Topical Review

Liquid structure under extreme conditions: high-pressure x-ray diffraction studies

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Abstract

Under extreme conditions of high pressure and temperature, liquids can undergo substantial structural transformations as their atoms rearrange to minimise energy within a more confined volume. Understanding the structural response of liquids under extreme conditions is important across a variety of disciplines, from fundamental physics and exotic chemistry to materials and planetary science. In situ experiments and atomistic simulations can provide crucial insight into the nature of liquid–liquid phase transitions and the complex phase diagrams and melting relations of high-pressure materials. Structural changes in natural magmas at the high-pressures experienced in deep planetary interiors can have a profound impact on their physical properties, knowledge of which is important to inform geochemical models of magmatic processes. Generating the extreme conditions required to melt samples at high-pressure, whilst simultaneously measuring their liquid structure, is a considerable challenge. The measurement, analysis, and interpretation of structural data is further complicated by the inherent disordered nature of liquids at the atomic-scale. However, recent advances in high-pressure technology mean that liquid diffraction measurements are becoming more routinely feasible at synchrotron facilities around the world. This topical review examines methods for high pressure synchrotron x-ray diffraction of liquids and the wide variety of systems which have been studied by them, from simple liquid metals and their remarkable complex behaviour at high-pressure, to molecular-polymeric liquid–liquid transitions in pnicogen and chalcogen liquids, and density-driven structural transformations in water and silicate melts.

Keywords: high-pressure, liquid structure, diffraction

(Some figures may appear in colour only in the online journal)

1. Introduction

Liquids are an intriguing state of condensed matter with a density close to that of the solid-state but with all atoms undergoing continuous diffusive motions, like a compressed gas, resulting in an absence of long-range structural order. Liquids occupy a relatively narrow pressure–temperature (p–T) regime and are one of the least prevalent states of matter in the known Universe with their very existence contingent upon a delicate balance between cohesive interatomic or intermolecular forces which impede vapourisation and entropic forces preventing crystallisation [1]. However, despite their precarious nature, the liquid state is key to sustaining life on Earth, as the...
active matrix for cell and molecular biology and for driving geochemical processes essential for maintaining a habitable planet [2, 3].

As illustrated by the $p-T$–depth profile of Earth in figure 1, the conditions within deep planetary interiors are extreme. Under these extreme conditions dynamic geophysical and chemical processes are dominated by changes in solid- and liquid-state structure. Crystalline solids can undergo first-order (and second-order) phase transitions at high-$p-T$ to form distinct polymorphic phases with the same stoichiometry but different crystalline structures. This is exemplified by seismic discontinuities in Earth’s transition-zone region that separates the upper and lower mantle, which are global-scale manifestations of the phase transition of the mineral olivine [$\alpha$-(Mg, Fe)$_2$SiO$_4$] to its high-$p$ wadsleyite [$\beta$-(Mg, Fe)$_2$SiO$_4$] polymorph at 410 km depth, its subsequent transition to spinel-structured ringwoodite polymorph [$\gamma$-(Mg, Fe)$_2$SiO$_4$] at 520 km, followed by decomposition to bridgmanite [(Mg, Fe)SiO$_3$] and magnesiowüstite [(Mg, Fe)O] at 660 km depth [4]. Such changes in mineral structure have a significant influence on mantle convection [5, 6] and the geochemical distribution and cycling of elements in the deep Earth [7]. The existence of similar abrupt and reversible liquid–liquid transitions between low and high density liquid structures at high-$p-T$ is the subject of considerable debate [8–12].

Whether first-order or continuous, understanding the nature of liquid–liquid transitions occurring at high-$p$ is important for discovery of new phases with unique physical properties, modelling material response to extreme conditions during industrial melt processes, and understanding geophysical processes controlled by magmatism. For example, changes in the atomic-scale connectivity and local polyhedral geometry in planetary melts in response to high-$p-T$ conditions determine the properties and behaviour of magma at depth, which in turn controls geochemical processes such as planetary-scale differentiation from primordial magma oceans and inter/intraplate volcanism that have shaped Earth over geological time. Structural information on metallic melts in deep terrestrial, gas giant, and exoplanet interiors is also important for understanding planetary core formation [16] or magnetic field generation [17], and such extreme conditions opens the possibility of forming exotic liquid states, such as liquid metallic hydrogen predicted in the deep interior of Jupiter [18].

Despite their characteristic absence of long-range structural symmetry, liquids do exhibit a high-degree of short-range order in their time average structure due to chemical bonding constraints, giving rise to well-defined coordination polyhedra and chemical bond lengths similar to the local structure in the corresponding crystalline solid-state. This short-range chemical order generally breaks down in liquids beyond the length-scale of a few atoms (2–5 Å), although different patterns of intermediate range order may occur beyond the next nearest neighbour length-scale of $\sim$5–20 Å [19–21]. The bulk structure of liquids can be measured using a range of

Figure 1. Pressure and temperature versus depth profile of Earth’s interior using data from the preliminary reference Earth model [13] and estimated thermal structure of the Earth [14]. Photograph modified from the NASA ‘Blue Marble’ image [15].
complementary diagnostic probes including neutron or high-energy x-ray diffraction (XRD), nuclear magnetic resonance spectroscopy (NMR), x-ray absorption spectroscopy (XAS), and Raman scattering [22, 23]. Melts in the deep Earth and other planetary bodies are generally inaccessible for direct measurement, so in order to understand their structure and properties the extreme high-\(p\)-T conditions experienced at depth must be reproduced in the laboratory.

For ambient-\(p\) (1 atm) liquid-state studies, high-T can be generated using a variety of resistive heating (RH) furnaces with the sample held in a refractory or metallic container. However, conventional furnaces have limited maximum working temperatures and there is a risk of chemical reaction and contamination of the liquid signal by the containment material. This limitation is overcome in containerless levitation with laser heating (LH) methods [24–27] which have been successfully exploited for measuring the structure of liquid metals and oxide melts in combination with NMR spectroscopy [28–34], Raman scattering [35], XAS [36–40], and neutron [41–47] or synchrotron XRD [45–59]. Wire heating, in which a micro-scale volume of liquid is held by surface tension within a small hole (~0.5–1 mm) drilled into the hotspot of a Pt–Rh/Ir heating wire [60], has also been successfully applied for the study of high-T liquid structure by Ramon spectroscopy [61–70], XAS [71–74], and small/wide angle x-ray scattering [75].

For experiments at non-ambient-\(p\), the generation of high-p relies upon the simple relation

\[
p = \frac{F}{A},
\]

where \(F\) is the force applied over a cross-sectional area \(A\). Pressure cells for high-\(p\) research can be classified into two distinct types: large volume devices which generate high-\(p\) by maximising the applied force, or the diamond anvil cell (DAC) which generates high-\(p\) by reducing the area over which the force is applied. To generate the simultaneous high-\(p\)-T conditions required for liquid-state studies, pressure cells are typically equipped with RH assemblies. In a DAC, laser-heating may also be employed. Large volume devices include piston-cylinder apparatus, which can achieve moderately high-\(p\)-T conditions of up to ~5 GPa and 1800 K, corresponding to lithospheric or lunar core depths, or the multi-anvil (MA) apparatus which are utilised for routine generation of conditions up to ~25 GPa and 2500 K, corresponding to transition-zone depths [76]. By exploiting smaller, micro-scale samples, the DAC can routinely generate conditions of the core-mantle boundary (120 GPa, 3000 K) and beyond.

Although synchrotron x-ray and neutron diffraction are both well established techniques for high-\(p\) solid-state crystallography [77, 78], diffraction studies of liquids at high-\(p\) remain challenging. This is due to the technically demanding task of generating the simultaneous high-\(p\)-T conditions necessary for melting combined with the requirement to accurately isolate the diffuse liquid scattering signal from the large background contributions arising from the apparatus containing the sample. High-\(p\) liquid diffraction studies have, therefore, been most widely undertaken at synchrotron facilities [79–81], where the high flux and micro-focussed x-ray beams are more suited to probing the small liquid volumes under compression by comparison to neutrons. Synchrotron XRD is a powerful tool by itself but a range of other techniques can also deliver highly complementary information on liquid structure. In situ XAS techniques are also commonly employed at synchrotron facilities and provide site-specific information on the local high-\(p\)-structure of liquids [82–85]. Raman spectroscopy has been exploited for geological fluids and melts at \(p\)-T conditions up to a few tens of GPa and \(\sim\)900 K [86–89], but measurements at higher \(T\) are extremely limited due to thermal emission from the hot sample dominating the Raman signal [35, 90]. High-\(p\) liquid-state NMR spectroscopy has been applied predominantly to biochemical studies such as protein folding/unfolding dynamics at up to ~1 GPa [91–94]. Although NMR spectroscopy is technically feasible in a DAC up to ~100 GPa and \(\sim\)1050 K [95–97], these conditions are generally restricted to solid-state measurements of hydrogen nuclei. The technique could, however, be ideal for studying liquid metallic hydrogen which is predicted under compression even at low \(T\) [18, 98, 99]. High-\(p\) NMR studies of the structure of oxide melts normally accomplished by ex situ NMR measurements of permanently densified glasses [100–109].

For a complete description of the structure of liquids, experimental data are commonly interpreted using atomistic models generated by computer simulations [110]. Reverse Monte Carlo (RMC) [111–114] and empirical potential structure refinement (EPSR) [115, 116] are commonly employed inverse simulation methods to generate a three dimensional structure fitted precisely to diffraction or spectroscopy data. In RMC atoms are moved randomly with moves accepted or rejected depending if they improve the fit, while in EPSR a classical potential is optimised to predict a structure in good agreement with the experimental data. However, the structural solutions obtained from these inverse methods are not unique and caution is needed to avoid over-interpretation of the resulting atomistic model which can have a strong dependency on the starting configuration or potential supplied [117, 118]. Molecular dynamics (MD) simulations generate dynamic models of liquid structure by solving Newton’s equations of motion for a given system of atoms [119]. In \textit{ab initio} or first principles MD, interatomic interactions are described by electronic structure calculations using a quantum mechanical method, such as density functional theory [120]. Although \textit{ab initio} MD can provide highly accurate predictions of liquid structure and properties, the computational cost is very high and remains limited to small systems (typically a few 100 atoms) and timescales (up to several 100 ps). In classical MD interatomic forces are computed from a classical potential [121], enabling computation of much larger systems (>10000 atoms) and longer timescales. However, classical potentials can be of limited accuracy and \textit{in situ} measurements of liquid structure are thus essential to provide an effective test of theoretical predictions from classical or \textit{ab initio} MD and, therefore, enable their extension to \(p\)-\(T\) conditions that are difficult to achieve experimentally [122].

This topical review is primarily focussed on \textit{in situ} XRD studies of liquid structure at high-\(p\). The review details the essential theory and sample environments for liquid
determination of polymer and biological structures. Since in the late 1960s, several groups have employed AD-XRD to study in situ liquid diffraction at high-$p$ and the wide variety of liquid-state studies reported in the literature, from simple to not-so-simple liquid metals, molecular to polymeric transformations in pnictogen and chalcogen liquids, and density-driven structural changes in water and silicate melts. The review concludes with a future perspective on in situ liquid diffraction studies.

2. High pressure liquid diffraction theory

This section provides an overview of the essential theory required for the processing and interpretation of high-$p$ liquid diffraction data measured by synchrotron XRD. For a more exhaustive treatment of the theoretical background of liquid diffraction methods, the reader is referred to the excellent review by Fischer et al [117] and references therein.

The general principle of a typical angle-dispersive XRD (AD-XRD) experiment of a liquid in a DAC is illustrated in figure 2. The sample is aligned to the focal point of a high-energy synchrotron x-ray beam of wavelength $\lambda$ and the x-ray photons are scattered elastically from the electron density distribution in the liquid. In contrast to the sharp Bragg diffraction peaks observed for crystalline solids, liquid diffraction patterns consist of a series of broad diffuse rings representative of a disordered structure. Diffraction data for liquids at modern synchrotron sources are usually measured using a two-dimensional detector array and integrated, after geometrical and incident beam polarization corrections [123, 124], to obtain the one-dimensional scattering intensity $I(Q)$ as a function of the elastic scattering vector

$$Q = \frac{4\pi}{\lambda} \sin \theta,$$  

where $\theta$ is one half of the scattering angle. The key data processing steps are illustrated in figure 3. The scattering signal $I_s(Q)$ arising solely from the liquid sample is obtained from the relation

$$I_s(Q) = I(Q) - a(Q)I_b(Q),$$  

where $I_b(Q)$ is the background scattering intensity measured for the pressure cell with no sample present (figure 3(a)). Accurately distinguishing the diffuse liquid diffraction signal from this background intensity is one of the major obstacles for accurate correction of x-ray intensities at high-$p$. Perfect characterisation of $I_b(Q)$ is difficult, requiring careful measurements of the unpressurised pressure cell using empty recovered gaskets to match the anvil separation during the high-$p$ experiment. The scaling factor $a(Q)$ in equation (3) accounts for attenuation of the incident beam in the presence of a sample. In theory, this can be quantified from the sample attenuation coefficient. However, in practice this is contingent upon the sample geometry which is often not explicitly known as a function of pressure such that $a(Q)$ is typically found empirically to achieve optimal subtraction of the cell background. Cell background scattering can be minimised by constructing the pressure vessel from x-ray transparent materials, reducing the fraction of non-sample components within the beam path, and increasing the volume of the sample, where feasible, to maximise the sample signal to background ratio. In addition to these steps, the diffraction signal arising solely from the liquid sample can be isolated by employing a multichannel collimator, consisting of an array of collimators in radial alignment [125–128]. In energy-dispersive mode, background features, including crystalline Bragg diffraction peaks, may also be eliminated by selective combination of data recorded at different fixed scattering angles $2\theta$.

