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Charge fluctuations and concentration fluctuations at intermediate-range distances in the disordered network-forming materials SiO_2, $SiSe_2$, and $GeSe_2$

Carlo Massobrio,[1] Massimo Celino,[2] and Alfredo Pasquarello[3,4]
[1]*Institut de Physique et de Chimie des Matériaux de Strasbourg, 23 rue du Loess, BP43, F-67034 Strasbourg Cedex 2, France*
[2]*Ente per le Nuove Tecnologie, l'Energia e l'Ambiente, ENEA, C.R. Casaccia, CP 2400, I-00100 Roma, Italy*
and Istituto Nazionale per la Fisica della Materia, Unità di Ricerca Roma1, Italy
[3]*Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL),*
CH-1015 Lausanne, Switzerland
[4]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*
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We calculate the concentration-concentration partial structure factor $S_{\mathrm{CC}}(k)$ and the charge-charge structure factor $S_{zz}(k)$ of liquid SiO_2, amorphous $SiSe_2$ and liquid $GeSe_2$ using first-principles molecular dynamics. These systems are characterized by the occurrence of intermediate range order, as evidenced by a first sharp diffraction peak (FSDP) at low k values in the total neutron structure factor. We show that a FSDP in the concentration-concentration partial structure factor $S_{\mathrm{CC}}(k)$ is generally associated with a small departure from chemical order. This feature tends to vanish either when sufficiently high levels of structural disorder set in, or, oppositely, when the chemical order is essentially perfect. For none of these networks, a FSDP is observed in the charge-charge structure factor $S_{zz}(k)$, i.e., fluctuations of charge do not occur over intermediate range distances. The constraint of charge neutrality is at the very origin of the appearance of fluctuations of concentration. These are observed when the atoms occur in configurations with different coordinations.

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I. INTRODUCTION

Partial structure factors are useful tools to elucidate the atomic structure of disordered systems.[1] These quantities provide information on the range of spatial correlations and can be employed to identify relevant constitutive units. For a binary system made of A and X atoms in concentrations c_A and c_X, respectively, the Bhatia-Thornton concentration-concentration partial structure factor $S_{\mathrm{CC}}(k)$ is defined as

$$S_{\mathrm{CC}}(k) = c_A c_X + c_A^2 c_X^2 \{[S_{AA}(k) - S_{AX}(k)] + [S_{XX}(k) - S_{AX}(k)]\}, \tag{1}$$

where $S_{AA}(k)$, $S_{AX}(k)$ and $S_{XX}(k)$ are the Faber-Ziman partial structure factors. Fluctuations of concentration are reflected by the presence of positive or negative peaks in $S_{\mathrm{CC}}(k)$. These correspond to preferred correlations among atoms of the same kind or of different kind on length scales associated with the value of k. Insensitivity to the chemical nature of the neighbors [i.e., $S_{AA}(k)=S_{AX}(k)$ and $S_{XX}(k)=S_{AX}(k)$ in Eq. (1)] yields $S_{\mathrm{CC}}(k)=c_A c_X$.

A first sharp diffraction peak (FSDP) at low values of k in the total neutron structure factor of liquid and glasses is commonly interpreted as a signature of structural order extending well beyond nearest neighbors.[2] This kind of extended structural organization is termed intermediate range order (IRO). The relationship between the FSDP and specific structural arrangements has long been the object of several interpretation schemes.[2–15] Two of them are frequently invoked.[2,13] The first considers the FSDP as a distinct signature of crystalline-like layers, its position being related to the interlayer separation.[6–8,13] In particular, it was emphasized that quasilattice planes do occur in amorphous silica.[13] The second approach highlights the occurrence of characteristic low density regions in covalent glasses, by successfully accounting for the position of the FSDP in a variety of AX_2 disordered systems.[2,5,10] In this picture, basic structural units ("clusters") are decorated by interstitial "voids," leading to correlation distances typical of intermediate range order. The general validity of such models for the appearance of the FSDP in the total neutron structure factor has been recently tested within the framework of accurate first-principles molecular dynamics calculations.[16] A clear assessment of their predictive power and limitations was reached, based on quantitative criteria applied to configurations of liquid SiO_2 (l-SiO_2) and liquid $GeSe_2$ (l-$GeSe_2$).[17,18]

