Ordering on different length scales in liquid and amorphous materials

Philip S Salmon and Anita Zeidler

Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom
E-mail: p.s.salmon@bath.ac.uk and a.zeidler@bath.ac.uk

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Abstract. The ordering on different real-space length scales is considered for a variety of glass-forming materials, ranging from densely packed amorphous metals and hard-sphere glassy colloids, to simple tetrahedral systems that include amorphous silicon and patchy colloids, to decorated tetrahedral systems that include amorphous ice and network-forming glasses with the AX$_2$ stoichiometry (A = Si, Ge or Zn; X = O, S, Se or Cl). The ordering manifests itself as distinct peaks in the total structure factor $S(k)$, where $k$ denotes the magnitude of the scattering vector, with positions $k_i$ ($i = 1, 2$ or $3$) that scale with the nearest-neighbour distance. Different length scales emerge with complexity of the bonding scheme. A peak at $k_3$ is a generic feature associated with nearest-neighbour contacts, and is therefore present in $S(k)$ for all of the materials. A second longer-length scale emerges as a peak at $k_2 < k_3$ if the bonding scheme assumes a directional character, leading to the formation of tetrahedral motifs in amorphous silicon and patchy colloids, or to Se–Se–Se chain segments in glassy selenium. A third still-longer-length scale appears for AX$_2$ glasses as a first sharp diffraction peak at $k_1 < k_2$, where the scaled peak position depends on the character of the local network of A atoms. The geometrical origin of the peaks in $S(k)$ and corresponding partial structure factors is considered, and equations are given for predicting the peak positions. The change in system fragility with the emergence of ordering on different length scales is discussed, along with the effect of pressure.

Keywords: glasses (structural), slow relaxation, glassy dynamics, aging
1. Introduction

The objective of this paper is to identify and characterise the ordering that occurs on different real-space length scales in a variety of glass-forming materials. Motivation is provided by the need to (i) establish a common reference point for researchers working on different classes of glass-forming materials; (ii) provide a geometric origin for the peak positions in the total structure factor $S(k)$ that is measured by diffraction or calculated from simulation, where $k$ denotes the magnitude of the scattering vector; (iii) deliver a basis for interpreting the structural changes that occur in disordered materials under extreme conditions [1]; and (iv) search for relationships between the structural ordering on different real-space length scales and the dynamical properties of the liquid as the glass transition is approached. The length scales are identified by considering the relative positions of the peaks that occur at smaller $kd$ values when $S(k)$ is plotted against the scaled scattering vector $kd$, where $d$ denotes the nearest-neighbour distance.

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In order to explore these issues, representative $S(k)$ functions are considered for various classes of glass-forming systems that differ in respect of the complexity of the bonding scheme. The systems range from densely packed amorphous metals and hard-sphere glassy colloids, to simple tetrahedral systems that include amorphous silicon and patchy colloids, to decorated tetrahedral systems that include network-forming glasses such as silica. Oftentimes, it is convenient to use the Bhatia–Thornton [2] formalism in order to separate the contributions to the structure from topological versus chemical ordering. The Bhatia–Thornton number–number partial structure factor often makes a significant contribution to the $S(k)$ function measured in a neutron diffraction (ND) experiment. The relationship between the structure and dynamics of the melt is discussed by reference to the system fragility, originally defined in terms of the rate-of-change of the liquid viscosity with temperature as the glass transition is approached [3].

The paper is organised in the following way. The total structure factor $S(k)$ and related functions are defined in section 2. The different real-space lengths scales are identified in section 3 for the various classes of glass-forming systems. The Bhatia–Thornton [2] formalism is introduced in section 4 for tetrahedral network glass-forming systems with the AX$_2$ stoichiometry (A = Si, Ge or Zn; X = O, S, Se or Cl). The relationship between the glass structure and dynamics of the melt is discussed in section 5. The real-space manifestation of the peaks in $S(k)$ is illustrated in section 6 by using case examples provided by the metallic glass-forming liquid Au$_{0.81}$Si$_{0.19}$ and the network glass-former ZnCl$_2$. In section 7, the structure of AX$_2$ systems is again examined, but this time from the viewpoint of the different chemical species, where a point of debate concerns the nature of the A atom network. The contribution of this network towards the peaks in $S(k)$ is discussed in section 8 by reference to the Bhatia–Thornton number–number partial structure factor. Finally, conclusions are drawn in section 9.

### 2. Total structure factor $S(k)$

The total structure factor for a system comprising several chemical species is given by [4]

$$S(k) = 1 + \frac{1}{|\langle w(k) \rangle|^2} \sum_\alpha \sum_\beta c_\alpha c_\beta w_\alpha(k) w_\beta^*(k) [S_{\alpha\beta}(k) - 1],$$  \hspace{1cm} (1)

where $c_\alpha$ is the atomic fraction of chemical species $\alpha$; $w_\alpha(k)$ represents either the $k$-dependent x-ray atomic form factor with dispersion terms or the $k$-independent coherent neutron scattering length of chemical species $\alpha$; $\langle w(k) \rangle = \sum_\alpha c_\alpha w_\alpha(k)$ is the mean value of $w_\alpha(k)$; and $S_{\alpha\beta}(k)$ is a Faber–Ziman [5] partial structure factor. In general, $w_\alpha(k)$ is a complex number, and $*$ denotes the complex conjugate. The corresponding total pair-distribution function $G(r)$, which describes the real-space ordering, is obtained from the Fourier transform relation

$$G(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty dk \ k \ [S(k) - 1] \sin(kr),$$  \hspace{1cm} (2)
where \( r \) is a distance in real-space and \( \rho \) is the atomic number density. A similar Fourier transform relates \( S_{\alpha\beta}(k) \) to its partial pair-distribution function \( g_{\alpha\beta}(r) \). The coordination number of atoms of type \( \beta \) around an atom of type \( \alpha \) will be denoted by \( \bar{n}_{\alpha\beta} \).

### 3. Structural length scales

The \( S(k) \) versus \( kd \) functions for a variety of glass-forming materials are shown in figure 1. The results were obtained from ND versus x-ray diffraction (XRD) experiments on the bulk-metallic glass Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) which has good glass-forming ability \([6]\); a coherent x-ray scattering experiment on a colloidal glass of hard spheres of diameter \( d = 2340 \) Å in the polymethylmethacrylate (PMMA) system \([7]\); an XRD experiment on amorphous silicon prepared by self-ion implantation where the structure is based on a tetrahedral network \([8]\); simulations of a liquid tetrahedral patchy colloid of equally sized hard spheres of diameter \( d \) and number density \( \rho \) with \( \rho d^3 = 0.57 \), where each patch is defined by a cone with its apex at the particle centre and aperture \( 2\theta \), \( \theta \) is the angle between the cone axis and a generatrix, and \( \cos \theta = 0.92 \) \([9]\); a ND experiment on glassy Se which has a structure based on Se\(_n\) chains where \( n \) is an integer \( \geq 2 \) \([10]\); ND versus XRD experiments on the network-forming glass SiO\(_2\) where the structure is based on corner-sharing (CS) tetrahedral SiO\(_4\) units \([11, 12]\); and ND versus XRD experiments on the network-forming glass GeSe\(_2\) where the structure is based on both CS and edge-sharing (ES) tetrahedral GeSe\(_4\) units with a small fraction of homopolar bonds \([13, 14]\).

