-ray propagation direction in order to optimize the accessible momentum-transfer range. As a result, the measured scattering intensities depended not only on the detector solid angle and X-ray polarization factors (Equation 2.6), but also on the geometric projection associated with the sample rotation. These effects were incorporated into a combined detector correction applied on a pixel-by-pixel basis during data reduction.

Each detector image was loaded, subtracted by a measured dark signal, and filtered to remove pixels with intensities below the detector dark level. Additionally, pixels corresponding to detector gaps or saturated regions were masked and excluded from further analysis. The remaining detector intensities were then normalized by the polarization factor, detector solid angle, and sample-rotation correction prior to azimuthal averaging. Since the detector consists of a discrete array of pixels, the corrected detector images were integrated over the accessible momentum-transfer range to obtain one-dimensional scattering profiles as a function of Q . The experimental configuration and detector geometry at SACLA covered the momentum transfer region $Q \in [0.094, 2.714] \text{ \AA}^{-1}$ with a momentum resolution of $\delta Q = 0.0267 \text{ \AA}^{-1}$.

For each time delay sampled, the scattering patterns were collected over multiple runs, with each run containing 1,200 detector images. Measurements at each delay were accumulated for a total of 6–10 minutes, corresponding to approximately 2×10^4 diffraction patterns, with each pattern being $2,400 \times 2,400$ pixels in size. The top and bottom 15th percentile of snapshots, ranked according to the total pulse energy, were subsequently discarded to remove shot-to-shot outliers in the X-ray

pulse intensity. Finally, the remaining scattering profiles were sorted into six uniformly spaced pulse-energy bins according to the total pulse energy, with each bin containing the averaged scattering signal of all patterns within the corresponding energy range (detailed in Chapter 3).

LCLS

A similar analysis workflow was employed for the LCLS measurements. However, unlike SACLA, the pressure cell was not rotated, and the measurements were acquired using continuous delay scanning over the range 0–3.6 ps. A total of 5×10^4 scattering patterns, with each pattern being $1,064 \times 1,030$ pixels in size, were collected per run over 20 runs. After dark subtraction, detector correction, and azimuthal averaging, the detector images were grouped according to the pump–probe delay using a delay-bin width of 0.1 ± 0.075 ps. The patterns within each delay bin were then binned into six uniform pulse-energy bins, after filtering out the outlier snapshots. The experimental configuration and detector geometry at LCLS covered the momentum transfer region $Q \in [0.088, 2.113] \text{ \AA}^{-1}$ with a momentum resolution of $\delta Q = 0.025 \text{ \AA}^{-1}$.

Diamond Subtraction and Differential Scattering

Mathematically, the normalized scattering signal was computed as:

$$\tilde{S}(Q, \tau, E_{tot}) = \frac{h\nu}{CE_{tot}} \sum_{j \in Q_{bin}} \frac{I(\mathbf{Q}_j, \tau, E_{tot})}{N_{Q_j} \langle |\mathcal{P}|_j^2 \rangle d\Omega_j}, \quad (2.13)$$

where N_{Q_j} is the number of detector pixels contained within each Q -bin and $C = r_e^2 \rho L_{eff} N_A / M$ with L_{eff} being the effective sample thickness. In turn, L_{eff} was evaluated as:

$$L_{eff} = L e^{-L/L_{att}}, \quad (2.14)$$

where L_{att} is the X-ray attenuation length. The attenuation lengths were calculated by dividing the mass density with the mass attenuation coefficient, μ/ρ , tabulated in [98]. At 30°C and 10 keV (SACLA), $\rho = 0.99782 \text{ g/cm}^3$ (50 bar) and 1.0022 g/cm^3 (150 bar) [99] with $\mu/\rho = 4.944 \text{ cm}^2/\text{g}$; at 22°C and 9.6 keV (LCLS), $\rho = 0.99782 \text{ g/cm}^3$ (2 bar) with $\mu/\rho = 5.6156 \text{ cm}^2/\text{g}$. This yielded attenuation lengths of 2018.24 μm (50 bar), 2027.1 μm (150 bar), and 1776.87 μm for SACLA and LCLS, respectively.

Due to the presence of diamond windows in the flow-cell, additional corrections were required to isolate the liquid water scattering signal. In both experiments, reference measurements of the empty cell (without water) were recorded under identical X-ray energy conditions. The water scattering signal was then obtained by:

$$\tilde{S}(Q, \tau, E_{tot})_{\text{water}} = \tilde{S}(Q, \tau, E_{tot})_{\text{filled}} - \gamma \tilde{S}(Q, \tau, E_{tot})_{\text{empty}} \quad (2.15)$$

where $\tilde{S}(Q, \tau, E_{tot})_{\text{filled}}$ corresponds to measurements acquired with the water-filled pressure cell and $\tilde{S}(Q, \tau, E_{tot})_{\text{empty}}$ represents the empty-cell measurements containing only the scattering contribution from the diamond windows. The transmission factor, γ , accounts for signal attenuation through the water sample, as the diamond-window scattering in the filled-cell is reduced relative to the empty-cell measurement. The transmission factors were calculated using the Beer-Lambert law [100], by evaluating the exponential term $e^{-((\mu/\rho) \cdot (\rho L))}$, to give $\gamma = 67.3\%$ at SACLA and 57.1% at LCLS.

At SACLA, empty-cell measurements were acquired at time-zero ($\tau = 0$), and they were used to remove the static contribution from the diamond windows under the assumption that the window response does not exhibit strong time-dependent features on picosecond timescales. At LCLS, empty-cell measurements were recorded at pump-probe delays up to 2 ps and confirmed that no measurable dynamics were present in the diamond windows within experimental uncertainty. To further ensure that the extracted signal reflected only the structure of liquid water, the static scattering signal at time-zero was compared between SACLA and LCLS measurements and benchmarked against reference scattering data [2, 3] (details in Chapter 3). Moreover, the differential scattering signal was evaluated for both the filled-cell and empty-cell measurements as:

$$\Delta\tilde{S}(Q, \tau, E_{tot}) = \tilde{S}(Q, \tau, E_{tot}) - \tilde{S}(Q, \tau_0, E_{tot}), \quad (2.16)$$

where only the momentum-transfer range satisfying $\Delta\tilde{S}(Q, \tau, E_{tot})_{\text{filled}} > \gamma\Delta\tilde{S}(Q, \tau, E_{tot})_{\text{empty}}$ was retained for data analysis. This yielded a minimum accessible momentum transfer of $0.094 \text{ \AA}^{-1}$ for SACLA and $0.088 \text{ \AA}^{-1}$ for LCLS.

Uncertainty Quantification

The uncertainty associated with normalization, pulse-energy binning, and azimuthal averaging was propagated according to:

$$\sigma(Q, \tau, E_{tot})_{IE} = \frac{I(Q, \tau)}{E_{tot}} \sqrt{\left(\frac{\sigma(Q, \tau)_I}{I(Q, \tau)}\right)^2 + \left(\frac{\sigma_{E_{tot}}}{E_{tot}}\right)^2}, \quad (2.17)$$

where $\sigma(Q, \tau)_I$ represents the standard deviation from azimuthal averaging and $\sigma_{E_{tot}}$ accounts for energy fluctuations within each pulse-energy bin; detector-level uncertainties and pulse-to-pulse fluctuations were assumed to be statistically independent.

The uncertainty associated with subtraction of the empty-cell scattering was propagated as:

$$\sigma(Q, \tau, E_{tot})_{\text{water}} = \sqrt{\sigma_{\text{filled}}^2(Q, \tau, E_{tot}) + \gamma^2 \sigma_{\text{empty}}^2(Q, \tau, E_{tot})}, \quad (2.18)$$

where σ_{filled} and σ_{empty} correspond to the uncertainties calculated with Equation (2.17) for the

filled-cell and empty-cell measurements, respectively.

Lastly, the uncertainty associated with the differential scattering signal was evaluated as:

$$\sigma(Q, \tau, E_{tot})_{\Delta\tilde{S}} = \sqrt{\sigma^2(Q, \tau, E_{tot})_{\text{water}} + \sigma^2(Q, \tau_0, E_{tot})_{\text{water}}}, \quad (2.19)$$

where the residual uncertainties at time-zero were assumed to be uncorrelated with measurements acquired at later delays [79, 80].

2.5.2 Liquid Jet Measurements

For the liquid jet measurements, scattering patterns were collected using two MPCCD detectors, simultaneously covering two momentum transfer regimes: small- and wide-angle X-ray scattering (SAXS and WAXS). The SAXS detector consisted of $2,400 \times 2,400$ pixels and was aligned normal to the incident X-ray beam during the measurements. The detector covered the momentum transfer region $Q \in [0.01225, 0.5115] \text{ \AA}^{-1}$ with a momentum resolution of $\delta Q = 0.0005 \text{ \AA}^{-1}$ for $0.01225 \leq Q \leq 0.3125 \text{ \AA}^{-1}$ and $\delta Q = 0.001 \text{ \AA}^{-1}$ for $Q > 0.3125 \text{ \AA}^{-1}$. Meanwhile, the WAXS detector consisted of $2,200 \times 600$ pixels and was rotated 35° relative to the incident beam. The detector covered the momentum transfer region $Q \in [1.696, 3.396] \text{ \AA}^{-1}$ with a momentum resolution of $\delta Q = 0.01 \text{ \AA}^{-1}$ for $1.696 \leq Q \leq 2.04 \text{ \AA}^{-1}$ and $\delta Q = 0.03 \text{ \AA}^{-1}$ for $Q > 2.04 \text{ \AA}^{-1}$. This detector geometry ensured adequate resolution of the prominent structural features observed in liquid water (discussed in Chapter 4).

The raw detector images were processed similarly to the flow-cell measurements, on a shot-to-shot basis. Each detector image was corrected by subtracting periodically acquired dark measurements, filtering detector pixels below the detector dark level, and masking to exclude detector gaps, damaged pixels, and saturated regions. The corrected detector intensities were subsequently normalized by the detector solid angle and X-ray polarization factor. For WAXS, an additional geometric correction that accounts for the detector rotation was applied. Following that, azimuthal averaging was performed to obtain one-dimensional scattering profiles as a function of momentum transfer.

Measurements at each time delay were collected over 25 runs, with each run containing 1,200 diffraction patterns. Since the liquid jet measurements were also performed at 10 keV, $\mu/\rho = 4.944 \text{ cm}^2/\text{g}$ [98]. Given that the mass density at 20°C and atmospheric pressure is $\rho = 0.99821 \text{ g/cm}^3$ [99], the attenuation length remained close to the pressure cell measurements with $L_{att} = 2019 \text{ }\mu\text{m}$.

Unlike the pressure cell measurements, however, no empty-cell subtraction was required since the liquid jet geometry does not contain scattering contributions from diamond windows. Furthermore, to allow a systematic analysis of the pulse-energy dependence in later chapters of the thesis (Chapter 4) while minimizing asymmetry between the pump and probe pulse energies, only shots satisfying $|(E_{pump} - E_{probe})/E_{tot}| < 0.2$ were retained for further analysis. This criterion ensured approximately equal pulse energies between the pump and probe branches while reducing shot-to-shot

fluctuations in the deposited pulse energy.

The filtered scattering profiles were then grouped into seven equally spaced pulse-energy bins according to the total pulse energy. Within each energy bin, the normalized scattering intensity was computed according to Equation (2.13). In addition, the differential scattering signal for liquid water was calculated directly from Equation (2.16).

Uncertainty Propagation

The uncertainty in the normalized scattering intensity arises primarily from statistical fluctuations in the azimuthally averaged detector signal, shot-to-shot variations in the pulse energy, and subtraction of the reference delay signal at τ_0 . The uncertainty propagation described by Equations (2.17) and (2.19) was similarly applied to the liquid jet measurements. However, unlike the flow-cell measurements, no additional uncertainty associated with empty-cell subtraction was present due to the absence of diamond-window scattering. The combined uncertainty was propagated throughout all ensuing analysis steps, including Fourier transformation and fitting procedures.

Chapter 3

Observation of Nanometer-Scale Structural Dynamics

This chapter presents the time-resolved X-ray scattering measurements of liquid water obtained using the high-pressure flow-cell geometry at SACLA and LCLS. The measurements at SACLA were performed at pressures of 50 bar and 150 bar and acquired at discrete time delays spanning 0–100 ps. Meanwhile, the measurements at LCLS used continuous delay scanning over the range 0–3.6 ps. The chapter outlines detector calibration and validation for each dataset along with the measured scattering response.

3.1 SACLA Pressure Cell Measurements

3.1.1 Experimental Overview

The initial time-resolved scattering measurements performed at SACLA were aimed at investigating the long-term response of liquid water following hard X-ray ionization, as well as the pressure dependence of any observed dynamics. The pump–probe delays sampled at each pressure condition are summarized in Table 3.1. The corresponding pulse-energy distributions for both pressure conditions, after time delay averaging, are shown in Figure 3.1. The average pump pulse energies were $\bar{E}_{pump} = 2.74 \mu\text{J}$ and $2.84 \mu\text{J}$ at 50 bar and 150 bar, respectively. The corresponding average total pulse energies were $\bar{E}_{total} = 5.85 \mu\text{J}$ and $6.27 \mu\text{J}$ for the two pressure conditions, giving an approximately even average pump–probe splitting ratio of 46.8% and 45.3%, respectively. The majority of snapshots (>95%) had total pulse energies below $8.5 \mu\text{J}$.

Pressure (bar)	Time Delay (ps)
50	0, 0.2, 0.6, 1, 1.5, 2, 3, 6, 10, 20, 100
150	0, 0.2, 0.6, 1, 3, 10, 100

Table 3.1: **Summary of time delays scanned at SACLA using the pressure-cell.** The experiments were performed at 30°C for both pressure conditions.

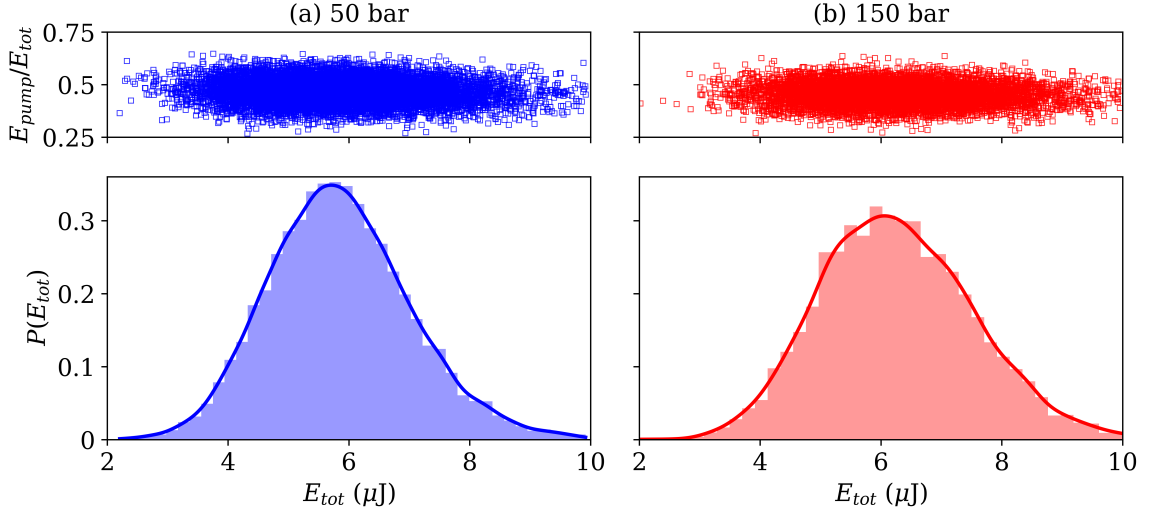


Figure 3.1: **Pulse-energy distribution for the SACLA pressure cell measurements.** The bottom row shows the probability distribution as a function of total pulse energy, while the top row shows the pump–probe energy splitting ratio. Results are averaged over all time delays at (a) 50 bar and (b) 150 bar.

3.1.2 Detector Calibration and Validation

As described in Chapter 2, the detector geometry encompassed the momentum transfer region of $Q \in [0.094, 2.714] \text{ \AA}^{-1}$. The detector geometry was calibrated using powder diffraction from silicon nanoparticles, yielding a sample-to-detector distance of 14.12 cm. Beyond geometric calibration, the reliability of the data reduction procedure was validated using the time-zero signal. In particular, the scattering response at $\tau = 0$ was plotted as a function of pulse energy and pressure and compared with reference data from the literature [2,3] to verify that no systematic dependence on experimental conditions was present. As shown in Figure 3.2(a), excellent agreement is observed across all pulse-energy and pressure conditions.

In addition, the diamond window scattering contribution was quantified by plotting the filled-cell signal at time-zero together with the scaled empty-cell response (scaled by the transmission factor γ), as shown in Figure 3.2(b). The diamond scattering is consistently at least a factor of two smaller than the filled-cell signal. This indicates that the diamond windows do not introduce a measurable

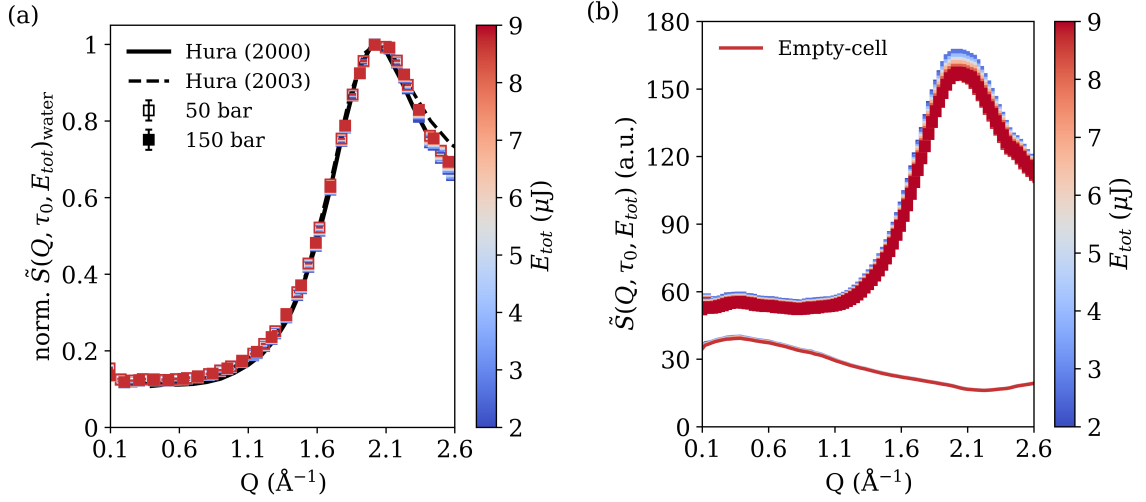


Figure 3.2: **Validation of the SACLA pressure cell measurements.** (a) Static time-zero response at 50 bar (unfilled squares) and 150 bar (filled squares) for all pulse-energy values. Results are overlaid on reference data from [2] at 27°C and [3] at 25°C. Each curve is normalized by its respective maximum and markers are plotted every third data point for visual comparison. Error bars in the present datasets were computed using Equation (2.18). The color bar indicates increasing pulse energy from 2 μJ to 9 μJ . (b) Time-zero scattering from the filled-cell at 50 bar and 150 bar (markers) compared with the scaled empty-cell (solid lines), where the latter is multiplied by the transmission factor $\gamma = 67.3\%$.

bias into the extracted water response.

3.1.3 Time-Resolved Scattering Response

The normalized differential scattering signal, $\Delta\tilde{S}(Q, \tau, E_{\text{tot}})$, obtained at 50 bar for a total pulse energy of $E_{\text{tot}} = 6 \mu\text{J}$ is illustrated in Figure 3.3. This pulse-energy bin was selected because it is close to the average total pulse energy across all time delays, $\bar{E}_{\text{tot}}$. Similar behavior was observed for all other pulse-energy bins, with the amplitude of the response increasing monotonically with the total pulse energy (details in Appendix A). The top panel presents the time-dependent scattering response as a contour map over the full momentum-transfer and pump-probe delay range investigated, while the bottom panel displays the individual line profiles. Positive values of $\Delta\tilde{S}(Q, \tau, E_{\text{tot}})$, highlighted in red, denote an enhancement in the scattering intensity relative to the reference liquid water structure, reflecting an increase in the spatial correlations on the respective length scale, whereas negative values correspond to a depletion of these spatial correlations.

Several distinct features are immediately apparent in the scattering response. First, a depletion in scattering intensity develops within the momentum-transfer range $1.6 < Q < 2.1 \text{ \AA}^{-1}$, accompanied by an adjacent enhancement between $2.1 < Q < 2.6 \text{ \AA}^{-1}$. This high- Q response appears promptly

following X-ray energy deposition and persists throughout the measured delay window. Previous X-ray scattering studies and molecular dynamics (MD) simulations have shown that the position of the principal water diffraction peak near $Q \approx 2 \text{ \AA}^{-1}$ is highly sensitive to temperature [2–4, 101, 102]. In particular, increasing temperature weakens the hydrogen-bond network of liquid water and shifts the diffraction peak toward higher momentum transfer, corresponding to shorter average intermolecular O–O distances. The observed negative and positive differential scattering signature here is therefore consistent with ultrafast heating of liquid water due to energy deposition by the incident hard X-ray pulse.

To quantify the temperature increase, the position of the diffraction peak was extracted from the time-resolved scattering signal, $\tilde{S}(Q, \tau, E_{tot} = 6 \text{ \mu J})_{\text{water}}$, and compared with established temperature-dependent calibrations [101], which demonstrate linear dependence up to the boiling point. At 0.2 ps, the water diffraction peak is located at $Q_{\text{peak}} = 2.019 \text{ \AA}^{-1}$, whereas at 0.6 ps, $Q_{\text{peak}} = 2.046 \text{ \AA}^{-1}$. By linearly interpolating the data in [101], the correlation between the sample temperature and the peak position was obtained as:

$$T = 462.8Q_{\text{peak}} - 625.5, \quad (3.1)$$

where T is the temperature in Kelvin and Q_{peak} is in inverse Angstroms. Using Equation (3.1), the maximum transient temperature increase induced by the pump pulse and measured by the delayed probe pulse is estimated to be $\Delta T \approx 12.5 \text{ K}$ at $6 \text{ \mu J}$. This suggests partial weakening of the hydrogen-bond network while maintaining the overall liquid structure [103]. Similar high- Q signatures on ultrafast timescales have also been reported in optical pump–probe scattering studies of liquid water [70, 104, 105]. A more detailed analysis of the temperature-dependent response and its dependence on the total pulse energy is presented in Chapter 4.

More notably, a feature emerges for $Q < 0.6 \text{ \AA}^{-1}$ on picosecond timescales. At early delays ($\tau = 0.6 \text{ ps}$), the low- Q response spans a broad momentum-transfer region and is marked with a local peak at $Q = 0.161 \text{ \AA}^{-1}$. While low- Q scattering signatures have previously been reported under extreme irradiation conditions associated with warm dense matter formation [106], where they were linked to strong ionization and non-equilibrium plasma dynamics, the present measurements are performed entirely within the liquid phase. The appearance of a distinct maximum in reciprocal space is therefore significant, as it points to the emergence of a preferred spatial correlation length within the irradiated liquid [107].

In X-ray scattering, the measured intensity arises from coherent interference between scattered waves, with the scattering amplitude given by a phase-weighted sum over atomic positions, Equation (2.5). For spatially uncorrelated density fluctuations, the phase factor averages out and no pronounced low- Q maximum is expected. The low- Q peak in $\Delta\tilde{S}(Q, \tau, E_{tot})$ hence implies the generation of correlated density perturbations over a given spatial length scale. Converting from momentum space to real space via the reciprocal-space relation, $L = 2\pi/Q$, yields a characteristic length scale of 3.9 nm .

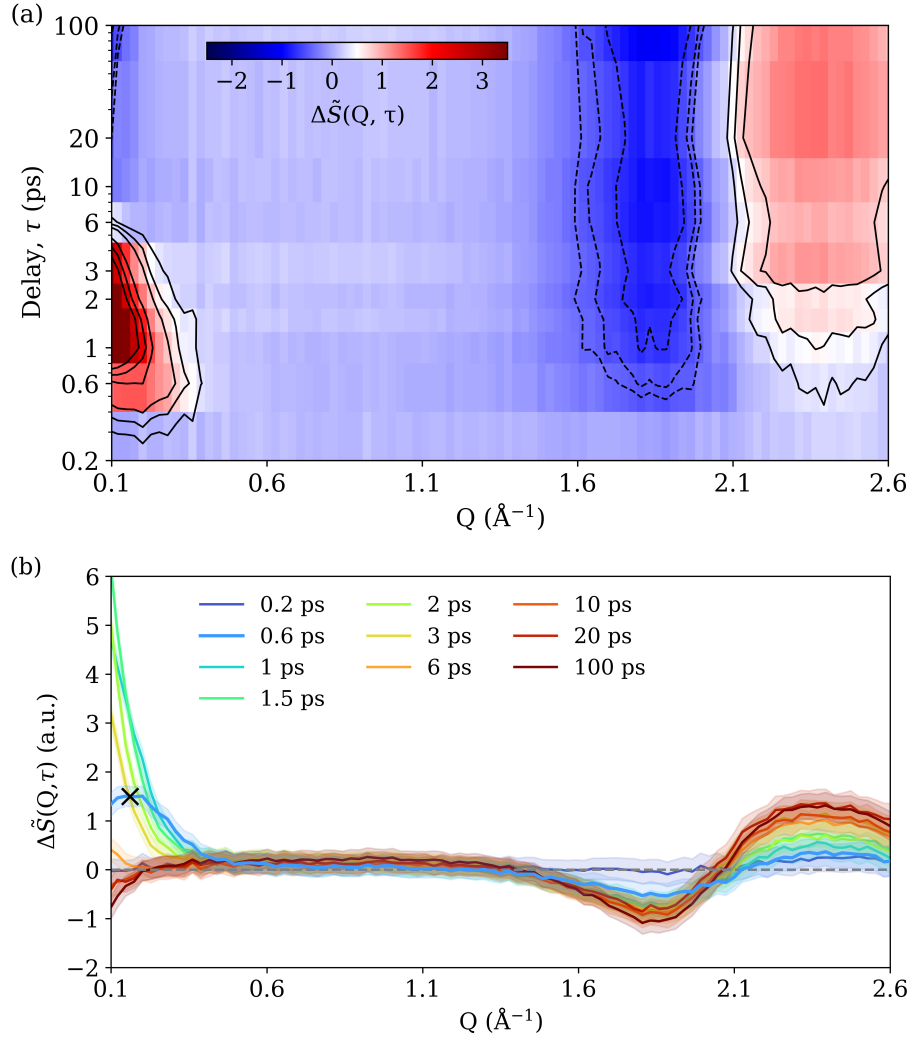


Figure 3.3: **Differential scattering signal of the SACLA pressure cell measurements at 50 bar.** (a) Contour map of the time-dependent scattering response for a pulse energy of $E_{tot} = 6 \mu\text{J}$. Dashed black lines denote negative contour levels ($-0.7, -0.5, -0.4$), while solid black lines indicate positive contour levels ($0.32, 0.55, 0.8, 1.5, 2, 2.5$). (b) Line plots of the time-dependent scattering response at $6 \mu\text{J}$. Shaded regions represent the propagated uncertainty evaluated using Equation (2.19). The marker highlights the local maximum at $\tau = 0.6$ ps.

The low- Q response grows in magnitude and shifts toward smaller momentum transfer with increasing time delay. For $\tau > 3$ ps, the response gradually decays until it is comparable to zero within experimental uncertainty for $\tau \geq 6$ ps. The appearance of this feature on nanometer length scales and picosecond timescales is qualitatively aligned with the formation of heterogeneous radiation track structures at the onset of the chemical stage of radiolysis (within 1 ps) [1, 44–47]. We return

to this interpretation in Chapter 5. Unlike previously reported valence-ionization dynamics in liquid water [35, 70, 108, 109], however, which evolve primarily on femtosecond timescales, the observed response persists well into the picosecond regime, indicating that hard X-ray core ionization produces significantly longer-lived structural perturbations in bulk liquid water.

3.1.4 Pressure Dependence

To investigate whether the low- Q response is sensitive to pressure-dependent thermodynamic parameters, additional measurements were performed at SACLA at an elevated pressure of 150 bar while maintaining identical temperature conditions and approximately equal pulse-energy distribution (Figure 3.1). Figure 3.4(a) shows the differential scattering response as a contour map for $E_{tot} = 6 \mu\text{J}$. As can be seen, the overall temporal evolution remains unchanged at elevated pressure: the high- Q negative–positive scattering signature associated with ultrafast heating is preserved, and the low- Q feature appears initially broad at 0.6 ps, increases in magnitude and shifts toward lower momentum transfer with increasing time delay, and eventually decays after $\tau = 3$ ps.

A more direct quantitative comparison between the two pressure conditions is presented in Figure 3.4(b), where the differential scattering profiles are overlaid at all available pump–probe delays (Table 3.1). Within experimental uncertainty, the scattering responses at 50 bar and 150 bar overlap across the low- Q and high- Q regions—the local maximum near $Q \approx 0.16 \text{ \AA}^{-1}$ exhibits very little shift in position with increasing pressure, and the amplitude and the shape of the thermal high- Q response is similar between the two measurements.

The absence of a substantial pressure dependence suggests that the observed dynamics are not strongly coupled to macroscopic thermodynamic changes over the investigated pressure range. More specifically, the persistence of the low- Q feature at elevated pressure indicates that the resulting structural perturbation is robust against moderate densification of the liquid. At 50 bar, the density of liquid water is $\rho = 997.83 \text{ kg/m}^3$, whereas at 150 bar, $\rho = 1002.2 \text{ kg/m}^3$ [99]. The increase in pressure thus corresponds to a marginal density increase of only $\sim 0.44\%$, which is in line with the negligible pressure dependence observed in the measured scattering response.

3.2 LCLS Pressure Cell Measurements

While the SACLA pressure-cell measurements revealed a reproducible low- Q structural response that evolves on picosecond timescales across both pressure conditions, the temporal sampling was limited by the discrete pump–probe delays accessible in the experimental configuration. Namely, the measurements probed delays at $\tau = 0, 0.2$, and 0.6 ps, followed by longer time delays up to 100 ps. However, the intermediate temporal windows between $0 < \tau < 0.2$ ps and $0.2 < \tau < 0.6$ ps were not resolved. In turn, this missing temporal region is of particular importance, as it bridges the transition between ionization events occurring on femtosecond timescales and the onset of the

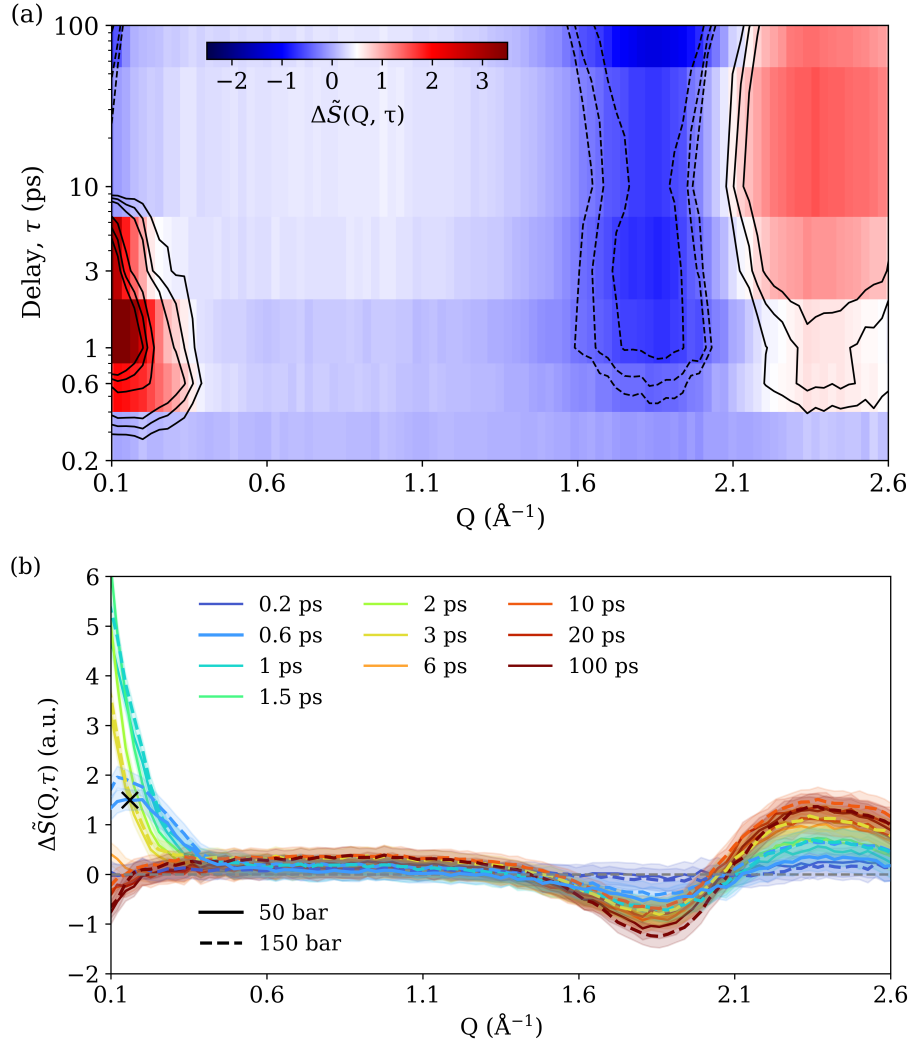


Figure 3.4: **Differential scattering signal of the SACLA pressure cell measurements at 150 bar.** (a) Contour map of the time-dependent scattering response for a pulse energy of $E_{tot} = 6 \text{ }\mu\text{J}$. Dashed black lines denote negative contour levels (-0.6 , -0.4 , -0.3), while solid black lines indicate positive contour levels (0.42 , 0.6 , 0.8 , 1.6 , 2.1 , 2.5). (b) Line plots of the time-dependent scattering response at $6 \text{ }\mu\text{J}$. Solid lines correspond to a pressure of 50 bar, whereas dashed lines illustrate the 150 bar dataset. Shaded regions represent the propagated uncertainty evaluated using Equation (2.19). The marker highlights the local maximum at $\tau = 0.6 \text{ ps}$.

chemical stage. For example, it is expected that the secondary electron ionization cascade concludes within 0.1 ps [110]. At the same time, electron hydration occurs within 0.26 ps [37, 73, 111, 112]. Both of these timescales lie within the unresolved temporal window. Accordingly, any scattering response evolving before 0.2 ps and between 0.2 and 0.6 ps may contain critical information about the

coupling between electron ionization and the formation of the observed nanometer-scale structural perturbations.