The significance of the appearance of a FSDP in the concentration-concentration partial structure factor $S_{\mathrm{CC}}(k)$ is even more contentious. Neutron-diffraction measurements showed a FSDP in the structure factor $S_{\mathrm{CC}}(k)$ of both liquid and amorphous $GeSe_2$ (l-$GeSe_2$ and a-$GeSe_2$).[19,20] However, first-principles molecular dynamics did not show any FSDP in the $S_{\mathrm{CC}}(k)$ of l-$GeSe_2$ yet featuring excellent agreement for the total neutron structure factor over the entire k range.[18] At variance, in the case of a-$GeSe_2$, for which the height of the FSDP in the $S_{\mathrm{CC}}(k)$ is strongly reduced, calculations by Zhang and Drabold do yield a sizeable FSDP in the $S_{\mathrm{CC}}(k)$.[21,22]

Very recently we considered a set of networks presenting a FSDP in the total neutron structure factor. We were able to rationalize the occurrence of a FSDP in the $S_{\mathrm{CC}}(k)$ as a signal for the departure from chemical order, and to identify systems of three different classes.[23] Class I encompasses networks showing perfect chemical order and the absence of any FSDP in the $S_{\mathrm{CC}}(k)$. This class includes systems like SiO_2 and GeO_2, which have been characterized either experimentally or by simulation.[17,24] Class II features network systems with a distinct FSDP in the $S_{\mathrm{CC}}(k)$. An extended set of such networks have been found experimentally.[25] This class is consistent with very moderate departures from chemical order, as confirmed by the structure of l-GeSe$_4$ and l-SiSe$_2$ obtained by simulation.[23,26,27] A network structure of class III has so far only been encountered in first-principles molecular dynamics simulations of l-GeSe$_2$.[18] Like for class I, no feature appears at the FSDP location in the $S_{\mathrm{CC}}(k)$. However, contrary to class I, the associated network shows a rich variety of structural motifs in the first-neighbor coordination shells.[18] The latter case precedes the disappearance of the FSDP from the total neutron structure factor as occurring for systems with a high degree of structural disorder, such as for l-GeSe$_2$ at high temperatures.[28]

In a recent paper, we carried out first-principles molecular dynamics simulations on l-GeSe$_4$.[23] Our purpose was twofold. First, we wanted to investigate the origin of the FSDP which appeared in the $S_{\mathrm{CC}}(k)$ of this system. Second, we wanted to compare the $S_{\mathrm{CC}}(k)$ with the charge-charge structure factor $S_{\mathrm{zz}}(k)$. Despite the high degree of ionicity in l-GeSe$_4$, we found that a pointlike charge model cannot describe the $S_{\mathrm{zz}}(k)$, as revealed by the differences between the $S_{\mathrm{CC}}(k)$ and the $S_{\mathrm{zz}}(k)$. These results showed that fluctuations of concentration and fluctuations of charge are uncorrelated on both the short- and the intermediate-range length scales. In particular, while the $S_{\mathrm{CC}}(k)$ exhibits a FSDP at low values of k, no features appear at the FSDP location in the $S_{\mathrm{zz}}(k)$.

In this paper, we calculate the charge-charge structure factor $S_{\mathrm{zz}}(k)$ for three AX_2 networks: l-SiO$_2$, a-SiSe$_2$ and l-GeSe$_2$. These systems are representative of the three classes (l-SiO$_2$: class I, a-SiSe$_2$: class II, l-GeSe$_2$: class III) which were introduced to relate the appearance of a FSDP in the $S_{\mathrm{CC}}(k)$ to the different degrees of departure from chemical order.[23] Our calculations reveal that no FSDP appears in any of the calculated charge-charge structure factors $S_{\mathrm{zz}}(k)$. These results provide evidence in support of the postulate advanced in Ref. 23 that no charge ordering is observed at IRO length scales irrespective of fluctuations of concentration occurring at the same length scales.

This paper is organized as follows. In Sec. II, we summarize the main features of our theoretical model. Section III is divided in three parts, each focusing on the results for the concentration-concentration and charge-charge structure factors of l-SiO$_2$, a-SiSe$_2$ and l-GeSe$_2$, respectively. Conclusive remarks are collected in Sec. IV.