The total liquid scattering signal $I_s(Q)$ can be separated into different coherent and incoherent components [117]. The total structure factor $F(Q)$ represents a thermal and spatial average of the liquid structure in reciprocal-space, arising from coherent interference of waves scattered from different atomic sites in the liquid, and is obtained after subtracting the theoretical self and incoherent scattering components from the total measured liquid scattering signal according to

$$F(Q) = \frac{1}{\gamma}I_s(Q) - \sum_{i=1}^{n} c_i [f_i(Q)^2 + f_i^*(Q)],$$  

where $n$ is the total number of chemical species $i$ with atomic fraction $c_i$. The $f_i(Q)$ and $f_i^*(Q)$ terms denote the x-ray form-factor (tabulated in reference [129]) and Compton scattering (tabulated in reference [130]), respectively, for a given atom. The factor $\gamma$ scales the measured intensity to fit the theoretical self and incoherent scattering in the mid-$Q$ ($\gtrsim 6$ A$^{-1}$) to

\[ \text{Figure 2. Illustration of the general principle of an angle dispersive XRD experiment for a liquid in a DAC in transmission geometry. A focussed high-energy x-ray beam with wavelength } \lambda \text{ is incident through the body of the upstream diamond anvil. X-rays scattered elastically from the sample produce a two dimensional diffraction pattern characteristic of the liquid and cell background.} \]
Figure 3. Data processing steps for total cross-section normalisation of in situ angle dispersive XRD measurements of a liquid at high-\textit{p}. (a) The total scattering intensity \( I(Q) \) measured for liquid gallium at 13 GPa in an RH-DAC [118] is shown together with the empty cell background scattering signal \( I_{\text{BG}}(Q) \), arising largely from the incoherent Compton scattering from the diamond anvils. (b) The scattering signal \( I_i(Q) \) arising solely from the incoherent Compton scattering from the diamond anvils. (c) The total scattering intensity \( I(Q) \), including the self and Compton scattering components. (c) The total structure factor \( S(Q) \) as obtained from equation (7).

\[ S(Q) = \frac{F(Q)}{\langle f^2(Q) \rangle} + 1. \]  

where the normalised total structure factor (figure 3(c)) is given by

The pair distribution function \( g(r) \) represents the radially averaged distribution of interatomic distances \( r \) in the liquid and is given by the Fourier transform relation

\[ g(r) - 1 = \frac{1}{2\pi^2\rho_0} \int_0^{Q_{\text{max}}} Q[S(Q) - 1] \sin(Qr) dQ. \]  

Here \( \rho_0 \) is the atomic number density i.e. the concentration of atoms per unit volume as derived from the mass density \( \rho \) by the relation \( \rho_0 = \rho N_A / M \), where \( N_A \) is Avogadro’s constant and \( M \) is the molecular mass. The \( g(r) \) functions measured for monoatomic liquid gallium at ambient-\( p \) and 13 GPa are shown in figure 4. The \( g(r) \) consists of a pattern of peaks and troughs corresponding to the distribution of interatomic distances in the liquid which tends to unity with increasing distance between atoms and zero at \( r \to 0 \) as a result of strong repulsive forces acting at small interatomic separations [135]. For a multicomponent system, \( g(r) \) contains the weighted sum of the individual partial pair distribution functions \( g_{\alpha\beta}(r) \). The finite maximum scattering vector \( Q_{\text{max}} \) accessible in a diffraction measurement results in peak broadening in \( g(r) \) and the appearance of spurious ‘termination ripples’ which can lead to over interpretation of experimental results. This is particularly problematic for high-\( p \) experiments for which the available scattering angle is often limited by the experimental apparatus.
These Fourier transform artefacts can be reduced by applying a damping modification function to \( S(Q) \) prior to Fourier transform [56, 136, 137] but this comes at the cost of a further reduction of resolution in \( g(r) \).

The normalisation of liquid XRD intensities can be optimised by considering the simple low-\( r \) behaviour of the differential correlation function

\[
D(r) = 4\pi \rho_0 r [g(r) - 1],
\]

where prior to the first interatomic distance \( r_{\text{min}} \)

\[
D(r < r_{\text{min}}) = -4\pi \rho_0 r. \tag{10}
\]

As there are no interatomic correlations in this region, any oscillations arise from experimental uncertainty e.g. systematic errors in the normalisation of \( S(Q) \) or Fourier transform artefacts. These errors can be minimised by subtracting the Fourier transform of the difference

\[
\Delta D_i(r) = D_i(r) - (-4\pi \rho_0 r), \quad \text{for } r < r_{\text{min}} \tag{11}
\]

from the reciprocal-space data over \( i \) iterations [138]. In high-\( p \) liquid diffraction experiments, the bulk liquid number density is often not known beforehand. Using this iterative auto-normalisation procedure, the liquid density can be refined by minimising a \( \chi^2 \) figure of merit

\[
\chi^2(\rho_0) = \int_0^{r_{\text{min}}} [\Delta D(r)]^2 \, dr \tag{12}
\]

which has a well-defined minimum [138, 139].

The average coordination number \( \bar{n} \), defined as the average number of \( \beta \) atoms surrounding a central atom \( \alpha \) in a coordination shell of inner and outer radius \( r_1 \) and \( r_2 \), respectively, is obtained via the integral

\[
\bar{n}_{\alpha\beta} = 4\pi \rho_0 c_{\beta} \int_{r_1}^{r_2} r^2 g_{\alpha\beta}(r) \, dr, \tag{13}
\]

where typically \( r_1 = 0 \) and \( r_2 \) is the position of minimum after the first peak in \( g(r) \). Hence, the average coordination number provides information on the nature of short-range chemical bonding. However, this simple geometric consideration may not accurately represent the genuine nature of chemical bonding in the liquid and, in contrast to crystalline materials, unless \( g(r = r_2) = 0 \) there is no absolute coordination structure. This is exemplified by the running coordination number \( n(r) \) which increases continuously as a function of \( r \) if there is no well-defined minimum after the first peak in \( g(r) \). For an ill-defined peak, the average coordination may be estimated by symmetrising the first peak in \( rg(r) \) or \( r^2 g(r) \) and computing twice the value of the integral up to the maximum of the first peak [140, 141]. For a multi-component liquid, if the peak of interest in \( g(r) \) cannot be attributed to a single \( g_{\alpha\beta}(r) \) then the contributions due to different partial correlations may be approximated by fitting the peak to a sum of appropriate (e.g. Gaussian) distribution functions [142, 143].

3. Sample environments for liquids under extreme conditions

There are several fundamental difficulties associated with measuring diffraction by liquids at high-\( p \), including (i) the technical challenge in itself of generating simultaneous high-\( p-T \) conditions, (ii) potential reactions between the liquid sample and surrounding containment media, (iii) the diffuse nature of the scattering signal from the disordered liquid structure which is compounded by (iv) small sample volumes and thick layers of material blocking direct access to the sample. Several of these difficulties can be overcome by exploiting the high flux, high-energy, and tightly focused x-ray beams produced at synchrotron radiation facilities, with further mitigation strategies including optimisation of the pressure vessel design to reduce the fraction of non-sample components in the x-ray path and utilizing x-ray transparent materials for construction of the cell components.

The first \textit{in situ} high-\( p \) liquid diffraction measurements were made in the early 1970s using a conventional powder x-ray diffractometer equipped with a tetrahedral anvil press to determine the structure of liquid sodium to 4.3 GPa [144, 145]. However, high-energy synchrotron x-rays are essential to probe the bulk structure of liquids effectively and to maximise the accessible \( Q \)-range for good resolution in \( g(r) \). From the mid-1980s MA apparatus have been widely used at synchrotron facilities, particularly at the Photon Factory (PF) and SPring-8 in Japan, for systematic measurements of the structure of liquid metals and semiconductor elements and their alloys [79, 146, 147], and subsequently adapted for silicate melts [148]. More recently, the Paris–Edinburgh press and DAC have been adopted for liquid diffraction measurements at synchrotron facilities around the world [80, 149, 150]. A general overview of these most widely used sample environments and their optimisation for diffraction studies of liquid structure at high-\( p-T \) is provided below.

3.1. Large volume devices

The MA apparatus is a well established large volume device for generating simultaneous high-\( p-T \) conditions. The MA apparatus applies multiple anvils to apply compression to a sample in four or more directions. High-\( T \) is achieved via a graphite or lanthanum chromite cylindrical resistive heater surrounding the sample assembly, with precise \( T \) measurements made using a thermocouple. The most widely used MA devices are the cubic-anvil ‘DIA’-type and 6–8 Kawai-type in which six first stage anvils and eight second stage anvils compress an octahedral sample and furnace assembly [151]. High-\( p-T \) conditions up to \( \sim 20–30 \) GPa and 3000 K can be routinely generated by MA apparatus, with higher-\( p \) in the megabar (1 Mbar = 100 GPa) range possible by employing e.g. sintered diamond anvil material and innovative anvil truncations [151–157]. While these large volume devices are readily exploited for \textit{ex situ} high-\( p-T \) experiments, the main disadvantage of MA devices for diffraction studies is the extremely limited angular access to the sample due to the bulky nature of the apparatus. To overcome these difficulties, MA devices
may be constructed using x-ray transparent cubic boron nitride anvils or with sintered diamond windows built into the anvils. To compensate for the limited angular range of the scattering aperture, energy-dispersive (ED)-XRD is typically used, where the diffraction signal is measured as a function of scattering vector $Q$ by varying the x-ray energy at fixed scattering angle.

The first MA apparatus for synchrotron applications was the MAX-80 installed in the early 1980s at the PF in Japan, adopting a cubic DIA-type design [158]. Now, almost all third generation synchrotron sources have beamlines with MA capabilities [151]. The MAX-80, MAX-90, and MAX-III devices at the PF and SPEED1500 Kawai-type double-stage apparatus at SPring-8 in Japan have been extensively exploited for high-$p$–$T$ diffraction studies of liquid metals and semiconductors [79, 146, 159]. Alternatively, the Paris–Edinburgh (PE) cell is a more portable large-volume device with wider accessible $Q$-range compared to the large-scale MA apparatus. The PE cell was originally developed in the late 20th century for in situ powder neutron diffraction experiments (for which a large sample volume is essential) with wide angular accessibility at high-$p$ up to ∼ 25 GPa [160, 161] and subsequently adapted for in situ high-$p$–$T$ synchrotron XRD experiments at the ESRF [149, 162–164]. In the last decade, a similar experimental setup was developed at HPCAT beamline 16-BM-B [80] of the Advanced Photon Source (APS), USA, providing routine ED-XRD measurements of silicate melts in the PE-cell with $Q_{\text{max}} \sim 20 \text{ A}^{-1}$ [80, 165–167]. Illustrated in figure 5, the silicate sample is encapsulated in a cell assembly with a graphite heater and other low density materials designed to limit the extrusion of cell materials and maintain large vertical access to the sample at high-$p$ [165, 166]. In combination with high-speed white-beam x-ray radiography, the PE-cell as been utilised for simultaneous structure and falling sphere viscosity measurements of liquids at high-$p$–$T$ [80, 168, 169], a technique originally developed for MA apparatus [170–176]. A drawback of the PE cell is that $T$ is not typically measured in situ and is instead estimated from a calibration of the heater-power performance, leading to uncertainties in $T$ of > 10% [164]. Liquid diffraction measurements in the PE cell are currently limited to conditions up to ∼ 7 GPa and 2300 K [80], although diffraction measurements of glasses have been reported into the Mbar regime using a double-stage PE cell [177–179].

3.2. The diamond anvil cell

The DAC is a compact device capable of generating ultra-high static pressures with only a moderate applied force by compressing a sample between the flat polished tips (culets) of two inclusion-free single crystal diamond anvils [186, 187]. A variety of DAC designs are available [188] for accommodation in a wide range of different experimental set-ups. The opposed anvil culets, polished to a few 10 s to 100 s of micron diameter, are separated by a thin gasket which acts as the seal of the sample chamber and is typically made from a hard metal foil such as rhenium. The sample is loaded under a microscope into a pressure chamber drilled (either mechanically, by spark erosion, or by laser ablation) into an indentation in the gasket preformed by the anvils. High-$p$ conditions of up to ∼ 1 Mbar can be routinely generated by simply squeezing the two opposing anvils towards each other by e.g. tightening spring-loaded screws (using Belleville spring washers) on the DAC [189] or using an inflatable metallic membrane [190]. Multi-Mbar pressures can be achieved using bevelled [191] or toroidal [192] anvils. Static pressures in the terapascal (1000 GPa) regime have also been reported using secondary micro-ball nano-crystalline diamond anvils [193, 194]. The simultaneous high-$p$–$T$ conditions required for liquid state studies in the DAC can be achieved by either resistive or laser heating techniques (figure 6).