Overall, although the SACLA measurements establish the existence of a low- Q response consistent with picosecond structural evolution, they do not fully resolve the early-time dynamics of this feature. This limitation motivated complementary measurements at LCLS. Unlike SACLA, the LCLS SDO was capable of sampling continuous pump-probe delays, albeit over a reduced maximum delay range of 3.6 ps. This enabled improved access to the sub-picosecond regime. Since the SACLA measurements demonstrated negligible pressure dependence, the LCLS measurements were conducted slightly above ambient pressure, at 2 bar, to provide a continuous fresh water supply in the flow cell.

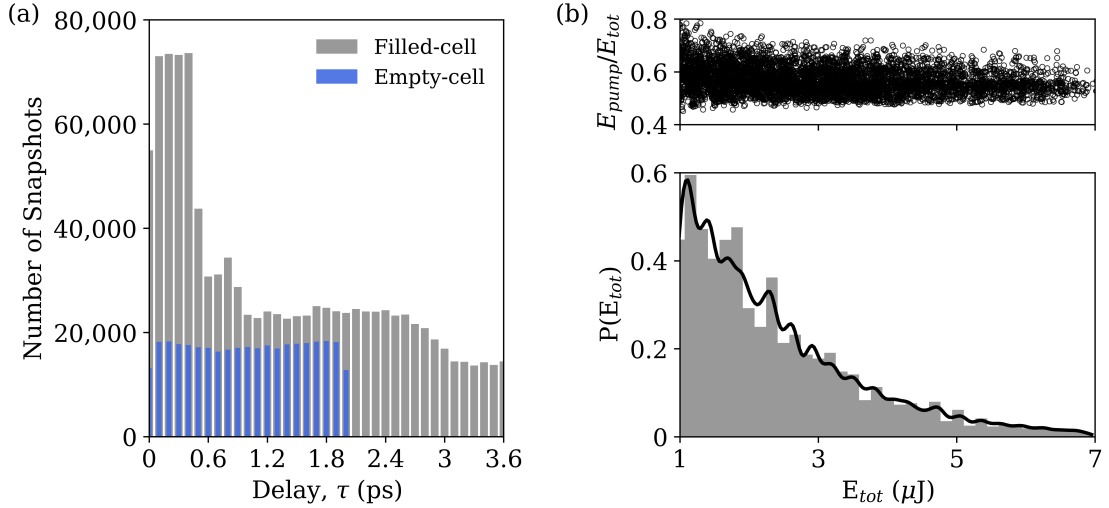


Figure 3.5: **Distribution of snapshots for the LCLS pressure cell measurements.** (a) Number of snapshots contained within each pump-probe delay bin after binning with a width of 0.1 ± 0.075 ps. Filled-cell measurements are shown in black and empty-cell measurements in blue. (b) Probability distribution of the total pulse energy (bottom panel) and pump-probe energy splitting ratio (top panel) for the filled-cell configuration, averaged over all sampled time delays up to 3.6 ps.

The distribution of snapshots after grouping into delay bins of width 0.1 ± 0.075 ps is shown in Figure 3.5(a) for both the filled-cell and empty-cell measurements. As detailed in Chapter 2, the empty-cell measurements were scanned only up to 2 ps, whereas the filled-cell measurements extended to the maximum accessible time delay of 3.6 ps. To improve temporal sampling within the unresolved time window identified in the SACLA measurements, a larger number of runs were acquired at early delays. At later delays, approximately 20,000 snapshots were collected per delay bin. The pulse-energy distribution is given in Figure 3.5(b). Unlike SACLA, where the SDO employed wavefront division [79], the LCLS SDO used amplitude splitting [80]. As a result, the total pulse-energy distribution was skewed toward lower energies. On average, the total pulse energy

measured at LCLS was $\bar{E}_{tot} = 2.35 \mu\text{J}$, with an average pump pulse energy of $\bar{E}_{pump} = 1.2 \mu\text{J}$. This corresponds to an average pump–probe splitting ratio of 51.1%.

3.2.1 Validation of Diamond Contributions

The detector geometry at LCLS encompassed the momentum transfer region $Q \in [0.088, 2.113] \text{ \AA}^{-1}$. The detector geometry was calibrated independently from the SACLA measurements using powder diffraction from a lanthanum hexaboride (LaB_6) standard [113] and refined using the pyFAI analysis package [114]. The distance between the detector surface and the X-ray sample interaction point was 20.72 cm.

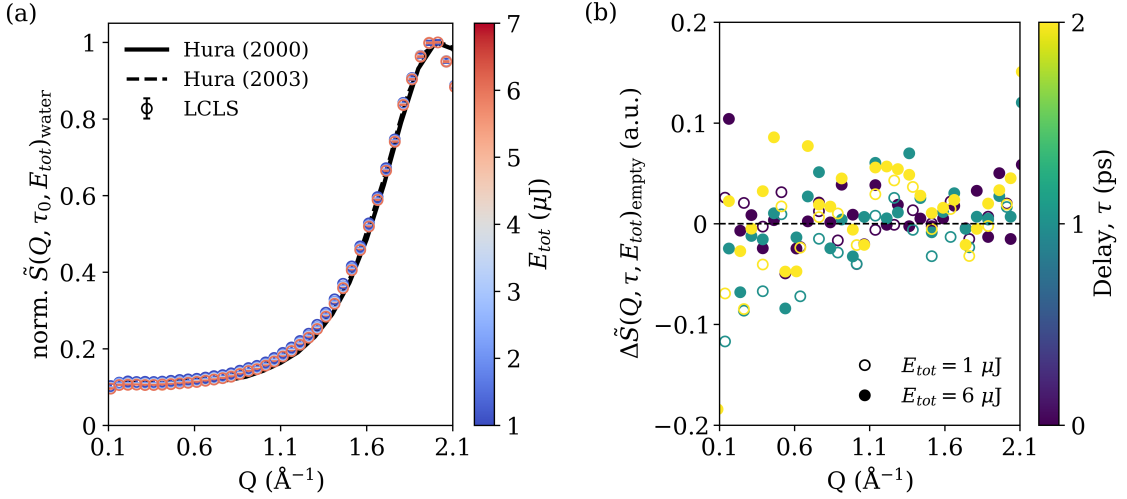


Figure 3.6: **Validation of the LCLS pressure cell measurements.** (a) Static time-zero response for all pulse-energy values. Results are overlaid on reference data from [2] at 27°C and [3] at 25°C. Each curve is normalized by its respective maximum and markers are plotted every second data point for visual comparison. Error bars in the present dataset were computed using Equation (2.18). The color bar indicates increasing pulse energy from 1 μJ to 7 μJ . (b) Differential scattering from the empty-cell at $\tau = 0, 1$, and 2 ps for a total pulse energy of 1 μJ (open circles) and 6 μJ (filled circles). Markers are plotted every third data point for visual comparison.

Figure 3.6(a) compares the normalized scattering signal, $\tilde{S}(Q, \tau, E_{tot})_{\text{water}}$, obtained using Equation (2.15) at a pump–probe delay of $\tau = 0$ (time zero), for all pulse energies with reference scattering curves for liquid water [2,3]. Overall, the measured scattering response agrees well with the literature values. A slight reduction in scattering is observed for $Q > 2.05 \text{ \AA}^{-1}$, which is attributed to masking near the detector edge. This does not affect the findings reported here, however, as the primary focus of the LCLS measurements is the early-time dynamics of the low- Q feature. Furthermore, since the linear correlation between the diffraction peak position and temperature is valid up to the boiling

point of water (Equation 3.1), corresponding to a maximum peak position of $Q \approx 2.16 \text{ \AA}^{-1}$, a reliable heating estimate could not be extracted from the LCLS dataset. Together with the validation shown in Figure 3.2(a), these results confirm the reliability of the detector calibration, azimuthal integration, and data-reduction workflow employed in both experiments.

The LCLS measurements also enabled a direct assessment of the time-dependent scattering dynamics from the diamond windows. As the LCLS experiment sampled the empty-cell response continuously up to 2 ps, this allowed computing the differential scattering response of the empty-cell in the same manner as the filled-cell configuration. Figure 3.6(b) compares the differential scattering signal evaluated from the empty-cell measurements at three representative pump-probe delays: time zero, 1 ps (intermediate stage), and 2 ps (late stage), for the lowest and highest available pulse-energy bins of $1 \text{ }\mu\text{J}$ and $6 \text{ }\mu\text{J}$, respectively. Across all delays and pulse energies, the differential scattering signal remains centered around zero and displays no pronounced time or energy dependence. This indicates that the diamond-window dynamics are negligible, if present at all, and suggests that they do not introduce measurable bias into the extracted liquid water scattering response.

3.2.2 Early-Time Structural Dynamics

The time-resolved differential scattering response measured at LCLS for a total pulse energy of $E_{tot} = 6 \text{ }\mu\text{J}$ is shown in Figure 3.7. The same pulse-energy bin is selected as in Section 3.1 to allow a direct comparison between the two datasets. In addition, to emphasize the low- Q structural dynamics identified in the SACLA measurements, the figures shown here focus on the momentum-transfer region below $Q = 0.5 \text{ \AA}^{-1}$. The full momentum-transfer range is provided in Appendix A. Figure 3.7(a) presents the differential scattering signal, $\Delta\tilde{S}(Q, \tau, E_{tot})$, obtained using Equation (2.16), as a contour map as a function of pump-probe delay and momentum transfer. Similar to the SACLA measurements (Figures 3.3 and 3.4), a broad positive low- Q feature emerges on sub-picosecond timescales. With increasing time delay, the feature narrows, shifts toward lower momentum transfer, and increases in magnitude. The response reaches its maximum amplitude near $\tau = 1.5 \text{ ps}$ before gradually decaying, within the accessible measurement window, for $\tau > 3 \text{ ps}$. This temporal evolution closely resembles the behavior observed at SACLA, indicating that the dynamics are reproducible across both XFEL facilities and experimental configurations.

The corresponding differential scattering line profiles are shown in Figure 3.7(b). Closely inspecting the profiles reveals the emergence of a statistically significant low- Q signal at $\tau = 0.4 \text{ ps}$. This time delay was not probed in the SACLA measurements and highlights the improved sub-picosecond temporal resolution achieved at LCLS. For $\tau < 0.4 \text{ ps}$, no statistically significant signal was observed within experimental uncertainty. Furthermore, the line profiles demonstrate that the low- Q feature develops progressively between $0.4 \leq \tau < 1.5 \text{ ps}$ rather than appearing abruptly at a single time delay. Within this temporal region, also, the scattering profiles exhibit distinct maxima

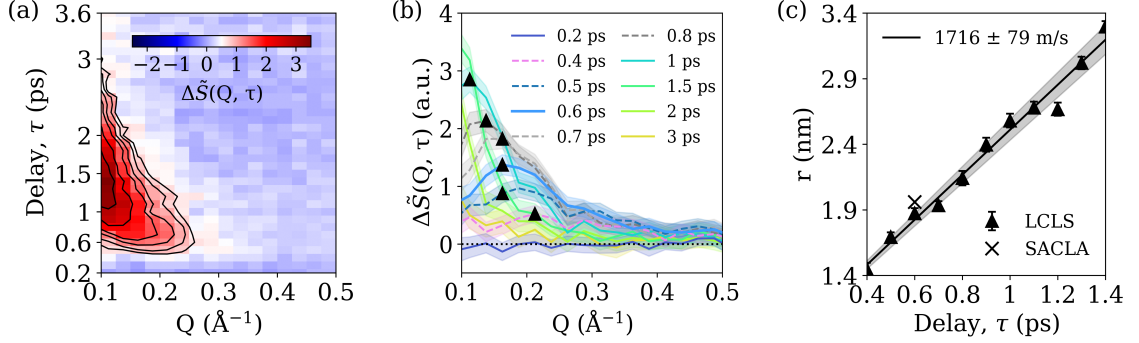


Figure 3.7: **Differential scattering signal and dynamics at LCLS.** (a) Contour map of the time-dependent scattering response for a pulse energy of $E_{tot} = 6 \mu\text{J}$. Black lines denote positive contour levels (0.7, 0.9, 1.2, 1.5, 2.2, 3, 4). (b) Line profiles of the time-dependent scattering response at $6 \mu\text{J}$. Shaded regions represent the propagated uncertainty evaluated using Equation (2.19). Markers indicate the local maxima at each time delay, computed using Equation (3.2). (c) Temporal evolution of the radial length scale from LCLS (triangles) and SACLA (cross). Error bars are calculated using Equation (3.3). The solid line shows a linear fit to the LCLS data with a slope of $1,716 \pm 79 \text{ m/s}$. The grey shaded region highlights the uncertainty of the fit.

for $Q < 0.3 \text{ \AA}^{-1}$. In contrast to the SACLA measurements, where only a single well-defined low- Q maximum at 0.6 ps was identified and no systematic tracking of peak evolution was required, here, the improved temporal sampling enabled observation of the peak evolution across multiple pump-probe time delays. As such, to ensure a robust determination of the peak position, a local centroid-based estimator was employed for all delays where a peak was clearly visible (between 0.4 ps and 1.5 ps).

For each delay, an initial peak location was first identified from the discrete maximum of $\Delta\tilde{S}(Q, \tau, E_{tot})$ within $Q < 0.5 \text{ \AA}^{-1}$. The peak position was then refined using an intensity-weighted centroid (first-moment) estimator [115]:

$$Q_{peak}(\tau, E_{tot}) = \frac{\sum_{i \in \mathcal{W}} Q_i \Delta\tilde{S}(Q_i, \tau, E_{tot})}{\sum_{i \in \mathcal{W}} \Delta\tilde{S}(Q_i, \tau, E_{tot})}, \quad (3.2)$$

where $\mathcal{W} = [i_{max} - 3, i_{max} + 3]$ denotes a symmetric window around the discrete maximum. This approach assumes that the true peak of an experimental signal can be locally approximated by a symmetric distribution where the center of mass provides a more stable estimator than the index of maximum value alone. Such an approach has been shown to be robust against experimental noise in X-ray diffraction measurements [116]. The uncertainty in the extracted peak position was

propagated according to [117]:

$$\sigma(\tau, E_{tot})_{Q_{peak}} = \sqrt{\frac{\sum_{i \in \mathcal{W}} (Q_i - Q_{peak})^2 \sigma^2(Q_i, \tau, E_{tot})_{\Delta \tilde{S}}}{\left(\sum_{i \in \mathcal{W}} \Delta \tilde{S}(Q_i, \tau, E_{tot})\right)^2}}, \quad (3.3)$$

where $\sigma^2(Q_i, \tau, E_{tot})_{\Delta \tilde{S}}$ is the propagated uncertainty calculated with Equation (2.19) at a given Q -value, Q_i , in the vicinity of the peak. To this end, of particular importance is the peak position at $\tau = 0.6$ ps, as it provides a quantitative comparison with the SACLA dataset. At this delay, the peak is located at $Q = 0.168 \text{ \AA}^{-1}$, evaluated from Equation (3.2). This corresponds to a characteristic real-space length scale of 3.74 nm ($L = 2\pi/Q$), which is in close agreement with the value of 3.9 nm obtained from the SACLA measurements (Figure 3.3(b)) and further supports the consistency between the two datasets.

To track the real-space evolution of the low- Q feature, the extracted peak position in momentum space is mapped onto a physical length scale. As opposed to a full Fourier-space inversion, where a periodic density modulation would correspond to a characteristic real-space length scale of $L = 2\pi/Q$, here we assume that the present signal arises from localized, approximately spherical density perturbations. In this case, the peak position can be associated with an effective radial length scale through the momentum-to-real space conversion of $r(\tau) = \pi/Q_{peak}(\tau)$. Relative to the characteristic length scale obtained from full Fourier-space inversion, this is equivalent to mapping the scattering peak with a radius rather than a full spatial period. Inherently, this assumption rests on the structural perturbation being azimuthally symmetric, an assumption that is revisited and validated in Chapter 4.

The evolution of the radial length scale is given in Figure 3.7(c) for $0.4 \leq \tau < 1.5$ ps at 6 μJ . As can be seen, the temporal evolution is approximately linear within experimental uncertainty. To better quantify this behavior, the radii were fitted using a weighted least-squares regression, $r(\tau) = a\tau + b$, with the propagated uncertainty from Equation (3.3) used as the weighting factor. From the fitted slope parameter, an effective propagation velocity of $1,716 \pm 79 \text{ m/s}$ was obtained. The fitted linear profile captures the SACLA data point from the 50 bar measurements (overlaid for comparison) within the uncertainty band, suggesting that the structural dynamics observed in both experiments originate from the same underlying mechanism and manifest as a uniformly expanding disturbance.

3.3 Summary

In summary, this chapter presented the time-resolved X-ray scattering measurements of liquid water enclosed in a high-pressure flow-cell. The experiments were performed at SACLA and LCLS and were designed to probe the structural response of liquid water over picosecond timescales following

hard X-ray ionization, while also assessing the influence of pressure on the observed dynamics.

At SACLA, the measurements were performed at 50 bar and 150 bar using discrete pump–probe delays spanning 0–100 ps and the momentum transfer region of $Q \in [0.094, 2.714] \text{ \AA}^{-1}$. The resulting normalized differential scattering intensity consisted of two primary components:

1. a high- Q negative–positive feature associated with ultrafast heating, and
2. a low- Q positive feature that emerges on sub-picosecond timescales.

The latter initially appears as a broad enhancement that increases in magnitude and shifts toward lower Q -values with increasing time delay before decaying after $\tau \approx 3$ ps. The features were observed consistently across pressure conditions, indicating that the dynamics are insensitive to moderate changes in macroscopic thermodynamic properties.

Additional measurements at LCLS, encompassing $Q \in [0.088, 2.113] \text{ \AA}^{-1}$, complemented the experimental campaign at SACLA by providing continuous time delay sampling and finer temporal resolution in the sub-picosecond regime, i.e., for $\tau < 1$ ps. The LCLS data confirmed the development of a similar low- Q feature at 0.4 ps, followed by gradual amplification between 0.4 and 1.5 ps. In addition, the temporal evolution observed at LCLS qualitatively and quantitatively reproduced the key characteristics observed at SACLA, including the appearance of a maximum in the normalized scattering intensity at 0.6 ps corresponding to a ~ 4 nm spatial correlation. This established the consistency of the results across distinct experimental configurations and detector geometries.

A central result from the analysis of the LCLS dataset was the evolution of the peak position in reciprocal space. By mapping this evolution into an effective radial length scale, the data revealed a linear increase with an effective propagation velocity on the order of $\sim 1,700$ m/s.

Despite the robustness of the aforementioned results, several important questions remain unresolved. First, although the low- Q feature was observed to decay for $\tau > 3$ ps, the long-time evolution of this decay could not be fully characterized within the accessible measurement window. In particular, it remained unclear whether the low- Q feature dissipated entirely or redistributed toward lower momentum transfer over the probed delays. This uncertainty was primarily driven by the second limitation, which originated from the detector geometry itself. More specifically, the detector geometry restricted the reliably accessible momentum-transfer region to $Q \geq 0.1 \text{ \AA}^{-1}$. In turn, the region below $0.1 \text{ \AA}^{-1}$ remained inaccessible, preventing direct observation of the nanometer-scale spatial correlations at later time delays. Taken altogether, these limitations motivated further investigation utilizing a different detector geometry. This forms the basis for the subsequent chapter, which presents time-resolved measurements in a liquid jet geometry.

3.4 Statement of Contributions

The work presented in this chapter was conducted as part of collaborative experimental campaigns at the SACLA and LCLS XFEL facilities.

My contributions included participating in both experimental campaigns, performing online data analysis during the beamtime, independently developing the offline data reduction and analysis tools used throughout this chapter, analyzing and interpreting the experimental results, preparing all figures, and writing this chapter. Although the overall experimental design was developed collaboratively, I contributed to planning the measurements by advising on the selection of pump-probe time delays to be scanned. The high-pressure flow cell was developed by Priyanka Muhunthan and Guillaume Vignat.

For the SACLA experiment, operation of the high-pressure sample environment was carried out by Haoyuan Li. X-ray beam delivery and operation were supported by Sanghoon Song and Yanwen Sun, while beamline operation and technical support were provided by Taito Osaka and Ichiro Inoue. Scientific direction and oversight of the project were provided by Diling Zhu and Matthias Ihme.

For the LCLS experiment, the high-pressure sample environment was operated by Priyanka Muhunthan, Taekeun Yoon, Guillaume Vignat, and Haoyuan Li. X-ray beam operation was supported by Yanwen Sun, Sanghoon Song, and Takahiro Sato. Scientific direction was provided by Diling Zhu and Matthias Ihme.

Chapter 4

Intrinsic Structural Dynamics from Jet Measurements

The previous chapter unraveled the structural dynamics of liquid water radiolysis initiated by hard X-ray ionization. From these measurements, a feature was identified between $0.1 < Q < 0.3 \text{ \AA}^{-1}$ that evolves on picosecond timescales and nanometer length scales. Due to the experimental geometry, however, access to momentum transfers below $\sim 0.1 \text{ \AA}^{-1}$ could not be achieved, leaving the dynamics not fully resolved, particularly for long time delays ($10 < \tau < 100 \text{ ps}$). This was overcome through a complementary experimental campaign at SACLA utilizing a liquid jet geometry. In addition, to obtain a wide momentum-transfer range, standalone SAXS and WAXS detectors were employed. The results of this experimental campaign are presented herein. The experimental setup and geometry are illustrated in Figure 4.1.

4.1 Experimental Overview

Similar to Section 3.1, the experiments were conducted at beamline 3 (BL3) [90] of SACLA with an X-ray energy of 10 keV. To investigate the influence of temperature on the structural dynamics, measurements were performed for a liquid water jet at ambient temperature (20°C) and heated jet at 80°C, both delivered at atmospheric pressure. The pump–probe delays sampled at each temperature condition are summarized in Table 4.1.

The corresponding pulse-energy distributions for the pump and probe pulses are shown in Figure 4.2 for the 20°C measurements, where the data are grouped according to the time delay and plotted cumulatively over all sampled delays. The pump–probe splitting ratio is also displayed for each snapshot. The pulse-energy distribution for the 80°C measurements is given in Section 4.8. In order to enable a systematic analysis of the pulse-energy dependence in this chapter, and as discussed in

Chapter 2, the snapshots were filtered at each time delay based on the relative pulse energies of the pump and probe beams—only shots satisfying $E_{pump}/E_{tot} = 0.5 \pm 0.1$ were retained, as indicated by the shaded region in Figure 4.2(a). This criterion ensured nearly symmetric probing conditions while reducing shot-to-shot variability.

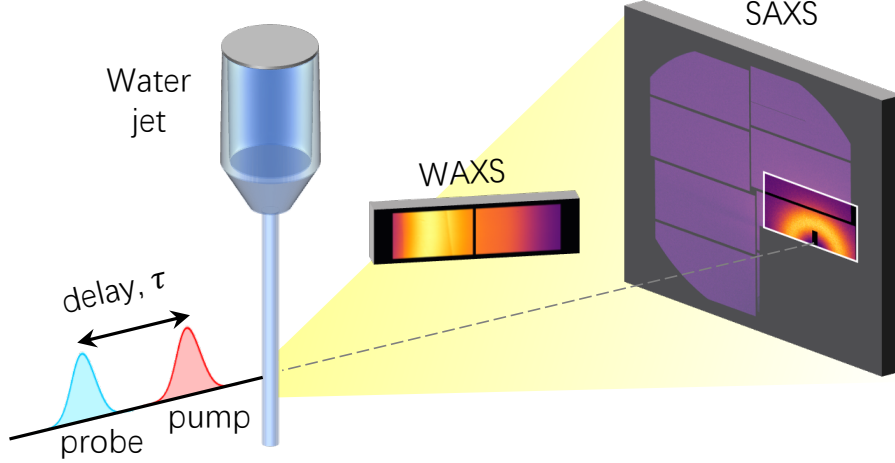


Figure 4.1: **Time-resolved hard X-ray scattering setup for the jet measurements at SACLA.** An XFEL pulse with a photon energy of 10 keV was used, and the scattered photons were collected by two MPCCD detectors covering the small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) regions. The SAXS detector was placed directly along the X-ray propagation axis, whereas the WAXS detector was rotated 35° off-axis. The water jet was enclosed within a helium chamber (not shown for clarity).

Temperature ($^\circ\text{C}$)	Time Delay (ps)
20	0.1, 0.8, 2, 6, 10, 15, 25, 40, 50, 75, 100
80	0, 0.8, 2, 6, 9, 10, 15, 18, 20, 22, 25, 30, 35, 40, 45, 50, 75, 100

Table 4.1: **Summary of time delays scanned at SACLA using the liquid jet.** The experiments were performed at atmospheric pressure for both temperature conditions.

The filtering procedure yielded $\sim 10,000$ snapshots at each time delay, which were subsequently grouped into seven equally spaced energy bins with $1 \mu\text{J}$ intervals. The lowest energy bin was centered around $E_{tot} = 2 \mu\text{J}$, whereas the highest was around $E_{tot} = 8 \mu\text{J}$. Averaged across all time delays, the mean pump pulse energies were $\bar{E}_{pump} = 2.22 \mu\text{J}$ and $2.73 \mu\text{J}$ at 20°C and 80°C , respectively. The corresponding mean total pulse energies were $\bar{E}_{total} = 4.47 \mu\text{J}$ and $5.62 \mu\text{J}$ for the two temperature conditions, giving approximately even average pump–probe splitting ratios of 49.7% and 48.6%, respectively. For both the pump and probe distributions, more than $>90\%$ of the snapshots had pulse energies below $5 \mu\text{J}$.

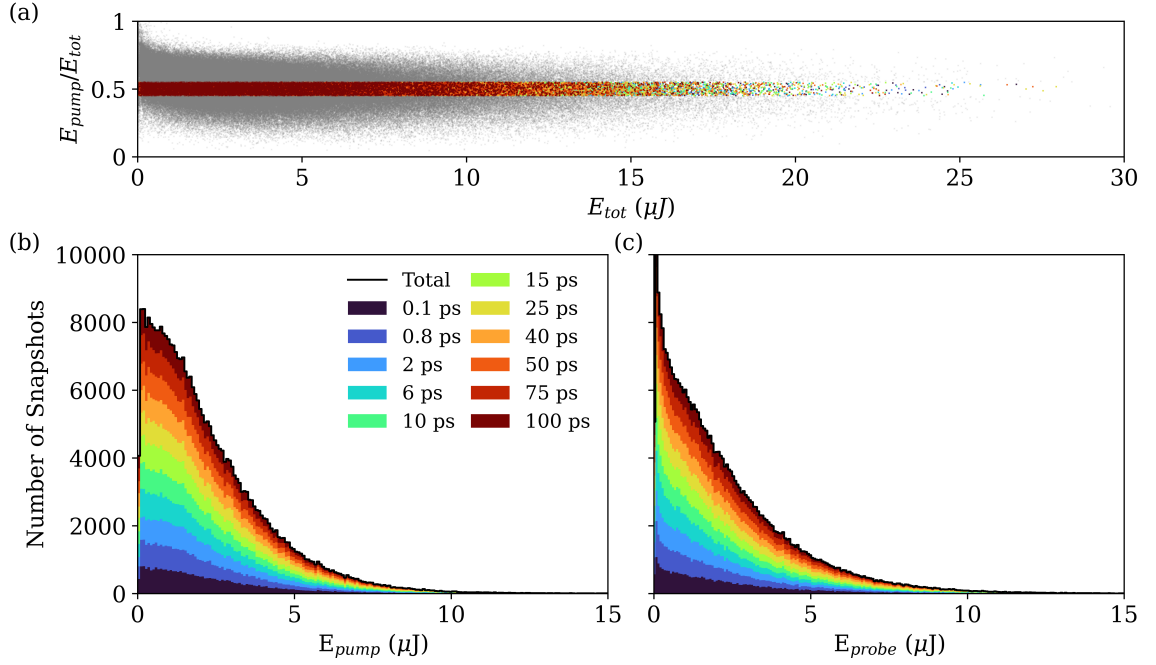


Figure 4.2: **Pulse-energy distribution for the SACLA jet measurements at 20°C.** (a) Pump-probe energy splitting ratio as a function of the total pulse energy. Grey markers denote the full dataset, whereas the colored markers highlight the filtered region around $E_{pump}/E_{tot} = 0.5$ retained for further analysis. Pulse-energy distributions at each time delay for the (b) pump and (c) probe pulses. Each successive time delay is cumulatively overlaid on earlier delays for visual comparison. The black curve outlines the total number of snapshots accumulated over all sampled delays.

4.2 Detector Masking, Calibration, and Validation

In order to maximize the accessible momentum-transfer range in the jet measurements, a refined detector masking procedure was also implemented. For the SAXS detector, in addition to masking detector edges and gaps, regions in the immediate vicinity of the beam stop were excluded from the analysis due to spurious saturation. For the WAXS detector, which was positioned off-axis relative to the X-ray interaction region (details in Section 2.5.2), a geometric shadow was present over a localized region of the detector surface. This region was likewise masked to ensure accurate resolution of the water diffraction peak and to enable reliable estimation of the heating response observed in Section 3.1. The resulting detector masks are shown in Figure 4.3 for both detectors.

Beyond masking corrections, each MPCCD detector was calibrated independently. Since the SAXS detector was positioned directly along the X-ray propagation axis, only minimal calibration was required beyond determination of the sample-to-detector distance. In turn, this was measured during the experiment to be 90 cm. The WAXS detector, on the other hand, required additional

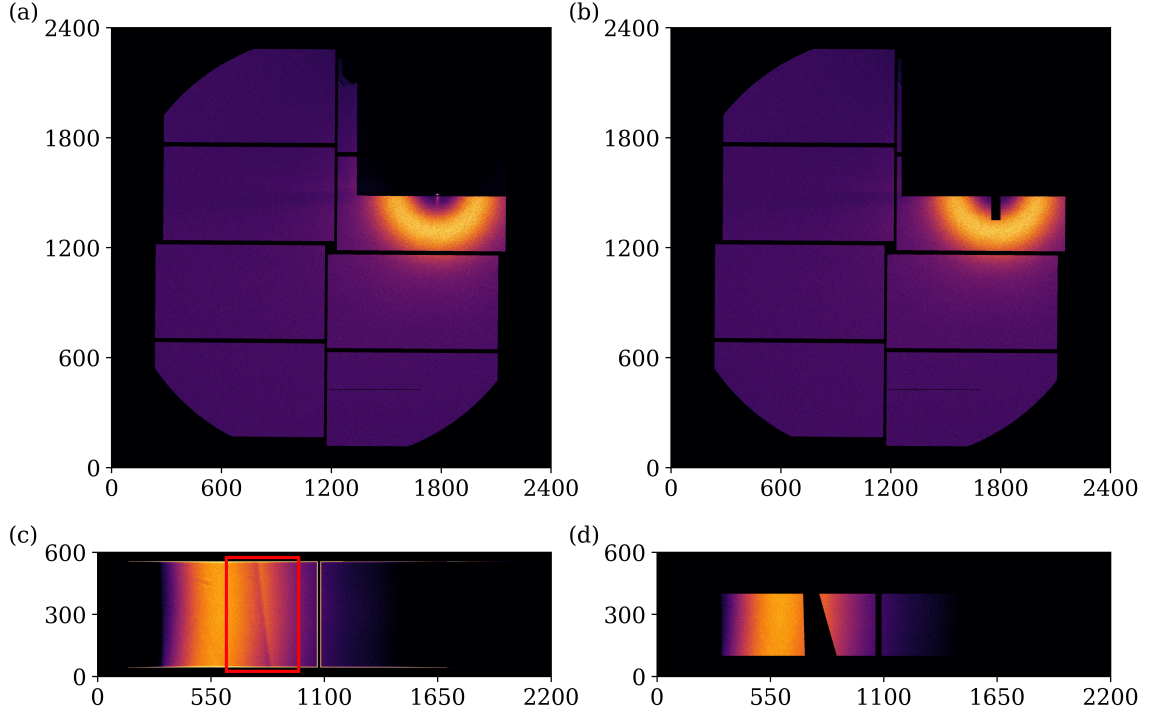


Figure 4.3: **Detector masks for the SACLA jet measurements.** Averaged SAXS detector image at $\tau = 2$ ps shown (a) before and (b) after masking. Averaged WAXS detector image at $\tau = 0.1$ ps shown (c) before and (d) after masking. The red rectangle highlights the shadow arising from the experimental geometry and off-axis detector rotation. A triangular mask was applied to exclude this region from the analysis.

calibration due to its off-axis placement. To this end, the detector geometry was optimized using pyFAI [114] with reference to a LaB₆ calibration standard [113] as follows. During the experiment, the scattering pattern from LaB₆ was measured. The observed diffraction-ring positions were then matched to the known reference ring positions [113] through the pyFAI optimization procedure [114]. This calibration yielded the detector solid angle, sample-to-detector distance, and momentum-transfer map (Q -map) required for azimuthal integration of the WAXS data. The sample-to-detector distance was determined to be 23 cm. Overall, the SAXS detector covered the momentum transfer region of $Q \in [0.01225, 0.5115] \text{ \AA}^{-1}$, whereas the WAXS detector encompassed $Q \in [1.696, 3.396] \text{ \AA}^{-1}$.

As an additional validation step, the near-time-zero response was examined for both the SAXS and WAXS detectors. Note that a true $\tau = 0$ measurement was not sampled in the jet experiment at 20°C. However, the LCLS measurements presented in Chapter 3 established the lack of statistically significant low- Q dynamics prior to $\tau = 0.4$ ps. As a result, the scattering response at $\tau = 0.1$ ps was adopted as the static reference throughout this section. This choice is validated in Figure 4.4,

which shows the normalized scattering signal from the SAXS detector at $\tau = 0.1$ ps and compares the WAXS signal against established reference datasets. For the latter, the most recent liquid water reference scattering data measured at 22°C [4] is overlaid to provide a stringent benchmark. Figure 4.4(a) demonstrates that the SAXS signal at $\tau = 0.1$ ps exhibits no systematic dependence on pulse energy, indicating the absence of detectable structural dynamics at this pump-probe delay. Moreover, Figure 4.4(b) confirms this behavior for the WAXS detector and further verifies the detector calibration and correction procedures. Together, these results justify the use of $\tau = 0.1$ ps as the static scattering reference.