II. THEORETICAL MODEL

In order to calculate the charge-charge structure factor $S_{\mathrm{zz}}(k)$, it is necessary to have access to the electron charge density. Simulations on the three systems considered in this work were carried out previously (Ref. 17 for l-SiO$_2$, Ref. 18 for l-GeSe$_2$, and Ref. 37 for a-SiSe$_2$). However, since the electron density had not been recorded, we here carry out new simulations. Overall, the technical ingredients are the same as in the original studies, to which we refer for a description of the short- and intermediate-range structure.[17,18,37]

The simulations are performed at constant volume on systems consisting of 72 atoms for l-SiO$_2$ (24 Si and 48 O atoms) and of 120 atoms for both a-SiSe$_2$ and l-GeSe$_2$ (40 Si/Ge and 80 Se atoms). The sizes of the periodically repeated cubic cells (10.7 Å, 15.6 Å, 15.7 Å, for l-SiO$_2$, a-SiSe$_2$ and l-GeSe$_2$, respectively) are taken to match experimental densities and are sufficiently large to cover the region of wave vectors in which the FSDP occurs. The smallest wave vectors compatible with our supercells are $k_{\mathrm{min}}=0.6$ Å^{-1} (l-SiO$_2$) and $k_{\mathrm{min}}=0.4$ Å^{-1} (a-SiSe$_2$, l-GeSe$_2$), significantly smaller than the FSDP wave vectors $k_{\mathrm{FSDP}}=1.6$ Å^{-1} (l-SiO$_2$) and $k_{\mathrm{FSDP}}=1.0$ Å^{-1} (a-SiSe$_2$ and l-GeSe$_2$). For each case, the region of wave vectors in which the FSDP appears is described by as much as eight discrete wave vectors compatible with the periodicity of our supercell. To substantiate our choice of the system size, we had previously carried out an analysis of the range of real-space correlations which are responsible for the appearance of the FSDP in the total and in the partial structure factors.[29] For a given partial pair correlation function $g_{\alpha\beta}(r)$, this range can be determined by truncating $g_{\alpha\beta}(r)$ at decreasing distances r_c, monitoring the behavior of the corresponding Fourier-transformed structure factor $S_{\alpha\beta}^{FT}(k)$ and comparing $S_{\alpha\beta}^{FT}(k)$ to the $S_{\alpha\beta}(k)$ directly calculated in reciprocal space. In Ref. 29, we showed that a well defined FSDP is present in $S_{\alpha\beta}^{FT}(k)$ when r_c extends up to $\sim\sqrt{2}L/2$, L being the size of our cubic simulations cells. For these values of r_c, reliable statistics can be collected for distances between independent atoms in the supercell.[30] These conditions are largely met in l-SiO$_2$, a-SiSe$_2$ and l-GeSe$_2$ for the sizes adopted in this study. Therefore, our calculations are suited to describe the correlations extending well beyond second nearest neighbors that characterize intermediate range order.

In our calculations, the electronic structure is described within density functional theory and evolves self-consistently during the motion.[31] Valence electrons are accounted for explicitly, in conjunction with pseudopotentials to account for core-valence interactions. A detailed description of our methodology is given in Ref. 31. In the case of l-SiO$_2$, the exchange and correlation energy is treated within the local density approximation.[32] A norm-conserving pseudopotential is used for silicon,[33] while an ultrasoft one is adopted for oxygen.[34] For a-SiSe$_2$ and l-GeSe$_2$, we resorted to a generalized gradient approximation,[35] with respective norm-conserving pseudopotentials generated as in Ref. 36.

For each system, the last configuration of the fully equilibrated trajectories from the previous studies[18,17,37] is taken as the starting configuration for the new simulation. In the case of a-SiSe$_2$, for which we generated six amorphous structures by quenching from the liquid, we chose to continue the evolution which gave the best agreement for the total neutron structure factor. The temperatures are maintained at the same values as in the original simulations: 3500 K for l-SiO$_2$, 300 K for l-SiSe$_2$, and 1050 K for l-GeSe$_2$. The total and the partial structure factors calculated for the new trajectories reproduce the data in the literature.[18,17,37] Charge densities recorded along the trajectories were used for the calculation of the charge-charge structure factor $S_{\mathrm{zz}}(k)$. Statistical averages were taken over time periods of 5 ps.