The wide transparency window of diamond enables a sample to be monitored in situ under compression using a range of optical microscopy, spectroscopy, and x-ray scattering techniques, while also enabling pressurised samples to be heated to temperatures in excess of 5000 K by infra-red (IR) lasers. Typically, a piece of Cr$^{3+}$-doped ruby is included in the sample chamber for pressure calibration, where $p$ is determined from the sensitive shift in the 694 nm ruby fluorescence peak [195–197]. Alternatively, $p$ may be determined from the Raman shift of the singlet peak of the diamond anvil at the culet surface [198, 199] or from the change in unit cell volume as determined from the Bragg reflections of an XRD calibrant placed inside the sample chamber. Synchrotron AD-XRD measurements in the DAC offer the advantage of fast data acquisition times (from a few seconds to several minutes) compared with much longer acquisition times (up to several hours) required for ED-XRD. However, liquid AD-XRD measurements in the DAC are often limited in $Q$-range accessibility. It
is, therefore, important to maximise the angular access on the downstream (scattering) side of the cell by using wide-opening anvil seats (e.g. Boehler–Almax type [200]) and high-energy (> 50 keV) x-rays to achieve a high enough $Q_{\text{max}}$, typically at least $\gtrsim 10$ Å$^{-1}$) for good resolution in real-space. The background scattering in a DAC experiment arises largely from the incoherent Compton scattering of diamond and can be reduced by using thinner [200] or perforated [201, 202] anvils.

3.2.1 Laser heating. High-$T$ conditions from 1500 K to > 5000 K are feasible in the LH-DAC, which has been widely adopted at synchrotron beamlines [203, 204] for e.g. high-$p$-$T$ sub-solidus crystallography and melting relations [198, 199, 205–213] and liquid structure measurements [182–184, 214, 215]. LH-DAC systems commonly employ tightly focussed lasers operating at near-IR ($\sim 1 \mu m$) wavelengths which are absorbed by free electrons in metallic materials. Temperature is measured in situ using spectroradiometry by fitting a blackbody function to the thermal emission measured from the heated region [216]. Temperature gradients are nominally very high (of the order of 100 K $\mu$m$^{-1}$ or more) which prevents total melting of the sample in the cell. Axial temperature gradients can be reduced by heating the sample from both sides and by surrounding the sample by a thermal insulating medium (e.g. KCl, Al$_2$O$_3$) to prevent heat dissipation through the highly thermally conductive diamond anvils (figure 7). However, this leads to significant contamination of the liquid diffraction signal by crystalline Bragg peaks (figure 6(a)) and risk of chemical reaction with the thermal insulation media. Radial temperature gradients are reduced by using beam shaping optics to achieve a wide flat top heating spot [208]. The use of micro-focussing x-ray optics such as Kirkpatrick–Baez mirrors are essential for LH-DAC synchrotron studies to ensure that the incident x-ray beam is smaller than the micro-scale heated region of the sample, thereby minimising any scattering signal from the unheated region. For diffraction studies, off-axis laser heating is preferable to prevent contamination of the diffraction signal with scattering from the laser mirrors. The major challenge for experimentalists during an LH-DAC experiment is ensuring good coupling of the two laser beams from each
A microfocused x-ray beam impinges on the heated region of the sample. Metal-free samples can be heated using a single laser beam from both sides. For CO2 (mid-IR) laser heating, the sample contains a metallic coupler and laser beams heat diamond anvils and ensure efficient heating. For near-IR laser DAC assembly [118, 219, 220], the sample can be placed either outside the cell, thereby heating the entire sample, or inside the cell, surrounding the anvils to provide more localised heating [185, 221–227]. Temperatures are typically monitored via a thermocouple positioned close to the sample. The highest operating temperature of an externally heated RH-DAC is generally limited to $\sim 1500 \text{ K}$ due to the high risk of graphitization of the unpressurised parts of the diamond anvils or thermal deformation of other cell components. However, the RH-DAC does offer some distinct advantages including precise control and enhanced stability of $T$ with reduced thermal gradients. Furthermore, resistive heating provides homogenous heating to achieve whole-sample melting over the entire sample and, therefore, provides a stronger and cleaner scattering signal from the liquid in comparison to the LH-DAC [118, 185] (figure 6(b)). An innovative internal resistive heating (IRH) technique was recently developed in Bristol, providing extremely homogenous heating of both metallic and insulating materials to at least 3000 K and 64 GPa, as confirmed by in situ synchrotron AD-XRD with simultaneous spectroradiometric measurements [228]. Although similar IRH techniques, including ‘fine-wire heating’, are well established for melting and resistivity measurements of metals [229–234], the application of IRH to non-metallic samples has been extremely limited [235, 236]. The Bristol IRH-DAC utilises a microfabricated heater filament placed inside the pressure chamber of a ‘split-gasket’, where the two sides of the gasket are isolated from each other by insulating epoxy. The sample is placed in a laser-drilled hole in the heating filament and electrical current transferred through the filament via the gasket.

Temperature stability in the RH-DAC is excellent, with $< 20 \text{ K}$ variation over several hours without user intervention, over an order of magnitude improvement on the LH-DAC. In combination with micro/nanofocus diffraction and spectroradiometry capabilities at synchrotron beamlines, the IRH-DAC has unprecedented potential for measuring the atomic-scale structure of wholly molten metal-free samples at deep lower mantle conditions [228].

### 3.3. Shock compression

Shock compression techniques offer an alternative approach to study the liquid state by subjecting a sample to a large controlled compression achieved by high velocity impact, explosion, or powerful laser pulse. As a shock front of duration $\sim 10^{-9} \text{ s}$ is driven through a sample, the material undergoes an irreversible sequence of disequilibrium states until it reaches a final super-isentropic compressed state lasting $10^{-8}$ to $10^{-6} \text{ s}$ [237]. Material characteristics of the shocked sample can be deduced from velocimetry and pyrometry diagnostics. Simultaneous time-resolved XRD or spectroscopy measurements of the shocked sample can be made to probe the atomic-scale characteristics. However, the low photon flux provided by conventional x-ray sources, and large background contributions, mean liquid diffraction studies are extremely limited and most studies to date have focussed on the solid state [238].

Modern x-ray free-electron laser (XFEL) facilities generate ultra-bright femtosecond flashes of x-rays which can be utilised for time-resolved diffraction measurements of shock compressed liquids. This has been exploited recently to measure the structure factors of liquid Bi [239] and liquid Sn [240] using laser compression at the matter in extreme conditions (MEC) [241] end station of the Linac Coherent Light Source (LCLS), USA. Here, a high energy laser pulse is incident on a plastic absorbing medium which rapidly ablates and expands at high velocity driving a compression wave through the sample. The XFEL pulse is timed to arrive at the sample at peak compression during the shock transit, where the scattered x-rays are recorded using two-dimensional detector arrays in
transmission geometry. An example raw diffraction image and integrated two-dimensional diffraction pattern of shock compressed liquid Sn at 51(1) GPa measured by Briggs et al [240] is shown in Figure 8. Some residual β-Sn diffraction peaks arising from uncompressed material ahead of the shock front are unavoidable and must be subtracted to obtain the underlying diffuse liquid scattering signal.

4. High pressure liquid diffraction studies

4.1. Structure of liquid metals

At ambient-\( p \), the majority of pure metallic liquids can be described as simple liquids [140]. This is a consequence of the collective de-localisation of the valence electrons of the constituent atoms with the remaining positively charged ionic cores occupying less than 10% of the total volume [135]. In the absence of hydrogen bonding or other electrostatic forces, the interatomic structure is governed solely by the strong short-range repulsion of these ion cores. The atomic interactions can be described by elastic collisions between impenetrable ‘hard-spheres’ of effective diameter \( \sigma \), represented by an interatomic potential \( V(r) \) with the form

\[
V(r) = \begin{cases} 
\infty, & \text{for } r < \sigma \\
0, & \text{for } r \geq \sigma.
\end{cases}
\] (14)

This model has an analytical solution represented by the Percus–Yevick [242] closure relation of the Ornstein–Zernike equation [243]. The particles in a simple liquid will pack in the most efficient way to balance repulsive forces with packing density

\[
\eta = \frac{\pi \rho_0 \sigma^3}{6}.
\] (15)

The Percus–Yevick structure factor \( S_{PY}(Q) \) and pair distribution function \( g_{PY}(r) \) have symmetric peaks equally separated by \( \sigma \) in real-space and \( 2\pi/\sigma \) in reciprocal-space, with ratios between the second and first peak positions of \( Q_2/Q_1 \approx 1.86 \) and \( r_2/r_1 \approx 1.91 \) [140]. Extensive x-ray and neutron diffraction measurements reveal that for a suitably selected packing density the \( S_{PY}(Q) \) closely resembles the experimental \( S(Q) \) functions for most liquid metals at ambient-\( p \), with nearest neighbour coordination numbers \( n \approx 11–12 \) consistent with close packing of hard spheres [140, 244]. These melts are categorised as type-I liquid metals [140] and include most transition metals, alkali liquids, the alkaline earths, and rare-earth elements.

However, the structure of some liquid metals or metalloids deviate from this simple hard-sphere description due to the varying tendency towards metallic or covalent bonding across the periodic table. Electrostatic interactions between the liquid atoms lead to anomalous behaviour and low-coordination numbers as the particles attempt to minimise the energy of the first coordination shell [245]. For example, diffraction measurements of the group 12 liquid elements zinc (Zn), cadmium (Cd), and mercury (Hg) are characterised by slightly asymmetric first peaks in \( S(Q) \) and \( g(r) \) with deviations in \( Q_2/Q_1 \) and \( r_2/r_1 \) from their ideal ratios [140]. Nevertheless, the coordination numbers of these type-II liquid metals remain essentially metallic at \( n \approx 10–11 \), consistent with a slightly distorted and loosely packed hard-sphere structure [140, 245].

Diffraction measurements of the polyvalent liquids gallium (Ga), silicon (Si), germanium (Ge), tin (Sn), arsenic (As), antimony (Sb), and bismuth (Bi) deviate more significantly from the simple hard-sphere model and are classified as type-III liquids [140, 245]. Signatures of a more complex structure of these melts include large deviations in the second and first peak positions of \( S(Q) \) and \( g(r) \) from their ideal values, the appearance of a shoulder or subsidiary peak on the high-\( Q \) side of the first peak in \( S(Q) \), a subsidiary peak between the two first maxima in \( g(r) \), and often exceptionally low coordination numbers [245]. The group 14 elements Si, Ge, and Sn experience a progressive reduction in the prominence of these anomalous features in \( S(Q) \) and \( g(r) \) with increasing atomic number (\( Z \)) and they are not observed at all in liquid lead (Pb), consistent with the reduction in covalent bond strength with increasing atomic radius. The group 14 elements undergo an interesting trend with increasing \( Z \) from the type-I hard-sphere-like structure of liquid aluminium (Al), to the anomalous complex type-III structure of liquid Ga, followed by the type-II liquid structure of indium (In) and back to the type-I structure of liquid thallium (Tl) [245].

The anomalous type-III liquid metals all exhibit an unusual negative slope in the melting curves on initial compression (figure 9). This behaviour is accompanied by a remarkable volume contraction on melting at ambient-\( p \) and can be understood by considering the Clausius–Clapeyron relation

\[
\frac{dp}{dT_m} = \frac{\Delta V_m}{\Delta S_m}.
\] (16)
where $\Delta V_m$ and $\Delta S_m$ denote the change in volume and entropy, respectively, between the solid and liquid states at the melting temperature $T_m$. The liquid-state entropy is always higher than in the solid-state and normally, the volume of a liquid is greater than the solid, resulting in a melting curve with a positive slope. A negative slope implies an increase in density on melting which requires a closer packed structure or change in bonding scheme in the liquid compared to the solid. This is exemplified by the everyday observation that ice floats on water, a consequence of the negative melting curve of $\text{H}_2\text{O}$. Higher contraction on melting is observed for steeper negative slopes, with values of around 10% ($\text{Si}$) [246], 6% ($\text{Ge}$) [246], 3.3% ($\text{Bi}$) [247], and 3.2% ($\text{Ga}$) [248]. The negative melting curves of the type-III liquid metals terminate in a solid–solid–liquid triple point (figure 9) associated with abrupt volume changes. A negative melting-curve on initial compression implies a melting curve maximum at negative (tensile-strained) pressure, similar to melting-curve maxima observed in other anomalous liquid systems such as alkali and chalcogenide elements [11]. In fact the melting curve for $\text{Sb}$ is already approximately flat close to ambient-$p$ with a gradual negative gradient at elevated-$p$ (figure 9). As a result it does not contract on melting at ambient-$p$, although the liquid-state expansion is unusually low at $<1\%$ [249].