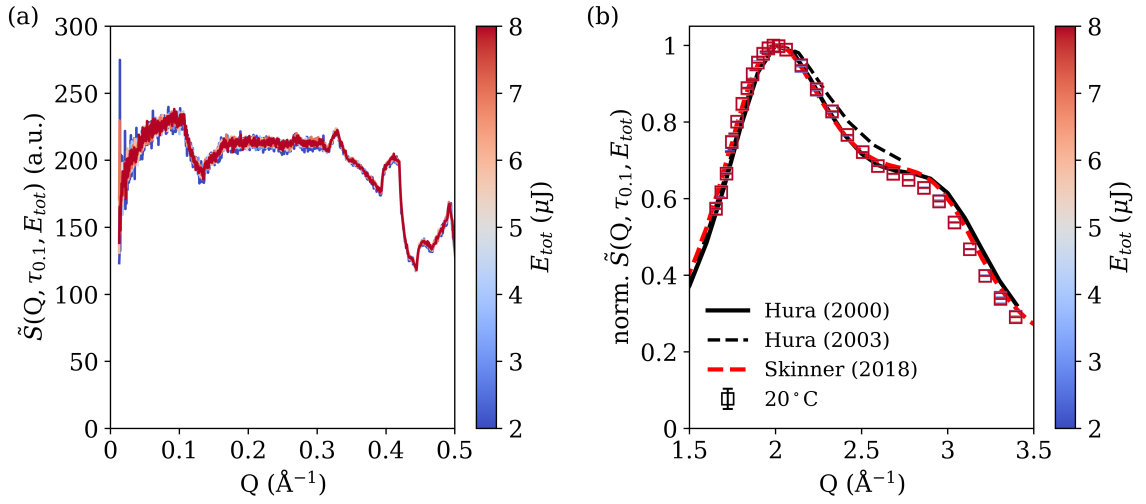


Figure 4.4: **Validation of the SACLA jet measurements at 20°C.** (a) SAXS profiles at $\tau = 0.1$ ps obtained after dark subtraction using Equation (2.13) for all pulse-energy bins. The color bar indicates increasing pulse energy from 2 μJ to 8 μJ . (b) WAXS signal for all pulse-energy values. Results are overlaid on reference data from [2] at 27°C, [3] at 25°C, and [4] at 22°C (Advanced Photon Source dataset). Each curve is normalized by its respective maximum. Markers are plotted every third data point for $Q \leq 2.04 \text{ \AA}^{-1}$ and at every data point otherwise to facilitate visual comparison. Error bars in the present dataset were computed using Equation (2.17).

4.3 Evolution of the Two-Dimensional Small-Angle X-ray Scattering Signal

Compared to the pressure-cell measurements presented in Chapter 3, the detector geometry in the jet measurements provided substantially improved access to the low- Q region, with the minimum accessible momentum transfer reduced by roughly an order of magnitude ($Q_{min,jet} \approx 0.1 Q_{min,cell}$). Hence, prior to performing azimuthal integration, the corrected two-dimensional SAXS detector images were inspected directly after masking, calibration, and pulse-energy filtering. Representative

detector images are illustrated in Figure 4.5.

As can be seen in Figure 4.5(a), at the lower pulse energy of $3 \mu\text{J}$, a faint, broad ring-like feature begins to emerge on the detector by 0.8 ps. At 2 ps, this feature is discernible and spans the low- Q region ($Q < 0.2 \text{ \AA}^{-1}$). With increasing time delay, the signal increases in intensity and progressively shifts toward the beam stop (dark notch at $Q_x = 0 \text{ \AA}^{-1}$), i.e., toward lower momentum transfer values. Unlike the pressure-cell measurements, however, the signal does not decay for $\tau > 3$ ps. Instead, the feature remains visible up to at least 10 ps.

The evolution of the low- Q feature is better elucidated at higher pulse energy ($6 \mu\text{J}$), as shown in Figure 4.5(b). At this higher pulse energy, the persistence of the low- Q response becomes more evident. Rather than decaying by 10 ps, the signal develops into multiple ring-like features that exhibit similar dynamics. In particular, the additional features initially appear broad, then sharpen, shift toward lower Q -values, and increase in magnitude with time delay. The persistence and multiplicity of these features indicate that the low- Q response is significantly longer-lived than previously inferred from the pressure-cell measurements. Even at $\tau = 75$ ps, a pronounced signal remains clearly visible, although it weakens substantially by 100 ps. This motivates quantitative analysis of the azimuthal symmetry and radial evolution presented in the following section.

4.3.1 Symmetry of the Structural Dynamics

The investigation of azimuthal symmetry provides important information about the physical origin of the observed low- Q dynamics. This is because photoelectron emission induced by linearly polarized X-rays, such as those employed at SACLA [90] and LCLS [91], is intrinsically anisotropic [118]. As such, it follows an angular distribution governed by the polarization axis [119]. Consequently, if the observed ring-like scattering features in Figure 4.5 originated primarily from directional electron dynamics, then a pronounced azimuthal dependence would be expected. Additionally, polarization-dependent scattering effects can introduce azimuthal intensity variations, although these effects are typically more significant in the wide-angle scattering regime [120]. Conversely, an isotropic scattering response in the SAXS regime would suggest that the dynamics are driven by radially symmetric structural perturbations in the liquid.

To investigate this, the azimuthal dependence of the low- Q rings was examined at three representative time delays ($\tau = 2, 10$, and 40 ps), as illustrated in Figure 4.6. The selected pump-probe delays were chosen such that they span qualitatively distinct stages of the dynamics: (a) $\tau = 2$ ps, where a single dominant ring-like feature is present; (b) $\tau = 10$ ps, where two rings are clearly resolved; and (c) $\tau = 40$ ps, where three ring-like features are visible simultaneously. For each feature, a circular contour centered on the calibrated beam position was overlaid on the two-dimensional detector images. The circular contour passed through the midpoint of the corresponding ring, determined by locating the maxima of the radially integrated intensity profile. The two-dimensional scattering intensity was then azimuthally sampled along each contour over the full angular range

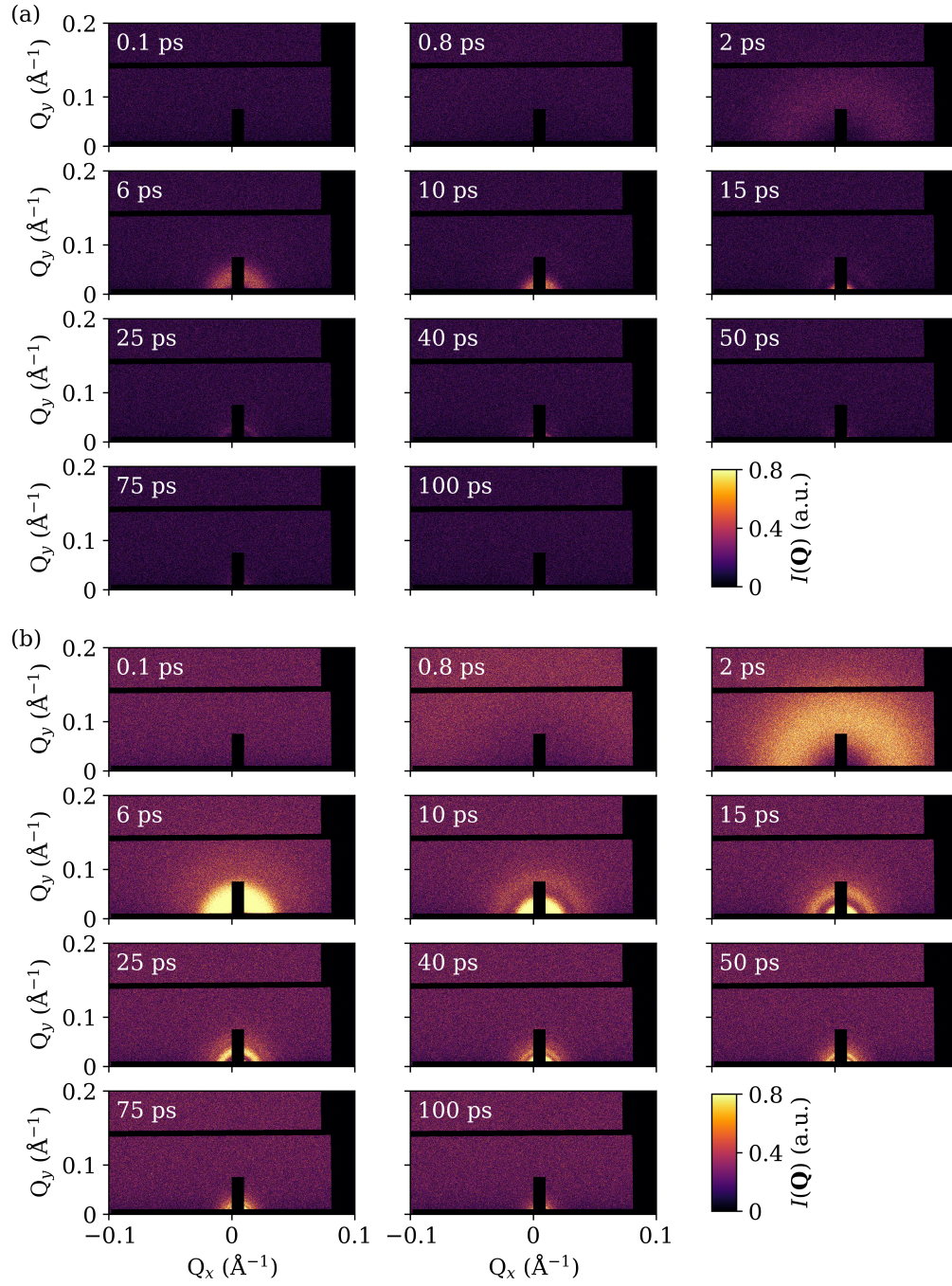


Figure 4.5: **Two-dimensional SAXS detector images for the SACLA jet measurements at 20°C.** Results shown are zoomed in on the low- Q region and are displayed for all sampled time delays measured at total pulse energies of (a) 3 μJ and (b) 6 μJ .

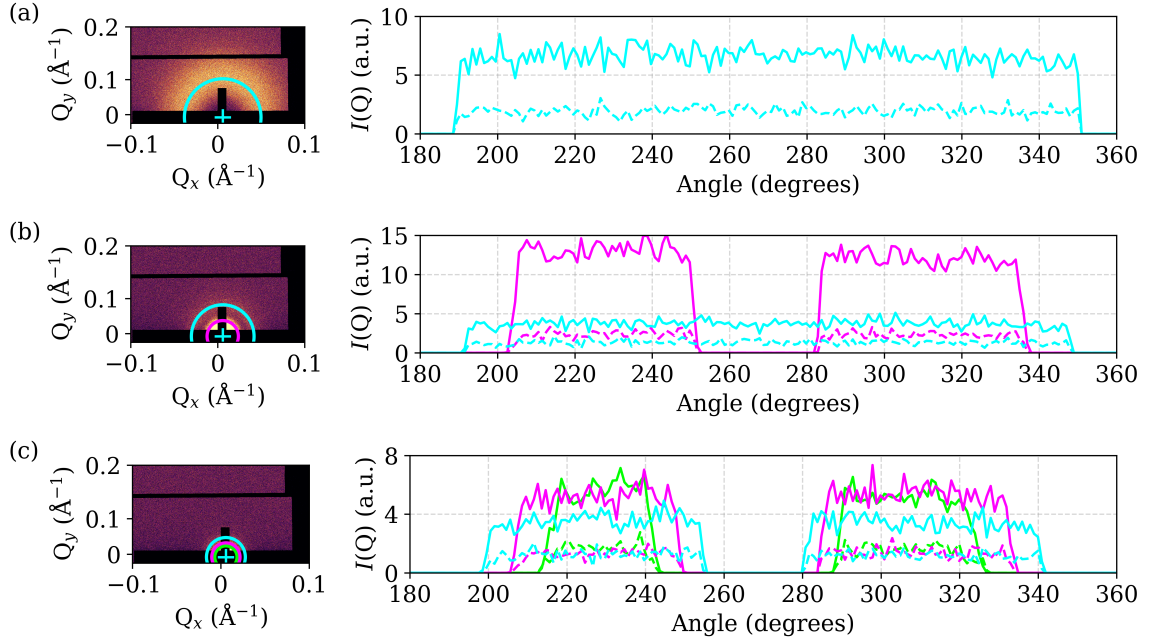


Figure 4.6: **Azimuthal analysis of SAXS detector images for the SACLA jet measurements at 20°C.** Results shown are for $\tau = 2$ ps (a), 10 ps (b), and 40 ps (c). The left column shows the two-dimensional images for $E_{tot} = 6$ μJ overlaid with circular contours at different radii: cyan (outermost), magenta (middle), and green (innermost). The cross marker represents the SAXS detector center. The right column shows the corresponding azimuthally integrated intensity profiles as a function of azimuthal angle for each radius. The integration was performed over a thin annular band extending ± 5 pixels about each radius, except for the innermost ring, where the integration spanned ± 4 pixels due to its proximity to the beam stop. Solid lines indicate results at a pulse energy of 6 μJ , while dashed lines correspond to 3 μJ .

between 0° – 360° for both pulse-energy conditions presented in Figure 4.5 (3 μJ and 6 μJ).

For all time delays and pulse energies, the azimuthal intensity does not demonstrate strong angular dependence—the scattering intensity remains approximately constant on either side of the beam stop and shows no preferred orientation relative to the X-ray polarization axis. Within the sensitivity of the SAXS measurement, this isotropy rules out a direct anisotropic electronic origin of the low- Q response. Rather, it favors a radially symmetric structural rearrangement in liquid water. Furthermore, the continued symmetry across multiple rings and time delays (Figures 4.6(b) and (c)) suggests that the dynamics evolve through the propagation of isotropic structural perturbations throughout the entirety of the measurement window, not just at early time delays.

4.4 Azimuthally Integrated SAXS Response

Since the two-dimensional SAXS response was found to be azimuthally symmetric, the scattering signal was reduced to one-dimensional radial profiles through azimuthal integration (details in Chapter 2). The resulting normalized differential scattering intensity, computed with Equation (2.16) with time-zero taken as $\tau = 0.1$ ps, is shown as a function of momentum transfer in Figure 4.7 for a total pulse energy of $6 \mu\text{J}$ at all sampled time delays. The ring-like features observed in Figure 4.5 manifest as local maxima in $\Delta\tilde{S}(Q, \tau, E_{tot})$. At the earliest sampled delay ($\tau = 0.8$ ps), the low- Q response remains weak and broadly distributed in momentum space. Nevertheless, it is marked by the formation of a faint peak at $Q_{peak} = 0.11 \text{ \AA}^{-1}$, corresponding to a characteristic length scale of 5.7 nm . Although the feature is broad, its appearance is consistent with the nanometer-scale response observed in the pressure-cell measurements (Figures 3.3, 3.4, and 3.7). Note that the relatively weak appearance of the signal at this delay reflects the substantially larger low- Q amplitudes reached at later pump-probe delays; this is in contrast to the pressure-cell measurements where the signal weakened at longer delays due to the restricted reciprocal-space window.

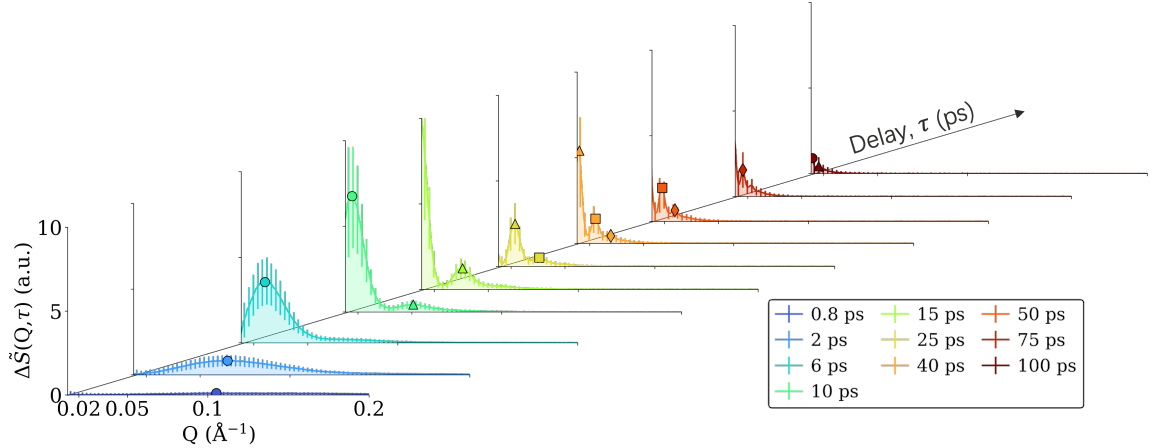


Figure 4.7: **Differential scattering signal of the SACLA jet measurements at 20°C .** Results are shown for a total pulse energy of $E_{tot} = 6 \mu\text{J}$. Error bars are computed using Equation (2.19), where $\tau = 0.1$ ps is taken as time-zero. Markers denote the local maxima at each time delay, determined using the procedure outlined in Section 3.2.2. Curves corresponding to successive pump-probe delays are offset for clarity, displayed on identical momentum-transfer and intensity axes.

With increasing pump-probe delay, the scattering intensity increases in magnitude, narrows in reciprocal space, shifts toward lower momentum transfer, and develops a single pronounced peak for $\tau < 10$ ps. Notably, this early-time behavior closely resembles the low- Q dynamics observed in the pressure-cell measurements, thereby confirming that the previously observed response is intrinsic to liquid water rather than being a consequence of any pressure-cell artifacts.

For time delays longer than 10 ps, however, the improved low- Q access reveals qualitatively

new behavior that was not attained in the earlier measurements. More specifically, as opposed to undergoing a monotonic decay, additional peaks emerge in the scattering intensity for $Q \leq 0.05 \text{ \AA}^{-1}$, with each successive peak appearing to follow similar dynamics as the first. The emergence of these peaks in this reciprocal space region explains why they were not detected in the pressure-cell measurements. In other words, while the intensity appeared to decay in the pressure-cell geometry for $\tau > 3 \text{ ps}$, it is now apparent that this is because the relevant features shifted outside the accessible momentum-transfer window. In fact, the scattering intensity in the present measurements remains prominent up to 75 ps. Only for $\tau = 100 \text{ ps}$ does it weaken sufficiently such that distinct peaks can no longer be reliably identified within experimental uncertainty.

The emergence of multiple well-defined peaks in the SAXS intensity points to the development of spatially coherent density perturbations within the liquid [121]. Furthermore, the progressive and continuous shift of the peaks toward lower momentum transfer suggests a sustained increase in the associated real-space length scales of these perturbations [107]. At the same time, the peaks become narrower and increase in magnitude with time delay, indicating that the perturbations evolve into higher-contrast structures [84]. Collectively, these findings are consistent with an outward propagation of density perturbations within the liquid.

4.4.1 Pulse-Energy Dependence

While the temporal evolution of the SAXS response establishes the existence of long-lived, propagating density perturbations, the origin of these perturbations and their mutual interactions remain unclear. Additional insight is obtained by characterizing the pulse-energy dependence of the scattering intensity. To do so, the differential signal is plotted in Figure 4.8 as a function of total pulse energy for the three representative time delays examined in Figure 4.6. As shown, the overall magnitude of the signal increases systematically with increasing pulse energy, while the spatiotemporal features and the positions of the local maxima remain unchanged. The invariance in peak positions holds across all observed peaks and all time delays (additional results are provided in Appendix A). This behavior suggests that the low- Q scattering response can be factorized into an energy-dependent amplitude and a universal spatiotemporal function:

$$\Delta\tilde{S}(Q, \tau, E_{tot}) = A(E_{tot})f(Q, \tau), \quad (4.1)$$

where the function $f(Q, \tau)$ is independent of pulse energy. This indicates that the pulse energy primarily changes the magnitude of the structural response rather than its characteristic length scales. As such, any additional contributions arising from interactions between density perturbations would either average out over the ensemble of scattering events or remain unresolved within the experimental Q -resolution.

The pulse energy scaling is explicitly quantified in Figure 4.9(a), which shows that the peak

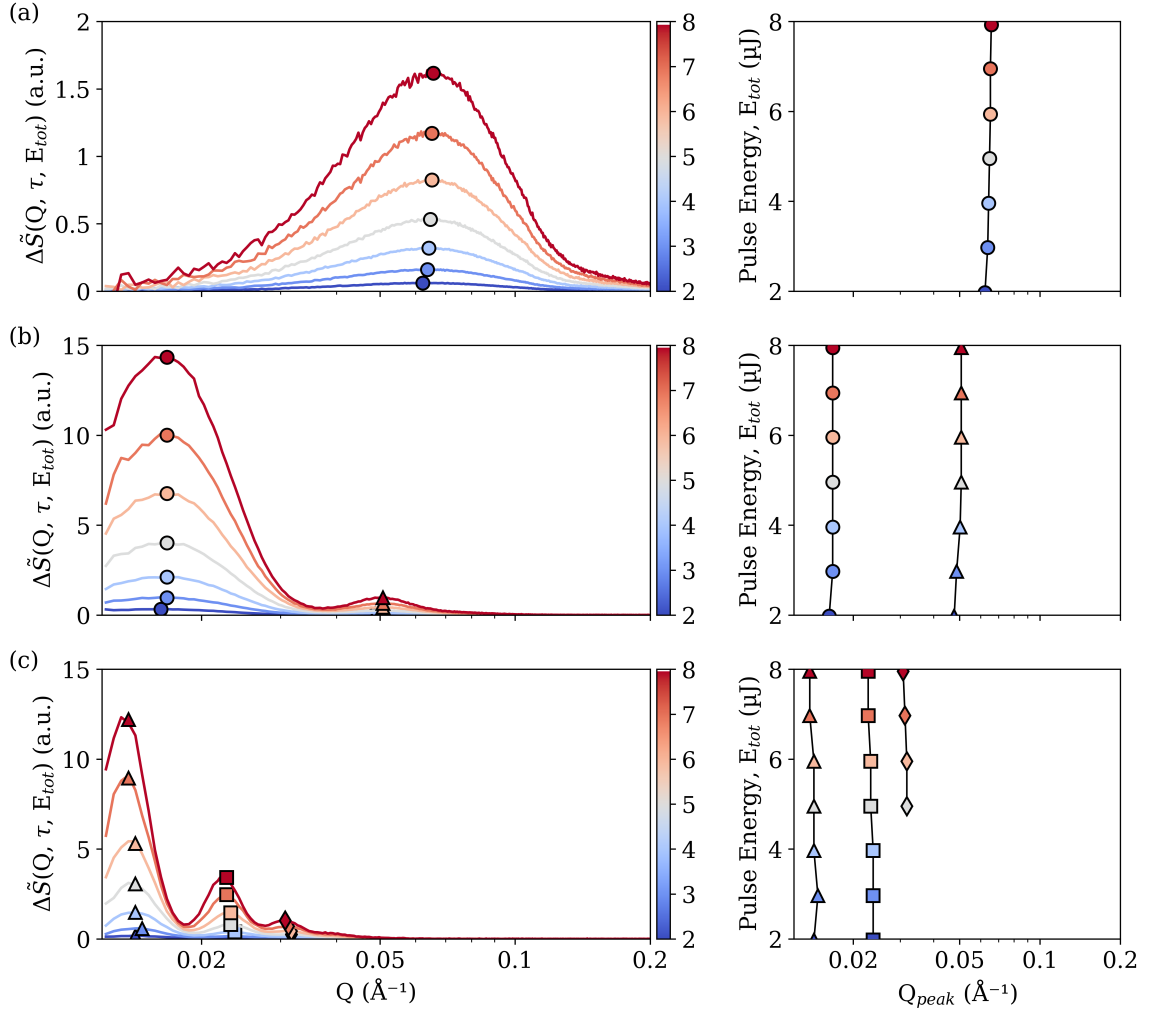


Figure 4.8: **Pulse energy dependence of the SACLA jet measurements at 20°C.** Results shown are for $\tau = 2$ ps (a), 10 ps (b), and 40 ps (c). The left column shows the differential scattering signal computed using Equation (2.16) with $\tau = 0.1$ ps taken as time-zero. The color bar indicates increasing pulse energy from 2 μJ to 8 μJ . Markers denote the local maxima at each corresponding delay, determined using the procedure outlined in Section 3.2.2. The right column tracks the position of the local maxima as a function of total pulse energy.

intensities scale quadratically with total pulse energy, i.e.:

$$A(E_{tot}) \propto E_{tot}^2. \quad (4.2)$$

Given that $E_{tot} = E_{pump} + E_{probe}$ from Equation (2.11) and that a symmetric pump-probe condition

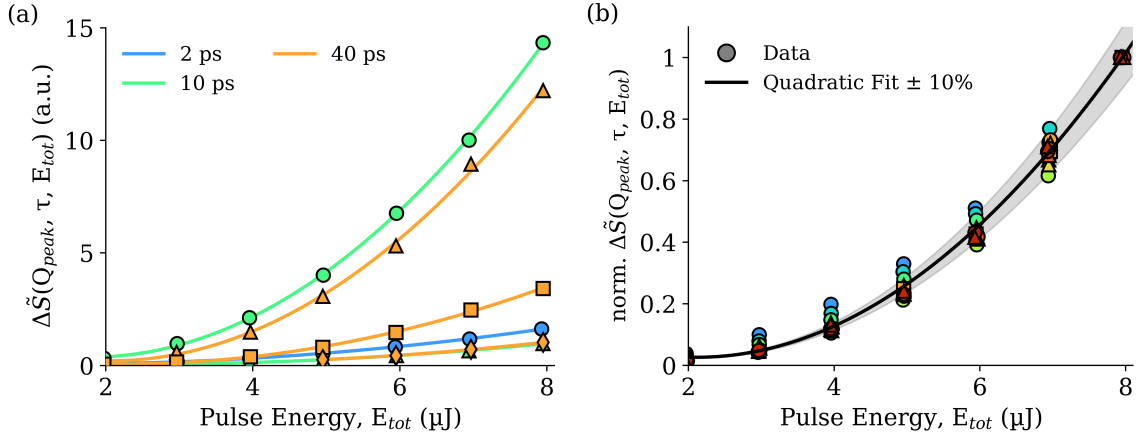


Figure 4.9: **Pulse energy scaling of the SACLA jet measurements at 20°C.** (a) Peak magnitude as a function of total pulse energy for $\tau = 2$ ps, 10 ps, and 40 ps. Solid lines denote quadratic fits through each set of peaks. (b) Normalized peak magnitude as a function of total pulse energy for all identified peaks and all sampled pump-probe delays between $2 \leq \tau \leq 75$ ps. Color coding and markers follow the convention defined in the legend of Figure 4.7. The solid line represents a common quadratic fit to all the data, with the shaded region indicating a $\pm 10\%$ deviation band. All peak magnitudes are normalized to their value at the highest total pulse energy bin ($8 \mu\text{J}$).

was used to filter the snapshots, this scaling is equivalent to a bilinear dependence:

$$\Delta\tilde{S}(Q, \tau, E_{tot}) = \frac{1}{4} E_{pump} E_{probe} f(Q, \tau). \quad (4.3)$$

For a fixed probe condition, Equation (4.3) yields a linear response with respect to the pump energy. Given that the pulse energy is directly proportional to the photon fluence (Equation 2.7), this implies that the low- Q dynamics arise from independent scattering sites within the X-ray illumination volume, where the magnitude of $\Delta\tilde{S}(Q, \tau, E_{tot})$ scales proportionally with the number of impinging X-ray photons. Equivalently, this indicates that each scattering site originates from a single-photon absorption event.

Importantly, the bilinear dependence is observed globally for all identified peaks and for all time delays at which the peaks are discernible (Figure 4.9(b)), where the normalized peak amplitudes collapse onto a single quadratic function within $\sim 10\%$ deviation. The results presented in Figures 4.8 and 4.9 therefore demonstrate that the system remains in a linear regime with respect to the X-ray irradiation over the explored energy range. We attribute the linearity to the incoherent superposition of independent contributions from non-interacting scattering sites formed as a result of X-ray ionization.

4.5 Real-Space Representation of the SAXS Signal

The pulse-energy scaling demonstrated that the observed low- Q response is brought about by independent scattering sites. Yet, the underlying source of these sites was not delineated. This is due to the fact that in reciprocal space, oscillatory features in SAXS profiles can stem from a wide variety of spatial morphologies, including spherical, cylindrical, and/or shell-like density distributions [121, 122]. Direct fitting of the experimental SAXS data using standard form-factor models, as well as recently developed unified descriptors [123], did not yield robust fits across all pump-probe delays. An improved understanding was thus sought by transforming the scattering signal into real space.

Unlike the pressure-cell measurements, where only length scales up to ~ 6 nm ($= 2\pi/Q_{\min, \text{cell}}$) could be reliably extracted due to the restricted low- Q range, encompassing only the first major peak for $\tau \leq 2$ ps, the expanded Q -space access of the jet measurements enabled reconstruction of transient real-space correlations up to length scales of ~ 50 nm. This substantially extended the resolvable spatial window and allowed direct deconvolution of the time-resolved signal.

To obtain real-space information on the transient structural dynamics, the differential scattering intensity was transformed into a radial density correlation function using a sine Fourier transform. For an isotropic liquid, the reduced pair distribution function (RPDF) is defined as [124]:

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q(S(Q) - 1) \sin(Qr) dQ, \quad (4.4)$$

where $S(Q)$ is the static structure factor. To isolate the pump-induced dynamics, the difference signal relative to time zero was considered, such that $\Delta G(r, \tau) = G(r, \tau) - G(r, \tau_0)$. Using Equation (4.4), this gives:

$$\Delta G(r, \tau) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q \Delta S(Q, \tau) \sin(Qr) dQ, \quad (4.5)$$

where $\Delta S(Q, \tau) = S(Q, \tau) - S(Q, \tau_0)$ is the unnormalized change in structure factor. The normalized differential scattering intensity, $\Delta \tilde{S}(Q, \tau)$, is related to $\Delta S(Q, \tau)$ through the atomic form-factor weighting (combining Equations 2.8 and 2.9):

$$\Delta \tilde{S}(Q, \tau, E_{\text{tot}}) = \Delta S(Q, \tau, E_{\text{tot}}) \sum_O |f_O(Q)|^2. \quad (4.6)$$

The dependence on pulse energy is retained in Equation (4.6) for clarity. As such, the experimentally accessible real-space signal can be written as:

$$\Delta G(r, \tau, E_{\text{tot}}) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q \Delta \tilde{S}(Q, \tau, E_{\text{tot}}) \sin(Qr) dQ. \quad (4.7)$$

The transformed quantity, $\Delta G(r, \tau, E_{tot})$, preserves the spatial correlations encoded in the scattering data and is used to track the propagation of the dynamics in real space. The transform was evaluated numerically on a discrete Q -grid, by first constructing a symmetric reciprocal-space signal over the interval $-Q_{max,jet,SAXS}$ to $+Q_{max,jet,SAXS}$, where $Q_{max,jet,SAXS} = 0.5115 \text{ \AA}^{-1}$ from Section 2.5.2. Following that, the fast Fourier transform (FFT) [125] was computed as part of the NumPy library [126] in Python v3.10.2. Since the scattering response is isotropic (Figure 4.6), the resulting transform is equivalent to the sine component of the Fourier transform. Direct numerical evaluation of the inverse Fourier integral yielded identical results within numerical precision. Finally, a truncation was applied at high- Q to suppress noise. The finite nature of the Q -range accessible in the experiment limited the achievable real-space resolution to $\Delta r = 1.23 \text{ nm}$ ($= 2\pi/Q_{max,jet,SAXS}$) and reduced sensitivity to spatial correlations beyond $r \geq 49.3 \text{ nm}$ ($= 2\pi/Q_{min,jet}$). As a result, the reconstructed real-space response is reliable only within the range $1.23 < r \leq 49.3 \text{ nm}$.

The real-space transform obtained for all sampled pump-probe delays at $E_{tot} = 6 \text{ \mu J}$ is shown in Figure 4.10(a) as a contour map. Corresponding results at other pulse energies are given in Appendix A. A negative $\Delta G(r, \tau, E_{tot})$ is observed at early time delays ($\tau < 10 \text{ ps}$) and for $r \lesssim 5 \text{ nm}$. This is followed immediately by an adjacent positive signal at larger distances. With increasing time delay, both features broaden in real space, while the positive component propagates to larger distances. The magnitude of both features remains comparable, which indicates an approximately balanced redistribution of density in the sample occurring on picosecond timescales and nanometer length scales following hard X-ray photoabsorption.

The evolution of the transformed signal is illustrated more clearly by line plots in Figure 4.10(b). At early delays, the response consists predominantly of a compact negative feature followed by a pronounced positive peak. As the delay increases, the positive peak broadens, decreases in amplitude, and migrates towards larger r . Concomitantly, the negative feature becomes increasingly extended in space. By $\tau \approx 10 \text{ ps}$, a secondary oscillation begins to develop upstream of the leading positive peak. The oscillation becomes prominent at 25 ps, consistent with the appearance of two peaks in reciprocal space in the scattering intensity (Figure 4.7). The observed negative-positive signature closely resembles the characteristic rarefaction-compression response expected from a propagating hydrodynamic density perturbation. In this interpretation, the negative component of $\Delta G(r, \tau, E_{tot})$ corresponds to a transient local density depletion near each isolated scattering site, whereas the positive feature reflects a compressive density enhancement that propagates outward into the surrounding liquid and dissipates with time.