The \( S(k) \) functions for network-forming glasses with the AX\(_2\) stoichiometry are characterized by three peaks with positions \( k_i \) (\( i = 1, 2 \) or 3) that scale with \( d \) such that \( k_1d \approx 2-3, k_2d \approx 4.6-4.9 \) and \( k_3d \approx 7.7-8.9 \), where the peaks at \( k_1 \) and \( k_2 \) are often known as the first sharp diffraction peak (FSDP) and principal peak, respectively \([15–21]\). In contrast, a peak at \( k_1 \) is absent in the \( S(k) \) functions for amorphous silicon, tetrahedral patchy colloids, and glassy selenium. Peaks at \( k_1 \) and \( k_2 \) are both absent for the metallic and hard-sphere colloidal glasses. This variability indicates ordering on real-space length scales that is present for some classes of material but absent for others. It is therefore valuable to identify several of the structural features that contribute towards the peaks at \( k_i \) in the \( S(k) \) functions.

According to the properties of Fourier transforms, a pair-distribution function with a well-defined shell of nearest-neighbours at distance \( d \) will manifest itself in \( S(k) \) as a function of periodicity \( 2\pi/d \) and amplitude that depends on \((kd)^{-1}\) \([19]\). The first maximum occurs at

\[
k_3d = 7.725 \approx 5\pi/2,
\]

which is known as the Ehrenfest relation. This expression gives the approximate position of the peak at \( k_3 \) for many different metallic glass-forming systems, which have structures based on densely packed polyhedra \([22]\), and for the colloidal glass shown in figure 1. In comparison, the Percus–Yevick equation gives a peak position at \( k_3d \approx 6.4\) –7.1 in \( S(k) \) for a system of hard spheres of equal diameter \( d \) and packing fraction 30%–50%, where the position increases with the packing fraction \([23]\). Equation (3)
also gives the approximate position of the peak at $k_3$ for the other classes of materials represented in figure 1.

From the properties of Fourier transforms, a sharp peak at $k_i$ in $S(k)$ is associated with real-space ordering of periodicity $2\pi/k_i$ that decays with a correlation length of $2\pi/\Delta k_i$, where $\Delta k_i$ is the peak width [19]. For a system based on tetrahedral motifs,
Table 1. The measured A–X bond distances $r_{AX}$, A–A nearest-neighbour distances for CS $r_{AA}^{CS}$ versus ES $r_{AA}^{ES}$ tetrahedra, and the intra-tetrahedral X–X distance $r_{XX}$ for several AX$_2$ glasses. Also listed are the A–A bond angles for CS $\theta_{AXA}^{CS}$ versus ES $\theta_{AXA}^{ES}$ tetrahedra. The bond angles were obtained from $r_{AX}$ and $r_{AA}^{CS}$ or $r_{AA}^{ES}$ by using the cosine rule: $\cos(\theta_{AXA}) = 1 - r_{AA}^{2}/2r_{AX}^{2}$.

| Glass   | $r_{AX}$ (Å) | $r_{AA}^{CS}$ (Å) | $r_{AA}^{ES}$ (Å) | $r_{XX}$ (Å) | $\theta_{AXA}^{CS}$ (°) | $\theta_{AXA}^{ES}$ (°) | Reference |
|---------|--------------|------------------|------------------|--------------|----------------|----------------|-----------|
| SiO$_2$ | 1.60(1)      | 3.08(1)          | —                | 2.62(1)      | 148.5(2.0)$^a$   | —              | [24]      |
| GeO$_2$ | 1.73(1)      | 3.16(1)          | —                | 2.83(1)      | 132(2)          | —              | [11, 25]  |
| ZnCl$_2$| 2.28(1)      | 3.75(1)          | —                | 3.70(1)      | 111(1)          | —              | [26, 27]  |
| GeS$_2$ | 2.22(1)      | 3.47(2)          | 2.91(2)          | 3.63(2)      | 103(2)          | 82(2)          | [28, 29]  |
| GeSe$_2$| 2.36(2)      | 3.57(2)          | 3.02(2)          | 3.89(2)      | 98(1)           | 80(1)          | [13, 14]  |

$^a$ An angle $\theta_{AXA}^{CS} = 151^\circ$ is reported from a reverse Monte Carlo analysis of ND data [30].

the base-to-apex distance in a regular tetrahedron is given by $(4/3)d$ where $d$ can be identified with the Si–Si bond distance in amorphous silicon, or the A–X bond distance within the AX$_4$ tetrahedron of an AX$_2$ glass. If the periodicity associated with $k_2$ is commensurate with this distance, it follows that $2\pi/k_2 \simeq (4/3)d$ or

$$k_2d \simeq 3\pi/2 \simeq 4.71.$$  

This equation is in accord with the peak positions reported in figure 1 for those materials that show a principal peak.

For AX$_2$ glass, the periodicity $2\pi/k_1$ associated with the FSDP is longer than the periodicity associated with the principal peak, and will therefore originate from a length scale that is longer than an intra-tetrahedral length scale. For an inter-tetrahedral A–X–A bond angle $\theta_{AXA}$, the associated nearest-neighbour inter-tetrahedral A–A distance is given by $r_{AA} = 2d\sin(\theta_{AXA}/2)$. If the periodicity $2\pi/k_1$ is commensurate with this distance, it follows that $k_1d \simeq \pi/\sin(\theta_{AXA}/2)$. For a bond angle $\theta_{AXA} = 150^\circ$, which is typical of CS A–X–A connections in glassy SiO$_2$ (table 1), $\sin(\theta_{AXA}/2) = (\sqrt{2} + \sqrt{6})/4$ and $k_1d \simeq 4\pi/\sqrt{2}(\sqrt{2} + \sqrt{6}) = 3.25$. For a bond angle $\theta_{AXA} = 90^\circ$, which is intermediate between the values found for CS versus ES A–X–A connections in glassy GeSe$_2$ (table 1), $\sin(\theta_{AXA}/2) = \sqrt{2}/2$ and $k_1d \simeq \sqrt{2}\pi = 4.44$. Both of these estimates give a scaled FSDP position that is larger than the experimental expectation of $k_1d \simeq 2–3$ (figure 1). The structural length scale associated with the FSDP is therefore longer than typical nearest-neighbour inter-tetrahedral distances, and will be discussed in sections 7.1 and 8.1.

