Phys. Status Solidi B 250, No. 5, 976-982 (2013) / DOI 10.1002/pssb.201248512

Disorder in Order: A special issue on amorphous materials honoring S. R. Elliott



## Anomalies of the first sharp diffraction peak in network glasses: Evidence for correlations with dynamic and rigidity properties

## Matthieu Micoulaut\* and Mathieu Bauchy

Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie, Boite 121, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received 30 October 2012, revised 19 December 2012, accepted 19 December 2012 Published online 14 February 2013

Keywords glasses, intermediate phase, molecular dynamics simulations, rigidity transitions, structure, supercooled liquids

\* Corresponding author: e-mail mmi@lptl.jussieu.fr, Phone: +33-1-44277240, Fax: +33-1-44275100

The structural and dynamical properties of densified sodium silicates are investigated using molecular dynamics (MD) simulations. From the analysis of the first sharp diffraction peak (FSDP) in the amorphous phase, it is shown that some of its characteristic parameters (position, width) in partial structure factors display minima in a certain pressure interval defining a window. The pressure window can be correlated with anomalies in transport properties (diffusion, viscosity) and their activation barriers. The count of topological constraints, sensitive to pressure and temperature, is also computed. In the pressure window, we find evidence that an adaptative behavior takes place as angular constraints soften and reduce the increasing network connectivity related strain induced by pressure. These findings display striking similarities with the Boolchand intermediate phase (IP) found in rigidity driven by composition. The present numerical results also suggest that structural signatures for the IP should be found from a detailed analysis of neutron structure factors involving the partials. Finally, on a more general ground, the present study links for the first time to the best of our knowledge characteristic features of the FSDP with transport properties in the liquid.

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** The first sharp diffraction peak (FSDP), or prepeak, is one of the most prominent features which appear in diffraction patterns of network-forming glasses and liquids [1, 2]. Given its position, typically at a wavevector of  $1-2 \text{ Å}^{-1}$ , it is supposed to be related to the presence of a non-random structural ordering at an intermediate lengthscale which also manifests in real space by well-defined peaks in the pair distribution functions up to 8-10 Å. Two decades ago, several interpretations were proposed in the literature in order to understand how and why the FSDP manifests. The first scheme highlights the possibility that clusters and low density regions (voids) contribute to the typical second and fourth-neighbor correlation distances giving rise to the FSDP [3]. Such elegant models have received support from numerical simulations on a variety of network glasses including SiO<sub>2</sub> or amorphous silicon [4]. On the other hand, it has been proposed that the FSDP is simply the result of a characteristic

distance involved in the inter-layer separation of crystallinelike structures [5] or quasilattice planes [6]. The latter ideas have served to understand the behavior of the FSDP in chalcogenides [7] which have, at least for some of them, a natural layered-like structure in their crystalline polymorphs [8]. This second scheme has been ruled out by an *ab initio* study of liquid GeSe<sub>2</sub> and SiO<sub>2</sub>, which has shown [9] that the appearance of an FSDP is not correlated to crystalline-like layers while cluster-void correlations were indeed found. Unfortunately, these layered-like structures also manifest in systems which do not exhibit a FSDP. Furthermore, the void-cluster model [4] fails to explain changes in the FSDP in alkali silicate glasses for which a heterogeneous distribution (channels) of modifier atoms is found [10]. Given the modified network structure, it becomes difficult to define voids. Furthermore, Li- and Na-silicates have an identical medium-range order structure but they differ substantially in terms of their FSDP intensity [11]. Finally, it has been

demonstrated [12] that both layers or voids can contribute to intermediate range order and the FSDP, as exemplified by a study on liquid ZnCl<sub>2</sub>.

Given these contradictory results on a controversial subject, one is left with the impression that, in fact, both layers or voids may contribute to the FSDP, and that their ratio may be highly system dependent, and may eventually be driven by *e.g.*, the underlying crystalline network structure. The FSDP also depends on the thermodynamic conditions as it is known that its intensity and position change with composition [13], pressure [14] and temperature [15], or even isotope substitution [16]. The debate on the origin of the FSDP is far from over, and there is space for entertaining new ideas, including new correlations that we describe in this contribution for the first time.