Note that a weak residual signal is observed downstream of the leading peak for $\tau = 6, 10$, and 15 ps. This arises from the discrete implementation of the sine Fourier transform and the construction of a symmetric reciprocal space over negative and positive Q -values. The downstream signal is not present when performing the inverse Fourier transform analytically. However, it is worth pointing out that the analytical formulation does not account for the finite nature of the Q -range

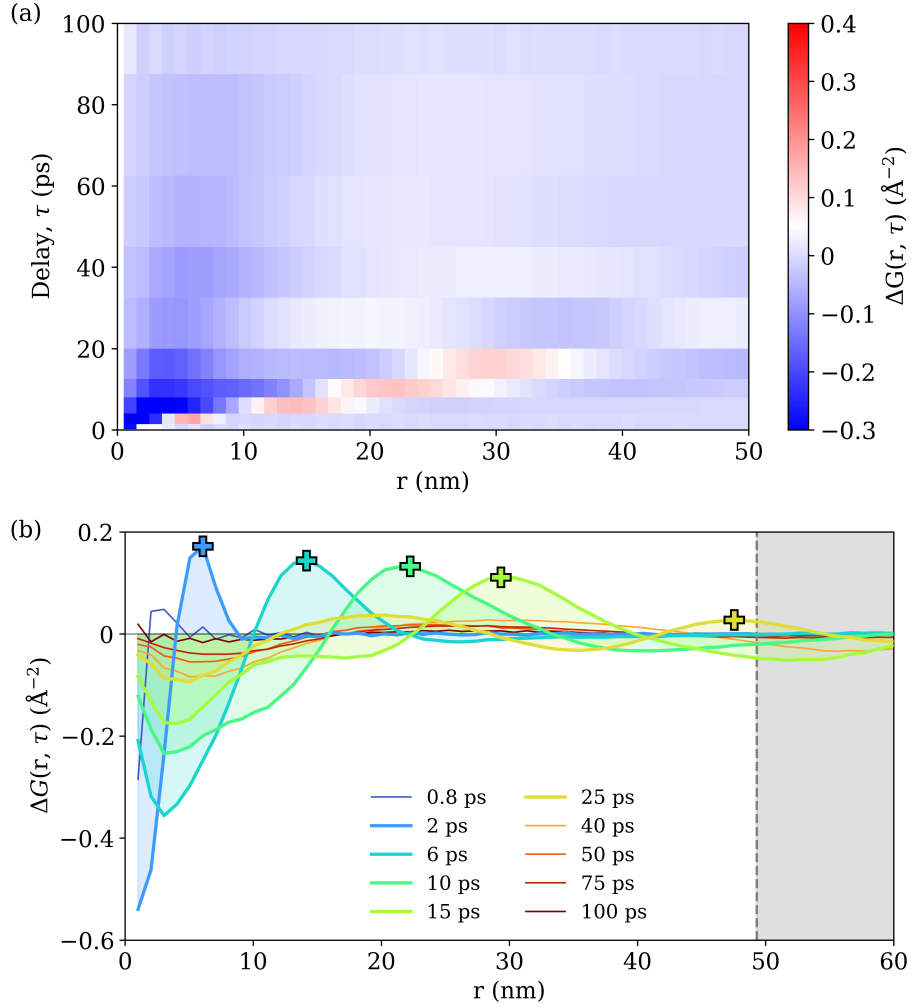


Figure 4.10: **Real-space representation of the SAXS response for the SACLA jet measurements at 20°C.** (a) Contour map of the reduced pair distribution function, $\Delta G(r, \tau, E_{tot})$, calculated with Equation (4.7) for $E_{tot} = 6 \mu\text{J}$. (b) Line plots of $\Delta G(r, \tau, E_{tot})$ at $6 \mu\text{J}$ for all sampled pump-probe delays. Selected time traces for which a peak is prominent within the experimental resolution are highlighted with thicker lines, while the remaining curves are shown with reduced opacity for comparison. Peak positions are indicated by cross markers. The grey shaded region denotes the inaccessible real-space range imposed by the minimum Q -value of the experiment, $Q_{min,jet} = 0.01225 \text{ \AA}^{-1}$.

measured in the experiment. As a result, it does not reproduce the true experimentally accessible real-space resolution. For this reason, the discrete transform described previously is retained—it provides the most consistent representation of the measured data. Nonetheless, the magnitude of these residual features is small ($<20\%$ of the maximum peak value). As such, they do not affect the

physical interpretation of the signal; this will be further demonstrated in Chapter 6.

4.6 Comparison with Pressure Cell Measurements

It is instructive to compare the present measurements with the pressure-cell measurements presented in Chapter 3 and draw parallels between the three datasets. This comparison serves not only to establish qualitative consistency in the observed dynamics but also to evaluate quantitative agreement between the independently measured results. This comparison is done in Figure 4.11.

In Figure 4.11(a)–(c), representative contour maps from the previous SACLA pressure-cell measurements and the present jet measurements are displayed for the same pulse-energy bin of 6 μJ . To facilitate direct comparison, the region below $Q \approx 0.1 \text{ \AA}^{-1}$ is overlaid with a semi-transparent grey rectangle. Under this condition, the contour maps exhibit remarkably similar behavior. In both cases, the low- Q response emerges near ~ 1 ps and evolves identically thereafter. This agreement demonstrates that the dynamics in both experiments are driven by the same physical mechanism, identified in this chapter to be a hydrodynamic response arising from isolated scattering sites.

In Figure 4.11(d), the extracted real-space peak positions from Figure 4.10(b) are mapped directly on those obtained from the LCLS measurements (Figure 3.7(c)) to provide an all-encompassing comparison. As can be seen, both datasets follow the same linear propagation trajectory with comparable slopes, which agree within 4%, within the uncertainty of the fitting. The consistency between the datasets and the quantitative agreement in the extracted propagation dynamics definitively show that the previously observed nanometer-scale response corresponds to the early-time evolution of the same long-lived density perturbation resolved in the present jet experiment. Importantly, this comparison further solidifies that the apparent decay observed in the pressure-cell geometry for $\tau > 3$ ps originated primarily from the restricted reciprocal-space window rather than from an inherent dissipation of the structural dynamics.

4.7 Wide-Angle X-ray Scattering Response and Transient Heating

The discussion has thus far revolved around the SAXS region. Yet, the WAXS region is sensitive to short-range intermolecular structure and hydrogen-bond network rearrangements in liquid water [4]. As such, it provides a complementary probe to SAXS for assessing local structural changes linked to energy deposition.

Figure 4.12(a) shows the WAXS profiles measured at all pump–probe delays for a total pulse energy of $E_{tot} = 6 \mu\text{J}$. Across all delays, the overall shape of the scattering signal remains unchanged. However, a systematic shift of the main diffraction maximum toward higher momentum transfer is observed with increasing delay. In liquid water, such a shift corresponds to a reduction in the average

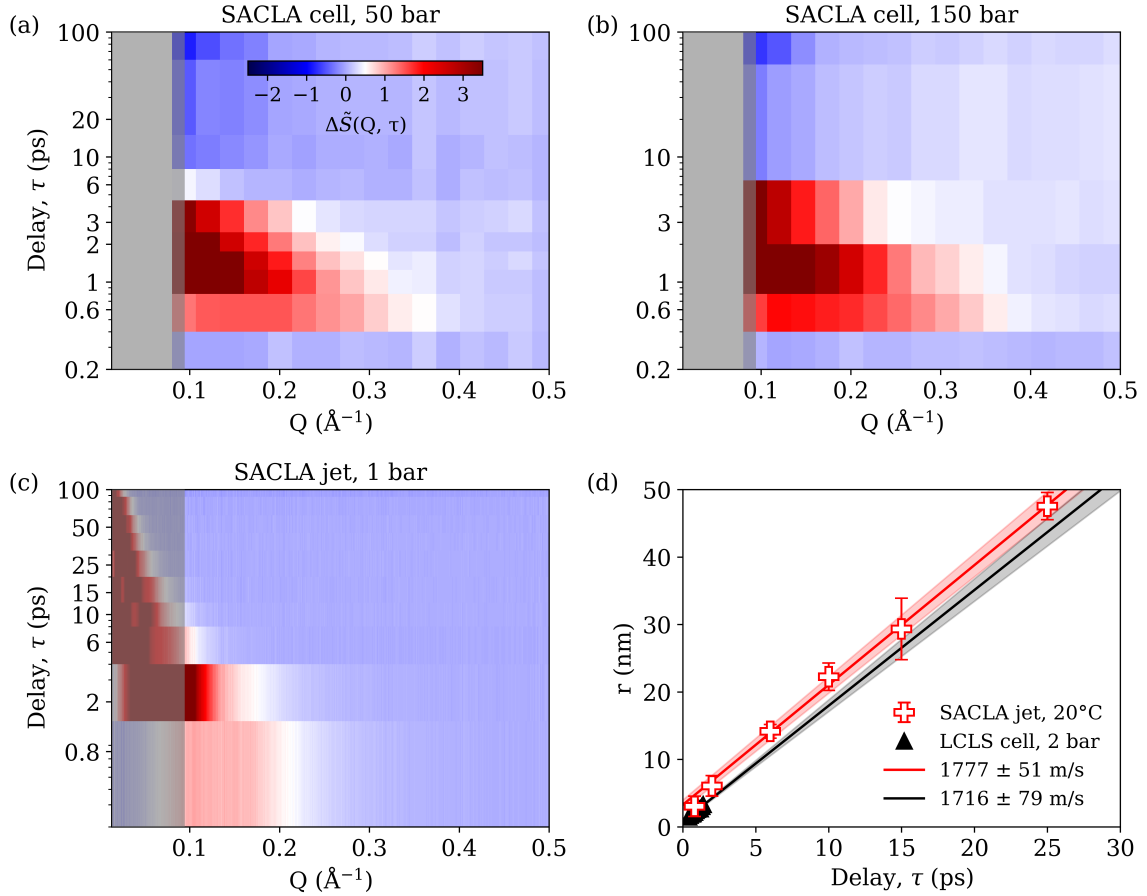


Figure 4.11: **Comparison between the pressure cell and jet measurements.** Contour maps of the time-dependent scattering response from the SACLA pressure cell experiments at (a) 50 bar and (b) 150 bar, and from the SACLA jet experiment at (c) 20°C and ambient pressure. The jet data are shown with the same color scale, and the grey shaded region denotes the momentum-transfer range inaccessible in the pressure cell detector geometry. All panels are generated for a total pulse energy of $6 \mu\text{J}$. (d) Temporal evolution of the extracted real-space length scale from LCLS (triangles) and SACLA jet measurements (crosses). Solid lines present linear fits to the data, with shaded regions highlighting the associated uncertainty in the fit parameters. Error bars indicate the uncertainty in the extracted peak position, estimated from the width of the RPDF peak and the local signal-to-noise ratio.

intermolecular O–O distance and is commonly associated with an increase in temperature [4,101,102]. No signatures of structural disruption or phase transition are observed within the accessible time window. This is illustrated more clearly in Figure 4.12(b), which presents the differential WAXS signal, $\Delta\tilde{S}(Q, \tau, E_{tot}) = \tilde{S}(Q, \tau, E_{tot}) - \tilde{S}(Q, \tau_{0.1}, E_{tot})$, for $E_{tot} = 6 \mu\text{J}$. A negative–positive feature similar to that observed in the pressure-cell measurements (Figures 3.3(a) and 3.4(a)) is recovered.

Together, these observations are consistent with moderate transient local heating induced by X-ray photon absorption, while preserving the underlying liquid-state structure. Furthermore, they demonstrate that the short-range structural response to hard X-ray irradiation is the same across the experiments despite the differences in geometries and thermodynamic conditions.

To quantify the transient heating effect, the position of the main diffraction peak was extracted for all delays and pulse-energy bins in Figure 4.12(c). The peak positions were determined by taking the derivative of the scattering curves with respect to Q , fitting the derivative with a third-degree polynomial, and finding the Q -value where the derivative is zero. Such an approach was followed previously to extract maxima in thermodynamic response functions [5]. Note that extracting the peaks with the method defined in Section 3.2.2 does not significantly change the findings.

The peak positions were then converted into an effective temperature using the calibration in Equation (3.1), and the transient temperature change, $\Delta T = T(\tau) - T(\tau_{0.1})$ was computed. The resulting evolution is given in Figure 4.12(d) for all pulse-energy bins. The maximum temperature rise does not exceed $\Delta T \approx 10^\circ\text{C}$, which is comparable to the maximum increase of 12.5°C obtained in the pressure-cell measurements (Section 3.1). These results additionally support the interpretation that the WAXS response primarily reflects transient heating of the liquid where the bulk-like liquid structure is retained.

Lastly, at longer pump-probe delays ($\tau \gtrsim 75$ ps), the inferred change in temperature displays a partial decrease toward $\Delta T = 2\text{--}4^\circ\text{C}$. Since the WAXS peak position reflects the average O-O distance and therefore the local temperature of the probed water, this decrease indicates thermal relaxation of the initially heated volume. The characteristic length scale over which thermal diffusion occurs can be estimated from $L_{th} \sim \sqrt{\alpha\tau_{th}}$, where α is the thermal diffusivity. Taking $\alpha = 1.43 \times 10^{-7} \text{ m}^2/\text{s}$ for liquid water at room temperature (20°C) [127] and $\tau_{th} \sim 100$ ps yields $L_{th} \sim 3.8$ nm. Note that such a decrease was not resolved in the pressure-cell measurements due to the more limited Q -space resolution. From Chapter 2, $dQ = 0.0267 \text{ \AA}^{-1}$ for the pressure-cell measurements, whereas $dQ = 0.01 \text{ \AA}^{-1}$ near the water diffraction peak in the jet measurements. Figure 4.12(c) shows that the late-time peak shifts are on the order of $0.01 \text{ \AA}^{-1}$, which matches the jet resolution but is smaller than the resolution of the pressure-cell measurements.

4.8 Temperature Dependence

To fully characterize the low- Q structural dynamics and assess their dependence on temperature, additional measurements were performed for a heated liquid water jet at 80°C . The sampled pump-probe delays are summarized in Table 4.1, and the corresponding pulse-energy distributions are provided in Figure 4.13. Although slightly higher pump and probe pulse energies were achieved for the heated jet, the overall distributions remained similar to those obtained at 20°C (Figure 4.2). For consistency, the snapshots were filtered using the same equally spaced energy bins and pump-probe

ratios employed in the room temperature case, and the same analysis workflow was likewise followed.

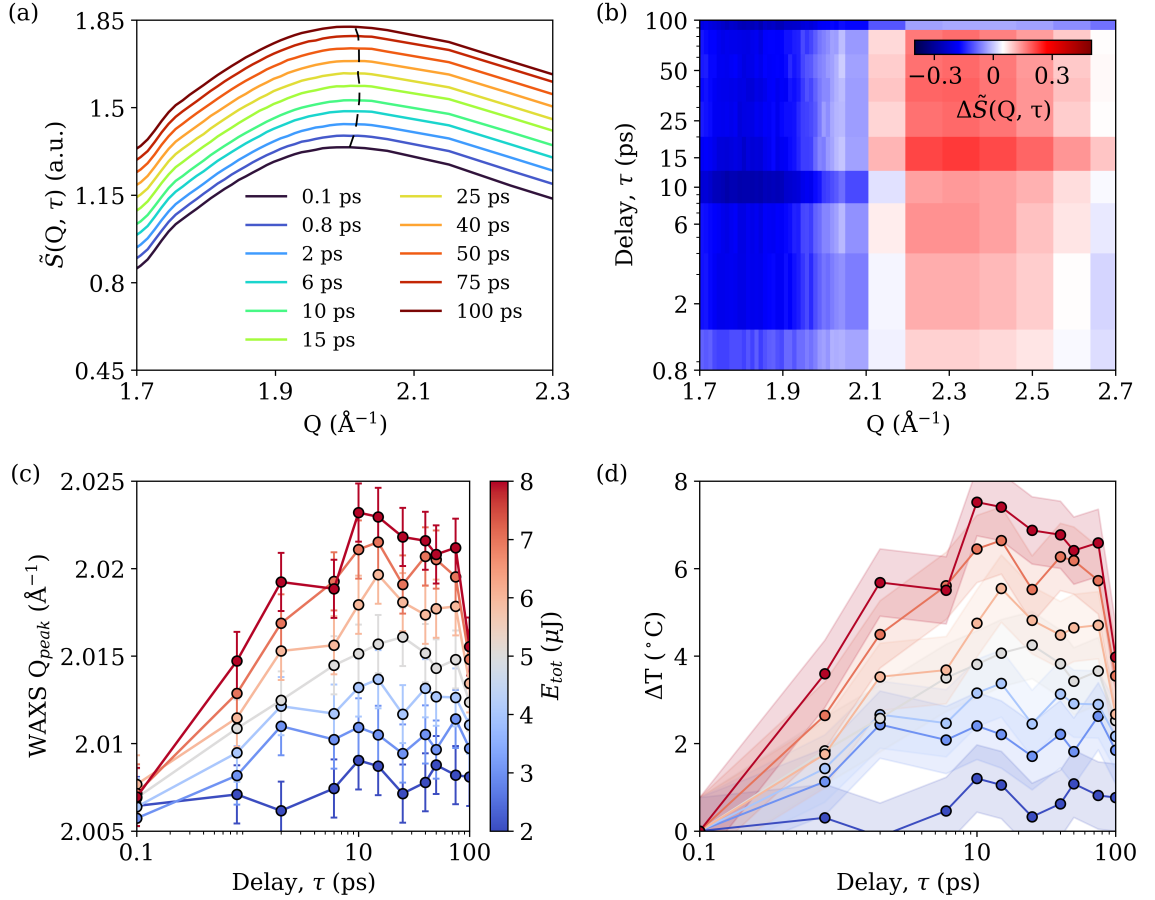


Figure 4.12: **Wide-angle X-ray scattering response for the SACLA jet measurements at 20°C.** (a) WAXS profiles as a function of pump-probe delay for a total pulse energy of $E_{tot} = 6 \mu\text{J}$. Each curve is vertically offset by 0.05 arbitrary units for clarity. The dashed black line connects the peak positions obtained using the derivative method [5]. The curves are zoomed in near the main water diffraction peak for emphasis. (b) Differential WAXS signal at $E_{tot} = 6 \mu\text{J}$. (c) Peak positions as a function of time delay for all pulse-energy bins. Error bars denote the propagated uncertainty from the derivative fitting procedure and the uncertainty in Equation (2.19). (d) Transient temperature change at all pulse energies. The temperature is estimated using Equation (3.1) with $\Delta T = T(\tau) - T(\tau_{0.1})$. Shaded regions represent the uncertainty obtained from the upper and lower bounds of the peak positions in panel (c). Colors correspond to the color bar in panel (c).

The scattering signal at time zero was validated in both the SAXS and WAXS regions using the optimized detector geometry and detector masks from Section 4.2. The validation results are given in Figure 4.14. Since elevated temperature reference datasets are not available in all of the literature used for validation at room temperature, we resorted to results measured at 77°C in [3]

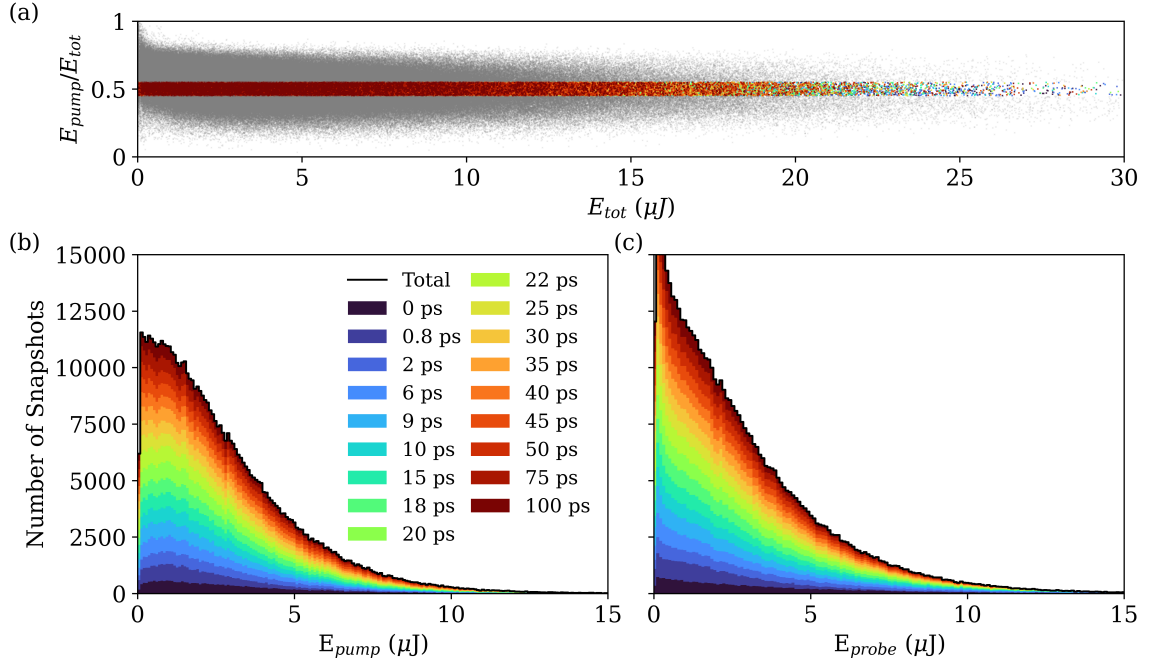


Figure 4.13: **Pulse-energy distribution for the SACLA jet measurements at 80°C.** (a) Pump-probe energy splitting ratio as a function of the total pulse energy. Grey markers denote the full dataset, whereas the colored markers highlight the filtered region around $E_{\text{pump}}/E_{\text{tot}} = 0.5$ retained for further analysis. Pulse-energy distributions at each time delay for the (b) pump and (c) probe pulses. Each successive time delay is cumulatively overlaid on earlier delays for visual comparison. The black curve outlines the total number of snapshots accumulated over all delays.

for comparison. Good agreement is obtained across the accessible momentum-transfer range. In addition, the SAXS signal at $\tau = 0$ exhibits no measurable dependence on pulse energy. This is consistent with the 20°C measurements at $\tau = 0.1$ ps (Figure 4.4(a)) and further supports the use of $\tau = 0.1$ ps as a suitable static reference for calculating the differential scattering signal in Section 4.4. For the present measurements, however, the scattering signal at time zero is employed to compute $\Delta\tilde{S}(Q, \tau, E_{\text{tot}})$.

The resulting differential scattering signal is shown in Figure 4.15 at all sampled time delays for a total pulse energy of $E_{\text{tot}} = 6 \mu\text{J}$. As can be seen, the low- Q response displays analogous behavior to that at 20°C (Figure 4.7). In particular, a single pronounced peak develops at early time delays, followed by steepening of the scattering intensity and migration of the peak toward lower momentum transfer. At later delays, additional peaks emerge that evolve similarly to the first peak. The close correspondence between the two cases suggests that the structural response is largely universal over the measured temperature range.

To directly compare the dynamics at the two temperatures, the pulse-energy dependence of

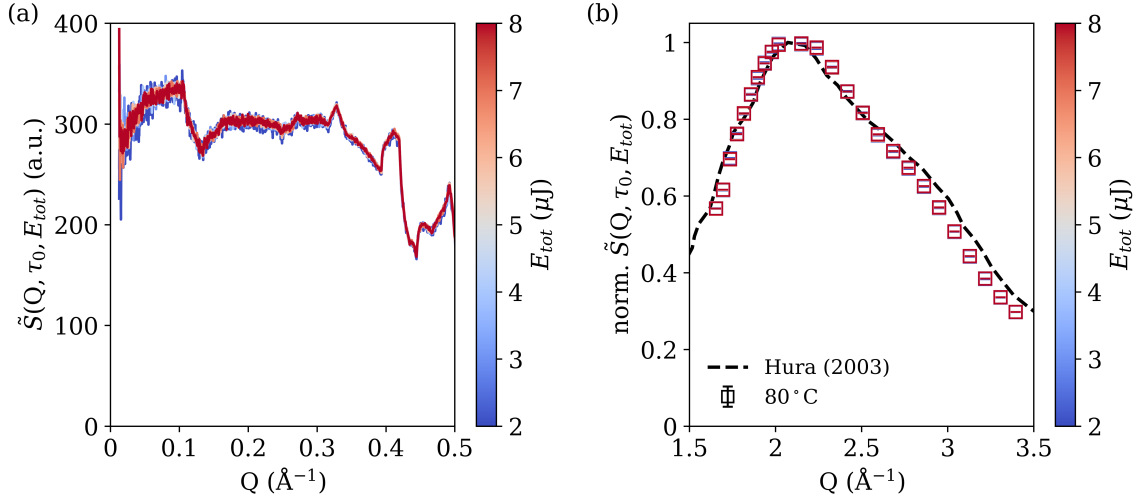


Figure 4.14: **Validation of the SACLA jet measurements at 80°C.** (a) SAXS profiles at $\tau = 0$ obtained after dark subtraction using Equation (2.13) for all pulse-energy bins. The color bar indicates increasing pulse energy from 2 μJ to 8 μJ . (b) WAXS signal for all pulse-energy values. Results are overlaid on reference data from [3] at 77°C. Each curve is normalized by its respective maximum. Markers are plotted every fourth data point for $Q \leq 2.04 \text{ \AA}^{-1}$ and at every data point otherwise to facilitate visual comparison. Error bars in the present dataset were computed using Equation (2.17).

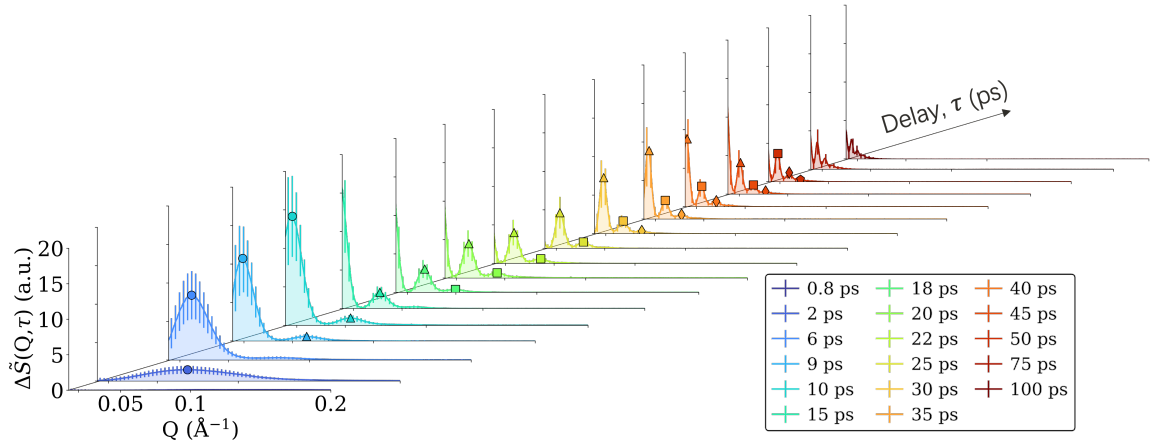


Figure 4.15: **Differential scattering signal of the SACLA jet measurements at 80°C.** Results are shown for a total pulse energy of $E_{tot} = 6 \mu\text{J}$. Error bars are computed using Equation (2.19). Markers denote the local maxima at each time delay, determined using the procedure outlined in Section 3.2.2. Curves are offset for clarity and are displayed on identical axes.

the peaks at 80°C and their locations was investigated in Figure 4.16 for the same delays studied in Figure 4.8. Additional results are provided in Appendix A. Notably, the peak locations at 80°C

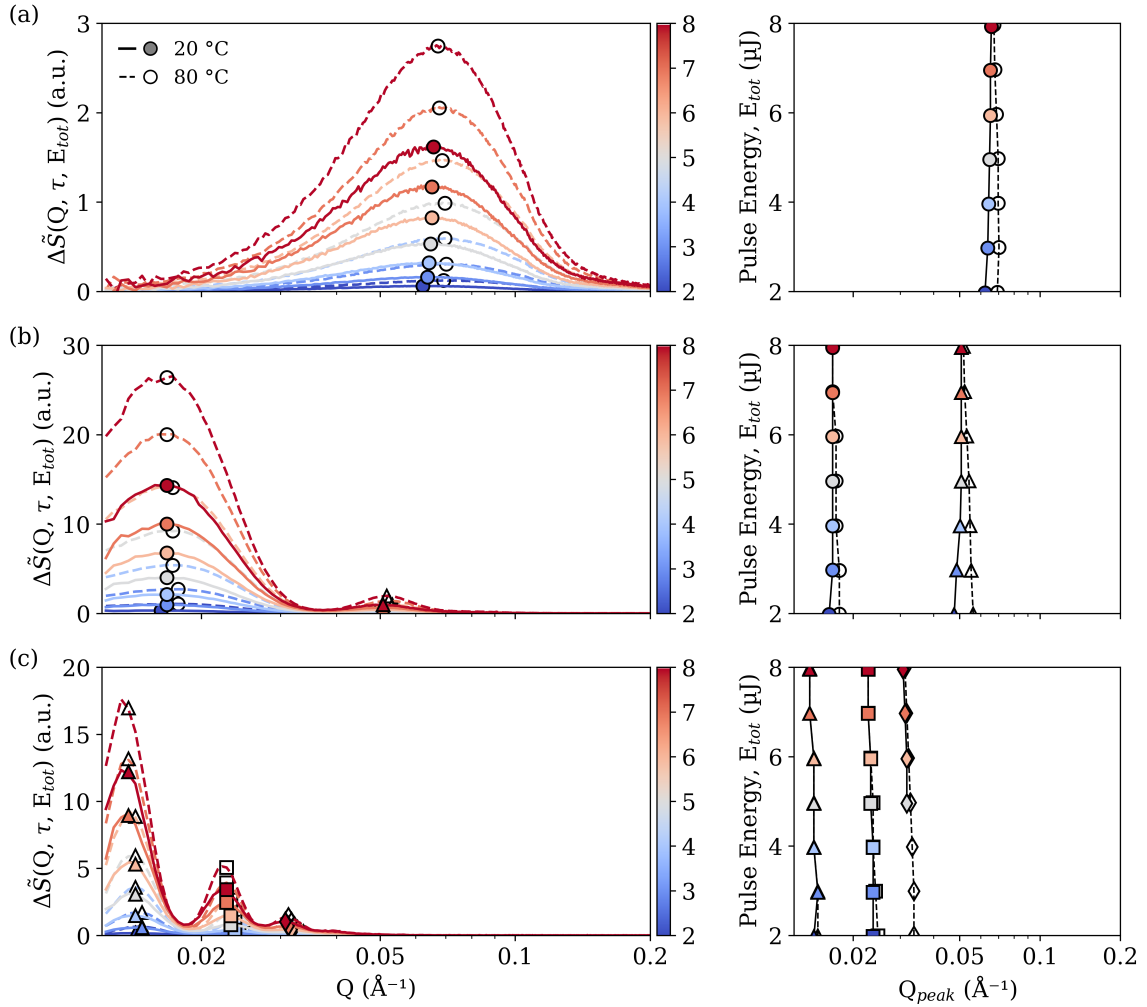


Figure 4.16: **Pulse energy dependence of the SACLA jet measurements at 80°C.** Results shown are for $\tau = 2$ ps (a), 10 ps (b), and 40 ps (c). The left column shows the differential scattering signal computed using Equation (2.16). The color bar indicates increasing pulse energy from 2 μJ to 8 μJ . Markers denote the local maxima at each corresponding delay, determined using the procedure outlined in Section 3.2.2. The right column tracks the position of the local maxima as a function of total pulse energy. Solid lines and filled markers correspond to the 20°C data, whereas dashed lines and open markers indicate the 80°C measurements.

coincide closely with those obtained at 20°C. Meanwhile, the overall signal magnitude is continuously amplified at elevated temperature. This amplification is linked to the reduced viscosity of liquid water at higher temperature and is discussed in more detail in Chapter 6. Since the peak evolution does not change significantly between the two temperature conditions, the same bilinear pulse-energy scaling is expected; this is indeed observed in Figure 4.17.

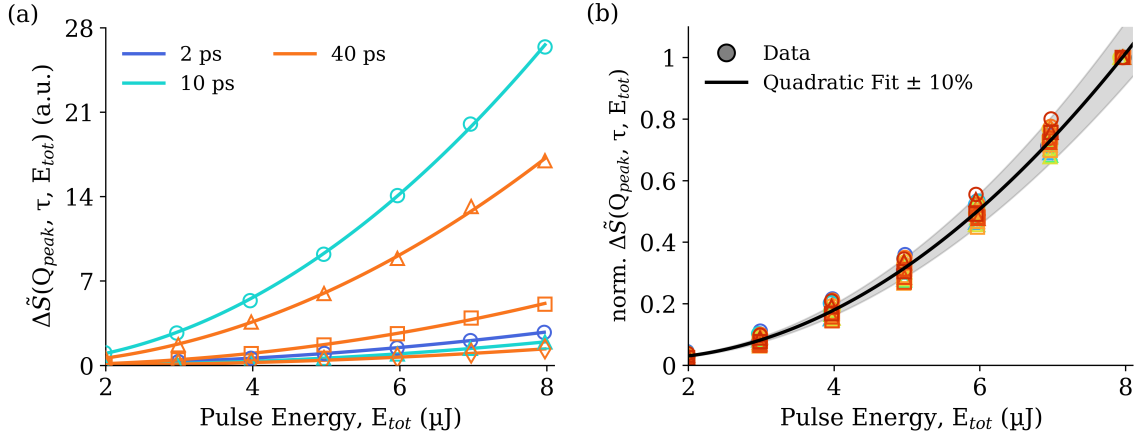


Figure 4.17: **Pulse energy scaling of the SACLA jet measurements at 80°C.** (a) Peak magnitude as a function of total pulse energy for $\tau = 2$ ps, 10 ps, and 40 ps. Solid lines denote quadratic fits through each set of peaks. (b) Normalized peak magnitude as a function of total pulse energy for all identified peaks and all sampled pump-probe delays between $0.8 \leq \tau \leq 50$ ps. Color coding and markers follow the convention defined in the legend of Figure 4.15. The solid line represents a quadratic fit to all the data, with the shaded region indicating a $\pm 10\%$ deviation band. Peak magnitudes are normalized to their value at the highest total pulse energy of $8 \mu\text{J}$.

Finally, the reduced pair distribution function (Equation 4.7) was also computed for the heated water jet at a total pulse energy of $6 \mu\text{J}$. The results are displayed in Figure 4.18(a) for selected time delays that are common between both datasets and lie within the experimentally accessible real-space length scales. The full dataset is presented in Appendix A. An identical rarefaction-compression pattern is observed as in Figure 4.10, albeit more magnified for the heated jet. The rarefaction is initially concentrated at small length scales ($r < 10$ nm) before broadening and decreasing in magnitude with increasing pump-probe delay. Simultaneously, a compressive front is visible that propagates toward larger distances with a pronounced peak while gradually attenuating. Tracking the peak positions for all the sampled time delays at 80°C reveals that the peak evolution is in line with that obtained at 20°C (Figure 4.10(b)).

Taken altogether, the SAXS and real-space analyses demonstrate that increasing the temperature primarily modifies the magnitude of the response while preserving its spatiotemporal evolution, propagation dynamics, and pulse-energy scaling. The persistence of the same reciprocal-space evolution, bilinear energy dependence, and rarefaction-compression propagation pattern across both temperatures strongly indicates that the low- Q dynamics are governed by the same underlying physical mechanism over the investigated temperature range, despite modest differences in the thermophysical properties of liquid water. Between 20°C and 80°C, the density decreases by only 2.6% [99], the speed of sound increases by $\sim 5\%$ [99], and the thermal conductivity changes by 12% [128]. These comparatively small variations are consistent with the nearly unchanged propagation dynamics and

characteristic length scales observed experimentally. In contrast, the dynamic viscosity decreases by $\sim 65\%$ over the same temperature range [129]. This substantial reduction in viscosity provides a potential explanation for the enhanced scattering amplitude observed at elevated temperature. The impact of thermophysical properties on the structural dynamics is examined within the hydrodynamic modeling framework in Chapter 6.