4. Topological versus chemical ordering

For a binary AX$_2$ system, it is instructive to identify the relative contributions to $S(k)$ from topological versus chemical ordering [18, 26]. Accordingly, it is helpful to rewrite equation (1) in terms of the Bhatia–Thornton [2] number–number (N–N), concentration–concentration (C–C) and number–concentration (N–C) partial structure factors, such that

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\[ S(k) = S_{NN}(k) + \left\{ \left[ w_A(k) - w_X(k) \right]^2 / \langle w(k) \rangle^2 \right\} S_{CC}(k) + 2 \left\{ \left[ w_A(k) - w_X(k) \right] / \langle w(k) \rangle \right\} S_{NC}(k), \]

where each term \( w_\alpha(k) \) is assumed to be a real number for simplicity of notation. The Bhatia–Thornton and Faber–Ziman partial structure factors are related by the expressions

\[ S_{NN}(k) = c_A^2 S_{AA}(k) + c_X^2 S_{XX}(k) + 2c_Ac_X S_{AX}(k) \]

(6)

\[ S_{CC}(k) = c_Ac_X \left\{ 1 + c_Ac_X [S_{AA}(k) + S_{XX}(k) - 2S_{AX}(k)] \right\} \]

(7)

\[ S_{NC}(k) = c_Ac_X \{ c_A [S_{AA}(k) - S_{AX}(k)] - c_X [S_{XX}(k) - S_{AX}(k)] \}. \]

(8)

In a diffraction experiment on a system for which \( w_A(k) = w_X(k) \), an incident neutron or x-ray cannot distinguish between scattering centres, and the measured total structure factor \( S(k) = S_{NN}(k) \). Similarly, for systems comprising a single chemical species such as amorphous Si or Se, \( S(k) = S_{NN}(k) \). The Fourier transform of \( S_{NN}(k) \) gives the number–number partial pair-distribution function \( g_{NN}(r) \), which describes the sites of two scattering centres separated by a distance \( r \), but cannot distinguish between the chemical species that occupy those sites. The number–number partial pair-correlation functions therefore give information on the topological ordering of the AX\(_2\) network [18]. By comparison, in a system for which \( \langle w(k) \rangle = 0 \), which is possible in ND because of the occurrence of negative coherent scattering lengths [31], the measured total structure factor \( S(k) = S_{CC}(k) \). The Fourier transform of \( S_{CC}(k) \) gives the concentration–concentration partial pair-distribution function \( g_{CC}(r) \), which will have a positive or negative peak at a given distance \( r \) when there is a preference for like or unlike chemical species at that distance, respectively. The concentration–concentration partial pair-correlation functions therefore give information on chemical ordering in the AX\(_2\) network. Lastly, the Fourier transform of \( S_{NC}(k) \) gives the number–concentration partial pair-distribution function \( g_{NC}(r) \), which describes the cross-correlation between the atomic sites described by \( g_{NN}(r) \) and their occupancy by a given chemical species.

In ND, the measured \( S(k) \) function often approximates \( S_{NN}(k) \) because of similarity between the coherent scattering lengths for many different chemical species. For example, in glassy GeSe\(_2\) the neutron scattering lengths of Ge and Se with natural isotopic abundances are \( b_\text{Ge} = 8.185(20) \) fm and \( b_\text{Se} = 7.970(9) \) fm [31], respectively, such that \( S(k) \simeq S_{NN}(k) \) for a ND experiment. For this material, the atomic numbers of Ge and Se are \( Z = 32 \) and \( Z = 34 \), respectively, such that \( S(k) \simeq S_{NN}(k) \) for an XRD experiment. Hence, conventional ND and XRD experiments on GeSe\(_2\) glass give the same information, which accounts for the similarity between the \( S(k) \) functions shown in figure 1. In comparison, for glassy SiO\(_2\) the neutron scattering lengths are \( b_\text{Si} = 4.1491(10) \) fm and \( b_\text{O} = 5.803(4) \) fm, and the atomic numbers of Si and O are \( Z = 14 \) and \( Z = 8 \), respectively. It follows from the weighting factors for the partial structure factors in equation (5) that \( S(k) \sim S_{NN}(k) \) for a ND experiment but not for an XRD experiment, which leads to a missing peak at \( k_0 \) in the x-ray measured \( S(k) \) (figure 1).

The measured \( S_{NN}(k) \) functions for glassy SiO\(_2\) [24], GeO\(_2\) [11, 25], ZnCl\(_2\) [26, 27] and GeSe\(_2\) [13, 14] are compared to the \( S_{NN}(k) \) functions for amorphous silicon [8] and germanium [32] in figure 2. The corresponding \( S_{CC}(k) \) and \( S_{NC}(k) \) functions for the
AX$_2$ glasses are shown in figures 3 and 4, respectively. Each set of partial structure factors was obtained by employing the method of isotope substitution in ND [4], with the aid of XRD in the case of SiO$_2$. Several of the parameters describing the real-space structures are summarized in tables 1 and 2. The results confirm that the ‘three peak’ character of the measured $S(k)$ functions for AX$_2$ glass originates from $S_{NN}(k)$, and show notable differences between the heights of the peaks positioned at $k_1$ and $k_2$. The $S_{CC}(k)$ functions are similar for all AX$_2$ glasses, with a main peak at the scaled position $k_2 r_{AX} \simeq 3\pi/2$. Often, there is a small peak at $k_1$, which indicates concentration fluctuations on an intermediate length scale [18, 33]. The $S_{NC}(k)$ functions for the AX$_2$ glasses also take similar forms with a large trough at the scaled position $k_2 r_{AX} \simeq 3\pi/2$, and a variation that emanates from differences in the network topology as evidenced by the $S_{NN}(k)$ functions shown in figure 2.
Figure 3. The measured concentration–concentration partial structure factor $S_{CC}(k)$ for glassy SiO$_2$, GeO$_2$, ZnCl$_2$ and GeSe$_2$. The data sets are plotted as a function of $kd$ where $d = r_{AX}$ is the A–X bond distance. The vertical arrow marks the position $kd = 3\pi/2$.

Figure 4. The measured number–concentration partial structure factor $S_{NC}(k)$ for glassy SiO$_2$, GeO$_2$, ZnCl$_2$ and GeSe$_2$. The data sets are plotted as a function of $kd$ where $d = r_{AX}$ is the A–X bond distance. The vertical arrow marks the position $kd = 3\pi/2$. 
### Table 2. The measured A–X coordination number \( \bar{n}_A^X \), A–A coordination numbers for CS \( \bar{n}_A^{A,CS} \) versus ES \( \bar{n}_A^{A,ES} \) tetrahedra, and X–X coordination number \( \bar{n}_X^X \) for several AX2 glasses. Also listed is the anion-packing fraction \( \eta_X \) calculated from equation (20).

| Glass   | \( \bar{n}_A^X \) | \( \bar{n}_A^{A,CS} \) | \( \bar{n}_A^{A,ES} \) | \( \bar{n}_X^X \) | \( \eta_X \) | Reference |
|---------|------------------|------------------|------------------|------------------|------------------|------------|
| SiO2    | 3.89(20)         | 4.06(20)         | -                | 5.99(30)         | 0.414(5)         | [24]       |
| GeO2    | 3.8(1)           | 4.1(2)           | -                | 6.7(1)           | 0.495(9)         | [11, 25]  |
| ZnCl2   | 3.9(1)           | 4.0(2)           | -                | 11.0(4)          | 0.647(9)         | [26, 27]  |
| GeS2    | 3.95(5)          | 3.2(1)           | 0.46(5)          | 9.2(2)           | 0.597(5)         | [28, 29]  |
| GeSe2   | 3.7(1)           | 3.2(3)           | 0.34(5)          | 9.3(2)           | 0.667(17)        | [13, 14]  |