Melting-curve maxima can be explained by considering a two state model proposed by Rapoport, originally developed to explain the unusual characteristics of water [256]. In this model, the liquid consists of two distinct coexisting states denoted low density liquid (LDL) and high-density liquid (HDL), with local structures reminiscent of corresponding low- and high-$p$ polymorphic crystalline solids. With increasing $p$, the LDL phase transforms continuously towards the HDL phase, culminating in a rapid change in concentration of the two phases predicted close to the melting-curve maximum.

The complex structures in type-III liquids can be understood in terms of an interplay between the random ionic packing and modulation of the local structure by Friedel oscillations in the effective interatomic forces beyond the first coordination shell [245, 257, 258]. As discussed above, the first peak in $S(Q)$ for a type-III liquid relates to the geometrical packing constraints of the repulsive hard-sphere cores with effective diameter $\sigma$ at $Q = \frac{2\pi}{\sigma}$. The high-$Q$ subsidiary peak, on the other hand, is associated with medium-range order with periodicity characteristic of the wavelength of the Friedel oscillations, producing a peak in reciprocal space at $Q_c = 2k_F$ (the diameter of the Fermi sphere), where $k_F$ is the Fermi wavenumber of the conduction electrons [259]. This is supported by electronic structure calculations which predict the modulation of random ionic packing by Friedel oscillations leads to weak covalent bonding effects in the light group 14 liquids Si and Ge [260]. Ab initio MD simulations predict tetrahedral fluctuations in the local structure [261–263], accounting for the unusually low average coordination numbers observed in these liquids. The return towards closed-packed metallic structures with increasing $Z$ (hence higher electron density) is driven by increasing non-local relativistic bonding effects damping the Friedel oscillation amplitude [260]. Fragments of tetrahedra are also found in liquid Sn but are absent in the close packed liquid Pb [264]. Si, Ge, and other type-III liquids, have a strong tendency to supercool. Diffraction measurements of levitated liquid Si and Ge show that the subsidiary peak in $S(Q)$ becomes significantly sharper with deeper supercooling [265–267]. This is consistent with a transition towards a metastable LDL structure consisting of tetrahedral clusters with covalent bonding reminiscent of the ambient-$p$ open diamond lattice crystalline structure [267].

Analysis of the periodic features present in early diffraction data of liquid metals (as tabulated by Waseda (1980) [140]) supports the link between Friedel oscillations and tetrahedral ordering. This is illustrated for Si, Ge, and Sn liquids in figure 10. Under ambient conditions, Si and Ge crystallise into a covalently bonded open diamond lattice structure with a coordination number of four. On melting, both elements undergo a semiconductor to liquid metal transition associated with an increase in coordination number to $\sim 6–7$ [140, 265, 268]. Sn adopts a body-centred-tetragonal ($\beta$-tin) structure above $13.2^\circ \text{C}$ and has a positive melting curve, in contrast to the negative slope observed for Si and Ge. Various different values of $\sim 7–11$ are reported for the coordination number of liquid Sn depending on the method of integration used [269]. For liquid Si and Ge, the position of the first peak $Q_1$ in $S(Q)$ is decoupled from the high-$Q$ reciprocal-space periodicity relating to local ordering. Instead, the subsidiary peak $Q_2$ marks the onset of periodicity $\Delta Q$ in reciprocal-space, which correlates inversely to the position of the nearest neighbouring peak $r_1$ in real-space via the simple Fourier relation $\Delta Q = \frac{2\pi}{r_1}$. 
Interestingly, the subsidiary peak at position \( r_s \), between the two first maxima \( r_1 \) and \( r_2 \), also marks the onset of periodicity \( \Delta r \) in real-space, which can be predicted from the position of the reciprocal-space subsidiary peak \( Q_s \) via the relation \( \Delta r = 2\pi/Q_s \). Supposing the real-space subsidiary peak at \( r_s \) relates to the distance between two atoms at adjacent vertices of a regular tetrahedron, then the distance between a central atom and a vertex is the circumsphere radius \( r_0 = r_s \sqrt{6}/4 \) [270, table I(i)]. As indicated in figure 10, this position represents the lower limit of the first interatomic distances in \( g(r) \) for liquid Si and Ge. However, \textit{ab initio} MD [263] and RMC [267] simulations predict liquid structures of Si and Ge that are reminiscent of the \( \beta \)-tin structure of the high-\( p \) crystalline polymorphs. The \( \beta \)-tin structure is characterised by flattened tetrahedral geometry, with four nearest neighbours and two additional neighbours arranged a further distance away perpendicular to the plane of the tetrahedron, giving a coordination number \( C_1 = 4 + 2 \), consistent with the value of \( n \sim 6 \) observed in the liquid. In a flattened tetrahedron arrangement, the interatomic distance between centre of vertex can be calculated by \( r_0 = r_s \sqrt{2} / 4 \) [263], which corresponds very closely to the nearest neighbour peak \( r_1 \) observed in the \( g(r) \) functions of liquid Si and Ge (figure 10). It is, therefore, apparent that the subsidiary peak \( Q_s \) is a signature of topological ordering of short-range distorted tetrahedral structures in these liquids. In contrast, while there remains some residual signature of the subsidiary peaks \( Q_s \) and \( r_s \) for liquid Sn, they are no longer coupled to the periodicity observed in either reciprocal- or real-space, and predicted tetrahedral bond lengths are no longer consistent with the position of the nearest-neighbour peak (figure 10). Instead, the first peak in \( S(Q) \) at \( Q_1 \) marks the onset of periodicity \( \Delta Q \) in reciprocal-space and is in closer agreement with the Ehrenfest relation \( Q_1 r_1 \approx 5\pi/2 \) for a dense packing of hard spheres [19]. Thus, the topological ordering in liquid Sn is dominated by a packing arrangement corresponding to a simple hard-sphere liquid.

4.2. Structure of type-I liquid metals at high pressure

The structure of type-I metallic liquid Al has been measured by Ikuta \textit{et al} [271] by ED-XRD up to 6.9 GPa and 1773 K using the PE press at the HPCAT beamline 16-BM-B [80] at the APS. The measured \( S(Q) \) functions reveal that over the \( p-T \) range explored there is no change in the ratio \( Q_2/Q_1 \) with increasing \( p-T \) conditions. Similar observations were reported by Shen \textit{et al} [214] in \( S(Q) \) data of liquid iron (Fe) up to 58 GPa and 2900 K (figure 11), as measured along the melting-curve using the LH-DAC at the GSECARS beamline 13-ID-D [272] at the APS. The first peak in \( S(Q) \) shifts to higher \( Q \) values with increasing \( p \) but retains the same shape, as evident by plotting the \( S(Q) \) as a function of the scaled momentum transfer.
(figure 11(b)), consistent with a close-packed hard-sphere liquid structure persisting from ambient to high-$p$. Understanding the structure and properties of Fe at high-$p$ is of considerable interest as it is the archetypal transition metal and the primary constituent of terrestrial planetary cores [273]. The high-$p$ diffraction measurement of liquid Fe [214] validates the linear extrapolation of the melting transition of Fe on the basis of the simplistic Lindemann criterion, which states that melting occurs when the thermal vibration amplitude exceeds a threshold value [274] and requires the structure to be invariant along the melting-curve [275]. The structural data also has important applications for interpreting the seismic wave speed parameter

$$\phi = V_p^2 - \frac{4}{3} V_S^2,$$

where the longitudinal $V_p$ and shear wave $V_S$ sound velocities are the primary observables in seismological studies. For a hard-sphere liquid, this seismic parameter $\phi$ is dependent upon $T$ and $\eta$ such that knowledge of the packing fraction of liquid Fe can be applied to determine the thermal structure of Earth’s molten outer core from global seismic measurements [276]. However, minor discrepancies observed between the model and experimental data at high-$Q$ (representative of local structure), may be indicative of a small deviation from hard-sphere behaviour at high-$p$ [214]. Kuwayama et al [277] recently extended the $p$-$T$ range of structural measurements of liquid Fe to 116 GPa and 4350 K using the LH-DAC at beamline BL10XU [278] at SPring-8, reporting densities $\sim 3\%-3.5\%$ lower than predicted by the hard-sphere model. Thus, while the hard-sphere model likely provides a good foundation for describing the structure of liquid Fe at high-$p$, consideration of slight perturbations in the standard hard-sphere model may be required to achieve perfect agreement with experimental measurements in the high-$Q$ region [214].

While predominantly Fe-rich (+5%-10% Ni), planetary cores also contain significant minor fractions of light elements such as Si, carbon (C), and sulphur (S). It is, therefore, important to understand the effect these light elements have on the structure of liquid Fe. The structure of liquid FeS was measured up to 5 GPa by Urakawa et al [279] using the MAX-80 system at the PF. In contrast to the close packed structure of pure Fe, liquid FeS exhibits a less organised covalent structure with a local Fe–S coordination number of six, leading to a higher compressibility compared to pure Fe melt [280–282]. However, AD-XRD measurements of Fe–FeS liquids by Morard et al [283, 284] using the PE-cell at beamline ID27 [181] at the ESRF, reveal that while S modifies the structure significantly at low-$p$, under core conditions liquid FeS adopts a more compact structure consistent with a hard-sphere liquid. This leads to a drastic increase in bulk modulus with the implication that appreciable concentrations of S could be dissolved in the Earth’s core and still be compatible with observed seismological sound velocities [284]. Several studies have also been reported for liquid Fe–Si [282, 284] and Fe–C [184, 285], with different incorporation mechanisms for Si (substitutional) and S or C (interstitial) suggested [286].

It should be noted that while the type-I liquids Al and Fe exhibit close to ideal compression behaviour, simulations using an ab initio random structure searching technique have predicted the crystal structure of Al transforms to an open-packed incommensurate host–guest structure at 3.2 TPa [287]. The predicted formation of complex open-packed crystalline solids in the TPa-regime has important implications for understanding the behaviour of liquid cores in super gas giant planets as it opens the possibility of similar transformations also occurring in type-I metallic liquids. Indeed, the likelihood of this occurrence is supported by the observation of simple-to-complex liquid–liquid transformations in the quintessentially metallic alkali elements which form open-packed structures in the GPa-regime (discussed in section 4.5).

4.3. Structure of type-II liquid metals at high pressure

Diffraction data for type II liquids, including the group 12 elements Zn, Cd, and Hg, are characterised by a slight asymmetry of the first peaks in $S(Q)$ and $g(r)$, with $Q_2/Q_1$ and $r_2/r_1$ ratios slightly lower than ideal values for a simple liquid. The liquid structures are correlated to the corresponding crystalline solids from which they melt with some slight distortion from hard-sphere packing [245, 288]. Few structural measurements have been made for these liquids at high-$p$. No diffraction measurements have been reported for liquid Zn, although XAS measurements indicate no change in local structure at pressures up to 1.6 GPa [289]. For Cd, liquid diffraction measurements have been reported up to 6.8 GPa and 873 K using an RH-DAC at beamline 12.2.2 [290] at the Advanced Light Source (ALS), USA [291]. The authors report no change in melt structure over the $p$-range studied. However, it should be noted that the $g(r)$ data is heavily broadened due to the truncation of $S(Q)$ at low $Q_{\text{max}} \sim 6.5$ Å$^{-1}$ and as such subtle changes in local structure may not be resolved. Liquid Hg is ideally suited for
liquid structure measurements due to its famously low melting point. Despite this, no structural measurements for liquid Hg have been reported in the liquid field close to the melting curve at high-p, although extensive studies of expanded liquid Hg have been made to test the existence of a predicted metal–insulator transition in the vicinity of the liquid–vapour critical point (1.67 GPa, 1749 K), with diffraction measurements revealing increasing asymmetry in the first peak in g(r) attributed to increasing non-metallic domains with longer bond lengths [292, 293].

It would be reasonable to expect the coordination number of these type-II liquids to increase from their ambient-p values of ~10 [140, 294] towards a more ideal close packed structure on the application of high-p. However, while the melting curve of Zn initially rises linearly in accordance with the Lindeman law, beyond 60 GPa there is a change in slope of dp/dTm [295]. This may be indicative of changes in liquid structure and associated subsolidus polymorphism, although no solid–solid transitions have been found thus far up to 140 GPa beyond the isomorphc hcp–hcp transition at ~10 GPa [295]. Similarly, the melting curve of Hg has a positive slope on initial compression but experiences a curvature towards lower gradient after 3–4 GPa, which as for Zn could be indicative of an underlying structural transformation in both the solid and liquid states. The high-p Si(\(Q \)) of type-II liquid In has been measured by Shen et al [296] at 6.3 GPa and 710 K, using an externally heated RH-DAC at the GSECARS beamline 13-ID-D [272] at the APS. The results show an increase in coordination number from \(n \sim 10\) at ambient-p [297] to 12, consistent with transformation from a more loosely packed distorted hard-sphere structure towards a close packed structure.