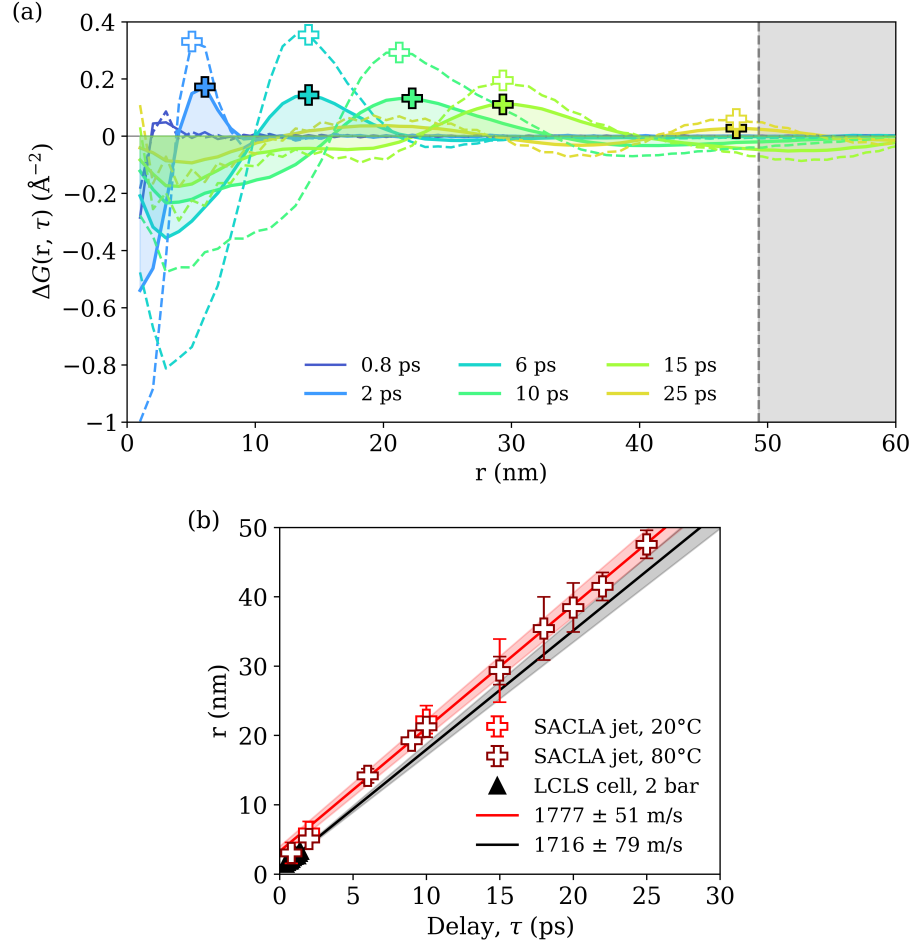


Figure 4.18: **Real-space representation of the SAXS response for the SACLA jet measurements at 80°C.** (a) Line plots of $\Delta G(r, \tau, E_{tot})$ for $E_{tot} = 6 \mu\text{J}$ at pump-probe delays common to both jet experiments. Solid lines and filled markers correspond to the 20°C dataset, whereas dashed lines and open markers indicate the 80°C measurements. The grey shaded region denotes the inaccessible real-space range imposed by the minimum Q -value of the experiment, $Q_{min,jet} = 0.01225 \text{ \AA}^{-1}$. (b) Temporal evolution of the extracted real-space peak positions from the LCLS (triangles) and SACLA jet measurements at 20°C (red crosses) and 80°C (dark red crosses). Solid lines denote linear fits to the data, with shaded regions highlighting the associated uncertainty in the fit parameters. Error bars indicate the uncertainty in the extracted peak position, estimated from the width of the RPDF peak and the local signal-to-noise ratio.

4.9 Summary

In this chapter, the transient structural dynamics of liquid water following hard X-ray ionization were investigated using time-resolved small- and wide-angle X-ray scattering measurements performed on a free-flowing liquid jet at SACLA. The measurements extended the accessible reciprocal-space range significantly beyond that achieved in the pressure-cell detector geometry discussed in Chapter 3, enabling direct observation of the low- Q structural response over substantially longer spatiotemporal scales. The reliability of the measurements was ensured through comprehensive detector calibration and validation procedures. The momentum-transfer axis was calibrated using standard scattering references, and the detector response at time zero was verified across all pulse energies, confirming that no systematic energy dependence influenced the extracted scattering features.

The SAXS measurements revealed the emergence of a pronounced low- Q scattering peak at early pump-probe delays (within the first 2 ps), corresponding to nanometer-scale structural correlations within the liquid. With increasing time delay, the scattering response increased in magnitude, narrowed in reciprocal space, and continuously shifted toward lower momentum transfer. Unlike the pressure-cell measurements, where the low- Q response appeared to decay after several picoseconds (~ 3 ps), the expanded reciprocal-space access of the jet detector geometry demonstrated that the dynamics instead persisted and evolved toward progressively lower momentum transfer. Multiple peaks were observed to emerge at later pump-probe delays (≥ 9 ps), pointing to the development of long-range spatial correlations extending over tens of nanometers.

The pulse-energy dependence of the SAXS response was investigated in detail. While the magnitude of the scattering signal increased systematically with deposited pulse energy, the peak locations and overall spatiotemporal evolution remained unchanged. Quantitative analysis demonstrated that the peak magnitudes scaled quadratically with total pulse energy, corresponding to a linear dependence with respect to the pump pulse energy at a fixed probing condition. This behavior indicated that the low- Q response originates from the incoherent superposition of independent, non-interacting scattering sites produced by X-ray ionization events.

An important characteristic of the SAXS response is that the scattering signal was observed to be azimuthally symmetric throughout the experiment—across all investigated pump-probe delays and pulse energies, the low- Q features showed no measurable angular dependence. This observation is in line with scattering sites that generate isotropic perturbations throughout the X-ray illuminated liquid volume.

To gain insight into the real-space origin of the scattering signal, the SAXS response was transformed into a reduced pair distribution function using a sine Fourier transform. The resulting real-space dynamics uncovered a pronounced rarefaction-compression pattern that propagated outward with increasing pump-probe delay. The compressive front exhibited linear propagation in time across the experimentally accessible length scales. The evolution of the real-space signal therefore demonstrated that the low- Q response corresponds to a propagating density perturbation within the

liquid, consistent with a hydrodynamic response originating from energy deposition.

Comparison with the pressure-cell measurements revealed excellent qualitative and quantitative agreement between the two experimental geometries. Restricting the jet measurements to the same reciprocal-space range accessible in the pressure-cell experiments recovered nearly identical low- Q dynamics. Furthermore, the extracted propagation velocities and characteristic length scales were found to agree closely across all datasets. These results conclusively showed that the nanometer-scale response previously observed in the pressure-cell measurements corresponds to the early-time evolution of the same long-lived density perturbation resolved in the present jet measurements.

The WAXS response was also analyzed to assess transient local heating within the liquid. A systematic shift of the main diffraction maximum toward higher momentum transfer was seen with increasing pump-probe delay, consistent with moderate heating of liquid water while preserving the underlying hydrogen-bond network. Quantitative analysis yielded a maximum transient temperature increase of approximately 10°C over the measured pulse energy range. No signatures of structural disruption or phase transition were evident, confirming that the measurements remained within the liquid phase throughout the experiment.

Finally, the temperature dependence of the low- Q dynamics was characterized through additional measurements performed at 80°C. Despite the elevated temperature, the SAXS response exhibited the same reciprocal-space evolution, pulse-energy scaling, and real-space rarefaction-compression dynamics observed at room temperature. The primary effect of temperature was an enhancement of the scattering magnitude, while the propagation dynamics and characteristic length scales remained nearly unchanged. These observations demonstrated that the low- Q structural response is governed by the same underlying physical mechanism over the investigated temperature range. Comparison with the thermophysical properties of liquid water suggested that the enhanced scattering amplitude at elevated temperature is associated primarily with the substantial reduction in viscosity, whereas the comparatively small changes in density, speed of sound, and thermal conductivity preserve the overall spatiotemporal evolution of the response.

Combined, the results presented in this chapter established that hard X-ray ionization of liquid water produces long-lived, propagating density perturbations that evolve hydrodynamically on nanometer length scales. The measurements further highlighted that these dynamics arise from independent scattering sites and persist robustly across a broad range of thermodynamic conditions.

4.10 Statement of Contributions

The work presented in this chapter was conducted as part of a collaborative experimental campaign at the SACLA XFEL facility.

I proposed the experiment and led its execution. My contributions included planning the measurements, performing the experiment, collecting the data, developing the online and offline data

analysis procedures, analyzing and interpreting the results, preparing all figures, and writing this chapter.

Operation of the liquid jet sample delivery system during the experiment was carried out by Taekeun Yoon. X-ray beam delivery and operation were supported by Yanwen Sun and Sanghoon Song, while beamline operation and technical support were provided by Taito Osaka and Ichiro Inoue. Scientific supervision during the experiment was provided by Matthias Ihme. Haoyuan Li assisted with the RPDF analysis.

Chapter 5

Physical Origin of the Low- Q Structural Dynamics

The findings presented in Chapters 3 and 4 outline that radiolysis initiated by hard X-rays induces an isotropic structural rearrangement in liquid water that evolves linearly in time, starting from nanometer length scales and sub-picosecond time delays. This chapter lays the physical framework underlying these findings, motivates modeling the dynamics with a continuum hydrodynamic formulation, and identifies the structural response as arising from the formation of radiation track structures, more specifically radiation spurs, in the low linear energy transfer (LET) regime. First, the ionization fraction is estimated. Second, the characteristic spur spacing is evaluated. Third, the role of radiolysis chemistry is discussed.

5.1 Experimental Signature of Hydrodynamic Propagation

We begin by revisiting one of the central observations from Chapter 4: the temporal evolution of the real-space scattering peaks. The extracted propagation velocities from the experiments were found to be between 1637–1828 m/s when factoring in the uncertainty of the fitted slopes. For comparison, the experimentally measured speed of sound in liquid water is 1482 m/s at 20°C and 1554 m/s at 80°C [130]. The observed propagation velocities thus appear to agree with the longitudinal acoustic velocity of liquid water, at least within $\sim 19\%$. The structural response also exhibited bilinear pulse-energy scaling, isotropic azimuthal propagation, smooth rarefaction–compression dynamics without the formation of sharp discontinuities in the reduced pair distribution function, and modest transient heating while preserving the overall liquid-state structure. Collectively, these observations suggest that the low- Q response corresponds to a weak, approximately linear hydrodynamic perturbation that modulates the density as it propagates through the liquid.

5.2 Ionization Fraction

Yet, a key question remains regarding the degree of ionization induced by the incident X-ray pulse. This question is of paramount importance because, at sufficiently large ionization fractions or pulse energies, warm dense matter [106] or micro-explosions are observed [131, 132]. Both phenomena significantly impact the ensuing structural dynamics. In the former case, the high degree of ionization gives rise to strong Coulomb interactions among the oxygen ions, leading to distinct non-equilibrium structures. In the latter, large energy deposition has been shown to drive non-linear shock-wave propagation in water jets and droplets. Although we observe no evidence for either phenomenon in the present experiments, it is still worthwhile to estimate the ionization fraction and verify that the current physical interpretation is justified.

Determining the exact number of ionization events is not straightforward, however, since several interaction channels are available for hard X-rays in water, as discussed in Chapter 2. At 10 keV, an incident photon undergoes primarily photoelectric absorption, as the photoelectric cross-section is two orders of magnitude larger than coherent and incoherent scattering [23]. In turn, this will eject a core-shell electron with sufficient kinetic energy to ionize secondary electrons. In principle, accurately resolving the resulting cascade of primary and secondary ionizations in liquid water requires Monte Carlo radiation transport simulations [133–136], which is beyond the scope of this thesis. Nevertheless, a first-order estimate of the ionization fraction can be obtained directly from tabulated photoelectric cross-sections.

Using tabulated cross-sections at 10 keV [23], the photoelectric cross-section for oxygen is:

$$\sigma_{\text{pe,O}} = 1.47 \times 10^{-22} \text{ cm}^2/\text{atom}, \quad (5.1)$$

where hydrogen is neglected due to its comparatively small contribution ($\sigma_{\text{pe,H}} = 4.55 \times 10^{-27} \text{ cm}^2/\text{atom}$). The ionization probability per water molecule is then approximated by:

$$P_{\text{ion}} = \Phi \sigma_{\text{pe,O}}, \quad (5.2)$$

where Φ is the incident photon fluence (Equation 2.7). Since only the pump pulse initiates the ionization dynamics, the photon fluence is determined by the pump pulse energy, $E_{\text{pump}} = BE_{\text{tot}}$, where B is the pump–probe energy splitting ratio. The number of incident photons is then given by $N_p = BE_{\text{tot}}/(h\nu)$. Taking $E_{\text{tot}} = 1 \text{ } \mu\text{J}$ and $B = 0.5$, corresponding to an even pump–probe splitting ratio, yields:

$$N_p = \frac{0.5 \times 1 \times 10^{-6} \text{ J}}{10 \times 1.602 \times 10^{-16} \text{ J}} \approx 3.12 \times 10^8 \text{ photons}. \quad (5.3)$$

Assuming a circular Gaussian beam profile with a FWHM diameter of 3 μm , the effective X-ray

illuminated area is:

$$A_{\text{beam}} = \pi w_0^2 = \frac{\pi w_{\text{FWHM}}^2}{2 \ln(2)} = \frac{\pi(3 \times 10^{-4} \text{ cm})^2}{2 \ln(2)} \approx 2.04 \times 10^{-7} \text{ cm}^2, \quad (5.4)$$

where $w_0 = w_{\text{FWHM}}/\sqrt{2 \ln(2)}$ is the $1/e^2$ beam radius of the equivalent Gaussian profile.

Substituting these values into Equation (5.2) gives:

$$P_{\text{ion}} \approx 2.25 \times 10^{-7} \text{ ionizations/molecule} \quad (5.5)$$

for a pulse energy of 1 μJ . This corresponds to approximately one ionization event per 4.4×10^6 water molecules. Since the photon fluence scales linearly with the pump pulse energy, the ionization probability likewise scales linearly. At the maximum total pulse energy measured experimentally, $E_{\text{tot,max}} = 8 \mu\text{J}$ (corresponding to a pump pulse energy of $B \times E_{\text{tot,max}}$), the ionization probability increases to:

$$P_{\text{ion,max}} \approx 1.8 \times 10^{-6} \text{ ionizations/molecule}, \quad (5.6)$$

corresponding to approximately one ionization event per 5.6×10^5 water molecules.

This estimate neglects the generation of secondary electrons, which can induce additional ionization events along their paths. However, even under the conservative assumption that each primary photoelectron generates as many as 10^3 secondary ionizations—obtained by dividing the incident photon energy (10 keV) by the minimum energy required to ionize a valence electron (11.2 eV [137])—the ionization probability remains at most 0.18%. Such a low ionization fraction is consistent with the modest heating, preserved liquid-state structure, and approximately linear hydrodynamic response observed from the experiments. Table 5.1 presents the ionization probability for a wide range of pulse energies.

Pulse Energy (μJ)	1 ionization every x molecules	mean separation	P_{ion} (%)
1	4444	~ 16 molecules	0.03
2	2222	~ 13 molecules	0.05
4	1111	~ 10 molecules	0.09
6	740	~ 9 molecules	0.14
8	555	~ 8 molecules	0.18

Table 5.1: **Ionization probability for a given total pulse energy.** P_{ion} is multiplied by 10^3 to provide an upper bound for secondary ionization. The mean separation between ionization events, expressed in units of molecular spacing, is estimated as $\sqrt[3]{P_{\text{ion}}^{-1}}$.

5.3 Radiation Spur Formation and Spacing

Next, we consider the development of the earliest pronounced scattering peak observed at $\tau = 0.6$ ps with a characteristic length scale of 3.9 nm (Figure 3.3). This timescale lies at the onset of the chemical stage of radiolysis and coincides with the expected formation of radiation track structures [40]. As discussed above, the dominant interaction channel for a 10 keV hard X-ray photon in liquid water is photoelectric absorption. This ejects a core photoelectron with a kinetic energy of 9.42 keV, after accounting for the oxygen K-shell binding energy of 538.2 eV [24]. The linear energy transfer of a 9.42 keV electron in water is 2.363 eV/nm [138], placing the present conditions firmly within the low-LET regime; the low-LET regime is conventionally defined to be between 0.2–3 eV/nm [139]. Under such conditions, analytical radiation track models [44–46] predict the emergence of spatially isolated Magee-type radiation spurs rather than dense overlapping tracks.

The spurs form as a direct consequence of the secondary electron cascade initiated by the photoelectron. Following photoelectric absorption, the core photoelectron possesses sufficient energy to ionize additional water molecules. As such, it undergoes repeated inelastic collisions along its path and deposits energy in the process. The average spacing between successive ionization events can be estimated from the ratio of the mean energy loss per collision, 60 eV [133, 140], and the LET:

$$\Delta x = \frac{60 \text{ eV}}{2.256 \text{ eV/nm}} \approx 26.6 \text{ nm}. \quad (5.7)$$

This estimate is consistent with the tabulated inelastic mean free path for an electron of similar energy (~ 9.5 keV) in liquid water [141]. Additionally, as this distance corresponds to the average spacing between neighboring ionization events, it represents the separation between spur centers.

Each primary ionization event generates low-energy (< 100 eV) secondary electrons [14] that likewise undergo repeated elastic and inelastic scattering until their energies fall below the excitation threshold of liquid water, 7.3 eV [38]. Owing to their large elastic scattering cross-sections [133], isotropic angular distribution [134], and short inelastic mean free paths (1 nm for 100 eV electrons) [141], these electrons deposit their energy and thermalize within nanometer-scale volumes, giving rise to localized regions of energy deposition known as radiation spurs with radii of 2–5 nm [52, 53]. The experimentally observed length scale of 3.9 nm is thus in reasonable agreement with these estimates.

Electron thermalization and hydration are also known to occur on sub-picosecond timescales (≤ 1 ps) [36, 37, 73]. As such, the development of the scattering peak at 0.6 ps falls squarely within the temporal range over which radiation spurs are expected to form. Rapid, spatially confined energy deposition events have long been theoretically predicted to induce a transient hydrodynamic response in the surrounding liquid [60, 62]. The close agreement observed in both the characteristic length scale and timescale hence lends support to the interpretation that the earliest measured scattering feature corresponds to the initial structural signature of a hydrodynamic response launched by individual radiation spurs. Within this framework, the longer-range structural modulations evident at later

pump–probe delays naturally reflect the subsequent evolution and propagation of this hydrodynamic response that emanates from the spurs.

A crucial aspect of this physical picture is the fact that the spurs remain non-interacting throughout the entirety of the measurement window—otherwise the response cannot be attributed to the superposition of independent contributions from individual spurs. To assess whether neighboring spurs can overlap on picosecond timescales, a characteristic diffusion timescale was estimated using:

$$\tau_D \sim \frac{(\Delta x)^2}{D}, \quad (5.8)$$

where D is the relevant diffusion coefficient. Using $D = 4.9 \times 10^{-9} \text{ m}^2/\text{s}$ [41], which is the mass diffusion coefficient of hydrated electrons in liquid water, the most mobile radiolytic species, yields $\tau_D \approx 144 \text{ ns}$. Even adopting the substantially larger thermal diffusivity of water, $D = 1.43 \times 10^{-7} \text{ m}^2/\text{s}$ [127], gives $\tau_D \approx 5 \text{ ns}$. Both timescales exceed the maximum experimental delay of 100 ps by more than an order of magnitude. Consequently, neither radical diffusion nor thermal transport can produce significant overlap between neighboring spurs during the measurement window. Given that the spurs have radii of at most 5 nm and are initially separated by approximately 26 nm, they remain well separated on picosecond timescales.

As a result, the aforementioned physical picture provides a possible explanation for all key experimental observations:

1. The initial scattering peak is ascribed to the hydrodynamic response launched by localized energy deposition within individual radiation spurs on nanometer length scales and sub-picosecond timescales.
2. The evolution into multiple peaks and the systematic migration toward smaller momentum-transfer values (i.e., larger length scales) portrays the outward propagation of this hydrodynamic response.
3. The observed rarefaction–compression pattern, the bilinear pulse-energy dependence, and the linear evolution of the real-space peak positions are all in line with a weak, approximately linear hydrodynamic regime.
4. Finally, the extracted propagation velocity, which is of the order of the speed of sound in liquid water, emerges as a direct consequence of acoustic-like density wave propagation inherent to linear hydrodynamic perturbations in the liquid.

5.4 Role of Radiolysis Chemistry

In the preceding sections, the observed structural dynamics have been interpreted primarily in terms of radiation spur formation and the resulting hydrodynamic response. A natural question is the extent to which radiolysis chemistry contributes to the measured signal on the measured timescales. To address this, radiolysis reaction networks, which allow estimation of the time-dependent concentrations of reactive species, were evaluated using established models from transmission electron microscopy and radiolysis chemistry literature [6, 41, 43, 49, 142].

In particular, the model developed by Schneider *et al.* [6] was implemented. The model provides a bulk (spatially averaged) representation of radiolysis chemistry by solving the coupled evolution of radiolytic species through a system of reaction-rate equations [41, 142]. The concentration of each species is governed by production and destruction terms arising from chemical reactions, together with a source term that accounts for energy deposition by ionizing radiation. As such, the formulation describes the average temporal evolution of the chemical species throughout the irradiated volume. The model tracks sixteen radiolytic species (e_{aq}^- , H^+ , H , H_2 , O^- , OH^- , OH , O_2 , O_2^- , HO_2 , HO_2^- , O_3 , O_3^- , H_2O_2 , HO_3 , and H_2O) and includes seventy-four reactions involving ionization equilibria, radical recombination, scavenging pathways, and molecular product formation.

The model was originally developed for continuous electron-beam irradiation conditions relevant to transmission electron microscopy. In the present experiments, however, ultrashort XFEL pulses are employed that deposit energy within ~ 10 fs. To account for this difference, the irradiation source term was modified to represent a step-function energy deposition event, such that the dose was applied only during the XFEL pulse duration and set to zero thereafter. Two limiting cases were considered: (i) homogeneous energy deposition corresponding to $3 \mu J$ distributed throughout the X-ray illuminated volume and (ii) localized energy deposition of 500 eV confined within a representative radiation spur volume (sphere of radius 2 nm). These cases provide upper and lower bounds on the expected concentrations of radiolysis products under the experimental conditions.

Figure 5.1 shows the calculated temporal evolution of the dominant radiolysis species following irradiation. As expected, hydrated electrons, hydroxyl radicals, and hydrogen atoms are produced rapidly following energy deposition, followed by the slower formation of molecular products such as H_2 , O_2 , and H_2O_2 on nanosecond timescales. Despite the large instantaneous dose delivered by the XFEL pulse, the resulting concentrations remain small, 10^{-2} – 10^0 M, compared with the molecular concentration of water, $[H_2O] = 55.6$ M. This is aligned with the low ionization fraction estimated in Table 5.1. Furthermore, the concentrations evolve on timescales that are significantly longer than the initial formation of the SAXS signal, suggesting that the earliest structural response is unlikely to be dominated by chemical reactions alone. Nevertheless, the formation of radiolytic species may still influence the subsequent evolution of the density perturbation through local changes in composition, energy redistribution, and coupled transport processes. Consequently, while the present analysis indicates that localized energy deposition and the resulting hydrodynamic response provide

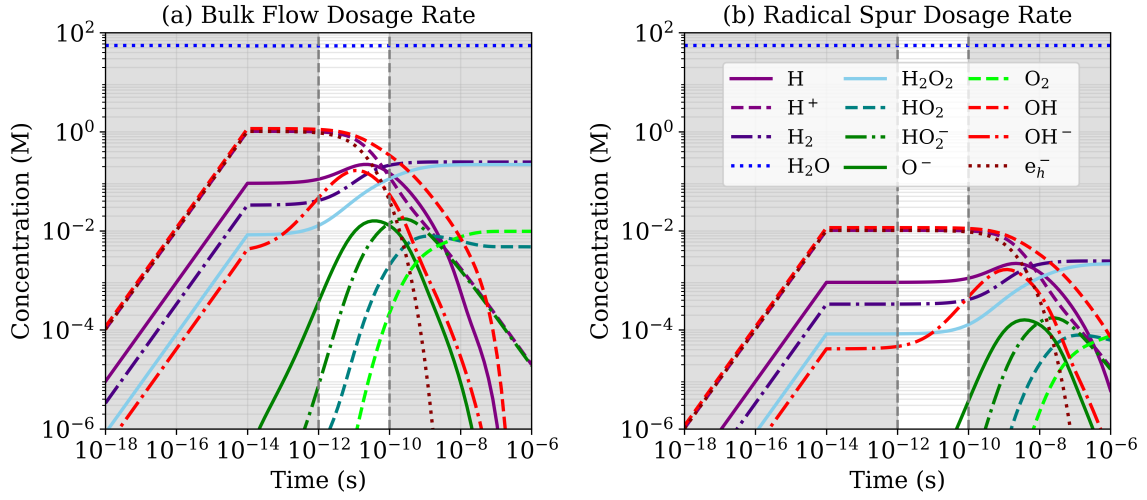


Figure 5.1: **Radiolysis reaction network model under the present experimental conditions.** Time-dependent concentrations of the major radiolytic species predicted using the model of Schneider *et al.* [6] for (a) energy deposition distributed throughout the X-ray illuminated volume (bulk flow scenario) and (b) localized energy deposition within a representative radiation spur (spur scenario). Species not shown remain below 10^{-6} M throughout the simulation. Both panels share the same legend, displayed only in panel (b) for clarity. The grey shaded region indicates timescales beyond the experimental pump-probe window.

the dominant contribution to the picosecond SAXS signal, radiolysis chemistry is expected to become increasingly more important at longer timescales and may contribute to the later evolution of the structural dynamics.

Chapter 6

Hydrodynamic Modeling

The preceding chapters examined the observed low- Q dynamics at both SACLA and LCLS, demonstrating that they can be attributed to a linear hydrodynamic response of liquid water due to localized energy deposition. If this interpretation holds, then the resulting structural dynamics should be captured within a continuum framework based on the conservation equations of mass, momentum, and energy. This chapter pursues such an approach by solving the Navier–Stokes and energy equations in radial coordinates and demonstrates that the experimentally measured dynamics can indeed be reproduced using a hydrodynamic model. The computational setup is illustrated in Figure 6.1, which defines the pertinent geometry and numerical grid used throughout the simulations.

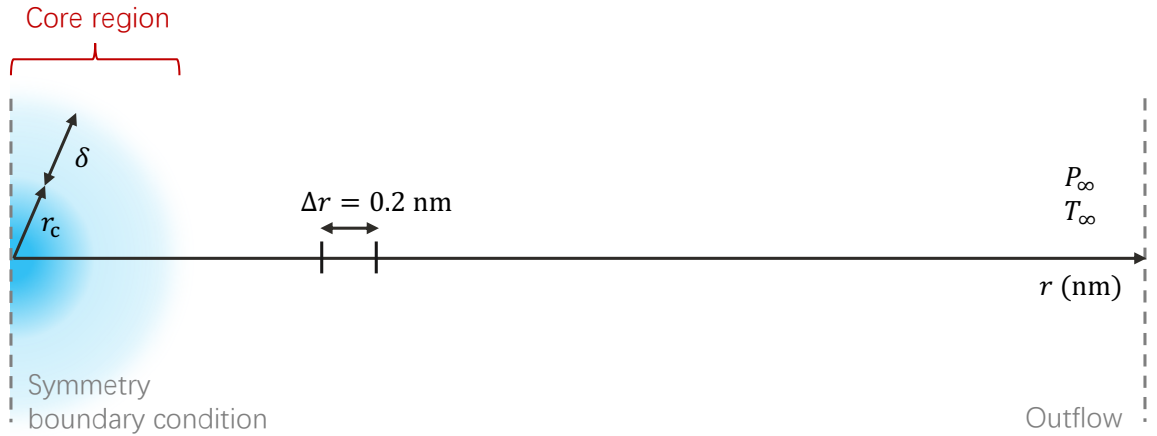


Figure 6.1: **Hydrodynamic model setup for the numerical simulations.** The governing equations are solved in radial coordinates on a numerical grid extending to $r_{\max} = 200$ nm with a spatial resolution of $\Delta r = 0.2$ nm. A symmetry boundary condition is applied at r_0 , taken to be $r_0 = 0.1$ nm to avoid division by zero, and an outflow boundary condition is imposed at $r = r_{\max}$. The core region is highlighted in blue and labeled in red.

6.1 Governing Equations

The response of liquid water to localized energy deposition is modeled using a spherically symmetric hydrodynamic framework. The adoption of a spherically symmetric continuum description is motivated by the results of Section 4.3, which demonstrated that the SAXS response remains azimuthally symmetric with no pronounced angular dependence, and by the radiation spur analysis presented in Chapter 5, which suggested that energy deposition occurs within localized, isotropic regions that remain sparsely distributed throughout the illumination volume. To this end, we solve the compressible Navier-Stokes equations in one spatial dimension (radial coordinate, r) together with energy conservation for a single-component fluid [143]:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho u) = 0, \quad (6.1)$$

$$\frac{\partial(\rho u)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2(\rho u^2 + p)) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \eta_L \frac{\partial u}{\partial r} \right) - \frac{4\mu}{r^2} u, \quad (6.2)$$

$$\frac{\partial(\rho E)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2(\rho E + p)u) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \eta_L u \frac{\partial u}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k \frac{\partial T}{\partial r} \right), \quad (6.3)$$

where ρ , u , p , and T denote the density, radial velocity, pressure, and temperature, respectively. Here, the quantity

$$E = e + \frac{u^2}{2} \quad (6.4)$$

is the specific total energy, where e is the specific internal energy, and the parameter

$$\eta_L = \frac{4}{3}\mu + \mu_b \quad (6.5)$$

is the longitudinal viscosity, composed of the shear viscosity, μ , and bulk viscosity, μ_b . In Equation (6.3), k denotes the thermal conductivity.

The system of equations is closed through a real-fluid equation of state based on the International Association for the Properties of Water and Steam (IAPWS) formulation for water [99], implemented via the open-source CoolProp library [144] in Python v3.10.2. The IAPWS formulation is chosen because it is widely regarded as the reference standard for liquid water and steam; it is based on a multi-parameter Helmholtz free energy equation of state that provides highly precise predictions of thermodynamic properties, through analytical derivatives, over a wide range of temperatures and pressures [145, 146].

In addition to the equation of state, transport properties are evaluated from corresponding IAPWS recommended correlations—the shear viscosity and thermal conductivity are both computed using the respective IAPWS formulation for water [128, 129]. These formulations are thermodynamically consistent with the underlying IAPWS-95 equation of state and ensure reliable calculation of the transport properties across the state space. The bulk viscosity is modeled separately using an

empirical temperature-dependent relation based on acoustic spectroscopy measurements [147]:

$$\mu_b = 2.47 \times 10^{-3} + 3.3 \times 10^{-6} \cdot \max(373.15 - T, 0). \quad (6.6)$$

At each time step, the thermodynamic state is determined from the density and internal energy, from which the pressure, temperature, viscosity, thermal conductivity, and other derived properties are obtained. As such, although the temperature is not evolved explicitly, it is recovered directly from the equation of state at each time step.

6.2 Numerical Implementation

The governing equations are solved numerically using a conservative finite-volume framework in spherically symmetric coordinates, with the evolved state vector being $\mathbf{U} = (\rho, \rho u, \rho E)$. As the structural dynamics are comprised of compressible density perturbations generated by localized energy deposition, a numerical scheme capable of resolving wave propagation in the presence of potentially steep gradients near the deposition region is required. Spatial fluxes are hence evaluated using MUSCL (Monotonic Upstream-centered Scheme for Conservation Laws) reconstruction [148], which achieves third-order accuracy in smooth regions through piecewise polynomial reconstruction of primitive variables. This is combined with an HLLC (Harten-Lax-van Leer-Contact) approximate Riemann solver [149], which provides a robust estimate of the intercell flux by resolving the characteristic wave structure of the Riemann problem. Unlike simpler approximate solvers, HLLC explicitly restores the contact wave, which is essential for accurately capturing density variations within the fluid [150].

To address the stiffness introduced by viscous and thermal diffusion processes, time integration is handled using first-order Lie–Trotter operator splitting [143], whereby each global time step is decomposed into inviscid, viscous, and thermal conduction sub-steps. The inviscid time advancement is performed using a third-order strong stability-preserving Runge-Kutta (SSP-RK3) scheme [151], with the time step determined adaptively from a Courant-Friedrichs-Lewy (CFL) condition based on the maximum local speed. The viscous and thermal diffusion terms are integrated using implicit backward-Euler discretizations [152] to ensure numerical stability at small grid spacing. Fundamentally, each implicit sub-step reduces to a tridiagonal linear system that is solved at every global time step. The splitting is formulated in conservative form, guaranteeing the discrete conservation of mass, momentum, and energy throughout the computational domain.

The computational domain extends to 200 nm with a uniform grid spacing of $\Delta r = 0.2$ nm, providing sufficient spatial extent and resolution to resolve the initial perturbation and its subsequent propagation, respectively. The domain size was selected based on the experimentally inferred propagation velocity of 1.77 nm/ps (Figure 4.18(b)). At this velocity, and assuming continuously linear propagation, the hydrodynamic wave would travel 177 nm over the maximum pump–probe delay of

100 ps. The chosen domain size thus allows the propagating wave to remain within the computational domain throughout the simulation without interacting with the outer boundary. A symmetry (reflective) boundary condition is imposed at the origin, while non-reflecting outflow conditions are applied at the outer boundary.

6.3 Initial Conditions

The hydrodynamic equations require specification of the initial thermodynamic state immediately following energy deposition. However, the precise microscopic state of a radiation spur is not known *a priori*. This is because ionization events [53] and radiation track structures [153] are inherently stochastic processes, leading to variations in the spatial distribution and magnitude of the deposited energy. Furthermore, mapping highly non-equilibrium excitation and ionization events that take place during the physical stage of radiolysis onto coarse-grained thermodynamic variables is generally not uniquely determined [154, 155]. As a result, hydrodynamic descriptions typically introduce a model for the initial energy density, temperature, or pressure field based on estimated spur dimensions and energy deposition characteristics [58, 131, 156–158]. Here, two distinct initial conditions were considered. In the first, energy deposition is represented as an isochoric temperature perturbation, corresponding to rapid local heating before significant volumetric expansion can occur. In the second, the deposited energy is modeled as an isothermal density perturbation, corresponding to an initially compressed fluid region.