5. Structure and the melt fragility

5.1. Network-forming systems

In figure 2, the \( S_{NN}(k) \) functions for the AX2 glasses originate from melts with dynamical properties that vary at different rates as the liquid is cooled and the glass transition temperature \( T_g \) is approached [3]. For experiments in which the liquid viscosity \( \eta \) is measured, this behaviour can be quantified in terms of the fragility index

\[
m = \frac{d \log_{10} \eta}{d(T_s/T)} \bigg|_{T=T_g},
\]

where \( T \) is the absolute temperature. The viscosity of ‘strong’ systems such as BeF2, SiO2 and GeO2 shows an Arrhenius temperature dependence, which manifests itself in terms of small values of \( m \). More fragile glass-forming systems with larger \( m \) values include ZnCl2, GeS2 and GeSe2.

Figure 5(a) shows the dependence of \( m \) on the A–A–bond angle \( \theta_{AXA}^{CS} \) for CS tetrahedral units in several network-forming AX2 glasses. The fragility index is small and approximately invariant for large \( \theta_{AXA}^{CS} \) values that are typical of BeF2, SiO2 and GeO2, but increases as \( \theta_{AXA}^{CS} \) reduces below \( \sim 120^\circ \) and ES tetrahedra become more numerous in materials such as GeS2 and GeSe2. Figure 5(b) shows the dependence of \( R_{k_1,k_2} \) on \( \theta_{AXA}^{CS} \), where the ratio of peak heights at \( k_1 \) and \( k_2 \) in \( S_{NN}(k) \) is given by

\[
R_{k_1,k_2} = \frac{S_{NN}(k_1) - S_{NN}(k \to 0)}{S_{NN}(k_2) - S_{NN}(k \to 0)}.
\]

This ratio decreases markedly with the bond angle when \( \theta_{AXA}^{CS} > 120^\circ \), and then levels at an \( R_{k_1,k_2} \) value of 0.3–0.7 for \( \theta_{AXA}^{CS} < 120^\circ \). The relative fragility of the AX2 materials therefore manifests itself in a competition between the ordering on length scales associated with the FSDP and principal peak in \( S_{NN}(k) \) [11].

Figure 5(c) shows the A–X–A bond angle distributions \( n(\theta_{AXA}) \) obtained from molecular dynamics simulations using a polarizable ion model for tetrahedral AX2 melts containing cations A and anions X [41, 42]. In this ionic model, the anion polarizability \( \alpha_X \) was varied systematically in order to control \( \theta_{AXA} \) and find the effect of structural change on the melt fragility. The fragility of the liquid was assessed from
the temperature dependence of the cation self-diffusion coefficient $D$ via the Vogel–Fulcher–Tammann (VFT) equation

$$D = D_0 \exp \left[ -B / (T - T_0) \right],$$

(11)

where $D_0$ is the self-diffusion coefficient in the infinite temperature limit, $T_0$ is the temperature at which the diffusion coefficient becomes zero, and $B$ is a positive constant. The molecular dynamics results mimic those reported in figures 5(a) and (b). A small $\alpha_X$ value leads to a small liquid fragility, a large peak-height ratio $R_{k_1:k_2}$ and a single peak in $n(\theta_{AXA})$ that originates from CS tetrahedra. As $\alpha_X$ is increased to 15 au,
there is little change to the fragility, and $R_{k_1:k_2}$ decreases as the $A-X-A$ bond angle becomes more acute. Around $\alpha_X \simeq 15$ au, the anion polarizability provides sufficient screening of the Coulomb repulsion between cations to stabilize ES tetrahedral AX$_4$ units, and a second peak from these connections appears in $n(\theta_{AXA})$. The peak-height ratio $R_{k_1:k_2}$ shows little change with further increase in $\alpha_X$. According to the polarizable ion model, ES configurations are longer lived than their CS counterparts.

In both ZnCl$_2$ and GeSe$_2$, there is evidence of a fragile-to-strong transition on cooling the liquid from high temperatures [37, 43]. In the case of ZnCl$_2$, for example, the fragility index $m = 59$, extracted by fitting high-temperature viscosity data to the MYEGA equation [44], exceeds the value $m = 30$ found from calorimetry measurements made at temperatures nearer to $T_g$. This observation indicates a change in the dynamics, which is related to a conversion of ES to CS tetrahedral ZnCl$_4$ units as the melt is cooled [37, 45], i.e. ES promotes fragile behaviour [41]. A conversion from ES to CS tetrahedral AX$_4$ units on cooling the melt is also observed for GeSe$_2$ [13, 14, 33].

An FSDP is absent for amorphous silicon, which is usually prepared by a deposition or self-ion implantation technique [8], thus avoiding crystallization of the melt. Here, the melt fragility has not been measured, but the absence of an FSDP suggests that liquid silicon will be more fragile than any of the AX$_2$ glasses shown in figure 2. On the other hand, simulations using the Stillinger–Weber potential indicate a fragile-to-strong transition on cooling the melt, although a quantitative assessment of the fragility index is not provided [46]. An FSDP is also absent in $S(k)$ for (i) amorphous germanium, which is prepared in a similar fashion to amorphous silicon [32], and (ii) glassy selenium, which has a fragility index $m = 61.0(2.3)$ [47]. For the Ge$_{x}$Se$_{1-x}$ ($0 \leq x \leq 1$) system, the relationship between the melt topology as expressed by $S_{NN}(k)$ and glass-forming ability is described in [48].

### 5.2. AX$_2$ systems under pressure

In situ high-pressure ND and XRD experiments on glassy SiO$_2$ [49–52], GeO$_2$ [53–58] and GeSe$_2$ [59–61] show that the FSDP loses intensity and moves towards a higher $k$-value with increasing pressure as the principal peak gains intensity and sharpens. For SiO$_2$, the principal peak is a clear feature in the ND results at all pressures, and $S(k) \sim S_{NN}(k)$ (section 4). This peak is absent, however, in the measured x-ray $S(k)$ function under ambient conditions (section 4), but appears as a discernable feature with increasing density. For $^{73}$GeO$_2$, isotope enrichment ensures that the neutron $S(k)$ function approximates $S_{NN}(k)$ on account of the similarity between the coherent neutron scattering lengths of oxygen and the isotope $^{73}$Ge [21]. For GeSe$_2$, both the neutron and x-ray $S(k)$ functions are good approximations to $S_{NN}(k)$ (section 4). The measured $S(k)$ functions for $^{73}$GeO$_2$ and GeSe$_2$ are shown in figure 6.