In order to calculate $S_{zz}(k)$, we have taken into account the self-consistent valence electron density in the definition of the total charge density composed of ionic and electronic parts, $\rho_t(\mathbf{r}) = \Sigma_i z_i \delta(\mathbf{r}-\mathbf{r}_i) + \rho_e(\mathbf{r})$:

$$S_{zz}(k) = N^{-1}\langle z_v^2\rangle^{-1} \int d\mathbf{r} d\mathbf{r}' \rho_t(\mathbf{r})\rho_t(\mathbf{r}') e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \tag{2}$$

In our pseudopotential formulation, only the valence electrons are accounted for in $\rho_e(\mathbf{r})$, the ionic charges z_i being $z_A = +4$ and $z_X = +6$. In Eq. (2) the spherical average over the orientations of $\mathbf{k}$ is assumed implicitly, N is the number of atoms and $\langle z_v^2\rangle$ is an appropriate normalization factor, $\langle z_v^2\rangle = z_{vA}^2 c_A + z_{vX}^2 c_X$. In the expression for $\langle z_v^2\rangle$, $z_{vA} = +4$ and $z_{vX} = -2$ are the charges attributed to A and X atoms within a pointlike charge model (PLC). In the limit $k \to \infty$, $S_{zz}(\infty) = \langle z^2\rangle / \langle z_v^2\rangle$, with $\langle z^2\rangle = z_A^2 c_A + z_X^2 c_X$. For AX_2 systems this leads to $S_{zz}(\infty) = 3.66$.

When the PLC approximation is adopted, the total charge density becomes $\rho_t(\mathbf{r}) = \Sigma_i z_{vi} \delta(\mathbf{r}-\mathbf{r}_i)$. The charge-charge structure factor $S_{zz}(k)$ is now proportional to $S_{CC}(k)$ and reads

$$S_{zz}^{\mathrm{PLC}}(k) = N^{-1}\langle z_v^2\rangle^{-1} \sum_{ij} z_{vi} z_{vj} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)} = (c_A c_X)^{-1} S_{CC}(k). \tag{3}$$

III. RESULTS

A. Liquid SiO_2

In liquid SiO_2 the chemical order of the network is preserved to a very large extent.[17] Most of the Si atoms are at the center of tetrahedra linked by corner-sharing O atoms. The total neutron structure factor of l-SiO_2 exhibits a FSDP at $k = 1.6$ Å^{-1}.[17] In Fig. 1, we compare the structure factors $S_{zz}(k)$ and $S_{CC}(k)$ for l-SiO_2, the latter being normalized to 1 for $k \to \infty$ [see Eq. (3)]. No feature appears in the $S_{CC}(k)$ at the FSDP location, demonstrating that fluctuations of concentration do not arise in a system characterized by perfect short-range order. According to the classification introduced in Ref. 23, this network belongs to class I. The charge-charge structure factor $S_{zz}(k)$ strongly differs from the concentration-concentration structure factor $S_{zz}^{\mathrm{PLC}}(k)$. The main peak the $S_{zz}(k)$ is located at $k_M = 5.1$ Å^{-1}, followed by one deep minimum and shallow oscillations. Small marks close to the FSDP location are not significantly different from the basis line within statistical accuracy, meaning that no charge fluctuations occur at intermediate-range length scales. A departure from charge neutrality is therefore not expected for distances beyond $r \sim 1.5$ Å,[41] i.e., of the order of the nearest-neighbor distances.

Due to the strong ionicity of its bonding, l-SiO_2 is a prototype of chemically ordered network. Therefore, one would expect the pointlike model to describe satisfactorily structural and charge correlations. However, the striking differences between $S_{CC}(k)$ and $S_{zz}(k)$ in Fig. 1 show that this is by far not the case. The disparity between $S_{CC}(k)$ and $S_{zz}(k)$ illustrates that structural order and charge order are two distinct physical properties as a consequence of the distributed nature of the electron charge.