For the isochoric case, the system of equations is initialized at ambient conditions (294.15 K, 1 bar) with a spatially uniform density ($\rho = 998 \text{ kg/m}^3$). A localized temperature increase of 1 K is then imposed within a spherical region of radius 1 nm, with a smooth transition to the surrounding liquid over 1 nm. The temperature perturbation is chosen to remain within the single-phase liquid regime of the equation of state while providing a representation of a localized thermal disturbance. Larger temperature increases, including those comparable to the experimentally inferred heating, can transiently enter the vapor dome under ambient pressure conditions and are therefore beyond the validity of the present single-species formulation. A larger temperature perturbation under elevated pressure conditions is examined in Section 6.6. This temperature distribution yields an overall effective radius of 2 nm, in line with the earliest experimentally observed length scale of 3.9 nm (i.e., a characteristic radius of 1.8 nm) at $\tau = 0.6 \text{ ps}$ (Figure 3.3(b)). The corresponding pressure profile is determined self-consistently from the equation of state, generating an initial pressure gradient that drives the subsequent hydrodynamic response. Mathematically, the temperature profile is given by a smooth tanh function:

$$T(r) = T_\infty + \frac{\Delta T}{2} \left(1 - \tanh \left(\frac{r - r_c}{\delta} \right) \right), \quad (6.7)$$

where $T_\infty = 294.15 \text{ K}$ is the ambient temperature, $\Delta T = 1 \text{ K}$ is the temperature increase, $r_c = 1 \text{ nm}$ is the core radius, and $\delta = 1 \text{ nm}$ defines the transition width (interfacial thickness).

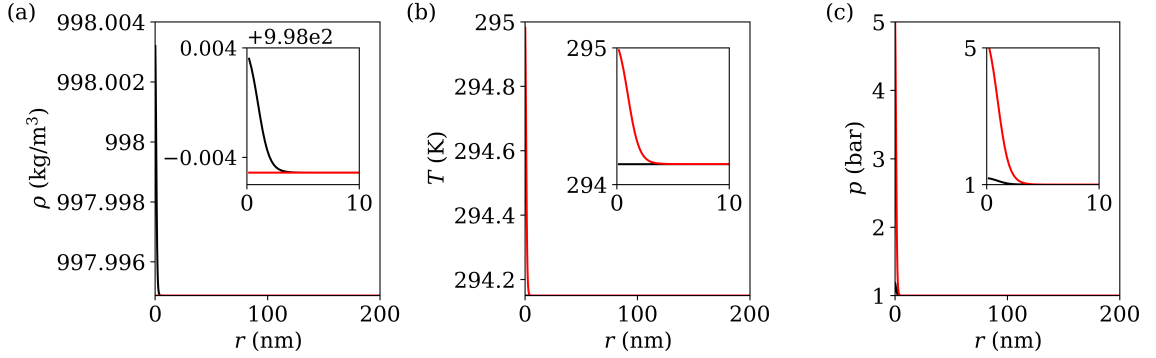


Figure 6.2: **Initial conditions for the hydrodynamic model.** Spatial profiles of (a) density, (b) temperature, and (c) pressure for the isochoric (red) and isothermal (black) initial conditions. Insets show a zoomed-in view near the core radius region.

For the isothermal case, the system of equations is initialized analogously, except that a localized density increase of 0.01 kg/m^3 is prescribed within the core region instead of a temperature increase. The magnitude of this perturbation is selected as a small numerical perturbation to remain within the stable liquid regime of the equation of state. The resulting pressure profile is again obtained self-consistently from the equation of state and an initial pressure gradient likewise drives the dynamics. The density profile is given by:

$$\rho(r) = \rho_{\infty} + \frac{\Delta\rho}{2} \left(1 - \tanh \left(\frac{r - r_c}{\delta} \right) \right), \quad (6.8)$$

where $\rho_{\infty} = 998 \text{ kg/m}^3$ is the ambient density, $\Delta\rho = 0.01 \text{ kg/m}^3$ is the density increase, and r_c and δ are identical to those defined in Equation (6.7). It is worth emphasizing that, in both cases, the isochoric and isothermal assumptions are only utilized to construct the initial conditions; the numerical solution does not enforce $\rho = \text{const.}$ or $T = \text{const.}$ for either case.

Figure 6.2 highlights the initial conditions for both scenarios. A parametric study investigating additional parameters, such as the magnitude of the temperature jump, core radius, and transition width is presented in Section 6.5.1.

6.4 Calculation of the Scattering Signal

The model yields the time-dependent radial density field, $\rho(r, \tau)$, which is used to compute the corresponding scattering signal for direct comparison with the experimentally measured SAXS response, $\Delta\tilde{S}(Q, \tau, E_{tot})$, at a given pulse energy. Assuming isotropic density fluctuations, the scattering

amplitude is obtained from the spherical Fourier transform of the density perturbation:

$$\Delta\rho(r, \tau) = \rho(r, \tau) - \rho_\infty, \quad (6.9)$$

where ρ_∞ is the equilibrium bulk density (approximated numerically by the far-field value at the outer boundary of the simulation domain). The scattering amplitude is then computed as:

$$A(Q, \tau) = \frac{4\pi N_A}{M} \int_0^{r_\infty} r^2 \Delta\rho(r, \tau) \frac{\sin(Qr)}{Qr} dr, \quad (6.10)$$

where the kernel $\sin(Qr)/(Qr)$ corresponds to the spherical Bessel function $j_0(Qr)$. The integration in Equation (6.10) is performed numerically using the trapezoidal rule with $r_\infty = 200$ nm being the spatial extent of the computational domain. Finally, the scattering intensity is calculated:

$$\Delta\tilde{S}(Q, \tau)_{\text{sim}} = |A(Q, \tau)|^2. \quad (6.11)$$

Physically, the expression in Equation (6.11) corresponds to the scattering intensity from a single scatterer with spherical symmetry [84].

6.5 Ambient Water Jet Results

The governing equations are solved for both initial conditions over a radial domain extending from 0.1 to 200 nm with a uniform grid spacing of 0.2 nm. The simulations were propagated to 100 ps, and the density, temperature, pressure, and radial velocity fields were recorded at regular time intervals of 1 ps. The corresponding scattering intensity was then calculated from the simulated density field using the procedure outlined in Section 6.4. The resulting SAXS signals are compared with the experimental response measured for the water jet at 20°C in Figure 6.3.

As shown, the isochoric temperature perturbation (Figure 6.3(b)) reproduces the main experimental features significantly more accurately than the isothermal density perturbation (Figure 6.3(a)). In particular, the isochoric model captures the development of the initially broad low- Q feature, its subsequent evolution toward lower Q , the emergence of multiple peaks at later pump-probe delays, and their eventual decay for $\tau \approx 100$ ps. Meanwhile, the isothermal model predicts the formation of several strong oscillating features that persist well beyond 100 ps.

These results are consistent with the experimentally determined reduced pair distribution function (Figure 4.10), which exhibited an approximately symmetric negative-positive response characteristic of a uniform density distribution rather than a compressed density perturbation. Moreover, previous ultrafast studies [8, 131, 159] have shown that energy deposition occurs on timescales substantially shorter than those required for large-scale density redistribution. As such, the picosecond response of the liquid is expected to be isochoric. The agreement between the experimental signal

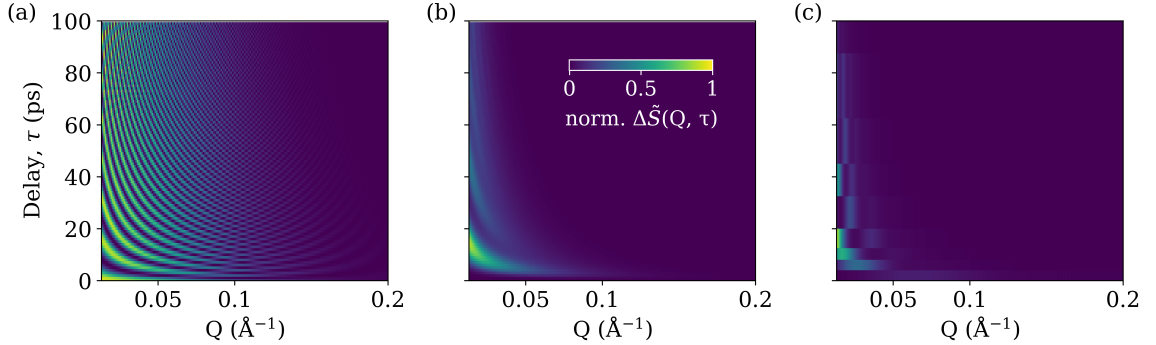


Figure 6.3: **Results from the hydrodynamic model for different initial conditions.** Contour map of the SAXS signal for (a) isothermal and (b) isochoric initial conditions. (c) Experimentally measured SAXS signal from the liquid water jet at 20°C for $E_{tot} = 6 \mu\text{J}$. All datasets are normalized by their respective global maxima to facilitate comparison and are displayed using a shared color bar corresponding to panel (b).

(Figure 6.3(c)) and the isochoric model further validates this assumption and provides additional support for this interpretation. For the remainder of this chapter, the isochoric initial condition is adopted for all subsequent simulations.

6.5.1 Parametric Study

Having established the appropriate initial condition, we next investigate the sensitivity of the model to the remaining assumed parameters, beginning with the size of the core region, r_c , which sets the characteristic length scale of the perturbation. We also consider variations in the transition width, δ , which controls the smoothness of the initial gradients, and the magnitude of the isochoric heating, represented by the temperature jump, ΔT . Each parameter is varied independently to assess its influence on the resulting hydrodynamic response and the corresponding scattering signal. To better isolate the impact of each parameter, we analyze the simulated SAXS intensity, $\Delta\tilde{S}(Q, \tau)$, at representative pump-probe delays of 2, 15, and 40 ps using one-dimensional line plots in momentum-transfer space. These time delays denote the early, intermediate, and late stages of the hydrodynamic evolution, respectively. All simulations are performed using the uniform density initial condition with $\rho_\infty = 998 \text{ kg/m}^3$.

Figure 6.4 shows the simulated SAXS response for different core radii, $r_c = 0.5, 1, 2$, and 3 nm at the selected time delays for fixed values of $\delta = 1 \text{ nm}$ and $\Delta T = 1 \text{ K}$. Ambient conditions (294.15 K, 1 bar) are used otherwise. As evident, the primary effect of increasing r_c is a systematic shift of the early-time ($\tau = 2 \text{ ps}$, Figure 6.4(a)) SAXS peak toward lower momentum transfer. Since larger real-space structures correspond to smaller reciprocal-space vectors ($Q \propto 1/L$), this behavior is consistent with larger core radii producing narrower features whose peak positions occur at lower Q .

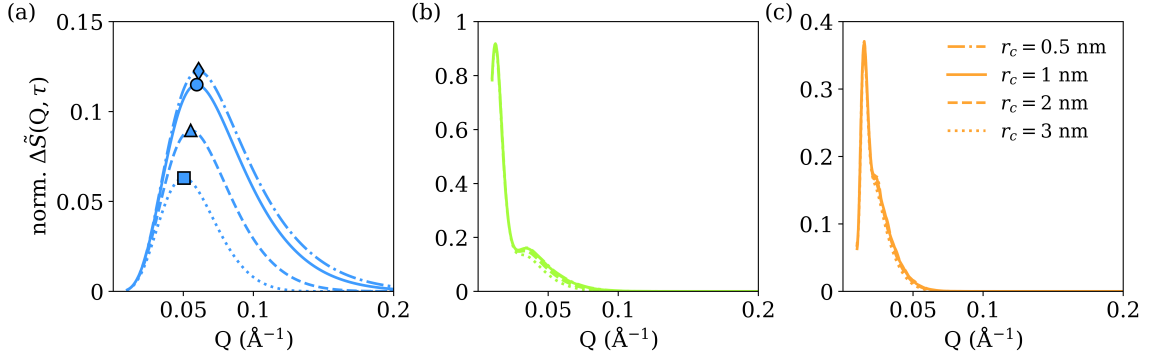


Figure 6.4: **Results from the hydrodynamic model for different core radii.** Line plots of the normalized SAXS intensity for (a) 2 ps, (b) 15 ps, and (c) 40 ps. Peak locations are highlighted by markers, and different line styles correspond to each core radius: dash-dotted lines ($r_c = 0.5$ nm), solid lines ($r_c = 1$ nm), dashed lines ($r_c = 2$ nm), and dotted lines ($r_c = 3$ nm). All datasets are normalized by their respective global maxima to facilitate comparison. The color scheme is consistent with that used in Figure 4.7.

Notably, while the early-time response is strongly dependent on the assumed core size, the subsequent hydrodynamic evolution remains qualitatively similar at later time delays (Figures 6.4(b) and 6.4(c) at 15 and 40 ps, respectively), indicating that r_c primarily sets the initial spatial scale of the energy deposition site rather than the underlying propagation dynamics. Comparison with the experimental SAXS signal (Figure 4.7), which displays a pronounced peak at $Q = 0.064 \text{ \AA}^{-1}$ for $\tau = 2$ ps, points to core radii in the range of $r_c = 0.5\text{--}1$ nm as providing the closest agreement; the simulated peak positions are at $0.061 \text{ \AA}^{-1}$ for $r_c = 0.5$ nm and $0.06 \text{ \AA}^{-1}$ for $r_c = 1$ nm, whereas larger values of $r_c = 2$ and 3 nm yield peaks at $Q = 0.056 \text{ \AA}^{-1}$ and $Q = 0.05 \text{ \AA}^{-1}$, respectively. As the difference between $r_c = 0.5$ and $r_c = 1$ nm is minimal in terms of the resulting peak position, the choice is instead guided by numerical considerations: the $r_c = 1$ nm case provides improved spatial resolution of the initial perturbation on the computational grid, with four grid points spanning the core region compared to only two for $r_c = 0.5$ nm. Therefore, it is chosen as the reference case.

With $r_c = 1$ nm and $\Delta T = 1$ K, the transition width was varied over the range $\delta = 0.5\text{--}3$ nm. Figure 6.5 shows the simulated SAXS response at the same selected time delays. Similar to increasing the core radius, increasing δ shifts the 2 ps (Figure 6.5(a)) scattering peak toward lower momentum transfer, from $Q = 0.066 \text{ \AA}^{-1}$ at $\delta = 0.5$ nm to $Q = 0.039 \text{ \AA}^{-1}$ at $\delta = 3$ nm, as larger values of δ increase the effective spatial extent of the initial perturbation. In addition, δ appears to strongly influence the width of the scattering profile, with smaller values giving broader SAXS features that extend to higher Q , whereas larger values yield narrower distributions. This behavior arises because a sharper interfacial transition spans shorter characteristic length scales and therefore larger reciprocal-space components.

In contrast to increasing r_c , increasing δ also impacts the dynamics at later times (Figures 6.5(b)

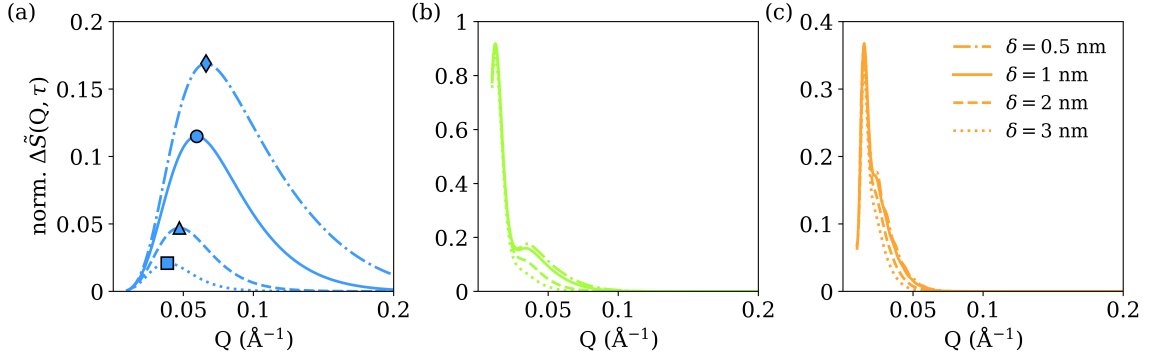


Figure 6.5: **Results from the hydrodynamic model for different transition widths.** Line plots of the normalized SAXS intensity for (a) 2 ps, (b) 15 ps, and (c) 40 ps. Line styles denote each case: dash-dotted lines ($\delta = 0.5$ nm), solid lines ($\delta = 1$ nm), dashed lines ($\delta = 2$ nm), and dotted lines ($\delta = 3$ nm). All other conventions follow Figure 6.4.

and (c)), with smaller transition widths producing more pronounced oscillatory features and larger values of δ leading to a more rapidly damped response. Physically, this reflects the dependence of the hydrodynamic driving force on the initial pressure gradient, which becomes stronger as the transition region becomes steeper. Comparison with the experimental SAXS signal at $\tau = 2$ ps (Figure 4.7) reveals that $\delta = 1$ nm provides the best overall agreement, reproducing the observed decay of the scattering intensity by $Q = 0.2 \text{ \AA}^{-1}$ and the peak position reasonably well. As a result, this value is adopted for subsequent simulations. Together, the selected values of $r_c = 1$ nm and $\delta = 1$ nm indicate that the deposited energy is distributed over a finite interfacial region, confined within a highly localized volume that is consistent with the expected dimensions of radiation spurs.

Lastly, the magnitude of the initial temperature increase in the core region was set to $\Delta T = 0.5$, 1, and 2 K, while holding $r_c = 1$ nm and $\delta = 1$ nm constant. The normalized SAXS response is presented in Figure 6.6(a), where we note that all curves collapse onto one another at each time delay. This demonstrates that the underlying hydrodynamic evolution is independent of the magnitude of the initial temperature perturbation. In other words, varying ΔT does not alter the characteristic length scales of the scattering response, the position of the SAXS peaks, or the overall shape of the reciprocal-space features. Such behavior is well-aligned with the linear hydrodynamic regime, in which the dynamics evolve self-similarly irrespective of the driving force.

The impact of ΔT becomes apparent when the normalization is removed (Figure 6.6(b)). Under this condition, the scattering intensity amplifies systematically with increasing temperature in the core region. Quantitatively, doubling ΔT from 0.5 to 1 K produces an approximately fourfold increase in the peak SAXS intensity, while a further doubling from 1 to 2 K yields another fourfold increase. The scattering signal therefore follows $\Delta \tilde{S}(Q, \tau) \propto (\Delta T)^2$. Since the simulated SAXS

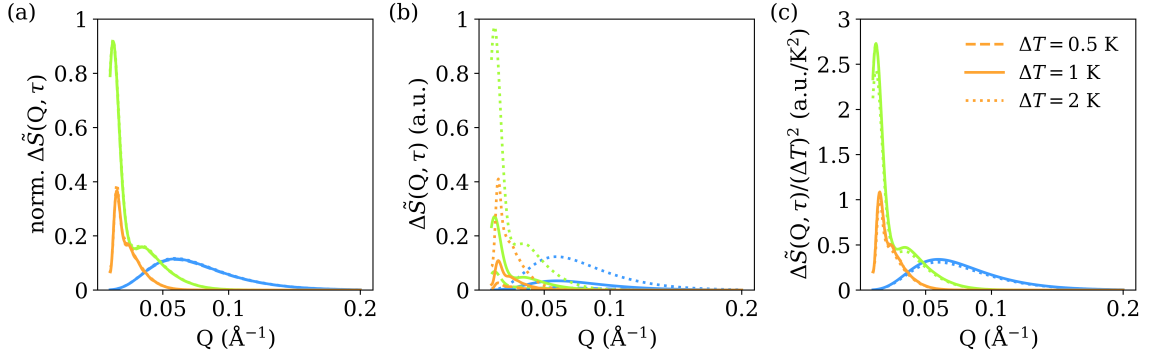


Figure 6.6: **Results from the hydrodynamic model for different temperature increases.** Line plots of the normalized SAXS intensity for (a) 2 ps, (b) 15 ps, and (c) 40 ps. Line styles denote each case: dashed lines ($\Delta T = 0.5$ K), solid lines ($\Delta T = 1$ K), and dotted lines ($\Delta T = 2$ K). All other conventions follow Figure 6.4.

intensity is proportional to the square of the density perturbation through a combination of Equations (6.10) and (6.11), this scaling implies that $\Delta\rho \propto \Delta T$. As a result, the hydrodynamic response remains linear across the range of temperature perturbations investigated.

This is further validated in Figure 6.6(c), which shows the one-dimensional scattering profiles normalized by $(\Delta T)^2$. As illustrated, the curves collapse onto one another to a large extent. Importantly, this behavior replicates the experimentally observed pulse-energy dependence (Figure 4.9), where the SAXS peak intensity exhibited quadratic scaling with the total pulse energy, reflecting a bi-linear dependence on the pump and probe pulse energies. The present simulations thus provide a physical basis for this observation by establishing that increased energy deposition generates proportionally larger density perturbations, which in turn produce a quadratic increase in the SAXS intensity through the relationship $\Delta\tilde{S}(Q, \tau) \propto |\Delta\rho|^2$.

6.6 Heated Water Jet and High-Pressure Results

The parametric study elucidated that the simulated SAXS response is predominantly controlled by the spatial extent of the initial perturbation region, yielding optimal agreement with the experimental data for $r_c = 1$ nm and $\delta = 1$ nm. However, variations in the initial temperature increase, ΔT , affected only the magnitude of the scattering intensity while leaving the spatiotemporal dynamics unchanged. As a result, unlike r_c and δ , the value of ΔT could not be directly constrained through comparison with the experimental SAXS signal, since the detector records the scattering intensity in arbitrary units and a one-to-one conversion between the measured and simulated amplitudes is not available. Yet, it is still imperative to establish a physically realistic estimate of the local temperature rise expected within the core region and determine whether the hydrodynamic response is robust

under experimentally relevant energy deposition conditions.

6.6.1 Estimating the Local Temperature Rise

An estimate of the local temperature rise can be obtained by considering the energy deposited during a single secondary ionization event induced by the photoelectron upon photoelectric absorption. As previously discussed, the photoelectron is emitted with 9.42 keV excess energy and loses its energy through repeated inelastic collisions approximately 26 nm apart (Chapter 5). The ionization cross-section for electrons in liquid water is largest below 100 eV [140], and Monte Carlo simulations suggest that the average energy deposited per ionization event is 60 eV [133]. Assuming that this energy is deposited within a region spanning 2 nm, consistent with both the experimentally observed length scale and the characteristic size identified in the parametric study (Section 6.5.1), the resulting local temperature increase can be estimated using:

$$E = mc_p \Delta T, \quad (6.12)$$

where $m = \rho V$ is the mass of water contained within the deposition volume, V , and c_p is the specific heat capacity of liquid water. Modeling the deposition volume as a sphere, motivated by the isotropic distribution of the low-energy secondary electrons [134] and in line with the two-dimensional isotropic scattering patterns observed experimentally (Figure 4.6), $V = 4\pi r_{\text{eff}}^3/3$ with $r_{\text{eff}} = r_c + \delta$. At 20°C [99], the specific heat capacity is $c_p = 4.184 \text{ kJ}/(\text{kg}\cdot\text{K})$. Substituting these values leads to an estimated local temperature rise of $\sim 69 \text{ K}$. Note that this value represents the transient temperature rise surrounding an individual ionization event and should not be directly compared with the experimentally inferred WAXS temperature increase, which corresponds to a spatial average over the entire illuminated volume; the smaller average temperature rise observed by WAXS arises from the limited fraction of the probed volume, estimated in Table 5.1, that undergoes such localized energy deposition events.

This local temperature estimate should be interpreted as an upper bound, as it assumes complete localization of the deposited energy within the effective core volume and rapid thermalization of the secondary electrons with the surrounding liquid. Although electron thermalization is expected to occur on sub-picosecond timescales [36, 37, 73], the deposited energy may initially be partitioned into non-thermal degrees of freedom, including transient electronic excitation, chemical rearrangement, and changes in the local hydrogen-bond network, before being converted into thermal energy. Furthermore, the ultrafast energy deposition occurs under effectively isochoric conditions, where transient pressure changes can modify the local thermodynamic response. The probabilistic nature of ionization events and the spatial distribution of secondary electron trajectories will also inevitably spread a fraction of the deposited energy beyond the assumed volume. Consequently, the actual local temperature rise may be somewhat lower than the value estimated above.

6.6.2 Universality of the Hydrodynamic Response

To test the generalizability of the simulated hydrodynamic response and to further assess the predictive capability of the model in reproducing the experimentally measured dynamics at elevated temperature and pressure, additional simulations were performed across thermodynamic conditions relevant to both the flow-cell and jet experiments. Specifically, three sets of cases are considered:

1. a pressure series for the SACLA cell configuration with $T_\infty = 303.15$ K (30°C), consisting of $P_\infty = 50$ and 150 bar;
2. a lower-pressure reference condition corresponding to the LCLS cell configuration at $T_\infty = 295.15$ K (22°C) and $P_\infty = 2$ bar; and
3. a heated jet condition at $T_\infty = 353.15$ K (80°C) and $P_\infty = 5$ bar.

All cases are simulated using a fixed initial temperature increase of $\Delta T = 1$ K, $r_c = 1$ nm, and $\delta = 1$ nm. While the experimental heated jet measurement was conducted at atmospheric pressure (case 3), simulations at this state are not thermodynamically stable within the present single-phase hydrodynamic framework. This is due to the combination of elevated ambient temperature and transient rarefaction following energy deposition, which drives the local thermodynamic state into the liquid-vapor coexistence region of the equation of state where the model is not applicable. To ensure thermodynamic consistency, the ambient pressure for this case is increased slightly to 5 bar. Note that this adjustment is not a fitting parameter, but a constraint required to maintain single-phase validity of the equation of state—as will be shown, it does not affect the observed hydrodynamic response.

In addition, to probe the response of the system under the maximum plausible energy deposition, an upper-bound scenario is considered for the high-pressure case ($P_\infty = 150$ bar), in which the initial temperature perturbation is increased to $\Delta T = 69$ K in the core region. This case acts as a physically motivated limit for the hydrodynamic response while remaining within the single-phase regime of the equation of state.

Figures 6.7(a)–(c) illustrate the simulated SAXS response calculated with the hydrodynamic model under the thermodynamic conditions corresponding to the pressure-cell measurements. In all three cases, the model reproduces the principal experimental features, starting from the development of the broad low- Q feature at sub-picosecond timescales, its evolution toward lower momentum transfer, to its eventual decay at longer time delays. Moreover, the secondary peak is clearly resolved in all simulations, whereas the higher-order peaks remain comparatively weak. Overall, the simulated dynamics are remarkably similar across the investigated pressure range, highlighting that the hydrodynamic response is largely insensitive to pressure under the experimentally explored conditions. This observation is fully consistent with the experimental results presented in Chapter 3, where the SAXS dynamics exhibited nearly identical spatiotemporal evolution despite a threefold increase in pressure from 50 to 150 bar.

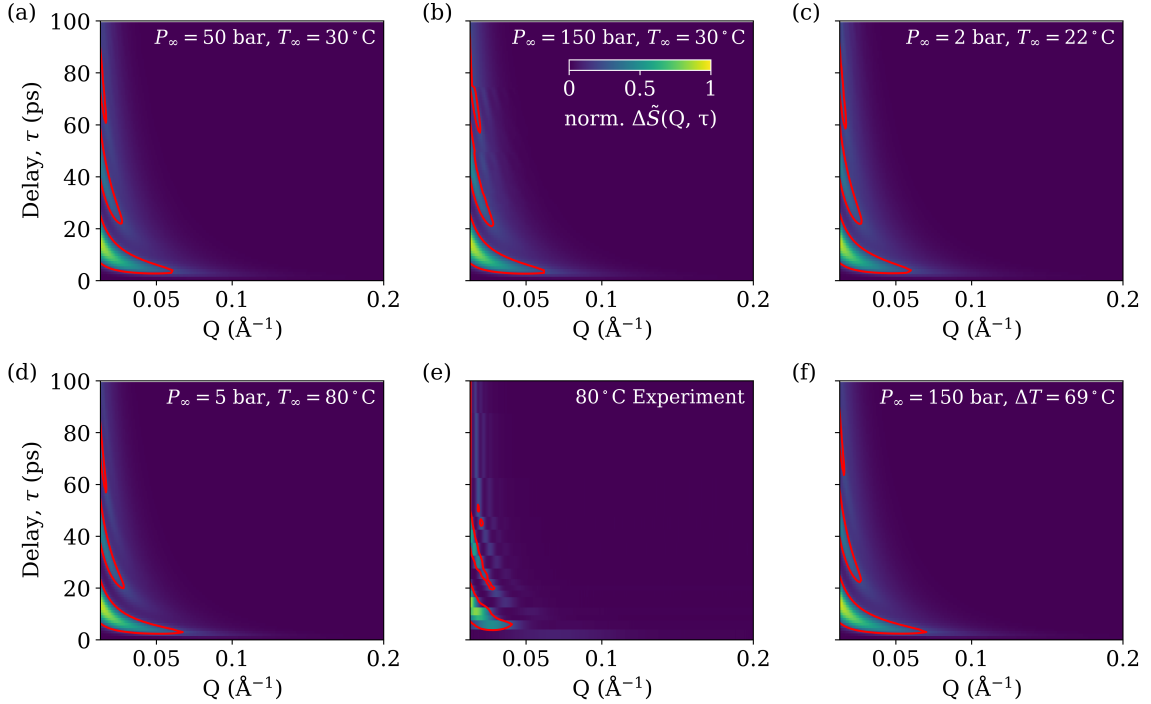


Figure 6.7: **Results from the hydrodynamic model across a wide range of thermodynamic conditions.** Contour maps of the simulated SAXS response with $r_c = 1$ nm and $\delta = 1$ nm at (a) $P_\infty = 50$ bar and $T_\infty = 30^\circ\text{C}$, (b) $P_\infty = 150$ bar and $T_\infty = 30^\circ\text{C}$, (c) $P_\infty = 2$ bar and $T_\infty = 22^\circ\text{C}$, and (d) $P_\infty = 5$ bar and $T_\infty = 80^\circ\text{C}$, all computed with $\Delta T = 1$ K. Panel (e) shows the corresponding experimental SAXS response for the heated jet measurement at 80°C and a total pulse energy of $6 \mu\text{J}$. Panel (f) presents the upper-bound simulation for $P_\infty = 150$ bar with $\Delta T = 69$ K and $T_\infty = 30^\circ\text{C}$. All datasets are normalized by their respective global maxima to facilitate comparison and are displayed using a shared color bar in panel (b). Red lines denote positive contour levels at 0.22, representing the evolution of the SAXS peaks.

Figure 6.7(d) shows the simulated SAXS response for the heated water jet condition, alongside the experimental counterpart in Figure 6.7(e). In contrast to the ambient temperature cases, both the simulation and the experiment display marginally more prominent higher-order oscillatory features, including apparent tertiary and quaternary peaks. As a result, the model successfully captures not only the evolution of the main low- Q peak, but also the sustained appearance of the higher-order oscillations at elevated temperature. This finding is particularly noteworthy because these additional features are only weakly developed under ambient temperature, yet emerge naturally in both the measured and the simulated elevated temperature cases.

From a physical perspective, increasing the ambient temperature modifies several thermophysical properties of water that enter the governing equations. Among those, the most significant change is

the reduction in viscosity, which decreases by roughly a factor of two between 20°C and 80°C. Reduced viscous dissipation, in turn, is expected to weaken the damping of the compression–rarefaction cycles generated by the initial perturbation, seen in Figures 4.10 and 4.18, allowing higher-order oscillations to persist for longer times. The agreement between the simulated and experimental SAXS response therefore lends support to the interpretation that viscous damping plays a dominant role in controlling the visibility and lifetime of the oscillatory features.

Finally, Figure 6.7(f) presents the simulated SAXS response for the upper-bound energy deposition scenario corresponding to $\Delta T = 69$ K at $P_\infty = 150$ bar. Despite the substantially larger temperature increase, the resulting dynamics remain qualitatively indistinguishable from those observed in the lower temperature rise simulations ($\Delta T = 0.5$ –2 K, Figure 6.6). The characteristic low- Q feature develops on the same timescale, evolves toward lower momentum transfer in a similar manner, and exhibits the same sequence of oscillatory peaks and decay. While not directly visible in normalized plots such as those in Figure 6.7, the chief difference lies in an overall increase in scattering magnitude, in accordance with the quadratic scaling discussed herein. This result demonstrates that the hydrodynamic response remains within the same dynamical regime even when the deposited energy approaches the maximum estimate derived from a single secondary ionization event. Furthermore, the fact that the SAXS behavior is similar over nearly two orders of magnitude in temperature rise indicates that the response is governed by hydrodynamic transport rather than the precise magnitude of the initial energy deposition.

6.6.3 Hydrodynamic Origin of the Oscillatory SAXS Features

The results presented thus far have established excellent qualitative agreement between the hydrodynamic model and the experimentally measured SAXS response over a wide range of thermodynamic and initial conditions. However, the model also enables access to parameters that cannot be measured directly, thereby offering additional insight into the physical origin of the observed scattering dynamics. In particular, one important observation from the analysis performed in Chapter 4 was the appearance of multiple peaks in the SAXS signal, which were hypothesized to originate from the development of successive compression–rarefaction cycles in the reduced pair distribution function. Yet, the reduced pair distribution function offers only an indirect representation of the underlying density field. In contrast, the hydrodynamic model explicitly solves for the time-dependent density profile, allowing this hypothesis to be tested directly.