At ambient pressure, the results for AX$_2$ glass-forming materials suggest that the peak-height ratio $R_{k_1:k_2}$ can be used as a marker of the system fragility. For the open network structures of strong glass-formers, $R_{k_1:k_2}$ decreases markedly (figure 5(b)) as the structural motifs become more densely packed (table 2), but there is little change to the fragility index (figure 5(a)). In comparison, for more densely-packed fragile glass-formers, the ratio takes a small $R_{k_1:k_2}$ value around 0.3–0.7. If this finding carries over to AX$_2$ materials under load [11, 21], the pressure-dependent behaviour of $R_{k_1:k_2}$ for SiO$_2$ [52]
and GeO₂ (figure 6(a)) will be indicative of a pressure-induced strong-to-fragile transition. In comparison, \( T_g \) for SiO₂ is observed to increase with pressure increasing from ambient to 0.6 GPa, which suggests a reduction in \( m \) for this pressure interval [62].

For oxide systems, the growth in height of the principal peak with pressure is accompanied by an increased oxygen-packing fraction, which can be used as a marker for predicting the transformation under load of tetrahedral \( AO_4 \) motifs to higher-coordinated polyhedral units [1, 63, 64].

### 5.3. Metallic and hard-sphere colloidal systems

As illustrated in figure 1 for glassy \( \text{Pd}_{42.4}\text{Ni}_{7.5}\text{Cu}_{30}\text{P}_{20} \), the \( S(k) \) functions for many metallic glass-forming systems feature a peak at \( k_3 \), but peaks at \( k_2 \) and \( k_1 \) do not appear. The liquids for these materials can vary from strong to extremely fragile, based on the reported values for the fragility index [65, 66]. For the Pd–Ni–Cu–P system, glass-forming ability is good, and the measured fragility index is \( m = 52.8–59.5 \) for \( \text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20} \) versus \( m = 75.8–76.2 \) for \( \text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20} \) [67].
The fragility of metallic glass-forming melts at temperatures substantially higher than \( T_g \) has been correlated with the height of the peak at \( k_3 \) in \( S(k) \) [68]. In this experimental work, the fragility was assessed from the VFT equation for the viscosity \( \eta \) as written in the form [69]

\[
\eta = \eta_0 \exp \left[ DT_0 / (T - T_0) \right],
\]

where \( \eta_0 \) is the viscosity in the infinite temperature limit, and \( T_0 \) is the temperature at which the viscosity diverges. The melt fragility increases with decreasing value of the parameter \( D \) [70]. The value of \( S(k_3) \) for the liquid was measured at different temperatures and extrapolated to \( T_g \), and the value of \( S(k_3) \) for the glass at \( T_g \) was also measured. If these results are denoted by \( S(k_3)_{\text{liquid},T_g} \) and \( S(k_3)_{\text{glass},T_g} \), respectively, then a structural fragility index \( \gamma = 100 \times [S(k_3)_{\text{glass},T_g} - S(k_3)_{\text{liq},T_g}] / S(k_3)_{\text{glass},T_g} \) can be defined. The value of \( \gamma \) was observed to increase with fragility of the liquid. We note that, in the case of metallic glasses, a ‘prepeak’ at \( k_2 \) can appear in \( S(k) \) if there is chemical short-range ordering, and originates from \( S_{CC}(k) \) [71].

The \( S(k) \) functions for hard-sphere colloidal glass-forming systems also feature a peak at \( k_3 \), but peaks at \( k_2 \) and \( k_1 \) do not appear (figure 1). Here, the interaction between hard spheres originates from excluded volume and is independent of temperature. Phase behaviour is controlled by the packing fraction \( \phi \). An increase in \( \phi \) will increase the viscosity and drive the system towards a glass, analogous to a decrease in temperature for a molecular glass-forming material. If \( \phi \) is regarded as the thermodynamic parameter that is analogous to \( 1/T \), then the exchange of \( T_0 \) for \( \phi/\phi_0 \) in the VFT formulation of equation (12) will give

\[
\eta = \eta_0 \exp \left[ D\phi / (\phi_0 - \phi) \right],
\]

where \( \phi_0 \) is the packing fraction at which the viscosity diverges. In this way, hard-sphere colloids are categorized as fragile glass-formers, with \( D \approx 1.15–1.65 \) from viscosity measurements or \( D \approx 0.5 \) from light scattering experiments [72]. In comparison, Berthier and Witten [73] argue that the reduced pressure \( Z(\phi) = P / \rho k_B T \) should be regarded as the thermodynamic parameter that is analogous to \( 1/T \), where \( P \) is the pressure, \( \rho \) is the number density and \( k_B \) is the Boltzmann constant. In this case, the exchange of \( T_0 \) for \( Z/Z_0 \) in equation (12), and the conversion from viscosity to the relaxation time \( \tau \) (\( = \eta / G_\infty \), where \( G_\infty \) is the high-frequency shear modulus [70]), gives

\[
\tau = \tau_0 \exp \left[ DZ / (Z_0 - Z) \right],
\]

where \( Z_0 \) is the reduced pressure at which the relaxation time diverges. Molecular dynamics simulations on a system of hard spheres with 8% polydispersity show fragile behaviour with \( D = 1.71(54) \) [74]. All of the \( D \) values for hard-sphere colloids are significantly smaller than \( D \approx 60 \) for silica [75], the prototypical strong glass-forming system. There does not appear to have been a systematic study of the variation in \( S(k) \) with fragility, akin to the investigation of liquid metals [68].

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6. Real-space manifestation of the peaks in $S(k)$

A peak at $k_i$ in $S(k)$ should manifest itself in real space as a damped oscillatory function of periodicity $2\pi/k_i$ with a correlation length that depends on the peak width [19]. A competition between the ordering on different length scales will therefore occur when more than one peak is present. In the following, we will consider this issue by reference to the structures of the liquid metal Au$_{0.81}$Si$_{0.19}$ [76] and the network-forming glass ZnCl$_2$ [26, 27]. For the metal, $S(k)$ has a sharp peak at $k_3$ but no peaks at $k_1$ or $k_2$, and is therefore similar to the structure factor for the amorphous metal shown in figure 1. For ZnCl$_2$, $S_{NN}(k)$ has a ‘three peak’ character with a large principal peak (figure 2). The Au–Si system provided the first metallic alloys to be vitrified by quenching from the liquid state, and the Au$_{0.81}$Si$_{0.19}$ composition is near a deep eutectic in the Au–Si phase diagram [77, 78].

The real-space results for Au$_{0.81}$Si$_{0.19}$ and ZnCl$_2$ are shown in figure 7 as the functions $r[G(r) − 1]$ and $r[g_{NN}(r) − 1]$, respectively. The large-$r$ behaviour was fitted using the expectation of a simple theory [76, 79–81]

$$rh(r) = 2|A|\exp(-a_0r)\cos(a_1r − \Theta),$$

where $h(r)$ denotes either $[G(r) − 1]$ or $[g_{NN}(r) − 1]$. The equation describes an oscillatory function of amplitude $|A|$, wavelength $2\pi/a_1$ and phase $\Theta$ that is exponentially damped with a decay length of $a_0^{-1}$.