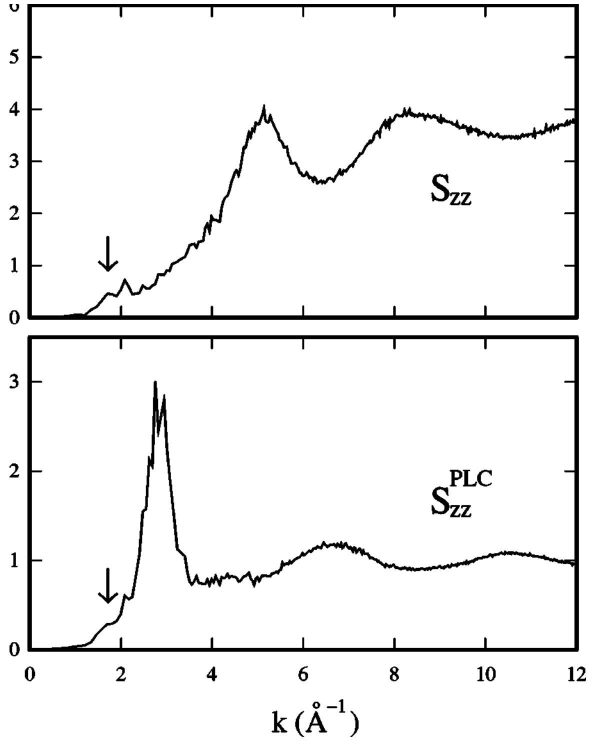

FIG. 1. Upper panel: charge-charge structure factor $S_{zz}(k)$ of liquid SiO_2 at $T = 3500$ K. Lower panel: concentration-concentration structure factor $S_{CC}(k)$ of liquid SiO_2 at $T = 3500$ K. $S_{CC}(k)$ is normalized as in Eq. (3), i.e., $S_{zz}^{\mathrm{PLC}}(k) = (c_A c_X)^{-1} S_{CC}(k)$. The arrows indicate the location of the FSDP in the total neutron structure factor ($k_{\mathrm{FSDP}} = 1.6$ Å^{-1}).

B. Amorphous $SiSe_2$

Amorphous $SiSe_2$ is characterized by a very high degree of chemical order and a small number of structural defects. Its total neutron structure factor exhibits a FSDP. No experimental partial structure factors are currently available. The atomic structure of a-$SiSe_2$ consists of both corner-sharing and edge-sharing connections. Edge-sharing connections are predominant, with a majority of Si atoms that belong to one or two fourfold rings.[37] Experimental evidence and first-principles molecular dynamics indicate that at least 1% of the bonds involving Si or Se atoms are homopolar.[37–39] These data are consistent with coordination numbers only slightly deviating from the values for a chemically ordered network (CON), $n_{\mathrm{Si}} = 3.95$, $n_{\mathrm{Se}} = 2.04$, $n_{\mathrm{Si}}^{\mathrm{CON}} = 4$, $n_{\mathrm{Se}}^{\mathrm{CON}} = 2$. Calculations on liquid $SiSe_2$ were carried out to produce a reliable starting configuration for the obtention of the amorphous phase.[27] In liquid $SiSe_2$ the presence of a small but distinct peak at the FSDP location in the concentration-concentration partial structure factor $S_{CC}(k)$ was correlated to the departure from chemical order.[27] Figure 2 shows that a prominent peak is clearly visible at the FSDP location in the $S_{zz}^{\mathrm{PLC}}(k)$ structure factor of a-$SiSe_2$. This feature can be ascribed to strong Si-Si IRO correlations, the FSDP being ab-