To investigate this behavior, Figure 6.8 displays the simulated density profiles at $\tau = 2, 15$, and 40 ps in panels (a)–(c), respectively, for the upper-bound scenario of $P_\infty = 150$ bar and $\Delta T = 69$ K (Figure 6.7(f)). The corresponding scattering intensities are shown in panels (d)–(f). The remaining thermodynamic conditions evolve similarly and are therefore omitted for clarity. Several observations can be made regarding the results. First, the simulated density profiles possess no residual structure downstream of the leading compression front. This confirms that the downstream features observed

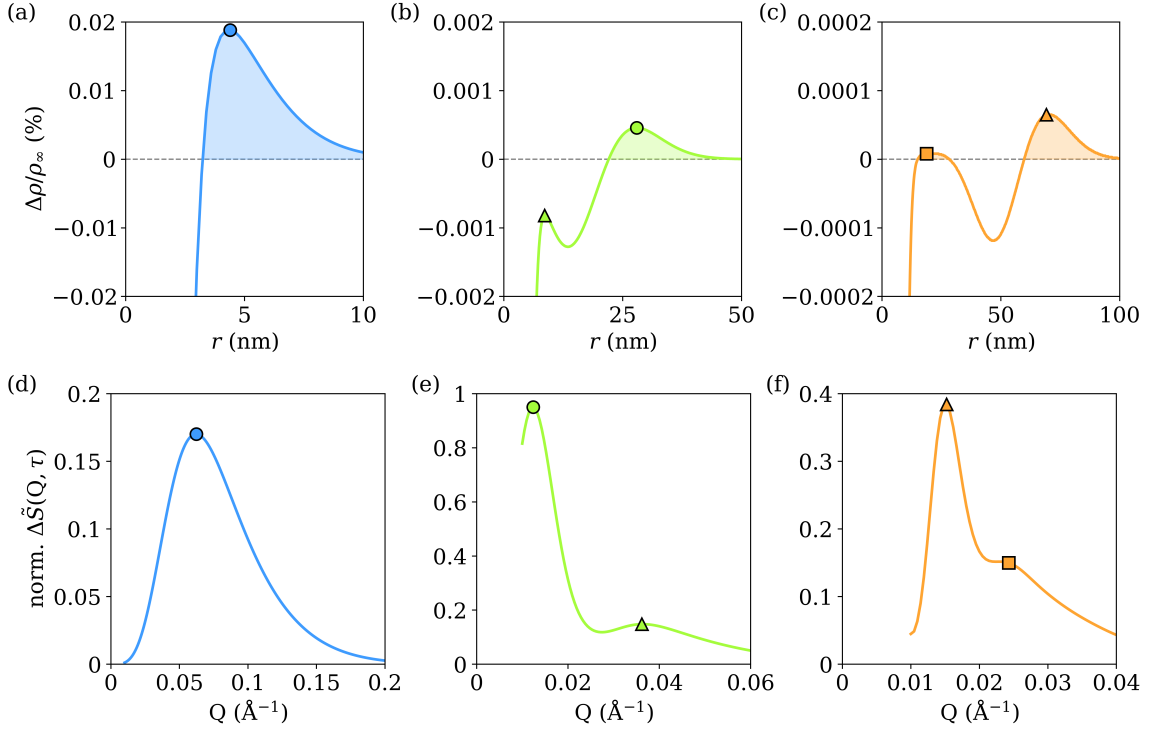


Figure 6.8: **Representative density and SAXS profiles from the hydrodynamic model.** Normalized change in density at (a) 2 ps, (b) 15 ps, and (c) 40 ps, shown for the upper-bound scenario corresponding to $P_\infty = 150$ bar, $T_\infty = 30^\circ\text{C}$, $\Delta T = 69$ K, $r_c = 1$ nm, and $\delta = 1$ nm. Markers denote the positions of the primary, secondary, and tertiary density maxima. The resulting SAXS response at the same time delays is presented in panels (d), (e), and (f), respectively, with peak positions indicated consistently in reciprocal space.

in the experimental RPDF (Figures 4.10 and 4.18) are artifacts of the inverse Fourier transform procedure, which involved mirroring the reciprocal-space coordinate and incorporated experimental noise, rather than signatures of a physical density perturbation.

Second, the simulations provide direct confirmation that the oscillatory SAXS features arise from successive compression–rarefaction cycles in the underlying density field. At early times, the density perturbation consists of a single localized compression front, producing one low- Q scattering peak (Figures 6.8(a) and (d)). As the hydrodynamic wave evolves, additional oscillations begin to develop in the density profile, giving rise to the secondary and tertiary peaks observed in the SAXS response (Figures 6.8(b,c) and (e,f)). In fact, the peak locations in reciprocal-space are consistent with Fourier reciprocity, namely the relation $Q = 2\pi/L$, where $L = 2r$ and r corresponds to the location of the compressive density peak.

Third, the density perturbation dissipates and disperses as it propagates through the liquid. This spatial spreading of the compressive wavefront is responsible for the narrowing of the scattering peaks

in momentum space, as it reflects the inverse relationship between characteristic length scales in real- and reciprocal-space. Conversely, the highly localized perturbation present at early times yields the broad scattering peak observed at $\tau = 2$ ps. This evolution illustrates how the propagation and dispersion of the density wave control the time-dependent SAXS curves.

As a further extension, the numerical model can be evaluated at Q -values below the experimental detection limit ($Q < 0.01 \text{ \AA}^{-1}$). Doing so reveals additional oscillatory features associated with longer-wavelength components of the density wave. In turn, these represent a continuation of the same compression–rarefaction dynamics, and no qualitative change in the hydrodynamic evolution is noted.

The analysis of the model is not limited to the scattering intensity, and a more systematic comparison with the experiments can be obtained by tracking the peak position of the leading compressive wavefront. In the SACLA jet experiments, this tracking was limited to ~ 25 ps, beyond which the signal crossed the real-space resolution limit of 49.3 nm imposed by the minimum accessible momentum transfer ($Q_{min,jet}$). The simulations, however, allow the wavefront to be followed over significantly larger spatial and temporal domains, extending to the full 100 ps simulation window and up to the maximum spatial extent of the computational domain (200 nm); this enables a complete characterization of the wave propagation dynamics throughout the experimentally measured time window.

Figure 6.9 shows the resulting peak trajectories for all simulated conditions (14 cases) presented in this chapter. Remarkably, all datasets collapse onto a single linear band, indicating a universal propagation law that is independent of pressure, temperature, and the magnitude and size of the initial perturbation. The experimental data for the heated water jet (Section 4.8) is also overlaid for completeness and lies directly on the same trend. Together with the previously established agreement between ambient and heated jet measurements (Figure 4.18(b)), this demonstrates that the model reproduces the experimentally observed propagation dynamics with high accuracy across all investigated conditions, both qualitatively and quantitatively. A linear fit to the simulated baseline case ($P_\infty = 1$ bar, $T_\infty = 294.15$ K, $\Delta T = 1$ K, $r_c = 1$ nm, and $\delta = 1$ nm) over the same experimentally accessible time window (0–25 ps) yields a propagation velocity of $1,719 \pm 12$ m/s, which is within 5% of the experimentally extracted values (Figure 4.18(b)). This alignment confirms that the hydrodynamic model encapsulates the dominant features of the observed dynamics within the single-phase, single-species framework. It also further verifies that the system remains within the linear hydrodynamic regime over the explored parameter space.

While the velocity extracted from the linear fits appears to exceed the thermodynamic speed of sound, this should not be interpreted as evidence for genuinely supersonic propagation. Rather, the experimentally extracted velocity corresponds to the motion of a fitted density maximum over a finite spatial and temporal observation window, which is not necessarily identical to the underlying acoustic wavefront velocity. Several factors may contribute to this distinction, including geometric

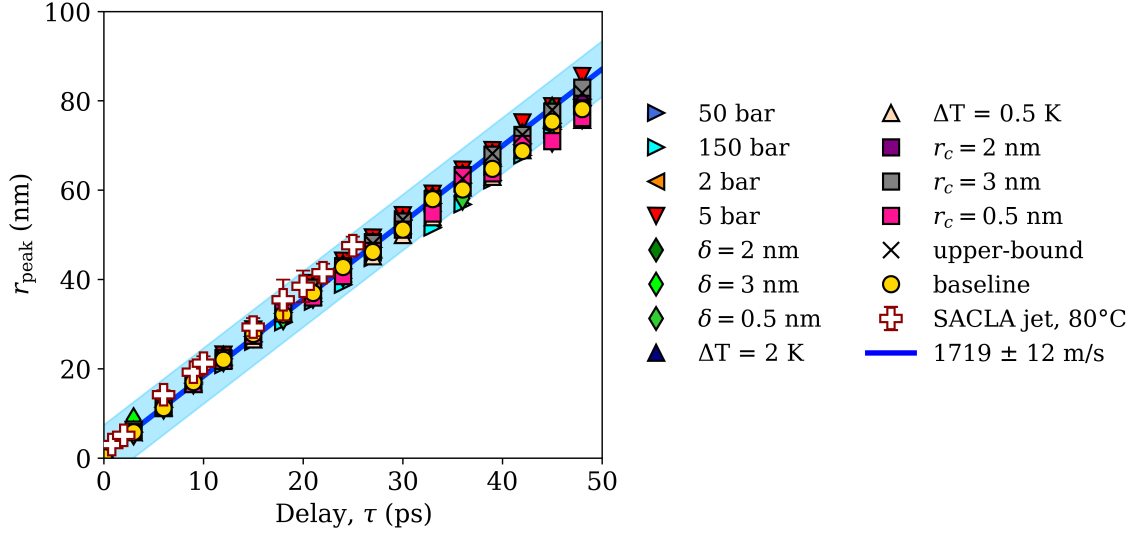


Figure 6.9: **Overlaid peak positions from the hydrodynamic model.** Position of the compressive density wavefront as a function of time for all simulation cases. Each case is denoted by a distinct marker and color, as indicated in the legend on the right. The experimentally extracted peak positions from the change in the reduced pair distribution function for the heated water jet are also included for comparison, where the error bars indicate the uncertainty in the extracted peak position. The solid line shows a linear fit to the baseline case (gold circles) over the time window 0–25 ps. The shaded region represents the standard deviation of the fit residuals.

spreading of the wave, finite pulse width, viscous and thermal attenuation, possible dispersive effects, and the limited fitting window used to determine the propagation speed. The following analysis therefore serves only as an illustrative demonstration that even an idealized spherical acoustic pulse naturally exhibits an apparent peak velocity that exceeds the asymptotic sound speed at early times.

To illustrate the apparent geometric origin of this discrepancy, consider the idealized solution of the spherical wave equation:

$$\phi(r, \tau) = \frac{f(r - c\tau)}{r}, \quad (6.13)$$

where ϕ is a generic wave variable taken here to represent the density perturbation $\Delta\rho$, c is the sound speed, and f describes the shape of the propagating pulse.

The peak position is obtained by taking the partial derivative of $\phi(r, \tau)$ with respect to the radius:

$$\left(\frac{\partial\phi}{\partial r}\right)_\tau = \frac{f'(r - c\tau)r - f(r - c\tau)}{r^2}, \quad (6.14)$$

and setting it zero, $\partial\phi/\partial r = 0$, which yields:

$$f'(r - c\tau) = \frac{f(r - c\tau)}{r}. \quad (6.15)$$

Assuming an idealized Gaussian pulse profile, f and f' can be written as:

$$f(r - c\tau) = \exp\left(-\frac{(r - c\tau)^2}{2\sigma^2}\right), \quad (6.16)$$

$$f'(r - c\tau) = -\frac{r - c\tau}{\sigma^2} f(r - c\tau), \quad (6.17)$$

where σ is the pulse width. Substituting Equations (6.16) and (6.17) into Equation (6.15) gives:

$$c\tau - r_{\text{peak}} = \frac{\sigma^2}{r_{\text{peak}}}, \quad (6.18)$$

where r_{peak} denotes the location of the $\Delta\rho$ maximum.

Differentiating Equation (6.18) with respect to time leads to the propagation velocity, v_{peak} :

$$v_{\text{peak}} = \frac{dr_{\text{peak}}}{d\tau} = \frac{c}{1 - \sigma^2/r_{\text{peak}}^2}. \quad (6.19)$$

For $r_{\text{peak}} \gg \sigma$, a Taylor expansion retaining only the first-order term gives:

$$v_{\text{peak}} \approx c \left(1 + \frac{\sigma^2}{r_{\text{peak}}^2}\right). \quad (6.20)$$

Within this simplified model, the velocity of the density maximum is predicted to be slightly larger than the true sound speed, with the correction scaling as $\sigma^2/r_{\text{peak}}^2$. As such, the correction is largest at early times when the characteristic propagation distance is comparable to the pulse width and rapidly decreases as the wave propagates and r_{peak} increases, eventually converging to the thermodynamic speed of sound. This qualitative behavior is consistent with the results presented in Table 6.1, which summarizes the extracted velocities for progressively extended fitting windows from the baseline and upper-bound simulation cases. As shown, the fitted velocity gradually decreases toward the sound speed predicted by the equation of state. For reference, $c = 1485.4$ m/s at ambient conditions (baseline case) and $c = 1534.4$ m/s at elevated pressure (upper-bound case) [99].

All in all, the results demonstrate that the hydrodynamic model provides a consistent description of the experimentally observed SAXS dynamics: it captures the one-dimensional evolution of the scattering signal, the emergence and progression of oscillatory features, the linear propagation of the density wavefront, and the effective velocities extracted from the limited temporal fitting windows. Combined, these findings support the interpretation that the measured response is consistent with the propagation of an acoustic-like disturbance wave, induced by hard X-ray ionization, that modulates the density over picosecond timescales and nanometer length scales in the single-phase liquid regime.

Temporal Window	Speed (baseline)	Speed (upper-bound)
0–25 ps	1719 ± 12 m/s	1775 ± 9 m/s
0–50 ps	1623 ± 10 m/s	1688 ± 7 m/s
0–75 ps	1561 ± 10 m/s	1639 ± 5 m/s
0–100 ps	1530 ± 11 m/s	1613 ± 4 m/s

Table 6.1: **Summary of extracted propagation velocities from the hydrodynamic model.** The table reports the fitted propagation speed of the leading density wavefront obtained over progressively increasing temporal fitting windows for both the baseline and the upper-bound simulation cases. For a detailed description of each case, see Section 6.5 and Section 6.6, respectively.

6.7 Influence of Thermophysical Properties

To delineate the role of key thermophysical properties appearing in the governing equations, including sound speed, viscosity, and thermal conductivity, we now examine their individual influence on the simulated dynamics. As such, the numerical simulations for the baseline condition were repeated assuming (i) no thermal conduction, (ii) no viscosity, and (iii) neither viscosity nor thermal conduction. The resulting SAXS contour maps are shown in Figure 6.10(a)–(c).

The contour maps clearly illustrate the impact of viscosity in attenuating the oscillatory response. When viscosity is removed, the higher-order SAXS features become substantially more prominent, persisting for longer times and appearing with greater contrast (Figures 6.10(b) and (c)). This behavior is consistent with the role of viscous dissipation in damping successive compression–rarefaction cycles. On the other hand, thermal conduction influences the evolution in a more subtle manner. In its absence, the secondary oscillations are less pronounced, reflecting the role of thermal diffusion in redistributing energy from the heated core region and sustaining the temperature and pressure gradients that ultimately bring about subsequent compression–rarefaction cycles (Figure 6.10(a)). Overall, these calculations show that the long-time evolution of the SAXS response is controlled predominantly by viscous damping, while thermal conduction provides a secondary correction. Nevertheless, the results highlight that both phenomena are necessary to reproduce the experimentally measured dynamics precisely.

With the role of the individual transport mechanisms established, we next investigate how the response changes when the thermophysical properties are altered through the choice of liquid. To this end, the model is applied to liquid CO₂ and ethanol, representing a non-polar and polar liquid, respectively. The simulations are performed in an identical fashion to those for water, with the only modifications being the equations of state and the evaluation of the corresponding transport properties. For CO₂, the equation of state is given by [160], while for ethanol it is described in [161]. The viscosity and thermal conductivity are likewise calculated using the appropriate constitutive relations for each liquid: [162, 163] for CO₂ and [164, 165] for ethanol. In addition, the bulk viscosity of CO₂ is modeled as $\mu_b = 10^{-5}$ Pa·s, whereas for ethanol the approximate relation $\mu_b = 1.4\mu$ is

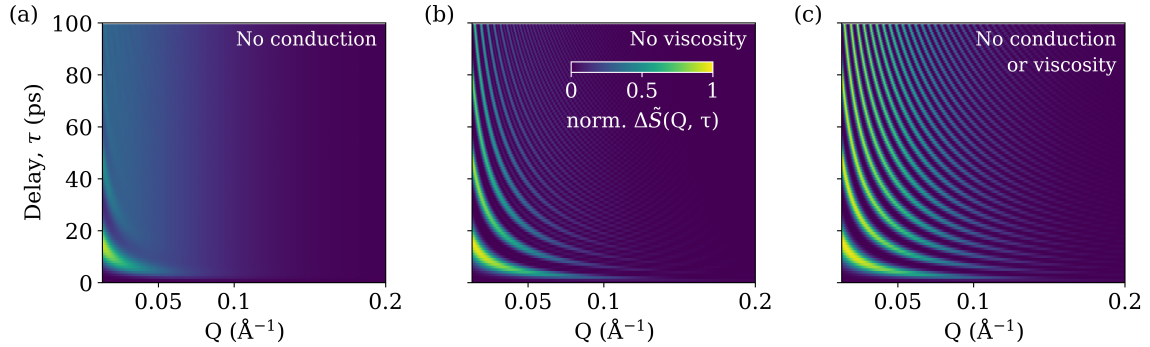


Figure 6.10: **Influence of transport mechanisms on the predicted hydrodynamic response.** Contour maps of the normalized SAXS intensity for (a) no thermal conduction, (b) no viscosity, and (c) no viscosity and no thermal conduction. All simulations were performed using the same initial perturbation parameters as the baseline water case. The responses are normalized by their respective global maxima to facilitate comparison.

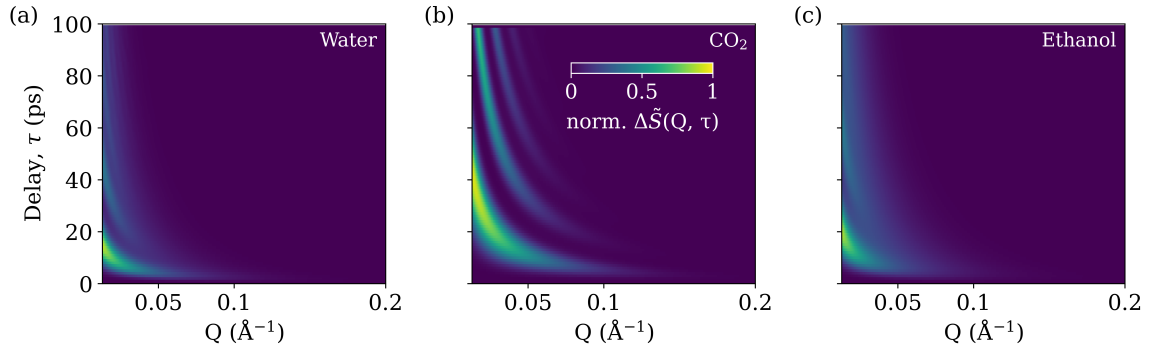


Figure 6.11: **Influence of fluid thermophysical properties on the predicted hydrodynamic response.** Contour maps of the normalized SAXS intensity calculated for (a) water, (b) liquid CO₂, and (c) ethanol. All simulations were conducted using $\Delta T = 1$ K, $T_\infty = 294.15$ K, $r_c = 1$ nm, and $\delta = 1$ nm. For water and ethanol, $P_\infty = 1$ bar, whereas for CO₂, $P_\infty = 150$ bar was used to attain liquid conditions. The responses are normalized by their respective global maxima for comparison.

employed [166].

The resulting SAXS responses are given in Figure 6.11, where the baseline water response from Figure 6.3(b) is included for comparison. The most noticeable difference is observed for CO₂, where the propagation of the SAXS signal lags behind that of water and ethanol. Moreover, the response exhibits more prominent higher-order oscillatory features (Figure 6.11(b)). In contrast, ethanol shows a slightly delayed propagation compared to water, with a moderate reduction in the amplitude of the higher-order oscillations (Figure 6.11(c)). These differences can be primarily attributed to variations in the speed of sound, which controls the propagation velocity of the density wavefront, and viscosity, which governs the attenuation of the oscillatory features.

	20°C H ₂ O	80°C H ₂ O	CO ₂	Ethanol
μ (mPa·s)	1.002	0.354 (↓ 64.7%)	0.071 (↓ 92.9%)	1.2 (↑ 19.8%)
k (W/(m·K))	0.6	0.67 (↑ 11.7%)	0.086 (↓ 85.7%)	0.167 (↓ 72.2%)
c (m/s)	1485	1534 (↑ 3.3%)	470 (↓ 68.4%)	1160 (↓ 21.9%)

Table 6.2: **Summary of thermophysical properties for ambient water, heated water, CO₂, and ethanol.** The values for each property are evaluated from the respective equations of state and constitutive relations. Values in brackets denote the relative difference with respect to the ambient water condition.

A summary of the relevant thermophysical properties is provided in Table 6.2 for ambient water, heated water at 80°C, CO₂, and ethanol. As indicated therein, and despite large changes in the thermal conductivity, the impact on the dynamics is minimal. However, a change in the sound speed, which is significantly lower in CO₂, leads to a marked delay in the wavefront propagation. Similarly, the reduced viscosity of CO₂ results in weaker damping of the higher-order features. Ethanol, on the other hand, which has a viscosity slightly higher than that of water, demonstrates stronger damping of the oscillations, while its moderately reduced sound speed yields a slower overall evolution of the response.

This is further corroborated in Figure 6.12, which shows the temporal evolution of the compressive wavefront peak position and magnitude for the three fluids. The extracted propagation velocities are 1,534 m/s for water, 592 m/s for CO₂, and 1,259 m/s for ethanol (Figure 6.12(a)). These values follow the same ordering as the corresponding speeds of sound (1,485, 470, and 1,160 m/s, respectively), confirming that the propagation of the SAXS response is governed by acoustic transport. The fact that the extracted velocities monotonically exceed the sound speeds is also consistent with the previously put forth discussion on the finite temporal fitting window. Importantly, the magnitude of the deviation remains comparable across all three liquids, indicating that the effect is geometric in nature rather than fluid specific.

The temporal evolution of the peak magnitude likewise reflects the influence of the transport properties (Figure 6.12(b)). Over the 100 ps simulated window, the peak intensity in water and ethanol decreases by approximately three orders of magnitude, whereas the CO₂ peak magnitude drops by only two. This slower attenuation can be mainly attributed to the considerably lower viscosity of liquid CO₂, which is roughly an order of magnitude smaller than that of ambient water. Dissipative losses are hence reduced and the oscillatory features remain discernible for longer times. Ethanol, whose viscosity is slightly larger ($\sim 19\%$ larger) than water, exhibits marginally stronger damping and weaker oscillatory behavior.

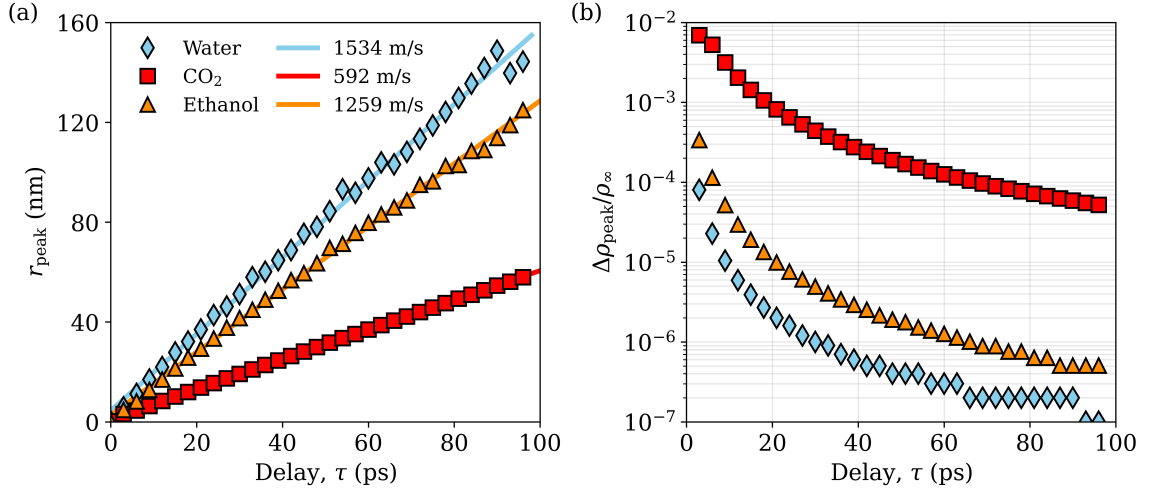


Figure 6.12: **Temporal evolution of the compressive density wavefront predicted by the hydrodynamic model for water, liquid CO₂, and ethanol.** (a) Position of the compressive wavefront peak as a function of time. Symbols represent the extracted peak positions, and solid lines show linear fits to the data. (b) Peak magnitude of the compressive wavefront as a function of time for each fluid.

6.8 Discussion

A practical outcome of the hydrodynamic framework is that it provides predictive capability for future ultrafast scattering experiments. This is because while experiments are inherently limited by the available momentum-transfer range and temporal sampling window, which are in turn constrained by the detector geometry and split-and-delay optics, the numerical model can be extended well beyond these limits. This capability makes it possible to estimate the lifetime, propagation distance, and oscillatory behavior of the density perturbations, offering access to regions of reciprocal space and timescales that cannot be measured directly.

Furthermore, the simulations presented in this chapter have shown that the evolution of the SAXS response following hard X-ray ionization is largely governed by the speed of sound and attenuated by viscous dissipation. Consequently, fluids with substantially different thermophysical properties are expected to exhibit distinct experimental signatures. For example, the delayed response predicted for liquid CO₂ indicates that longer pump–probe delays would be required to capture the same stage of the hydrodynamic evolution observed in liquid water. At the same time, liquids with larger sound speeds would require relatively shorter delays. As a result, the model serves not only as a tool for interpreting SAXS measurements, but also as a blueprint for designing future experiments, guiding beamline scientists and research staff and identifying the temporal windows required to observe the relevant dynamics.

Perhaps the most significant outcome of the hydrodynamic model is that a continuum description based on the Navier–Stokes equations successfully reproduces the experimentally measured response, despite the disparity in spatiotemporal scales. As the initial perturbation responsible for driving the observed SAXS signal is localized to a region only a few nanometers in size, and the ensuing dynamics evolve on picosecond timescales, one might reasonably expect atomistic effects, such as intermolecular interactions or deviations from local thermodynamic equilibrium, to play a dominant role. However, the simulations demonstrate that the experimentally resolvable dynamics are sufficiently well described by the hydrodynamic continuum formulation, coupled with an appropriate equation of state and reliable transport properties. This conclusion is supported by several independent findings.

First, the model captures the two-dimensional evolution of the SAXS signal across a broad range of thermodynamic conditions and deposited energies. Second, it correctly predicts the emergence and progression of the oscillatory features observed in both reciprocal- and real-space. Third, the extracted propagation velocities agree quantitatively with the experiments and naturally explain the apparent faster-than-sound speed obtained from finite temporal fitting windows in the experiments. Finally, the same formulation remains consistent when applied to liquids with different thermodynamic properties, forecasting expected changes in propagation speed and damping. Altogether, these results suggest that the experimentally observed dynamics are governed by hydrodynamic transport rather than molecular-scale processes, at least on the spatiotemporal scales probed in this work.

Nonetheless, the model possesses several limitations. Most notably, the formulation is restricted to the single-phase liquid regime and therefore cannot describe thermodynamic trajectories that enter the liquid–vapor coexistence region. The model is also formulated for single-species systems and cannot be applied to multi-species mixtures. Finally, the energy deposition process is represented by an effective temperature perturbation instead of an explicit treatment of electron transport and thermalization. These all present opportunities for future work, discussed next in Chapter 7.

Chapter 7

Conclusions and Outlook

This thesis advances the fundamental understanding of liquid water radiolysis and hard X-ray condensed-matter interactions. More specifically, it characterizes the response of liquid water subject to hard X-ray irradiation on nanometer length scales and picosecond timescales, a regime that has remained largely unexplored in conventional experimental approaches. Through a combination of three experimental campaigns conducted at two X-ray free electron laser facilities, theoretical analysis, and the development of a first-principles numerical model based on the governing flow equations, the thesis establishes a holistic interpretation of the ultrafast dynamics in the chemical stage of radiolysis. To this end, the main findings from each chapter are summarized below.

7.1 Main Findings

Chapter 2 introduced the theoretical and experimental foundations required for the remainder of the thesis. It outlined the principles of hard X-ray scattering techniques, the X-ray free electron laser facilities employed in this work, and the instrumentation used to collect the data. Particular emphasis was placed on time-resolved X-ray scattering as a tool for probing non-equilibrium dynamics. The chapter also described the liquid jet and pressure-cell sample environments, data reduction procedures used to extract reciprocal-space information from the measured scattering signals, and the uncertainty propagation methodology.

Chapter 3 presented the first time-resolved X-ray scattering measurements of liquid water following hard X-ray ionization using a high-pressure flow-cell geometry; the experiments were conducted at SACLA and LCLS. Experiments performed at SACLA revealed the emergence of a previously unobserved transient low- Q scattering feature on sub-picosecond timescales, along with a traditional high- Q heating signature corresponding to a temperature increase on the order of 13 K. The low- Q response appeared initially as a broad enhancement that subsequently increased in magnitude, developed a distinct peak in momentum space corresponding to a characteristic length scale of 3.9 nm

within 0.6 ps, shifted toward lower momentum transfer with increasing delay, and decayed after 6 ps. The feature was observed consistently across pressure conditions of 50 and 150 bar, suggesting that the dynamics are largely insensitive to variations in pressure.

The experiments at SACLA were complemented by measurements at LCLS performed at 2 bar, which leveraged the continuous split-and-delay optics available at the facility to probe the early-time evolution of the low- Q signal. These measurements reproduced the low- Q response observed at SACLA and yielded a characteristic length scale of 3.74 nm, in excellent agreement with the 3.9 nm value extracted from the high-pressure measurements. This demonstrated that the observed structural dynamics are indeed insensitive to pressure. Moreover, the LCLS measurements enabled tracking the evolution of the low- Q peak over time delays spanning 0–3.6 ps, revealing an apparent linear propagation corresponding to an effective velocity of approximately 1,700 m/s. Due to the pressure-cell detector geometry and the utilization of diamond windows to enclose the cell, however, momentum transfer values below $Q = 0.1 \text{ \AA}^{-1}$ were not accessible. As such, this prevented direct observation of the long-time evolution of the signal at larger real-space length scales. These limitations motivated the development of the liquid jet experiments presented in the following chapter.

Chapter 4 extended the investigation of the low- Q structural response using time-resolved SAXS and WAXS measurements performed on a free-flowing liquid water jet at ambient conditions and elevated temperature at SACLA. The jet detector configuration significantly expanded the accessible momentum transfer range, by roughly an order of magnitude, enabling the dynamics to be tracked over substantially larger length scales and longer pump–probe delays than was possible in the prior experiments. The jet measurements definitively showed that the low- Q signal does not simply decay after a few picoseconds; rather, it continues to evolve toward lower momentum transfer while developing multiple oscillatory features, i.e., peaks in reciprocal space, associated with long-range density correlations. Analysis of the WAXS response confirmed a transient temperature increase on the order of 10 K, consistent with the pressure-cell measurements. This provided additional evidence that both datasets probe the same underlying energy deposition and relaxation dynamics.

A systematic analysis of the pulse energy and temperature dependence of the SAXS features indicated that the low- Q peak positions are independent of both pulse energy and temperature. The pulse energy dependence displayed quadratic scaling with total pulse energy, which amounts to a linear dependence on pump energy at fixed probe conditions, signifying that the response arises from independent scattering sites within the X-ray illumination volume. In contrast, the effect of increasing temperature was a monotonic amplification of the overall signal magnitude without noticeably impacting the spatiotemporal scales. The SAXS response was also determined to be azimuthally symmetric across all investigated time delays, pointing to the absence of any measurable angular dependence in the scattering signal.

Transformation of the SAXS response into real space additionally revealed a traveling rarefaction–compression pattern whose compressive wavefront evolved linearly in time with an effective velocity

of 1,777 m/s. The velocity remained unchanged across temperature and pulse energy. Combined, these findings are consistent with an interpretation that the measured response corresponds to a long-lived density perturbation, originating from statistically independent scattering events, generated by hard X-ray ionization and governed by a universal mechanism.

Chapter 5 tied the experimental observations together and provided a physical interpretation of the low- Q structural response. In particular, the microscopic origin of the dynamics was substantiated through an analysis of radiation-induced energy deposition processes in liquid water. By comparing the measured velocities with the speed of sound and estimating the ionization fraction under the relevant pulse energy conditions, the measured signal was linked to photoelectrons ejected during hard X-ray photon absorption. The photoelectrons undergo inelastic collisions and produce spatially confined radiation spurs, which, in turn, act as nanometer-scale regions of energy deposition within which electron thermalization occurs on sub-picosecond timescales. The resulting localized heating due to thermalization drives the initial perturbation and gives rise to the structural response. This interpretation was supported by calculating the spur separation and showing that individual spurs remain well separated over the experimental time window. Together with the observed linear scaling in pulse energy, this validated the independence of the scattering sites. Finally, Chapter 5 also demonstrated that radiolysis chemistry does not play a prominent role in the dynamics.

Chapter 6 developed a hydrodynamic framework based on the Navier–Stokes equations to characterize the experimentally observed SAXS dynamics. Within this formulation, electron thermalization was modeled as a weak temperature perturbation under isochoric conditions. Thermophysical properties were determined from equations of state based on multi-parameter Helmholtz free energy formulations and constitutive relations. The model successfully reproduced the key experimental observations across all measured conditions: it captured the two-dimensional evolution of the scattering signal, the emergence and propagation of oscillatory features in both real- and reciprocal-space, and the shift toward lower momentum transfer at later delays.

In addition, the model elucidated the origin of the oscillatory behavior—by explicitly analyzing the resulting density field, we showed that the temperature perturbation generated an equivalent pressure rise that launched an acoustic wave that modulated the local density profile. Systematically varying transport coefficients and initial conditions in the simulations also revealed that the observed dynamics are strongly dependent on the speed of sound and viscous damping. The former was found to govern the rate at which the low- Q signal shifts toward lower momentum transfer values, while the latter controlled the attenuation of successive oscillatory features. The dynamics were robust with respect to moderate changes in thermodynamic parameters otherwise.

Moreover, the extracted propagation velocities from the model and the experiments were directly compared, and excellent agreement was obtained overall with consistent values across all datasets. Lastly, the model was employed to rationalize the apparent faster-than-sound speed propagation observed in the experiments. In turn, this was attributed to the finite temporal fitting window and

spherical spreading of the wavefront, rather than being from any true supersonic transport. All in all, Chapter 6 showed that the experimentally observed SAXS response is reproducible within a continuum, compressible hydrodynamic framework despite the separation of length scales and timescales between atomistic-level ionization events and large-scale density modulations.