For the metal, the large-$r$ fit to $r[G(r) − 1]$ reproduces most of the features in this function at all $r$ values. The fitted periodicity of $2\pi/2.721 = 2.31$ Å matches that expected from the position of $k_3$. The oscillatory character of this function manifests itself in a plot of $\ln |r[G(r) − 1]|$ versus $r$ (figure 7) as a periodically repeating function, where the decay length $a_0^{-1}$ can be obtained from a straight line fit to the repeated maxima. For ZnCl$_2$, $r[g_{NN}(r) − 1]$ shows more complexity than found for the metal, and the large-$r$ fit does not reproduce the features at smaller $r$ values: there are competing length scales that originate from the ‘three peak’ character of $S_{NN}(k)$. Nevertheless, the large $r$ behaviour is oscillatory with a periodicity given by $2\pi/k_2$, which is consistent with the sharpness and height of the principal peak at $k_2$ in $S_{NN}(k)$.

For glassy ZnCl$_2$, the measured $rg_{CC}(r)$ and $rg_{NC}(r)$ functions also have a large-$r$ periodicity given by $2\pi/k_2$ [26], as befits the magnitude and sharpness of both the principal peak in $S_{CC}(k)$ (figure 3) and the principal trough in $S_{NC}(k)$ (figure 4). A fit to the large-$r$ behaviour of $rg_{CC}(r)$ or $rg_{NC}(r)$ using equation (15), with $h(r)$ set at either $g_{CC}(r)$ or $g_{NC}(r)$, reproduces most of the features in a given function at all $r$ values [81].

7. Structure of tetrahedral network-forming glasses

The measured $S_{AA}(k)$, $S_{XX}(k)$ and $S_{AX}(k)$ partial structure factors for several AX$_2$ glasses are plotted as a function of $kd$ in figures 8–10, where $d$ is chosen to be the A–A distance $r_{AA}^{CS}$ for CS AX$_4$ tetrahedral units, the X–X intra-tetrahedral distance $r_{XX}$, or the A–X bond distance $r_{AX}$, respectively. The values of these parameters are listed in table 1. In these materials, the networks are built from tetrahedral AX$_4$ motifs, and a
point of debate concerns the nature of the local A atom network that is formed from the linked motifs. For example, if the AX₄ motifs are corner sharing, then the local A atom network is expected to be approximately tetrahedral, i.e. there will be X-decorated AA₄ tetrahedral units as shown in figure 11.

7.1. A–A correlations: tetrahedrality of the local A atom network

In figure 8, the \( S_{AA}(k) \) versus \( kr_{AA}^{CS} \) functions for several AX₂ glasses are compared to the \( S(k) \) versus \( kr_{AA} \) functions for amorphous silicon [8] and germanium [32], where the nearest-neighbour distances \( r_{AA}^{CS} \) are listed in table 1 and the bond distances \( r_{AA} \) are listed in table 3. A local tetrahedral network for amorphous silicon and germanium is illustrated by a ratio of second to first neighbour distances that is close to the value of \( \sqrt{8/3} = 1.633 \) for a regular tetrahedron, and by A–A–A bond angles that are close to
the ideal intra-tetrahedral angle of 109.47° (table 3). The A atoms are, however, under-coordinated, as indicated by a coordination number \(\bar{n}_A^A < 4\), which is likely to originate from vacancy-type defects or voids [8, 32]. Also shown in figure 8 is \(S_{OO}(k)\) versus \(kr_{OO}\) for low density amorphous (LDA) ice [82], where \(r_{OO}\) is the nearest-neighbour O–O distance (table 3). In LDA ice, the hydrogen atoms of the water molecules are arranged between pairs of oxygen atoms according to the ice rules [83]. A local tetrahedral network for the oxygen atoms is supported by the measured values for the O–O coordination number, ratio of second to first neighbour distances, and O–O–O bond angle (table 3).
Figure 8 shows similarity between the $S(k)$ functions for amorphous silicon and germanium and the $S_{AA}(k)$ functions for glassy SiO$_2$ and GeO$_2$, which supports the notion of an A atom network that is locally tetrahedral. The scaled FSDP position $k_{1r_{AA}^{CS}}$ for these AX$_2$ glasses is similar to the scaled peak position $k_{2r_{AA}} \approx 4.7–4.8$ for amorphous silicon and germanium, which suggests that

$$k_{1r_{AA}^{CS}} \approx 3\pi/2,$$

i.e. the FSDP originates from a length scale that is commensurate with the base-to-apex distance within an X-decorated AA$_4$ tetrahedron. The presence of these tetrahedral configurations in glassy SiO$_2$ and GeO$_2$ is supported by an A–A coordination number $\bar{n}_{A,CS} \approx 4$ (table 2). For SiO$_2$ and GeO$_2$, the ratio of second to first neighbour distances in the measured $g_{AA}(r)$ functions is 1.66(1) or 1.61(1), respectively, and the A–A–A bond angle estimated from these peak positions is 112(4)$^\circ$ or 108(4)$^\circ$, respectively [11, 24, 25].

Figure 8 shows that the FSDP position in $S_{AA}(k)$ for ZnCl$_2$ and GeSe$_2$ is shifted towards a smaller value as compared to SiO$_2$ and GeO$_2$. This shift corresponds to a reduction in the A–X–A bond angle $\theta_{CS}^{AXA}$ (table 1), and to an increase in the anion-packing fraction $\eta_X$ (table 2). For ZnCl$_2$ and GeSe$_2$, the scaled FSDP position $k_{1r_{AA}^{CS}}$ is closer to that expected from the A–A distance along the edge of a regular X-decorated AA$_4$ tetrahedron, i.e. $2\pi/k_1 \approx \sqrt{8/3}r_{CS}^{AA}$ such that

$$k_{1r_{AA}^{CS}} \approx 2\pi\sqrt{3/8} = 3.848.$$  

The presence of X-decorated AA$_4$ tetrahedral motifs in ZnCl$_2$ glass is supported by the Zn–Zn coordination number $\bar{n}_{Zn,CS}^{Zn} = 4.0(2)$ (table 2), and by the Zn–Zn–Zn bond angle distribution that has a broad peak around 112$^\circ$ [27]. In comparison, the overall Ge–Ge coordination number for GeSe$_2$ is given by $\bar{n}_{Ge}^{Ge} = \bar{n}_{Ge,CS}^{Ge} + \bar{n}_{Ge,ES}^{Ge} \approx 3.54$, which indicates a sub-tetrahedral coordination environment (see section 8.1).

For glassy selenium, it is notable that the Se–Se bond angle of 104(1)$^\circ$ is close to the ideal intra-tetrahedral angle of 109.47$^\circ$. This similarity in bond angles for the chain-like conformations of glassy Se follows from the presence of two lone-electron pairs on each Se atom, and is likely to account for a scaled peak position $k_{2r_{SeSe}}$ that is similar to the scaled peak position $k_{2r_{AA}}$ for amorphous silicon and germanium (see figures 1 and 2).