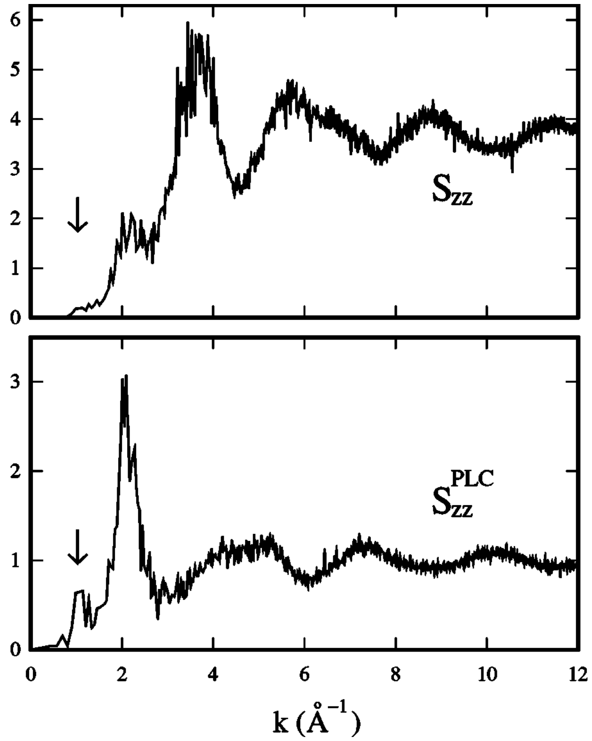

FIG. 2. Upper panel: charge-charge structure factor $S_{zz}(k)$ of amorphous $SiSe_2$ at $T=300$ K. Lower panel: concentration-concentration structure factor $S_{CC}(k)$ of amorphous $SiSe_2$ at $T=300$ K. $S_{CC}(k)$ is normalized as in Eq. (3), i.e., $S_{zz}^{PLC}(k)=(c_A c_X)^{-1}S_{CC}(k)$. The arrows indicate the location of the FSDP in the total neutron structure factor ($k_{FSDP}=1.0\ Å^{-1}$).

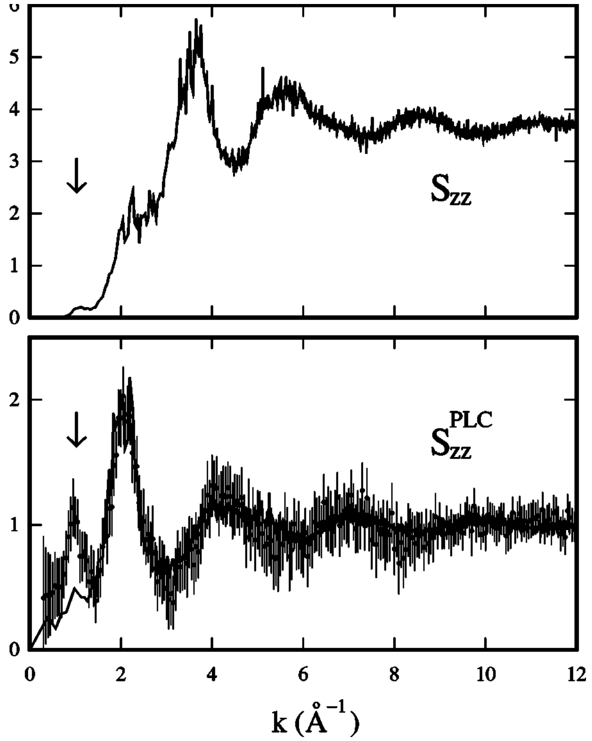

FIG. 3. Upper panel: charge-charge structure factor $S_{zz}(k)$ of liquid $GeSe_2$ at $T=1050$ K. Lower panel: concentration-concentration structure factor $S_{CC}(k)$ of liquid $GeSe_2$ at $T=1050$ K. $S_{CC}(k)$ is normalized as in Eq. (3), i.e., $S_{zz}^{PLC}(k)=(c_A c_X)^{-1}S_{CC}(k)$. Full line: present results, dots with error bars: experimental results. (Ref. 19) The arrows indicate the location of the FSDP in the total neutron structure factor ($k_{FSDP}=1.0\ Å^{-1}$).

sent in the calculated Se-Se partial structure factor.[40] Amorphous $SiSe_2$ forms a network representative of class II.

The charge-charge structure factor $S_{zz}(k)$ does not show any peak at the FSDP location (Fig. 2). Interestingly, a distinct bump can be noticed in the $S_{zz}(k)$ at a k value corresponding to the main peak in the $S_{zz}^{PLC}(k)$, $k_M \sim 2$ Å^{-1}. Therefore, both fluctuations of concentrations and fluctuations of charge occur at short-range length scales. However, while fluctuations of charge are suppressed for distances beyond $r \sim 3.8$ Å,[41] fluctuations of concentration persist for larger distances, as proved by the peak at $k_{FSDP}=1$ Å^{-1}. The behavior found for a-$SiSe_2$ indicates a sensitivity of the fluctuations of concentration over IRO length scales to the presence of a small number of structural defects. These defects are responsible for the appearance of a FSDP in the $S_{CC}(k)$, otherwise absent in a network showing perfect chemical order (cf. the case of l-SiO_2 in Sec. III A). We note that the condition of charge neutrality over IRO length scales is not affected by the small deviation from chemical order found in a-$SiSe_2$.