Here we investigate by molecular dynamics (MD) the behavior of the FSDP with changing pressure in a model silicate glass, 2SiO<sub>2</sub>-Na<sub>2</sub>O (called NS2 hereafter). Results show that the characteristic features of the FSDP (peak position, peak width) display anomalies (extrema) with pressure in a certain pressure interval. In the latter, dynamic anomalies in diffusion or viscosity take place in the liquid [17, 18], and corresponding activation energies are found to be minimum. These are signatures of a rigid intermediate phase (IP) that is determined from MD-based topological constraint counting, a phase located between a lowconnected (low density) flexible phase, and a highly crosslinked (high density) stressed rigid phase [19, 20]. In contrast with previous studies on the subject, rigidity is not tuned by composition as in base network glasses [21], but by pressure which induces an increase in e.g., the Si coordination number [22], thus in network connectivity and rigidity. Our results therefore provide a clear evidence that the IP has some explicit structural signatures coming from the FSDP. Experimentally, corresponding investigations-based solely on the neutron or X-ray total structure factor have been unsuccessful [13, 23, 24]. Recently however, an X-ray absorption near edge structure (XANES) experiment has shown that there are weak structural signatures of the IP [25]. Here, it is shown that the IP should be detected from neutron diffraction through a detailed analysis of the partial structure factors. On a more general ground, it is shown for the first time that the structural properties at intermediate range order embedded in the characteristic features of the FSDP at low temperature, are associated with dynamical properties of the corresponding glass-forming liquid. The latter correlations should be useful for an improved understanding of the nature of the IP and the FSDP.

At this point, and before presenting the details of the calculations and the connection with rigidity theory, it is probably useful to review some of the salient features of the IP which is one of the most intriguing discoveries [26] in the field of network glasses. According to the seminal work of Phillips and Thorpe [27, 28], and following the pioneering work of Maxwell on mechanical trusses, glasses with a low connectivity (or a low network mean coordination number  $\overline{r}$ ) have usually more degrees of freedom  $n_{\rm L}$  than mechanical

constraints  $n_{\rm c}$  imposed by nearest-neighbor (bond-stretching, BS, and bond-bending, BB) interactions  $(n_c < n_L)$ . Such networks are flexible because local deformations are possible which manifest in model networks due to lowfrequency (floppy) modes in the vibrational density of states [29]. Since  $\overline{r}$  can be increased by appropriate compositional or pressure changes, at some point the network will undergo a rigidity transition and one will have a stressed rigid phase characterized by  $n_{\rm c} > n_{\rm L}$  with nearly no more local deformations possible. However, when  $n_c$  nearly balances  $n_L$ , during cooling and relaxation the network can adapt over a finite compositional (or pressure) domain to reduce the stress imposed by the increased number of constraints, thus leading to a special phase, an IP, that is rigid but unstressed [30]. This has led to the introduction of self-organized networks [19, 20, 31] as a clue for the understanding of the IP.

Experimentally, one of the most obvious signatures of the IP arises from a modulated differential scanning calorimetry (mDSC) measurement [30]. The latter splits the usual DSC signal into a reversing part which tracks the temperature modulation at the same frequency, and a residue, characterized by a non-reversing heat flow,  $\Delta H_{\rm nr}$ , which contains most of the kinetic events associated with the slowing down of the relaxation close to the glass transition. In the IP, it has been found that  $\Delta H_{nr}$  nearly vanishes [26]. The use of calorimetric methods to detect the boundaries of the IP has not been without controversy, mostly because the measurement of  $\Delta H_{\rm nr}$  is hardly reproducible without special care. First, one has to take into account frequency corrections [32] in order to avoid spurious effects arising from the frequency-dependence of the specific heat [33]. Secondly, this quantity appears to be extremely sensitive to impurities and inhomogeneities [34]. Careful sample preparation has therefore become the very crucial prerequisite prior to the investigation of the IP [35, 36].