### 4.4. Development towards hard-sphere behaviour in type-III liquid metals at high pressure

Several ED-XRD studies of the high-p structure of group IV liquids have been reported using the MA apparatus at the PF and SPring-8 synchrotron facilities. Funamori and Tsuji [298] measured the structure of liquid Si just above the melting curve at four pressures up to 23 GPa. Under initial compression, up to at least 8 GPa, the height and position of the first and second peaks in Si(\(Q \)) increase slightly, while the ratio \(Q_2/Q_1\) remains close to the ambient-p value of 2.07 [140]. There is little change in the intensity of the subsidiary peak \(Q_s\) over this \(p\)-range, characteristic of a mixed metallic and covalent bonding scheme in the liquid. Meanwhile, the coordination number increases from ~6.4 at ambient-p [140] to ~7 at 8 GPa, accompanied by a slight reduction in nearest-neighbour bond length. These observations indicate that on initial compression the structure of liquid Si contracts near uniformly with only small changes in bonding. At higher-p the metallic domain increases and the liquid transforms to a denser structure more closely resembling a type-II liquid metal, as demonstrated by a rapid reduction in the ratio \(Q_2/Q_1\) to 1.92 at 23 GPa, an increase in coordination number to \(n \sim 9\), and the near disappearance of the subsidiary peak \(Q_s\) [298]. Structural models of the liquid, generated using potentials refined to fit experimental data using the Schommers algorithm, reproduce the marked densification and increase in local coordination number after 8 GPa but indicate the topological packing density remains loose at 23 GPa [304].

Tsuji et al [147] reported additional measurements of Si together with the other group IV liquids Ge and Sn, noting a more continuous anisotropic compression of liquid germanium compared to Si. However, their \(Q_2/Q_1\) ratios for high-p liquid diffraction measurements of Si [147, 298], Ga [118, 299], Ge [147, 300], Sn [240, 301, 302], and Bi [239, 303]. The ideal values \(Q_2/Q_1 = 1.86\) and \(r_2/r_1 = 1.91\) consistent with a simple hard-sphere liquid are indicated by the dotted lines.

![Figure 12. Ratio of peak positions (a) \(Q_2/Q_1\), and (b) \(r_2/r_1\) from high-p liquid diffraction measurements of Si [147, 298], Ga [118, 299], Ge [147, 300], Sn [240, 301, 302], and Bi [239, 303]. The ideal values \(Q_2/Q_1 = 1.86\) and \(r_2/r_1 = 1.91\) consistent with a simple hard-sphere liquid are indicated by the dotted lines.](image-url)
As discussed in section 4.1, the structure of liquid Sn more closely resembles that of a simple liquid at ambient-\(p\) compared to Si and Ge. However, the \(S(Q)\) features a small but distinct shoulder on the high-\(Q\) side of the first peak and a non-ideal ratio \(Q_2/Q_1 \approx 1.96\) reflecting anisotropy in the liquid structure [140]. ED-XRD measurements of liquid Sn reported by Katayama and Inamura [301] at 2.0 and 5.3 GPa reveal a reduction in prominence of the high-\(Q\) shoulder in \(S(Q)\) and a reduction in ratio \(Q_2/Q_1\) to \(\sim 1.92\), indicating a reduction in covalent bonding. Narushima et al. [302] extended the ED-XRD measurements of liquid Sn to 19.4 GPa revealing a very close to ideal ratio \(r_2/r_1 \sim 1.92\). The coordination number increases slowly, although the reported values (7.5 at low-\(p\) to 7.8 at 19.4 GPa) are much lower than the value of 10–11 reported in several works for this type-II liquid at ambient-\(p\) [140, 269]. This discrepancy likely arises from the cut-off value chosen for integration over the first peak in real-space which, if too low, may not adequately reflect the asymmetry of the peak. The ratio \(Q_2/Q_1 \sim 1.92\) remains constant up to 19.4 GPa with some small residual asymmetry in the first peak in \(S(Q)\), very similar to the \(S(Q)\) functions observed for liquid Si and Ge at 20 GPa and indicative of an anisotropic local structure persisting in the liquid even at this high-\(p\). Similar behaviour is observed for the liquid iso-electronic alloy InSb [305]. These findings contrast with classical and ab initio MD simulations which indicate a complete disappearance of the shoulder by 20 GPa associated with the loss of fragments of tetrahedral ordering in the liquid [306]. The failure of these computational models to predict the experimental findings may be due to the simulation cell of 144 or 256 atoms being too small to adequately probe the medium range order. Recent diffraction measurements of shock compressed liquid Sn reported by Briggs et al. [240] at the MEC endstation [241] of the LCLS XFEL facility, and accompanying ab initio MD simulations, reveal a liquid structure above 50 GPa with coordination number of \(\sim 12\) consistent with a close-packed hard-sphere liquid. Examination of the \(S(Q)\) and \(g(r)\) data published in this study reveals \(Q_2/Q_1\) and \(r_2/r_1\) ratios shown in figure 12 are very close to the ideal values expected for a simple liquid.

In contrast to the group 14 elements Si, Ge, Sn, and Pb which evolve towards more ideal metallic liquid behaviour with increasing \(Z\) (as the tendency towards covalent bonding reduces), the group 13 elements undergo an anomalous trend from the type-I liquid Al, to type-III liquid Ga, back to the distorted but more ideal type-II liquid In [245]. This departure from the type-I liquid Al to type-III liquid Ga, back to the disreduces), the group 13 elements undergo an anomalous trend from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers) from simple behaviour for liquid Ga may be understood from its mixed metallic-covalent bonding (including Ga\(_2\) dimers). The authors suggest the anisotropic liquid structure at low-\(p\) consists of a mixture of two local structures similar to the Ga-I and Ga-II (bcc) crystalline solids. With increasing \(p\) the structure undergoes non-uniform contraction, characterised by an increase in coordination number to 10.5 at the highest pressure of 5.6 GPa achieved. A gradual reduction in the fraction of Ga-I like local structure from \(\sim 20\%\) at 0.64 GPa to zero by 7.5 GPa was predicted with a complete transformation to a simple liquid structure by \(\sim 15\) GPa [299].

Drewitt et al. [118] recently reported the structure and melting curve of liquid Ga up to 26 GPa using an externally heated RH-DAC at beamline I15 Diamond Light Source (DLS), UK. The measured \(S(Q)\) functions are shown in figure 13 together with the results generated from 600 atom ab initio MD simulations which accurately reproduce the experimental data, including the subsidiary peak in \(S(Q)\). With increasing \(p\) the coordination number increases continuously, approaching a close-packed hard-sphere liquid value of 12 at \(\sim 20–25\) GPa. However, the first peak in \(S(Q)\) remains asymmetric in the experimental measurements and a distinct shoulder is resolved in the simulation result, indicative of some residual structural anisotropy. In order to understand the development of local structural ordering at high-\(p–T\) a topological cluster analysis of the simulation trajectories was performed using the topological cluster classification (TCC) algorithm [311]. In the TCC scheme, the local environment of particles is compared to a predefined library of clusters representing the minimum energy motifs for classical atoms. The abundance of larger clusters in liquid Ga increases at high-\(p–T\) conditions [118]. The results show that although the liquid tends to adopt an increasingly hard-sphere-like structure above the melting curve at high-\(p–T\), there remains a large deviation of \(> 40\%\) from this simple model over all \(p–T\) space. The greatest deviation is found close to the melting curve, where fivefold symmetric partially icosahedral (10B) and crystalline (11F) motifs are most prevalent (figure 14). These motifs have significantly lower values of local two-body excess entropy compared to other structural arrangements. The authors postulate that the competition between regions of exceptionally low configurational entropy formed by these radically different structural motifs with five-fold symmetry and crystal-like ordering may provide a mechanism for stabilising a metastable metallic glass phase in the supercooled liquid below the melting curve at high-\(p\) [118].

The lanthanide and actinide metals lanthanum (La), praseodymium (Pr), neodymium (Nd), and neptunium (Np) experience an unusually small volume change on melting [312]. Cerium (Ce) and plutonium (Pu) both experience a negative volume contraction on melting and negative slopes in their melting curves, with Pu exhibiting one of the most complex solid-state phase diagram of any element [312–314]. Although their liquid structures are not known, the anomalous melting behaviour of these heavy lanthanide and actinide
elements points to the formation of complex structures in the liquid state consistent with type-III liquid metals. An HDL to LDL phase boundary in liquid Ce, rising from the melting curve minimum and ending at a liquid–liquid critical point at \( \sim 21 \text{ GPa} \), has been predicted by Cadieu et al [315] on the basis of free-energy calculations of mixed structures of trivalent Ce\(^{f_0}\) (LDL) and tetravalent Ce\(^{f_1}\) (HDL). The authors report liquid diffuse scattering measurements in the region of the first peak in \( S(Q) \) using the LH-DAC at HPCAT beamline 16-BM-B [80] at the APS. These measurements are consistent with the calculated LDL and HDL structures at low and high-\( p \), respectively, with a crossing of the HDL to LDL boundary at 13 GPa between 1550 and 1900 K [315]. However, the fully corrected and normalised \( S(Q) \) data are not reported, and the observed trend in diffuse melt signal is tentative. Further experimental measurements of the heavy lanthanide and actinide liquids are needed to confirm these predictions.

4.5. Molecular to polymeric liquid–liquid transitions in pnicogen and chalcogen liquids

The pnicogen (group 15) and chalcogen (group 16) elements form low-dimensional covalently bonded structures including molecules, layers, chains, and rings at ambient-\( p \). In contrast to the group 14 elements Si and Ge, which undergo a semiconductor-to-metal transition on melting accompanied by an increase in coordination number, these open packed crystalline structures melt into liquids with very low coordination numbers (e.g. 2 [Se, Te] or 3 [P, As]). Many of the pnicogen and chalcogen liquids exhibit maxima in their melting curves at high-\( p \), accompanied by large and rapid \( p \)-induced changes in their physical properties, such as electrical conductivity and density, which have been interpreted as indicative of liquid–liquid phase transitions [316]. These findings have inspired researchers to search for structural transformations that may accompany a change in properties [79].

In the solid-state, phosphorous (P) adopts a variety of different forms, including white phosphorous, consisting of tetrahedral \( P_4 \) molecular units, red phosphorous with an amorphous network structure, and black phosphorous, the most stable form under ambient conditions, with puckered sheets of linked atoms in an orthorhombic pleated honeycomb structure. Early \textit{ab initio} MD simulations of liquid P by Hohland Jones [317] predicted a transition from a molecular liquid of tetrahedral \( P_4 \) molecules to a polymeric network forming liquid at high-\( T \). Subsequently, Katayama et al [318] measured the structure of liquid P by ED-XRD using the MA apparatus at SPring-8. At low-\( p \), the orthorhombic black phase of P melts into a molecular liquid of \( P_4 \) tetrahedra, reminiscent of the white phosphorous crystal. At \( \sim 1 \text{ GPa} \), the \( S(Q) \) of liquid P is characterised by a so-called first sharp diffraction peak (FSDP) at \( \sim 1.4 \text{ Å}^{-1} \), indicative of ordering on intermediate length scales and attributed to intermolecular correlations between \( P_4 \) molecules [319, 320]. On compression over a very narrow \( p \)-range of \( < 0.05 \text{ GPa} \) between 0.96 GPa and 1.01 GPa, coinciding with a maximum in the melting curve, Katayama et al [318] observed a sudden change in the liquid \( S(Q) \), with the disappearance of the first peak and a new peak emerging at \( \sim 2.45 \text{ Å}^{-1} \). Analysis of the corresponding \( g(r) \) data revealed real-space features consistent with a transformation from a molecular to polymeric liquid (illustrated in figure 15).
The abrupt and reversible transition between these two distinct forms of liquid, with no detectable intermediate state, is indicative of a first-order liquid–liquid phase transition. Further MD simulations [321–323], and x-ray radiography and absorption measurements, showing that the transition is accompanied by a discontinuous change in density of $\sim 40\%$ [324], support the interpretation of a first-order transition from a molecular to polymeric liquid. Monaco et al [326] measured the liquid–liquid transition line over an extended temperature range using a resistively heated PE-cell at beamline ID30 [163] at the ESRF, revealing the transition is both $T$- and $p$-driven with only the polymeric liquid form stable at high-$T$, bearing semblance to the $T$-driven $\lambda$-transition in liquid sulphur (S) (discussed below).

Under ambient conditions, arsenic (As) crystallises into an unusual rhombohedral (A7) crystal structure with coordination number of 3, arising from a Peierls distortion of simple cubic structure (sc) due to the half-filled $p$ valence band [327]. At 25 GPa, the Peierls distortion is suppressed and the A7 structure transforms to the sc-type [328]. Neutron diffraction measurements by Bellissent et al [329] revealed three-fold coordinated units remain in the liquid. This resemblance to the A7 structure led to speculation of the Peierls-type distortion persisting in the liquid-state. Hafner et al [330] argued the threefold coordination could equally be explained by the Friedel modulation, although the Peierls distortion is generally favoured in subsequent MD simulation studies [331–334]. MD simulations predict a transition to a sixfold-coordinated liquid at high density [331, 332]. Chiba et al [335, 336] and Ohmura et al [334] reported the structure of liquid As from ED-XRD measurements just above the melting curve up to $\sim 17$ GPa using the MA apparatus at the PF and SPring-8. The results reveal a disappearance of a pre-peak observed in $S(Q)$ indicative of a loss of intermediate range order associated with correlations between As$_4$ molecules [334, 336]. The coordination number undergoes a continuous increase on compression, with the $r_2/r_1$ ratio and bond angle distributions (from $ab$ initio MD calculations) similar to the high-$p$ sc structure above $\sim 7$ GPa [334].