7.2. X–X correlations

Figure 9 shows similarity between the $S_{XX}(k)$ versus $kr_{XX}$ functions for the AX$_2$ glasses, with a main peak at

$$k_{2r_{XX}} \approx 7.725,$$

where $r_{XX}$ is the nearest-neighbour X–X distance (see equation (3)). For a regular AX$_4$ tetrahedron, this distance is given by $r_{XX} = \sqrt{8/3}r_{AX}$, so equation (18) can be rewritten as

$$k_{2r_{AX}} \approx 7.725\sqrt{3/8} = 4.731.$$
There is some variation between the $S_{XX}(k)$ functions that is related to different anion-packing fractions. For an AX$_2$ system of number density $\rho$ containing spherical X atoms of radius $r_X$, the anion-packing fraction is given by $\eta_X = \frac{8}{9} \rho \pi r_X^3$. If each AX$_4$ motif is a regular tetrahedron containing touching X atoms, then $r_{XX}/r_{AX} = \sqrt{\frac{8}{3}}$ and $r_{XX} = 2r_X$. It follows that the anion-packing fraction can be written as

$$\eta_X = 16\sqrt{2}\pi \rho r_{AX}^3/27\sqrt{3}. \quad (20)$$

The packing fractions thus calculated are listed in table 2.

Systems with the lowest anion-packing fractions, namely SiO$_2$ and GeO$_2$, show the largest FSDP in $S_{XX}(k)$ (figure 9). In comparison, the anion-packing fraction for ZnCl$_2$ is close to the value of $\simeq 0.64$ for a dense random-packing of equally sized hard spheres [84, 85], and the FSDP in $S_{XX}(k)$ is a comparatively small feature. Figure 12 shows that the associated Cl–Cl–Cl bond angle distribution is similar to the bond angle distribution for a dense randomly-packed system, where these $n(\theta)$ distributions are normalized by $\sin(\theta)$ in order to remove the effect of a finite sampling volume that would otherwise suppress a finite bond angle distribution at $\theta \simeq 180^\circ$ [27]. The anion-packing fraction for GeSe$_2$, as calculated from equation (20), is larger than the dense random-packing limit. The high value may originate from the comparable size of Ge and Se atoms, i.e. the Se atoms in a tetrahedral GeSe$_4$ unit should not be regarded as touching spheres. Notwithstanding, the Se–Se partial structure factor for GeSe$_2$ is similar to the Cl–Cl partial structure factor for ZnCl$_2$, and both have a shoulder at $kr_{XX} \simeq 14.7$ on the third peak in $S_{XX}(k)$ (figure 9).
7.3. A–X correlations

Figure 10 shows that the $S_{AX}(k)$ functions for the AX$_2$ glasses are superposable over a wide range of $kr_{AX}$ values, with a large trough at

$$k_2r_{AX} \simeq \frac{3\pi}{2},$$  

which follows from the base-to-apex distance within an AX$_4$ tetrahedron (equation (21)). Each $S_{AX}(k)$ function displays an FSDP at $k_1r_{AX} \sim 2.28$–$2.48$, with a height that increases as $\eta_X$ decreases.

8. The FSDP and principal peak positions for AX$_2$ glasses

8.1. The FSDP in $S_{AA}(k)$ and $S_{NN}(k)$

As discussed in section 7.1, the FSDP position in $S_{AA}(k)$ is dependent on the bond angle $\theta_{AXA}^{CS}$. For the more open structures of SiO$_2$ and GeO$_2$ with $\theta_{AXA}^{CS} > 120^\circ$, the scaled FSDP position $k_1r_{AA}^{CS}$ is given by equation (16), which originates from a length scale that is commensurate with the base-to-apex distance within an X-decorated AA$_4$ tetrahedron. For the more compact structure of ZnCl$_2$ with $\theta_{AXA}^{CS} < 120^\circ$, the scaled FSDP position $k_1r_{AA}^{CS}$ is given by equation (17), which originates from a length scale
that is commensurate with the A–A distance along the edge of an X-decorated AA₄ tetrahedron. Equation (17) also gives a good approximation to the FSDP position for GeSe₂, even though the local network of A atoms is sub-tetrahedral with an overall A–A coordination number \(\bar{n}_A \approx 3.54\) (table 2). The latter originates from the presence of both ES and CS tetrahedra [13, 14], conformations that are also found in the structures of crystalline GeSe₂ and GeS₂ [88, 89]. Here, there are layers containing equal numbers of ES and CS GeX₄ tetrahedra, which have three or four nearest-neighbour Ge atoms, respectively, giving a mean Ge–Ge coordination number \(\bar{n}_{Ge} = 3.5\).

In an AX₂ glass, the nearest-neighbour inter-tetrahedral A–A distance is given by \(r_{AA}^{CS} = 2r_{AX} \sin (\theta_{AXA}^{CS}/2)\). Hence, equation (16) for the scaled peak position in \(S_{AA}(k)\) can be rewritten as

\[
k_1r_{AX} \simeq \frac{3\pi}{4 \sin (\theta_{AXA}^{CS}/2)},
\]

and equation (17) for the scaled peak position in \(S_{AA}(k)\) can be rewritten as

\[
k_1r_{AX} \simeq \frac{\sqrt{3}\pi}{\sqrt{8} \sin (\theta_{AXA}^{CS}/2)}.
\]

For a given AX₂ glass, the FSDP position \(k_1\) is similar for each of the Faber–Ziman partial structure factors [20, 21]. It follows, from the definition of the N–N partial structure factor (equation (6)), that equations (22) and (23) should also hold for the scaled FSDP position in \(S_{NN}(k)\). The resultant predictions for the scaled FSDP positions, as calculated using the \(\theta_{AXA}^{CS}\) values listed in table 1, are compared to the measured \(S_{NN}(k)\) functions in figures 2 and 6. At ambient pressure, equation (22) gives a good account of the scaled FSDP position in \(S_{NN}(k)\) for SiO₂ and GeO₂, and equation (23) gives a good account of the scaled FSDP position in \(S_{NN}(k)\) for ZnCl₂ and GeSe₂.