C. Liquid $GeSe_2$

The partial structure factors of l-$GeSe_2$ have been measured by Penfold and Salmon using the method of isotopic substitution in neutron diffraction.[19] A prominent FSDP characterizes the $S_{CC}(k)$, due to IRO correlations involving mostly Ge-Ge interactions. Accordingly, this network belongs to class II. By comparing the heights of the FSDP in the $S_{zz}^{PLC}(k)$ of a-$SiSe_2$ (present work, Fig. 2) and in the $S_{zz}^{PLC}(k)$ of l-$GeSe_2$ (experimental results of Ref. 19, see Fig. 3), it appears that fluctuations of concentration on IRO distances are higher in the latter case. The total neutron structure factor as obtained by first-principles molecular dynamics is in excellent agreement with the experimental one over the entire k range, and even the FSDP is accurately reproduced.[18] However, the distribution of the FSDP weight in the partial structure factors is different in theory and experiment. In particular, the FSDP is vanishing in the calculated $S_{zz}^{PLC}(k)$ (Fig. 3). This point has been extensively addressed in Ref. 29, where we showed that this disagreement is due to an insufficiently accurate description of Ge-Ge correlations. Indeed, the height of the FSDP in the Ge-Ge partial structure factor is underestimated. While this underestimation does not affect the total neutron structure factor because of compensation effects related to the other partials structure factors, this discrepancy is magnified in the $S_{CC}(k)$.

Calculations predict a predominant fourfold $GeSe_4$ coordination coexisting with a large variety of structural motifs.[18] This marked departure from perfect tetrahedral order shows that fluctuations of concentration on IRO distances are suppressed in the presence of a high concentration of defective units. Therefore, the absence of the FSDP in $S_{CC}(k)$ might result from two drastically different origins, i.e., from the establishment of perfect chemical order (as in l-SiO$_2$, class I) or from the occurrence of a high level of structural disorder (as in the simulations of l-GeSe$_2$, class III).

The charge-charge structure factor $S_{zz}(k)$ of l-GeSe$_2$ behaves similarly to the case of a-SiSe$_2$. The absence of any distinct feature at the FSDP location confirms that no charge ordering occurs at IRO scales in disordered network-forming materials, and this holds irrespective of fluctuations of concentration on the same length scale. The absence of any feature below the shoulder at $k_s \sim 2$ Å^{-1} in the $S_{zz}(k)$ is indicative that no departure from charge neutrality is expected for distances beyond $\sim$3.8 Å.[41]

IV. CONCLUSIVE REMARKS

We considered three AX_2 disordered networks, liquid SiO$_2$, amorphous SiSe$_2$ and liquid GeSe$_2$, characterized by the presence of intermediate range order, as evidenced by the appearance of a FSDP in the total neutron structure factor. We calculated the concentration-concentration structure factor $S_{CC}(k)$ and the charge-charge structure factor $S_{zz}(k)$ by taking time averages over equilibrium trajectories obtained via first-principles molecular dynamics. Depending on the level of chemical disorder, three different behaviors have been identified in the concentration-concentration structure factor $S_{CC}(k)$ at low k values. When the network is made of nondefective tetrahedral units, the FSDP in the $S_{CC}(k)$ is absent. A moderate departure from perfect chemical order is reflected by a distinct feature at the FSDP location in the $S_{CC}(k)$ structure factor. This mark disappears again for higher levels of disorder.

For all networks studied here, the charge-charge structure factor $S_{zz}(k)$ does not display any feature at the FSDP location. This result confirms previous evidence collected on liquid GeSe$_4$.[23] Moreover, it corroborates the postulate that no charge ordering occurs at intermediate length scales in disordered network-forming materials. The constraint of charge neutrality is responsible for the appearance of fluctuations of concentration on IRO distances. For a perfect network, this constraint does not require any local variation of the average concentration since all atoms of the same species are in the same valence states. Accordingly, no FSDP is found in the structure factor $S_{CC}(k)$. The situation changes in the presence of a moderate amount of chemical disorder, i.e., the occurrence of different valence states. For charge neutrality to hold over intermediate distances, the occurrence of different valence states has to correspond to local variations in the structural arrangement. As a result, the local concentration deviates from the average value, giving rise to fluctuations of concentration at IRO distances and to the appearance of a FSDP in the structure factor $S_{CC}(k)$.

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