In contrast to P and As, liquid Sb and Bi adopt an sc-like local structure at ambient-$p$ [337, 338] with anomalous features in their $S(Q)$ and $g(r)$ functions characteristic of type-III liquid metals [140]. ED-XRD measurements of liquid Sb to 9.4 GPa by Chiba et al [337] and liquid Bi to 7 GPa by Yaoita et al [303], both using the MAX-80 system at the PF, reveal similar continuous evolution towards hard-sphere-like behaviour as observed for other type-III liquids. Yaoita et al [303] reported $Q_2/Q_1$ and $r_2/r_1$ ratios for liquid Bi representative of a simple liquid by 6.8 GPa. At their highest measured $p$ of 7.3 GPa, the authors report sharp periodic peaks in $S(Q)$ which they attribute to a stacked-layer model of liquid structure. However, a more likely explanation is these peaks are simply Bragg reflections due to incipient crystallisation of the melt and/or reaction with the pressure media. Indeed, recent femtosecond XRD measurements of shock compressed liquid Bi made by Gorman et al [239] at the MEC endstation [241] of the LCLS XFEL are consistent with a close-packed liquid structure with CN $\sim 12$ persisting up to 68 GPa.

The chalcogen element S has a complex phase diagram, adopting a large number of different cyclic and polymeric forms [339]. The stable crystalline form S-I at ambient-$p$ consists of S$_8$ molecules, transforming to a polymeric solid S-II with helical chains at elevated $p$ [340] and metallisation at 83 GPa [341]. On melting at ambient-$p$ at 388 K, liquid S retains S$_8$ molecular liquid structure. At 432 K, liquid S undergoes the so-called $\lambda$-transition at 432 K, where the S$_8$ molecules breakdown to form long polymeric chains or rings. The $\lambda$-transition is marked by a distinct change in appearance, from a clear yellow liquid to a viscous red liquid accompanied by an anomalous, but continuous, change in density [342]. The length of chains reach a maximum at 460 K, before reducing at higher-$T$ leading to a reduction in viscosity. ED-XRD measurements of liquid S have been reported by Liu et al [343] in the range 5.6–7 GPa using the PE-cell at HPCAT beamline 16-BM-B [80] at the APS. The $S(Q)$ and $g(r)$ data show little variation with $p$, although it should be noted that the $S(Q)$ data contain large non-physical slopes at high-$Q$. With reference to $ab$ initio MD simulations [344], the results were interpreted as being consistent with a purely polymeric liquid at high-$p$ formed of chains. A reduction in coordination number observed at higher-$T$ is interpreted as evidence of a discontinuous transition associated with a drastic reduction in chain length from $\sim 500$ at 1000 K to $\sim 20$ at 1100 K [343]. Isobaric $ab$ initio MD simulations at 10 GPa reproduce this $T$-driven transition, observing reversible de-polymerisation to short helical chains at high-$T$ consistent with the short range order observed in the S-II phase [345]. While this structural transformation is accompanied by sharp changes in physical properties, including an electronic semiconductor–metal transition, there is no evidence of a density discontinuity that would indicate a first order transition. Instead, the process of chain breakage is driven by stabilisation of short chains with higher energy by their higher configurational entropy [345]. At higher-$p$, AD-XRD measurements by Sanloup et al [346] of cold-compressed amorphous S in a cryogenically cooled DAC indicate an amorphous–amorphous structural transformation in the vicinity of the crystalline S-III to S-IV transition between 65 and 70 GPa.
Henry et al [347] recently reported in situ AD-XRD and XAS measurements of the structure and density of liquid S in the low-\(p\) region below 3 GPa in a PE-cell at beamline ID27 [181] at the ESRF. The authors report abrupt discontinuities in density along various different \(p\)–\(T\) paths marking an LDL–HDL transition line, terminating in a liquid–liquid critical point. X-ray radiography images provide remarkable evidence of the formation and evolution of the interface separating two distinct regions of the liquid with different density across the transition line. The transition is also marked by a distinct shift in position and intensity of pre-peak at \(Q_p \approx 1.3 \text{ Å}^{-1}\) on the low-\(Q\) side of the first peak in \(S(Q)\). This pre-peak is at a similar position to the FSDP observed in liquid P, with its loss indicative of a collapse of intermediate range ordering on a length-scale of \(2\pi/Q_p = 4.8\) Å, which is consistent with a breakdown of the \(S_8\) ring structures. In real-space, changes are observed in the region of the second coordination shell at \(r = 4.45\) Å consistent with increased polymerisation in the HDL, as confirmed by Raman spectroscopy which show an increase in intensity of stretching modes assigned to polymeric chains [347]. It should be noted, however, that the changes observed in both \(S(Q)\) and \(g(r)\) are virtually identical to the changes observed in neutron diffraction measurements by Bellissent et al [348] (shown in figure 16), which track the \(T\)-driven polymerisation of liquid S through the \(\lambda\)-transition at ambient-\(p\). The discontinuous density changes along most of the \(p\)–\(T\) pathways reported (with the exception of path P2 [347]), may also be considered continuous within the experimental uncertainty, albeit with a change in slope (figures 2, S10, and S11 in Henry et al 2020 [347]). The observed changes in \(S(Q)\) are also much more subtle than those observed for liquid P and occur over a wider \(p\)-range. More work is thus needed to resolve if these observations are truly representative of a first order liquid–liquid transition or simply high-\(p\) manifestations of the \(\lambda\)-transition.

Crystalline Se and Te are semiconductors consisting of one-dimensional helical chain molecules with two-fold covalent bonding [349, 350]. At high-\(p\) in the solid state, Se and Te undergo semiconductor→metal transitions at 23 [351] and 4 GPa [352], respectively. Early ED-XRD measurements of liquid Se at high-\(p\) were made by Tsuji [159, 353] using the MAX-80 system at the PF, with later measurements at SPRing-8 reported by Katayama et al [354]. On melting at ambient-\(p\), the chain molecules are largely preserved in liquid Se [355], while liquid Te undergoes a semiconductor→metal transition with a liquid structure consisting of short entangled chains with a coordination number of 3 [356]. Initial compression of liquid Se proceeds via a reduction in interchain distance with little change in covalent bonding [79]. Above \(p \approx 3.5\) GPa, the \(S(Q)\) undergoes a gradual transformation [354], moving towards close resemblance of the \(S(Q)\) for metallic liquid Te in the vicinity of a melting curve maximum at 8.4 GPa [314, 353]. These changes are accompanied by an increase in coordination number to \(3 \pm 1\) [159], with electrical conductivity measurements indicative of a semiconductor→metal transition. Early structural and property measurements predicted an abrupt transition in the liquid at \(p \approx 5\) GPa [316, 357, 358]. However, ED-XRD measurements reported by Funamori and Tsuji [359] using the MA systems at the PF and SPRing-8 reveal a continuous increase in nearest neighbour bond length operating against the volume contraction, associated with an increase in coordination number to 4 at 6 GPa. With further increase in \(p\), the nearest neighbour bond length contracts as the coordination number increases continuously towards values consistent with a simple liquid at 22 GPa [359].

Limited high-\(p\) diffraction studies of chalcogenide liquid compounds have also been reported. Brazhkin et al [360] measured the structure of AsS by ED-XRD using an MA device at SPRing-8. Their data, combined with electrical conductivity measurements, reveal the liquid transforms from a molecular liquid to a high-viscosity non-metallic polymerised liquid at \(\approx 2\) GPa, followed by a transformation to a low-viscosity metallic liquid at \(\approx 4.7\) GPa. A combined diffraction and absorption spectroscopy study of liquid As\(_2\)Se\(_3\) to 4.4 GPa reveals a collapse in intermediate range order as manifested by the disappearance of the FSDP in \(S(Q)\) with little change in local structure from the three-fold coordination observed at ambient-\(p\) [361]. Crichton et al [362] measured the structure of liquid GeSe\(_2\) to 5.1 GPa using AD-XRD in a PE-cell at beamline ID30 [163] at the ESRF. At ambient-\(p\), the liquid structure consists of GeSe\(_4\) tetrahedra with approximately equal fractions of edge- and corner-sharing connectivity [363], giving the liquid a two-dimensional character in contrast to other tetrahedral liquids such as SiO\(_2\) or H\(_2\)O. Under compression, a change in connectivity from a two- to three-dimensional network-like liquid, as anticipated from the crystal structure of GeSe\(_2\), results in a breakdown in intermediate range order indicated by the near disappearance of the FSDP in \(S(Q)\) above \(\approx 2.5\) GPa [362]. In \(g(r)\), the Ge–Se bond distances increase on compression, indicating a gradual increase in coordination number [362]. Neutron and XRD studies of GeSe\(_2\) glass reveal the fourfold coordination of edge-sharing GeSe\(_4\) tetrahedra persist until \(\approx 8.5\) GPa, above which there is a gradual increase in higher coordinated units which are strongly associated with homopolar bonds [364, 365]. High-\(p\) neutron diffraction measurements of Ge\(_2\)S\(_2\) glass reveal a similar collapse in intermediate range order above \(\approx 2\) GPa consistent with a change from edge- to corner-sharing connectivity of Ge\(_2\)S\(_4\) tetrahedra [366].

4.6. Alkali metals: simple to complex liquid structure

The group 1 alkali elements with a single \(s\) electron in their valence band are considered archetypal free-electron metals. At ambient-\(p\), the structure factors of the liquid alkali’s are indicative of simple liquids, with \(Q_2/Q_1\) and \(r_2/r_1\) ratios consistent with ideal hard-sphere values [140]. However, the nearest-neighbour coordination numbers are slightly lower than expected for close-packing, consistent with the more open packed bcc crystal structures from which they melt. Conventionally, it was assumed that these simple metallic alkali liquids undergo uniform compression tending towards more close-packed structures at high-\(p\) [79, 147]. Indeed, in the solid-state the alkali metals transform from the bcc arrangement to a close-packed fcc structure on application of pressures of 7.5 GPa (Li), 65 GPa (Na), 11.6 GPa (K), 7 GPa (Rb), and 2.25 GPa (Cs) [367]. The first reported in situ diffraction experiment of a liquid at high-\(p\) measured the structure of the
liquid alkali sodium (Na) to 4.3 GPa [145]. Subsequent studies of alkali liquids were performed using the MAX-80 and MAX-90 large volume apparatus at the PF reporting the structure of liquid Na to 5.1 GPa [368], liquid Rb to 6.1 GPa [369], and liquid Cs to 4.3 GPa [370]. The diffraction data revealed the liquid alkali’s follow a uniform compression model at low-\(p\) up to at least \(\sim 3–4\) GPa with a slight deviation from ideal behaviour observed for liquid Rb and Cs at higher-\(p\) to accommodate a slight increase in coordination number [369].

In the early 2000s, theoretical and experimental work had found that the alkali group elements undergo a remarkable loss in metallic character at high-\(p\), where forced interactions between densely packed atoms give rise to non-spherical packing arrangements resulting in the formation of a myriad of low symmetry complex open-packed crystal structures, many of which feature incommensurate composite structures [367, 371, 372, 377–380]. These transitions in the solid-state are accompanied by remarkable complexity in their melting curves at high-\(p\), illustrated in figure 17 including multiple maxima and deep minima, as low as 200 K at 50 GPa for Li [371] and 300 K at 120 GPa for Na [372]. A maximum is also observed in the melting curve of hydrogen (H) at 65 GPa [99, 381] and similar complex phase diagrams and incommensurate crystalline forms are observed for the alkaline Earth elements [382–386].

The liquid structure of Cs was measured up to \(\sim 10\) GPa by Falconi et al [387] using AD-XRD in the RH-DAC at beamline 9.1 of the Daresbury Synchrotron Radiation Source (SRS), UK. The results reveal a striking reduction in coordination number attributed to a simple-to-complex liquid transformation. As in the earlier ED-XRD diffraction data, the measured \(S(Q)\) for liquid Cs at low-\(p\) initially displays characteristics consistent with a simple hard-sphere liquid. However, above 3.9 GPa, the first peak in \(S(Q)\) undergoes a reduction in intensity and develops an asymmetry on its high-\(Q\) side accompanied by a deviation in the \(Q_2/Q_1\) ratio from the ideal value. The Cs coordination number undergoes a reduction from \(\sim 12\) at low-\(p\) to \(\sim 7–8\) by 4.5 GPa where it remains stable on further compression to 9.8 GPa [387]. Gorelli et al [374] recently reported AD-XRD measurements of the structure of liquid Rb up to 23 GPa using an externally heated RH-DAC at beamline ID27 [181] at the ESRF. The \(S(Q)\) data are reproduced in figure 18. At low-\(p\) up to \(\sim 6\) GPa the \(S(Q)\) and \(g(r)\) data are consistent with a simple liquid with a high coordination number of 10–11. At 10 GPa the first peak in \(S(Q)\) appears asymmetric, developing into a shoulder at \(\sim 16\) GPa and a double peak at 23 GPa. These changes are accompanied by a reduction in coordination number to less than 8 above 20 GPa [374]. These remarkable simple-to-complex transitions in Cs and Rb liquids reflect their complex phase diagrams, both of

![Figure 16](image)

**Figure 16.** (a) Total structure factor \(S(Q)\) and (b) pair distribution function \(g(r)\) for liquid S at temperatures 130, 150, 170, 250, and 300°C. The six temperatures are represented by alternate dotted and solid curves. Enlargements of the first two peaks in \(S(Q)\) and third peak in \(g(r)\) are also shown. Reprinted figure with permission from [348]. Copyright 1990 by the American Physical Society.