### 8.2. The principal peak

As shown in figure 8, the principal peak position in \(S_{AA}(k)\) for AX₂ glasses is at

\[
k_2r_{AX}^{CS} \simeq 7.725.
\]

For these materials, the nearest-neighbour inter-tetrahedral A–A distance is given by \(r_{AA}^{CS} = 2r_{AX} \sin (\theta_{AXA}^{CS}/2)\), so the principal peak position can be rewritten as

\[
k_2r_{AX} \simeq 7.725/2 \sin (\theta_{AXA}^{CS}/2).
\]

The scaled peak positions thus calculated, using the \(\theta_{AXA}^{CS}\) values listed in table 1, vary with decreasing \(\theta_{AXA}^{CS}\) from \(k_2r_{AX} = 3.99\) for SiO₂ to \(k_2r_{AX} = 5.12\) for GeSe₂. For AX₂ glasses, the principal peak in \(S_{XX}(k)\) is at \(k_2r_{AX} \simeq 4.731\) (equation (19)), and the principal trough in \(S_{AX}(k)\) is at \(k_2r_{AX} \simeq 3\pi/2\) (equation (21)), where these features are associated with intra-tetrahedral correlations. Hence, the principal peak in \(S_{NN}(k)\) at \(k_2r_{AX} \simeq 4.6–4.9\) will have contributions from inter-tetrahedral
Figure 11. An X-decorated AA$_4$ tetrahedron in an AX$_2$ glass such as silica. The large (brown) A atoms are connected via small (red) X atoms to form a chemically ordered network of CS tetrahedral AX$_4$ motifs. Each A atom is at the centre of a tetrahedron of four other A atoms. If this tetrahedron is regular and $r_{AA}$ is the centre to apex (i.e. nearest-neighbour A–A) distance, then the base-to-apex distance is $4r_{AA}/3$ and the edge length is $\sqrt{8/3}r_{AA}$. The FSDP position in AX$_2$ glasses is associated with these longer distances (see the text).

Figure 12. Comparison between the Cl–Cl–Cl bond angle distribution for glassy ZnCl$_2$ generated by the reverse Monte Carlo (RMC) method (dark solid (black) curve), the bond angle distribution obtained from a hard sphere Monte Carlo (HSMC) simulation of the glass (broken (red) curve), and the bond angle distribution obtained from the large 7934 sphere random close-packing model of Bernal and co-workers [86, 87] (dark solid (blue) curve with sharp peak). Reprinted figure with permission from [27], Copyright (2010) by the American Physical Society.
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Table 4. The scaled FSDP and principal peak positions in the Faber–Ziman and Bhatia–Thornton partial structure factors for tetrahedral AX2 glasses. Several of the equations can be rewritten in terms of the A–X bond distance \( r_{AX} \) by noting that the A–A distance for CS AX4 units is given by \( r_{CS}^{AX} = 2r_{AX} \sin(\theta_{AXA}/2) \), and the X–X distance for a regular AX4 tetrahedron of touching X atoms is given by \( r_{XX} = \sqrt{8/3}r_{AX} \).

| A–A   | X–X   | A–X   |
|-------|-------|-------|
| \( k_1r_{CS}^{AA} \approx 3\pi/2^a \) | \( k_1r_{XX} \approx 3.6–4.1 \) | \( k_1r_{AX} \approx 2.28–2.48 \) |
| \( k_1r_{CS}^{AA} \approx 2\pi\sqrt{3/8}^b \) | — | — |
| \( k_2r_{CS}^{AA} \approx 7.725 \) | \( k_2r_{XX} \approx 7.725 \) | \( k_2r_{AX} \approx 3\pi/2 \) |
| N–N   | C–C   | N–C   |
| \( k_1r_{CS}^{AA} \approx 3\pi/2^a \) | \( k_1r_{AX} \approx 2.3–2.5 \) | \( k_1r_{AX} \approx 2.36–2.86 \) |
| \( k_1r_{CS}^{AA} \approx 2\pi\sqrt{3/8}^b \) | — | — |
| \( k_2r_{AX} \approx 3\pi/2 \) | \( k_2r_{AX} \approx 3\pi/2 \) | \( k_2r_{AX} \approx 3\pi/2 \) |

\( ^a \theta_{AXA} \geq 120^\circ \).
\( ^b \theta_{AXA} < 120^\circ \).

nearest-neighbour A–A correlations and from intra-tetrahedral A–X and X–X correlations. Nevertheless, as shown in figures 2 and 6, the scaled principal peak position in \( S_{NN}(k) \) is accurately approximated by equation (21) at ambient pressure.

9. Conclusions

The ordering on different real-space length scales has been considered for a variety of glass-forming materials. Different length scales emerge as peaks in \( S(k) \) with complexity of the bonding scheme. A peak at \( k_3 \) is a generic feature because it is associated with nearest-neighbour contacts at a distance \( d \), and its scaled position is given by \( k_3d \approx 7.725 \). A second (principal) peak appears at \( k_2 \) when the bonding scheme assumes a directional character, and is associated with a longer real-space length scale. Its position in a bare tetrahedral system such as amorphous silicon or germanium is given by the base-to-apex distance within an AA4 tetrahedron, such that \( k_2r_{AA} \approx 3\pi/2 \) where \( r_{AA} \) is the nearest-neighbour A–A distance. A third peak (the FSDP) appears at \( k_1 \) for AX2 glasses, and is associated with a still-longer (intermediate) real-space length scale. The total structure factor \( S(k) \) measured for a multicomponent system by ND often approximates the Bhatia–Thornton number–number partial structure factor \( S_{NN}(k) \), because of similarity between the coherent scattering lengths of many different chemical species.

Conceptually, an AX2 glass could be constructed from a disordered tetrahedral network of A atoms by decorating each A–A bond with an X atom, re-scaling the network, and relaxing the structure. If the resultant local network of A atoms remains open and tetrahedral, as for glassy SiO2 and GeO2, the scaled FSDP position is given by equation (16), which follows from the base-to-apex distance within an X-decorated...
AA₄ tetrahedron. Alternatively, if the local network becomes more densely packed, as for glassy ZnCl₂, the scaled FSDP position is given by equation (17), which follows from the A–A distance along the edge of an X-decorated AA₄ tetrahedron. In the case of GeSe₂, equation (17) also gives a good approximation for the scaled FSDP position, even though ES tetrahedra are present and the local network of A atoms is sub-tetrahedral with n̄ₐ ≃ 3.54. For AX₂ glass, the principal peak at k₂ has contributions from nearest-neighbour inter-tetrahedral A–A correlations and from intra-tetrahedral A–X and X–X correlations, but its scaled position is given by equation (21), which follows from the base-to-apex distance within an AX₄ tetrahedron. The peaks at k₂ and k₃ are therefore associated with ordering on length scales that are commensurate with the size of local network-forming motifs, and with the arrangement of these motifs on an intermediate range, respectively [1]. A summary of the scaled FSDP and principal peak positions in the partial structure factors for AX₂ glasses is given in table 4.

For AX₂ glasses, the peak-height ratio Rₘ₃₃:ₘ₄₄ changes markedly with the A–X–A bond angle for strong glass-forming systems such as SiO₂ and GeO₂, in which the AX₄ structural motifs are sparsely packed, but not for more fragile materials such as ZnCl₂, GeS₂ and GeSe₂, in which the motifs are more densely packed. For glassy SiO₂ and GeO₂ under pressure, the behaviour of Rₘ₃₃₄₄ points towards a pressure-induced strong-to-fragile transition. The absence of an FSDP in SNN(k) for amorphous silicon and germanium suggests that these materials are more fragile than their AX₂ counterparts. The fragility of metallic glass-forming melts has been correlated with the height of the peak at k₃ in S(k) [68]. An analogous investigation for glass-forming hard-sphere colloids does not appear to have been made.

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Data access statement

The data sets created during this research are openly available from the University of Bath Research Data Archive at https://doi.org/10.15125/BATH-00600 [90].

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