7.2 Future Work

While this thesis contributes to the understanding of radiation-induced structural dynamics in liquid water by addressing key gaps in the evolution of the chemical stage of radiolysis, additional work is still needed. This work can be broadly categorized into improvements in experimental methodology, supplementary measurements, extensions of the theoretical modeling, and the development of sophisticated numerical simulation frameworks. Addressing these directions would enable a more comprehensive description of the ultrafast dynamics in potentially more complex fluid systems and fully bridge the connection between microscopic energy deposition processes and macroscopic hydrodynamic modulations across a wide range of spatiotemporal scales.

7.2.1 Experimental Improvements

From an experimental perspective, several advancements would enhance the ability to probe and track ultrafast radiation-induced dynamics in liquids. A primary limitation of the present measurements arises from the accessible momentum transfer and temporal windows, which are constrained by detector geometry, beamline configuration, and split-and-delay optics. One avenue for improvement is hence the extension of the accessible low- Q range beyond $Q = 0.01 \text{ \AA}^{-1}$. This is routinely achieved in Ultra-Small-Angle X-ray Scattering (USAXS) experiments [167], although a time-resolved USAXS implementation is not yet available. Nonetheless, such capability would allow direct observation of longer wavelength density modulations at later pump-probe delays, in regimes where current measurements indicate sustained evolution toward larger length scales.

Similarly, increasing the available time delay window would be particularly beneficial for slower propagating systems, such as liquids with reduced sound speeds (e.g. liquid CO_2), where the relevant hydrodynamic response evolves on significantly longer timescales than water. This, however, would necessarily require improvements in state-of-the-art detector sensitivity, as the scattering features and overall signal magnitude progressively weaken with time. As such, the development of highly sensitive detectors with expanded dynamic range is also an avenue worth exploring.

7.2.2 Additional Measurements

Beyond the beamline configuration itself, the experimental methodology employed herein can be utilized for further investigations. A natural next step is to perform the experiments on liquids with

more diverse thermophysical properties. Such studies would not only allow the robustness of the observed signal to be tested across varying conditions, but it would also provide a means to delineate the validity limits of the present hydrodynamic model.

Taking the experiments one step further would involve extending the measurements to multi-component systems, where liquids are combined in binary or ternary mixtures. These studies would provide an opportunity to investigate how intermolecular interactions modify the collective response of the fluid, through documenting changes in the experimentally extracted propagation velocity and successive damping of higher-order features. Measurements across different mixture fractions could additionally provide insight into how individual thermophysical properties combine to govern radiation-induced density transport in complex fluids.

Another opportunity arises from the sensitivity of the measured SAXS response to the underlying transport properties of the liquid. As demonstrated in Chapter 6, the propagation velocity is governed primarily by the speed of sound, whereas the attenuation of successive oscillatory features depends strongly on viscous damping. This suggests that ultrafast SAXS measurements may ultimately provide a means of experimentally determining transport properties under transient X-ray irradiation conditions. By fitting the measured spatiotemporal evolution using the hydrodynamic framework developed in this thesis, quantities such as the effective speed of sound, the bulk viscosity, and potentially even the thermal conductivity could be inferred from radiation-induced density perturbations.

Finally, one of the most decisive experimental tests of the physical interpretation developed in this thesis would involve systematically varying the pump photon energy. The present experiments employed hard X-rays in the low-LET regime, which generate energetic photoelectrons that initiate extended secondary electron cascades and produce spatially separated radiation spurs. In contrast, tuning the pump energy to the oxygen K-edge (~ 540 eV) would fundamentally alter the radiation track structure. Under these conditions, the photoelectron carries only a few electron volts of kinetic energy, Auger–Meitner decay dominates the subsequent relaxation, and secondary spur formation is expected to be strongly suppressed. If the interpretation proposed in this thesis is correct, the resulting SAXS response should differ substantially, exhibiting a more localized, shorter-lived, and weaker structural perturbation associated primarily with a single Auger spur. This would inherently result in a markedly different reciprocal-space evolution than that observed for hard X-ray ionization. Conversely, employing a high-LET ionizing source, such as alpha particles, would produce densely overlapping radiation tracks rather than isolated spurs. In this regime, the assumption of independent scattering sites would no longer be expected to hold, and the bilinear pulse-energy scaling established in Chapter 4 would likely break down as neighboring perturbations begin to nonlinearly interact.

7.2.3 Modeling Extensions

From a modeling perspective, several opportunities exist to extend the formulation developed in this thesis. These are:

1. **Incorporating multi-phase dynamics into the framework.** While the assumption of a single-phase liquid regime is justified for the experimental conditions investigated in this work, owing to the modest transient heating observed in the WAXS signal and the relatively low ionization fractions estimated, sufficiently large pulse energies (on the order of mJ or higher) could drive the local thermodynamic state into the liquid–vapor coexistence region. Under such conditions, cavitation, phase separation, and vapor–bubble formation may become important. At present, these effects are not captured by the model and would require a multi-phase extension.
2. **Adding functionality for multi-component mixtures.** As all the experiments in this thesis were performed on liquid water, the hydrodynamic model was developed for pure liquids. However, many technologically and scientifically relevant systems involve multi-component mixtures, including aqueous solutions and alcohol–water mixtures. The functionality to handle mixture thermodynamics and transport models would therefore open up pathways that significantly broaden the applicability of the model. Note that such an extension would inherently require reliable thermophysical property data, validated mixing rules, and accurate equations of state for each species to ensure thermodynamic consistency in resolving the coupled evolution of the density perturbation.
3. **Explicit treatment of electron transport and thermalization.** In the present formulation, the interaction of the hard X-ray pulse with the liquid is represented through an effective temperature increase. While this approximation successfully reproduces the experimentally observed dynamics, a more rigorous treatment would explicitly model photoelectron transport, secondary electron cascades, and energy thermalization. Coupling a radiation-transport solver directly to the hydrodynamic model, for example, would provide a more complete connection between the microscopic ionization events and the macroscopic density evolution.
4. **Generalized hydrodynamic and non-equilibrium effects.** Transport coefficients in the model were treated as scale-independent and evaluated from equilibrium constitutive relations. Yet, departures from classical continuum behavior are plausible at nanometer length scales and picosecond timescales [168–170]. Future developments could investigate these effects and quantify their impact on the relaxation process and overall hydrodynamic evolution. Tackling this problem would help bridge the gap between molecular and continuum descriptions of liquid dynamics, while providing a more stringent testbed to assess the validity of the Navier–Stokes equations under extreme non-equilibrium conditions.

Beyond its interpretive value, the hydrodynamic framework developed in this work has the potential to serve as a predictive tool for future XFEL experiments, particularly if some or all of the aforementioned extensions are implemented. Even without these extensions, in its current form, the model can be used to provide first-order estimates of the lifetime, characteristic length scales, propagation velocity, and expected magnitude of X-ray radiation-induced density perturbations prior to performing a measurement. This information can then be utilized to optimize detector placement, select appropriate pump–probe delays, and identify experimental conditions most likely to maximize signal visibility. In this regard, the model may ultimately evolve from a tool for interpreting ultrafast hard X-ray pump–probe scattering experiments into a platform for guiding their design.

7.2.4 Numerical Simulations

Finally, a promising future direction is the development of fully multiscale simulation frameworks capable of connecting atomistic-level ionization processes to macroscopic-level structural changes. Due to the incompressible nature of liquids and the low momentum transfer values over which the dynamics evolve, large system sizes of at least 10^6 molecules need to be resolved. Achieving this will likely leverage hybrid methodologies.

Two potential routes are particularly attractive. The first involves Monte Carlo methods, which can probabilistically account for and statistically sample multiple ionization pathways, including photoelectron generation, Auger–Meitner decay, and secondary electron cascades [136, 171]. Information obtained from these calculations could then be incorporated into large-scale molecular dynamics simulations through physically motivated source terms or modified interaction potentials. The second route involves non-adiabatic quantum dynamical approaches [172, 173], which explicitly account for coupled electronic and atomic motion while being computationally tractable for system sizes substantially larger than those that can be treated with a full quantum mechanical framework. Pursuing either of these research directions would provide more direct insight into how localized electronic excitations and ionization events evolve into collective density perturbations and eventually give rise to the hydrodynamic response observed experimentally.

Realizing this vision, however, remains a significant challenge, and continued advances in theoretical formulations, radiation-transport codes, molecular dynamics simulations, and quantum mechanical treatments of condensed-phase systems will be essential for establishing a truly predictive multiscale description of radiation-induced dynamics in liquids.

7.3 Final Remarks

In summary, this thesis has established a clear link between hard X-ray ionization and the emergence of long-lived nanoscale density perturbations in liquid water on the picosecond timescale.

Through a combination of ultrafast X-ray scattering experiments, theoretical analysis, and hydrodynamic modeling, it has been shown that the observed low- Q response can be understood as the propagation of an acoustic wave that emanates from radiation spurs, formed during the chemical stage of radiolysis due to localized energy deposition by secondary electrons, and modulates the density. Complementary to this finding, the results also suggest that continuum hydrodynamics remains remarkably effective at describing liquid dynamics on nanometer length scales and picosecond timescales. This provides a foundation for future investigations of radiation-induced structural dynamics in liquids and opens new opportunities for connecting microscopic ionization processes with macroscopic transport phenomena.

Appendix A

Supplementary Data and Pulse-Energy Results

This appendix presents additional differential scattering data from the SACLA and LCLS pressure-cell measurements and the SACLA jet measurements discussed in Chapters 3 and 4. The figures include contour maps and corresponding line profiles of the normalized differential scattering response, $\Delta\tilde{S}(Q, \tau, E_{tot})$, for pulse-energy bins not shown in the main text. For the SACLA pressure-cell dataset, results are provided for both pressure conditions (50 bar and 150 bar) in Figures A.1 and A.2, respectively. For the LCLS dataset, the full momentum-transfer region is displayed in Figure A.3. The additional data demonstrate behavior that is consistent with the primary results in the main text—the same high- Q and low- Q features are observed. The principal difference across pulse-energy conditions is an amplification of the scattering signal with increasing pulse energy.

For the SACLA jet dataset, Figure A.4 shows the pulse energy dependence at both ambient and heated conditions for time delays not displayed in the main text. These include $\tau = 6, 15, 25$, and 50 ps. Time delays exceeding 50 ps do not exhibit pronounced peaks and are therefore not shown. Figure A.5 illustrates the systematic amplification in the reduced pair distribution function for the ambient water jet over pulse energies between 3–8 μJ . Figure A.6 presents the reduced pair distribution function as a contour map and line plots for the full time delay spectrum probed at 80°C. As can be seen, the results evolve similarly to the 20°C condition, except that the magnitude of the signal is amplified in accordance to the reduced viscosity.

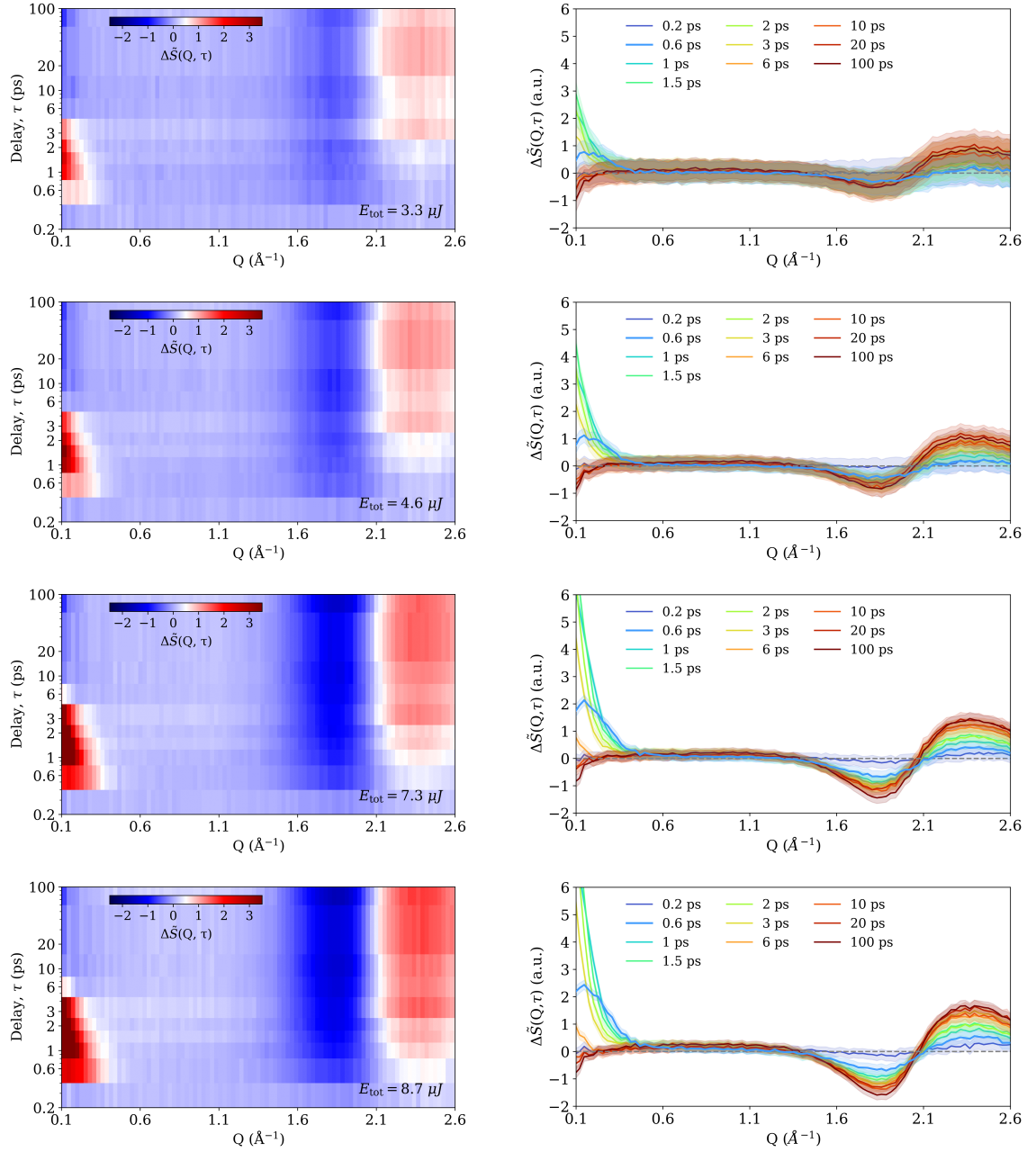


Figure A.1: Differential scattering signal from SACLA at 50 bar for $E_{tot} = 3.3, 4.6, 7.3$ and $8.7 \mu\text{J}$ (from top to bottom). The left column displays the results as a contour map, whereas the right column presents the individual line plots. Shaded regions correspond to the uncertainty calculated with Equation (2.19) from the main text.

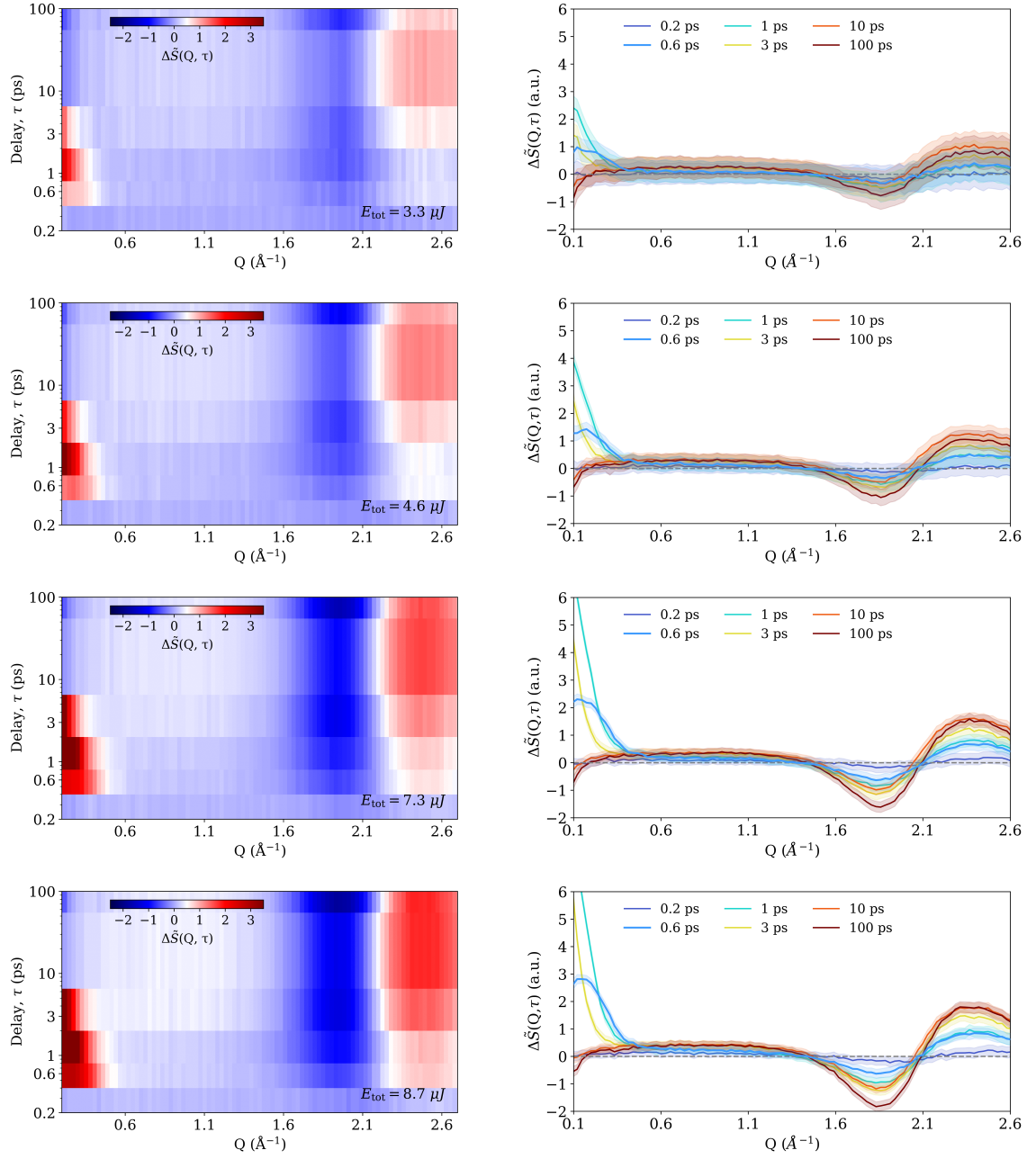


Figure A.2: Differential scattering signal from SACLA at 150 bar for $E_{tot} = 3.3, 4.6, 7.3$ and $8.7 \mu\text{J}$ (from top to bottom). The left column displays the results as a contour map, whereas the right column presents the individual line plots. Shaded regions correspond to the uncertainty calculated with Equation (2.19) from the main text.

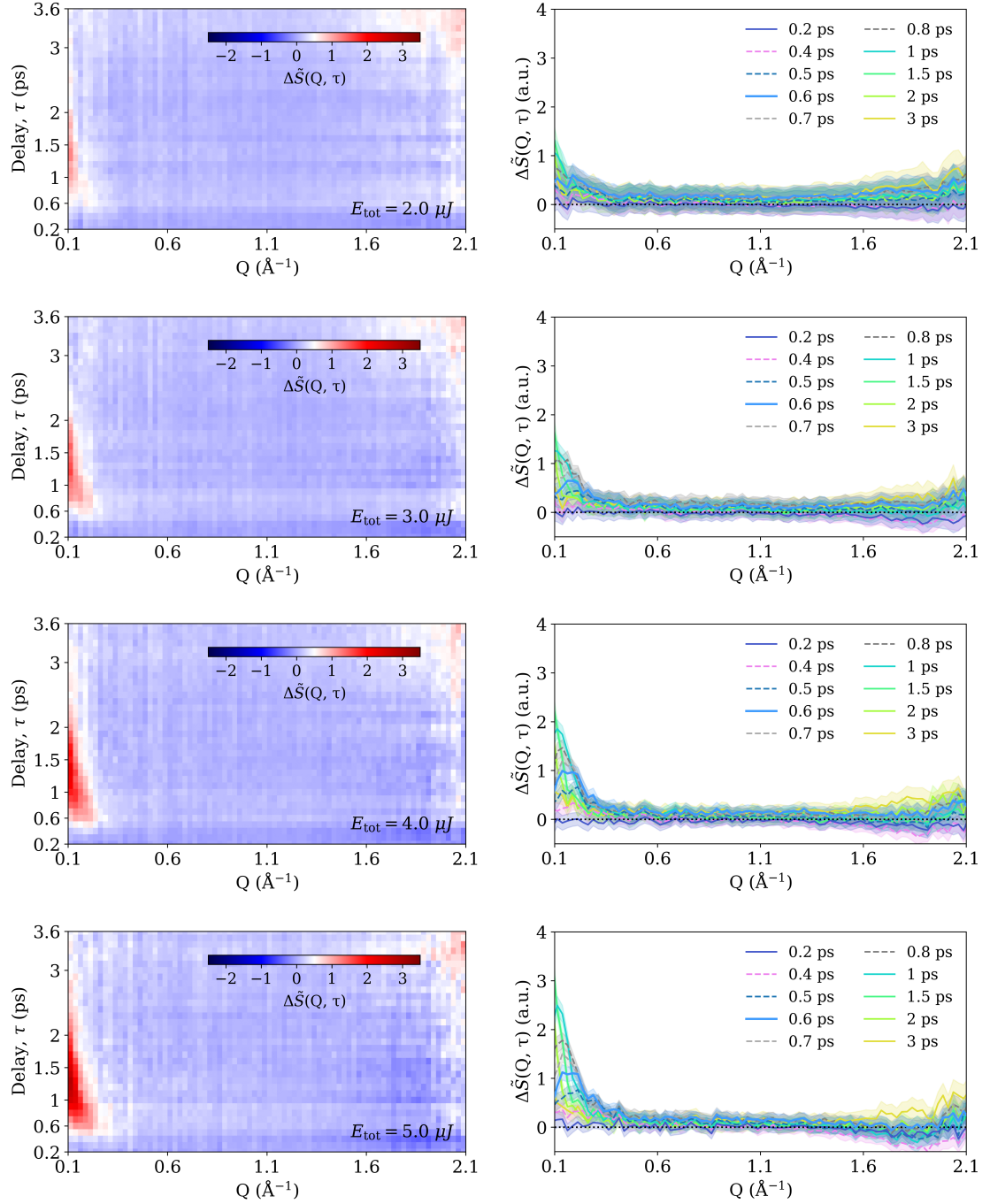


Figure A.3: Differential scattering signal from LCLS at $E_{tot} = 2, 3, 4$ and $5 \mu\text{J}$ (from top to bottom). The left column displays the results as a contour map, whereas the right column presents the individual line plots. Shaded regions correspond to the uncertainty calculated with Equation (2.19) from the main text.

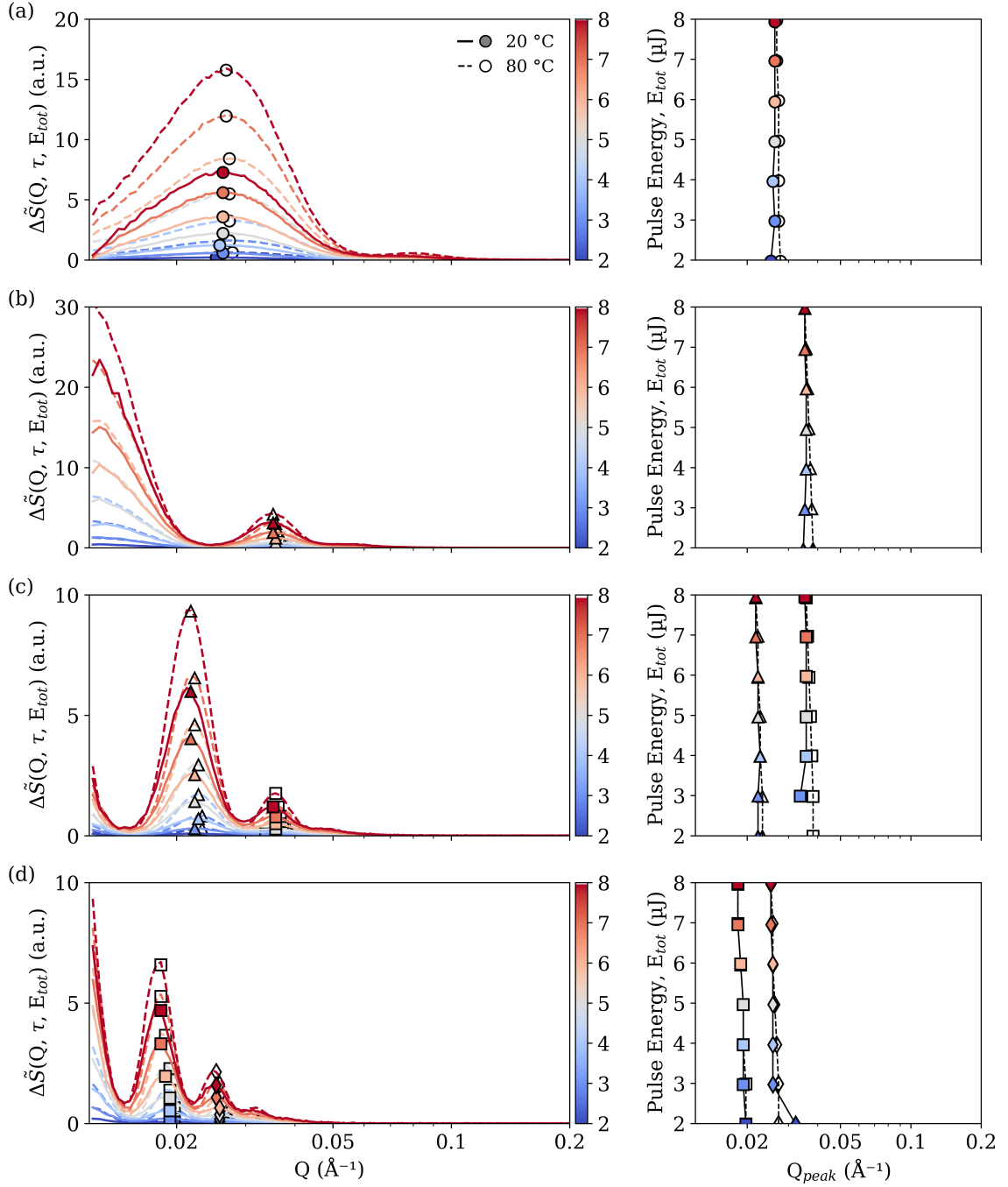


Figure A.4: Pulse energy dependence of the SACLA jet measurements at 20 °C (solid lines, filled markers) and 80 °C (dashed lines, open markers). Results shown are for $\tau = 6$ ps (a), 15 ps (b), 25 ps (c), and 50 ps (d). Markers denote the local maxima at each corresponding delay, determined using the procedure outlined in Section 3.2.2.

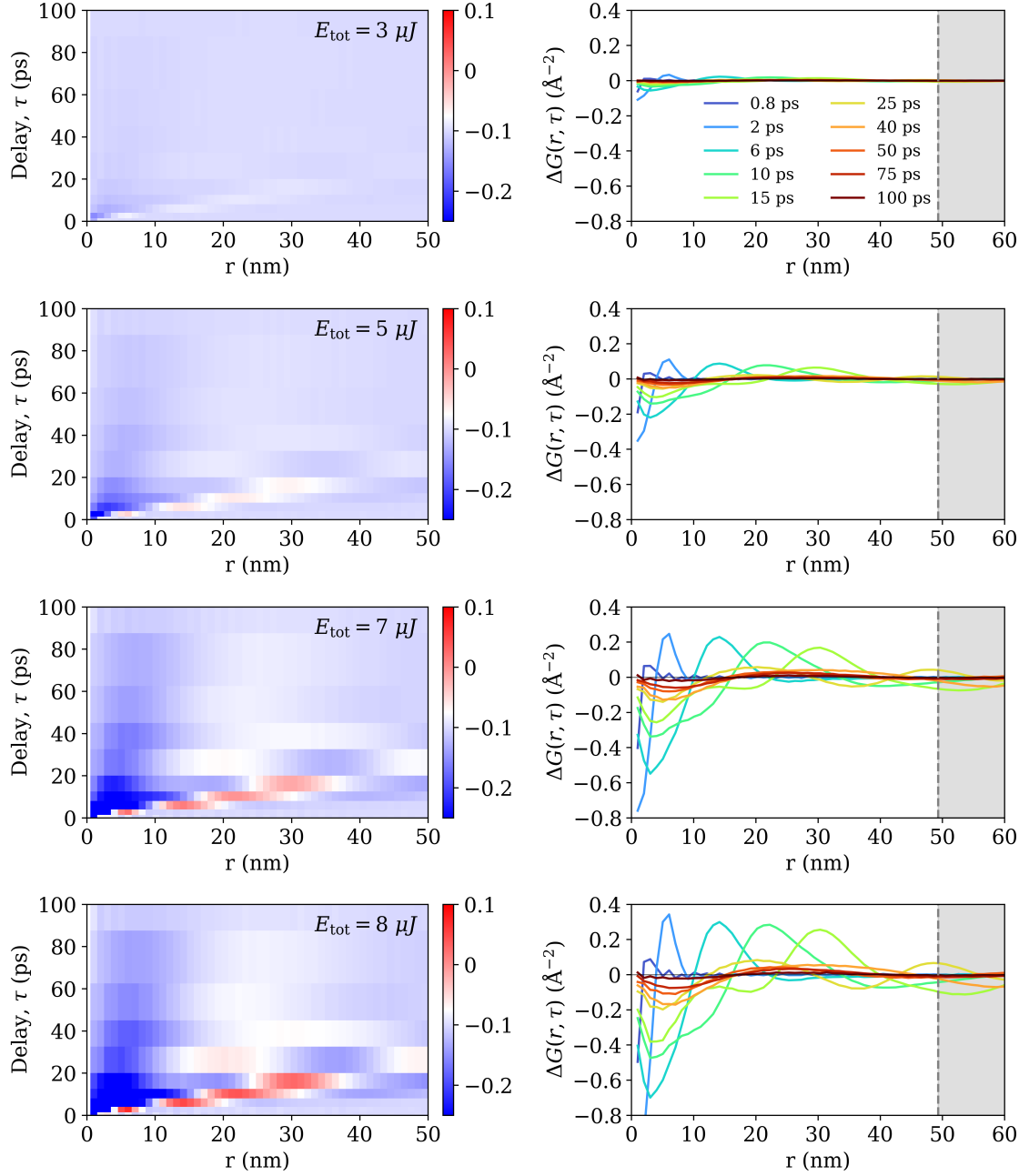


Figure A.5: Reduced pair distribution function for the 20°C water jet at $E_{\text{tot}} = 3, 5, 7, \text{ and } 8 \mu\text{J}$ (from top to bottom). The left column displays the results as a contour map, whereas the right column presents the individual line plots.

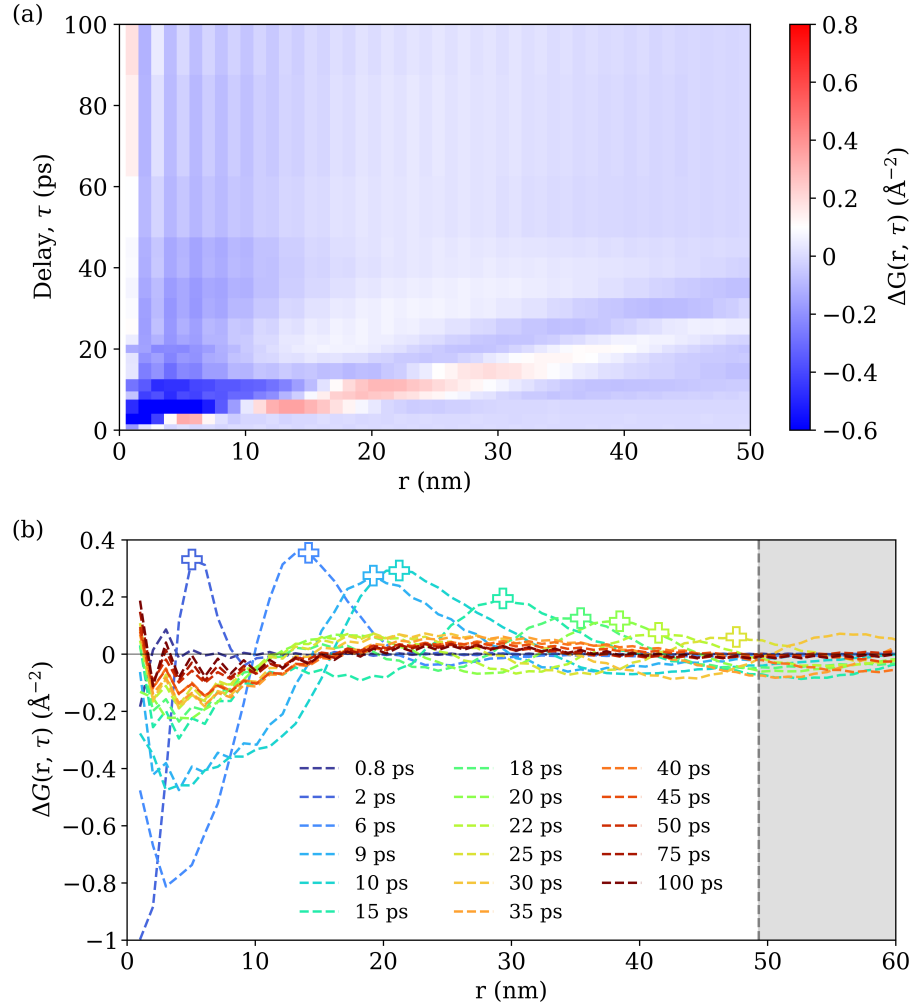


Figure A.6: (a) Contour map of the reduced pair distribution function, $\Delta G(r, \tau, E_{tot})$, calculated with Equation (4.7) for $E_{tot} = 6 \mu\text{J}$ for the SACLA jet measurements at 80°C . (b) Line plots of $\Delta G(r, \tau, E_{tot})$ at $6 \mu\text{J}$ for all sampled pump-probe delays at 80°C . Peak positions are indicated by cross markers. The grey shaded region denotes the inaccessible real-space range imposed by the minimum Q -value of the experiment, $Q_{min,jet} = 0.01225 \text{\AA}^{-1}$.

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