![Figure 17](image)

**Figure 17.** High pressure melting curves for the alkali metals (a) Li [371] (red), Na [372] (black), and (b) K [373] (red), Rb [374] (black), Cs [375, 376] (blue).
which feature two melting curve maxima below 4 GPa (Cs) and 13 GPa (Rb) (figure 17). After the initial bcc–fcc transition, in a narrow region of stability below the melting-curve minimum in the range 4.2–4.3 GPa, solid Cs undergoes an isomorphic fcc–fcc transition into a complex incommensurate host–guest structure with 84 Cs atoms in the unit cell [388]. Further compression, Cs transforms to a bcc (Cs-IV) structure, with further transitions occurring at higher-$p$ [389]. Similarly, solid Rb transforms to an orthorhombic stacking structure, with 52 atoms in the unit cell at 13 GPa [390], followed by a transition to an incommensurate structure at 16 GPa [391].

DFT calculations of Cs and Rb liquids reveal that the continuous LDL–HDL transformations observed in these liquids are driven by the progressive $s$–$d$ hybridisation and localisation of valence electrons in interstitial regions [392, 393]. This manifests as a pseudo gap opening in the electronic density of states at the Fermi energy leading to structural symmetries with minimum energy at reciprocal lattice vectors at $2k_F$, which are incompatible with a simple crystal structure resulting in the formation of complex incommensurate phases and lower melting point [392, 394–397]. While there is no long range order in liquids, energy minimisation via preferential scattering of electrons with periodicity $2k_F$ will lead to a peak in $S(Q)$ at the Fermi energy [392, 396], a condition encapsulated by Friedel oscillations (discussed in section 4.1) responsible for the subsidiary peak at $Q = 2k_F$ in the $S(Q)$ of complex liquids [396].

XRD measurements of lighter alkali liquids are more challenging due to their weaker scattering signals and higher chemical reactivity. Shu et al [398] recently overcame these difficulties to measure the structure of liquid lithium (Li) by multi-angle ED-XRD under isothermal compression to 11.5 GPa using a LiF cylindrical capsule in a cupped-Drickamer–toroidal cell assembly in the PE-cell at the APS. At ambient-$p$, the first peak in $S(Q)$ of liquid Li coincides with reflections expected for both bcc-Li (110) and fcc-Li (111) phases [399]. However, in the solid-state, Li undergoes a bcc–fcc transition below the melting curve at ~9 GPa (figure 17). The value of $Q_1$ in the liquid $S(Q)$ increases gradually under compression and above 8.7 GPa is consistent with the position and $p$-evolution of the fcc-111 reflection. This indicates a gradual mixing of bcc-like to fcc-like local ordering takes place under compression, with fcc-like ordering becoming dominant in the vicinity of the melting curve maximum and underlying solid-state bcc–fcc transition [398]. As for Cs and Rb liquids discussed above, a recent MD simulation study of liquid K predicts a continuous transition between 10 and 20 GPa (above the melting curve maximum, see figure 17) from a metallic liquid to an ‘electride’ structure (in which electrons are localised in interstitial regions) accompanied by a reduction in coordination number [400]. Despite the lower coordination the electrode liquid is denser than the underlying fcc solid, resulting in the negative melting curve (equation (16)). This is not the result of more efficient packing, since fcc represents the closest possible packing for spheres. Instead, because the electrode ions are smaller than the atoms they can adopt closer packed structures with electrons adopting any shape required to fit the interstitial site [400].

More experimental work is needed to investigate the liquid structure of the alkali (including H) and alkaline Earth elements to further explore the simple–complex transformations which are expected in these liquids on the basis of their complex melting behaviour and solid state structures.

4.7. Water

Water, the essential solvent for life on Earth, was one of the earliest liquids to be studied by XRD [401]. Water is an anomalous liquid with a negative melting curve and expansion on freezing at 0°C to form solid ice. Despite the apparent simplicity of the water molecule (H$_2$O), strongly directional H bonding and sizeable quantum motions of the light H ions lead to a complex phase diagram with more than 17 crystalline and several amorphous ice structures reported to date, including a high-$T$ superionic phase at Mbar pressures [402]. At low-$T$, amorphous ice adopts two distinct structures, a dense form denoted high-density amorphous (HDA) ice and an expanded form denoted low-density amorphous (LDA) ice. Under ambient conditions, liquid water consists of imperfect tetrahedral arrangements ordered by H-bonding, with significant fractions of trigonal motifs consistent with the molecular H$_2$O electron density, and bifurcated interactions [403].

As a result of the very small x-ray scattering cross-section of H, XRD measurements of liquid water provide information predominantly on the oxygen–oxygen (O–O) correlations. In contrast, neutron diffraction is sensitive to light nuclei such as H in water, although neutron scattering measurements are impaired by strong incoherent scattering of natural H. This is often mitigated by using H–deuterium (D) mixtures. The x-ray $S(Q)$ for liquid H$_2$O at ambient-$p$ has a double first peak, similar to the $S(Q)$ observed for the anomalous type-III liquid
metals [407, 408]. A variety of x-ray [409–412] and neutron diffraction [404, 413, 414] studies of liquid water have been reported using fluid pressure vessels optimised for scattering experiments at pressures below 1 GPa. On initial compression, the liquid structure undergoes continuous densification via compaction of the second coordination shell to fill the void space in the network structure (figure 19) while the local tetrahedral order of the first coordination shell remains largely intact [404, 412].

The first diffraction measurements of the structure of liquid water in a DAC were reported by Eggert et al [138, 415] using a modified membrane driven DAC at beamlines ID09 and ID30 at the ESRF. Their results reveal the compaction of the second coordination shell, manifested by the collapse in the second O–O peak in g(r), is accompanied by a dramatic reduction in height of the second peak in S(Q) becoming a much diminished shoulder of the 1st main peak at 1.1 GPa [415]. Strässle et al [416] measured the structure of liquid heavy water (D2O) up to 6.5 GPa using a PE-cell with a pyrophyllite gasket and graphite heater design [417] at the PEARL instrument at ISIS neutron facility, UK. As for the x-ray data, a similar reduction in the second peak is observed in the S(Q) measured by neutron diffraction. Empirical structure refinement of their measured S(Q) data indicates that water approaches a structure consistent with a simple liquid but with persisting H-bonding resulting in a distorted tetrahedral local structure, similar to the structure of very high-density amorphous ice [416, 418]. Weck et al [419] measured the structure of H2O and D2O liquids up to 4.5 GPa by AD-XRD in an RH-DAC at beamlines ID30 and ID09 at the ESRF. The results show a continuous reduction in intensity and ultimate disappearance of the second peak in S(Q) by ∼ 2 GPa with a simultaneous increase in intensity and shift of the first peak to higher-Q to give an S(Q) consistent with that of a simple liquid. This is accompanied by a rapid increase in the O–O coordination number to ∼ 10 at 1.5 GPa and 12 at 4.5 GPa reflecting the evolution to a close packed liquid structure [419].

Goncharov et al [420] have reported AD-XRD measurements of liquid water to 57 GPa using the LH-DAC facilities at both the APS and ESRF. A 10 μm thick 40 × 40 μm2 square foil of iridium was used as the laser coupler, with a central 10 μm diameter hole containing the hot portion of the liquid sample. The measured S(Q) data are limited in Q-range but indicate little structural development occurring beyond 4 GPa [420]. Katayama et al [406] reported ED-XRD measurements of liquid water along the melting curve to 17.1 GPa (figure 20) using the MA apparatus at Spring-8. Their results, combined with MD simulations, confirm the rapid transformation to a densely packed simple liquid structure by 4 GPa. At higher-p, the volume contraction proceeds predominantly via reduction of the intermolecular O–O bond length [406].

4.8. Silicate melts

Most natural magmas contain silica (SiO2) in high (rhyolite) or moderate (basalt) fractions together with other oxide components, including MgO, FeO, CaO, and Al2O3 [421]. Knowl-
edge of the atomic-scale structure of silicate melts at high-$p$ is important for understanding the mechanisms of densification and dynamical properties (hence mobility) of magmas at depth, which are important parameters in geochemical models of e.g. large scale differentiation of primordial magma oceans during planetary formation, element partitioning and chemical alteration of the mantle during upward or lateral migration of melts, mantle melting in subduction-zone and mid-ocean ridge settings, and interpreting of seismic anisotropy or discontinuities [23]. However, in situ structural measurements of silicate liquids are challenging due to their high melting points and the limited x-ray sensitivity of low-Z materials. For this reason, high-$p$ diffraction studies have generally focussed on silicate glasses as proxies for silicate melts [178, 422, 423].

Extensive in situ x-ray or neutron diffraction measurements of pure SiO$_2$ glass [424–431], and its structural analogue germania (GeO$_2$) [177, 432–437], have been made in the last two decades revealing the mechanisms that drive structural transformations in these oxide glasses [422, 438]. At ambient-$p$, the structure of pure silica glass is characterised by ring structures enclosing open regions in a network of corner shared SiO$_4$ tetrahedra. At high-$p$ the structure experiences two key densification regimes beginning with the steady collapse of medium range order via closure of the ring structures, as manifested in the measured $S(Q)$ by a continuous reduction in height of the FSDP and shift from $5 \pm 1$ Å$^{-1}$ to higher-$Q$ values. This is followed at $\sim 10–15$ GPa by a continuous transformation from a tetrahedral to octahedral glass network structure by $\sim 30–40$ GPa [55, 439]. On further compression, the coordination number increases continuously approaching an average value of $\sim 7$ at 172 GPa [430, 431] (figure 21).

There exists a compelling interrelation between the $p$-driven changes in local structure and medium range order in oxide glasses which can be rationalised in terms of the packing arrangement of oxygen atoms [422, 438–441]. The upper limit of stability of tetrahedral units occurs at an oxygen packing fraction $\eta_O \sim 0.58$, consistent with random loose packing of hard spheres [439]. Ring closure in pure SiO$_2$ glass proceeds via the so-called ‘zipper’ mechanism formulated by Zeidler et al [429], in which a new bond between a SiO$_4$ tetrahedron and bridging oxygen within a ring leads to the creation of a distorted square pyramidal SiO$_6$ motif spanning the ring void [437, 439]. On further compression, these fivefold coordinated units transform to octahedra in a process that is largely completed by $\eta_O \sim 0.64$, corresponding to random close packing of hard spheres [439]. In XRD measurements, these transformations are marked by the emergence of a new peak in $S(Q)$ at $\sim 3$ Å$^{-1}$, bearing striking resemblance to the subsidiary peak discussed earlier for type-III liquid metals (section 4.1) and water (section 4.7). This peak appears at ambient-$p$ in neutron diffraction measurements of SiO$_2$ glass, and in other glass-forming materials with directional bonding, where it is often denoted the ‘principal peak’ and is associated with topological ordering beyond the first coordination shell [442–445]. Hence, the development of this peak at high-$p$ can be attributed to an increase in topological ordering associated with a more densely packed structure [182, 446]. Consequently, this peak should disappear at extremely high-$p$ as the local Si–O structure proceeds beyond six-fold coordination towards a simple metallic-like liquid structure. Indeed, laser-driven shock experiments of SiO$_2$ and ab initio MD simulations indicate an Si–O coordination of 9 in the liquid at 3.6 times the normal solid density accompanied by changes in conductivity to metallic-like values [447–449]. The potential existence of liquid metallic silicate at extreme conditions has profound implications for e.g. magnetic field generation via a silicate dynamo in the early Earth or in magma oceans of super-Earth exoplanets [450].

As the fundamental constituent of natural magmas, pure SiO$_2$ is an important starting point. However, natural melt compositions contain modifier cations which disrupt the silicate network polymerisation via the formation of non-bridging oxygen atoms. Moreover, glass structure is not representative of fragile liquids [42, 54], a taxonomy that includes de-polymerised silicate melts [451], in which viscosity exhibits a marked deviation from Arrhenius behaviour compared to strong glass forming liquids such as pure silica [452]. In general, fragile liquids quench less readily to a glass and in situ high-$p$–$T$ measurements are, therefore, essential to probe the melt structure. A full description of the atomic-scale structure of silicate melts at high-$p$ and its influence on thermodynamic behaviour of magmas at depth, can be achieved by combining the strengths of in situ diffraction data and property measurements (e.g. in situ x-ray falling sphere viscosity [80, 175, 176, 453, 454], absorption contrast density [455–463] measurements), and predictions from ab initio [464–481] or classical MD simulations [182, 482–497].

The first in situ diffraction measurements of silicate liquids at high-$p$ were performed by Funamori et al [148] in 2004 on wollastonite (CaSiO$_3$) and enstatite (MgSiO$_3$) liquids at up to 6 GPa using the MAX-80 and MAX-III cubic MA apparatus at the PF, Japan. They revealed that, as for pure silica, the primary mechanism of structural change in this $p$-range involves transformations in the network and local structure of the modifier cations, with larger changes indicated on initial compression for CaSiO$_3$ compared to MgSiO$_3$. Yamada et al [498, 499] used the MAX-80 apparatus to measure the structure of hydrous silicate melt in the forsterite–enstatite (Mg$_2$SiO$_4$–MgSiO$_3$) system to 6.9 GPa. Water has a depolymerisation effect on the silicate melt network [471, 500].
However, the FSDP shifts to lower-$Q$ above 3 GPa indicating re-polymserisation of the melt structure, which causes an increase in melt viscosity. This has the potential to increase their residency time in the asthenosphere and could be responsible for the low seismological wave velocities observed at the lithosphere–asthenosphere boundary [499, 501].

In the last decade, the PE-cell has been widely exploited for measurements of silicate melts at $p$ up to 10 GPa, including albite (NaAlSi3O8) [165], jadeite (NaAlSi2O6) [166, 440, 502], fayalite (Fe2SiO4) [167], diopside (CaMgSi2O6) [440], and basaltic melts [459, 463]. A compilation of the structure, density, and viscosity of silicate melts at high-$p$ by Wang et al [440] reveals a reduction in isothermal viscosity for polymerised melts occurs up to $p \sim 3–5$ GPa, before encountering a turnover to normal (positive) dependence [503]. Wang et al attributed this viscosity turnover to the packing limit of tetrahedra, as discussed above. Below this limit, the melt structure is highly compressible and structural transformations are dominated by the collapse in medium range order associated with changes in network connectivity and a reduction in the inter-tetrahedral bond angle. Above the tetrahedral packing limit, the structural response is dominated by increasing co-ordination numbers of both the network forming and modifier atoms [440].

While the local Si–O structure is readily probed in diffraction measurements of silicate melts and glasses, determining the coordination environment of other major elements represents a greater challenge due to significant overlap of correlations at higher distances in $g(r)$ [23]. This difficulty is made worse in high-$p$ experiments in which the resolution in real-space may be restricted by experimental limitations for achieving a sufficiently high $Q_{\text{max}}$. MD simulation studies of liquid silicates reveal that the coordination number of other network formers and modifier cations in silicate glasses increases more rapidly on initial compression compared to Si [182, 474, 475, 479, 480, 485–487, 492]. Experimental information available from x-ray and neutron diffraction measurements of Mg-silicate glasses at high-$p$ reveal an immediate increase in Mg-O coordination from an average of $\sim 4.5$ at ambient-$p$ to $\sim 6–7$ at 20 GPa [504–506]. ED-XRD measurements of liquid fayalite (Fe2SiO4) reported by Sanloup et al [167] up to 7 GPa using the PE-cell at HPCAT beamline 16-BM-B [80], APS, reveal a rapid continuous increase in Fe–O coordination from $\sim 4.5$ at ambient-$p$ [56] to 7.1 at 7 GPa. This accelerated development of Fe-O coordination in liquid silicates compared to Mg-O coordination may be responsible for the higher compressibility of fayalite melt observed in comparison to molten Mg-rich San Carlos olivine [167, 485].

Only two studies to date report in situ diffraction of silicate melts above 10 GPa, both utilizing the LH-DAC [182, 215]. Sanloup et al [215] measured the structure of liquid basalt to 60 GPa at beamline P02.2 [180] at the Petra-III synchrotron in Germany. Despite the weak liquid scattering signal compared to the cell background and crystalline SiO2 thermal insulation layers, liquid diffraction intensities were successfully isolated and show an evolution under compression consistent with measurements of silicate glass; the FSDP reduces in intensity and shifts to higher-$Q$ values, indicating a collapse of medium range order in the silicate network, and a second peak at $\sim 3.3$ Å$^{-1}$ develops at higher-$p$ conditions [215]. The measurements reveal an increase in Si–O coordination number from 4 at ambient-$p$ [56] to 6 at 35 GPa in molten basalt, consistent with octahedral coordination observed in pure SiO2 glass [55, 427]. Early equation of state measurements using shock-compression methods showed that silicate liquids are more compressible than mantle minerals, resulting in predictions of a melt-crystal density crossover at depth [507–509]. The densities of liquid basalt, as determined via the iterative self-normalisation of the x-ray scattering intensities (equations (9)–(12)), indicate that liquid basalt is denser than the seismological density profile of the solid mantle at $p \gtrsim 40$ GPa, thereby implying that natural melts of basaltic composition may be gravitationally stable in the deep lower mantle [215]. This supports the Labrosse et al [510] layered model of a crystallising magma ocean in the early Earth, in which a stable dense magma ocean is formed at the base of the mantle. Subsequent in situ density measurements of silicate glasses using x-ray contrast techniques similarly predict the accumulation of Fe-rich silicate melts above the core mantle boundary [511, 512].

4.9. Development of chemical and topological structure in aluminosilicate liquids

It is known from ex situ NMR spectroscopy and XAS measurements of permanently densified aluminosilicate glasses ($p$–$T$-quenched from up to 12 GPa) that Al coordination changes occur at far lower pressures than for Si [103, 106, 108, 513]. Hence, modifications in Al coordination and connectivity may have a greater influence than Si on controlling melt densification in the shallow upper mantle. However, large transient drops in $p$ during $T$ quench may result in a significant underestimate of the abundance of highly coordinated units in these ex situ studies of recovered glasses [109].

Drewitt et al [182] reported in situ AD-XRD measurements of calcium aluminate (CaAl2O4) and anorthite (CaAl2Si2O8) glasses and melts to $\gtrsim 30$ GPa using the CO2 LH-DAC facility at beamline ID27 [217], ESRF, France. Despite significant contamination of the liquid signal by Bragg reflections from the thermal insulation media (figure 6(a)), the corrected $S(Q)$ data shown in figure 22 is in good general agreement with both the ambient-$p$ measurements of the glass and levitated liquids and the high-$p$ evolution predicted from accompanying ab initio and classical MD simulations using the aspherical ion model potentials developed for the Ca–Mg–Al–Si–O system [45, 46, 482]. The limited $Q_{\text{max}}$ and statistical accuracy of the high-$p$ diffraction data leads to considerable peak broadening in real-space [182]. Nevertheless, the nearest neighbour Al–O coordination numbers obtained from the experimental measurements are in good overall agreement with simulation results [182, 514].

This combined in situ XRD and MD simulation study revealed that at high-$p$ aluminate and aluminosilicate melt structures undergo changes in chemical and topological order. At ambient-$p$, the structure of aluminosilicate liquids and
et al. CaAl$_2$O$_4$ at 2500 K and 0, 10, and 30 GPa are also shown, where pressures indicated in parentheses. Simulation snapshots of liquid levitated liquids (red curves) or in the DAC (blue curves) at AIM-MD simulations (black curves), and AD-XRD of the glass or AlO$_4$ or SiO$_4$ tetrahedra[182]. On initial compression, the network of AlO$_6$ units on initial compression, which accelerates above 5 GPa with AlO$_6$ units becoming the dominant structural coordination is accompanied by the development of polyhedral connectivity via the formation of edge- and face-sharing networks. At 10 GPa, ~95% Ca- and 50% Al-centred polyhedra belong to single clusters, increasing to 100% Ca- and 90% Al-centred units at 30 GPa [182]. The simulations reveal an increase in O–O coordination which plateau’s at 11 at 10 GPa, consistent with random close packing of hard spheres. This change is accompanied by the development of the familiar topological peak in $S(Q)$ at 3.1 Å$^{-1}$ (figure 22) which is indicative of an increase in topological ordering associated with a more densely packed structure.

Recent in situ synchrotron XRD measurements of an aluminosilicate glass in a double-stage PE cell suggest the Al–O coordination number of ~6 remains constant up to 110 GPa based on the observation that densification proceeds via a uniform contraction of the Al–O bond length beyond ~30 GPa [517]. While MD simulations reproduce this contraction in bond distance, they also predict a continuous increase in Al–O coordination number to values approaching ~7 at 100 GPa [514, 518, 519], although it should be noted that coordination numbers for glass and melts under hot-compression are consistently higher than values obtained for cold-compressed glass [519].

### 5. Future perspectives

This review encapsulates the tremendous progress that has been made in the last 40 years to determine the structure of liquids at high-$p$ using in situ synchrotron XRD techniques. The large-volume MA apparatus was the work-horse of early work, with extensive diffraction measurements of liquid metals and semiconductors leading to important discoveries, including the continuous transformation of anomalous liquid metals towards simple close packed structures and the molecular to polymeric liquid–liquid transition in liquid P [79]. However, the MA apparatus has limited utility for diffraction studies of low-Z multicomponent liquids as the limited $Q$-range due to the large obstructive anvil assemblies results in relatively poor resolution in real-space data. These limitations may be overcome in future upgrades of MA devices at synchrotron facilities using innovative anvil materials and configurations.

The large-volume PE-cell is a portable alternative to the MA apparatus with wider accessible $Q$-range. ED-XRD measurements of liquid silicates are now routine in the PE-cell at $p$–$T$ conditions up to ~7 GPa and 2300 K with $Q_{\text{max}}$ ~ 20 Å$^{-1}$ [80, 165, 166]. Generating higher $p$–$T$ conditions in the PE-cell is limited by extrusion of the cell assembly containing the heater and sample capsule at high-$p$, which reduces the anvil separation and hence limits accessibility to the sample for in situ measurements. Future developments in the PE-cell technology may involve adapting double stage configurations [179] to incorporate heating elements. In situ neutron diffraction with isotope substitution (NDIS) measurements of glass structure can also be made in the PE-cell to isolate specific pair correlations at high-$p$ [365, 422, 434, 437]. However, neutron diffraction of liquids in the PE-cell is currently limited to $p$–$T$ conditions of ~7 GPa and < 1000 K with typically low data quality due to...
the difficulty in manufacturing hermetically sealed heating assemblies from materials with sufficiently low neutron scattering cross-sections [416, 417, 520–523]. Development of suitably transparent PE-cell heating assemblies for neutron diffraction will open up the possibility of performing in situ NDIS measurements of liquids in the PE-cell, which will enable unprecedented resolution of structural correlations in multicomponent liquids at high-\(p\)–\(T\).

The LH-DAC is the only device available at synchrotron facilities for routine diffraction measurements of liquids at deep mantle and planetary core conditions. However, the LH-DAC has a number of drawbacks for liquid diffraction measurements including strong temperature gradients, which prevent total melting of the sample, and chemical reaction with thermal insulation media, making isolation of a clean diffraction signal arising solely from the liquid sample very difficult to achieve. The increased flux and nano-focus capabilities of the ‘fourth-generation’ diffraction-limited storage ring upgrades, currently being implemented at major synchrotron radiation facilities around the world, will allow more precise measurement of the diffuse liquid signal from a micro-scale heating spot in an LH-DAC experiment. The signal to background ratio for liquids in an LH-DAC can also be improved significantly by employing a multichannel collimator [128]. Nevertheless, large temperature gradients and poor stability will remain a limiting factor on the accuracy of measured LH-DAC data.

RH-DAC devices are now available for routine experiments at moderate high-\(p\)–\(T\) conditions, providing homogeneous heating and wholesale melting of the sample, thereby providing a stronger and cleaner liquid diffraction signal compared to the LH-DAC [185]. The innovative IRH-DAC recently developed in Bristol is capable of extremely stable heating of metallic or insulating materials to at least 3000 K and 64 GPa, offering a viable alternative to the LH-DAC [228]. The temperature uncertainties are an order of magnitude smaller than in the LH-DAC with more precise temperature control. In combination with micro/nanofocus and spectromicroscopy capabilities at synchrotron beamlines, the IRH-DAC offers the prospect of high-quality diffraction measurements of wholly molten samples at deep lower mantle conditions [228]. The technique will be particularly useful for determining the structure of refractory liquids at extreme conditions.

Finally, the development of XFEL accelerators now allow diffraction measurements of laser shocked liquids to be made using femtosecond x-ray pulses [240]. XFEL pulses can also be utilised to induce extreme \(p\)–\(T\) conditions within a DAC by isochoric x-ray heating with simultaneous diffraction measurements [524]. These advances in time-resolved diffraction of liquids under dynamic compression may be exploited for exploring the structure of exotic liquid states under super-extreme conditions, e.g. metallisation of liquid oxides [447–449] or metal–insulator transitions in type-I liquid metals [287] emulating the behaviour of liquid alkali metals and the incommensurate host–guest structures observed in the crystalline solids-state [378, 379].

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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