Unfortunately, while many studies have spent time lambasting on  $\Delta H_{\rm nr}$  measurements, other alternative and obvious signatures of the IP and some of its anomalous properties have been overseen [26]. Figure 1 displays a survey of some of such properties for three families of glasses with widely different chemical bonding, although they display similar features in terms of rigidity: covalent  $Ge_xSe_{1-x}$  [34, 37], ionic (1 – x)AgPO<sub>3</sub>–xAgI [38] and ionocovalent (1 - x)GeO<sub>2</sub>-xNa<sub>2</sub>O glasses [39]. In all, rigidity is tuned by a change in composition. When the atomic sizes are comparable (e.g.,  $r_{\text{Ge}} = 1.22$  Å, and  $r_{\text{Se}} = 1.17$  Å for the covalent radius in Ge-Se), it has been found that because of the absence of stress [19], networks will pack together more easily in the IP as manifested by a minimum in the molar volume (Fig. 1a and c). The stress-free nature of the IP has been detected from pressure experiments [37] showing the vanishing of the threshold pressure (Fig. 1a) prior to a pressure-induced Raman peak shift. The latter behavior serves usually to measure residual stresses in crystals. Finally, in ionic conductors (Fig. 1b), onset of ionic conduction appears only in the flexible phase when the network can be more easily deformed at a local level because





**Figure 1** (online color at: www.pss-b.com) A survey of different quantities showing an anomalous behavior in the IP. (a) Raman threshold pressure  $P_c$  [37] and molar volume [34] (right axis) in Ge<sub>x</sub>Se<sub>1-x</sub> as a function of Ge composition. (b) Ionic conduction and zero-frequency permittivity (right axis) in (1 - x)AgPO<sub>3</sub>-xAgI as a function of AgI composition [38]. (c) IR-TO vibrational frequency and molar volume (right axis) in (1 - x)GeO<sub>2</sub>-xNa<sub>2</sub>O as a function of Na<sub>2</sub>O composition [39]. The gray areas correspond to the reversibility windows determined from mDSC. The flexible phase is signaled.

of the presence of floppy modes [38] thus promoting mobility. This leads to an exponential increase of the conductivity. However, in the IP an intermediate conductive regime sets in, which also shows anomalous behavior for a typical jump distance [40], dc permittivity  $\varepsilon(0)$  (Fig. 1b) [38] or the frequency  $v_{TO}$  [39] associated with the imaginary part the complex dielectric function (Fig. 1c).

In the following, we build on these concepts and investigate numerically the structural and dynamical properties of a densified sodium silicate glass and liquid. We analyze the rigidity of such systems and identify the IP. Obvious correlations emerge from the investigations, and these are discussed in the following.

**2** Computational methods We now consider a 3000 atom  $Na_2O-2SiO_2$  (NS2) ensemble containing 660 silicon, 670 sodium, and 1670 oxygen atoms. A two-body Teter potential [41] has been used as interaction potential, and its accuracy has been demonstrated for structure [42] and dynamics [10, 18]. Transport properties (diffusion and viscosity) have been found to be comparable to experimental data, and are substantially improved with respect to alternative potentials [43].

After an equilibration stage at 6000 K over 1 ns (loss of initial configuration), the integration time using the Verlet algorithm being 2 fs, the system has been placed at various (T, P) thermodynamic conditions. At a first stage, we have used an NPT Ensemble to calculate the box size, prior to a simulation in NVT Ensemble for the accumulation of the trajectory. For instance, a pressure of -1.9 GPa corresponds to a box length of 32.39 Å allowing to recover the experimental density  $\rho = 2.37$  g cm<sup>-3</sup> at 300 K [44].

Next, we examine the structure of the glassy NS2 by following the total neutron weighted structure factor  $S_N(k)$  with pressure. Our results are then compared with a constraint analysis [45] introduced recently, which allows to identify the boundaries of the IP, together with calculated dynamical properties at 2000 K: diffusion *D* (computed from the long-time limit of the mean-square displacement), viscosity  $\eta$  (computed using the Green–Kubo formalism), and corresponding activation energies  $E_A$  which are extracted from an Arrhenius plot of both *D* and  $\eta$ . We refer the reader to Ref. [18] for the details on the calculation of these transport properties.

**3 Results** In Fig. 2 we show the total computed structure factor, obtained from a linear combination of the partial structure factors  $S_{ij}(k)$ , defined by

$$S_{\rm N}(k) = \frac{\sum\limits_{i,j} c_i c_j b_i b_j S_{ij}(k)}{\left(\sum\limits_i c_i b_i\right)^2},\tag{1}$$

where  $S_{ij}(k)$  have been calculated from the Fourier transform of the pair distribution functions. As seen from the figure, at ambient pressure the computed  $S_N(k)$  reproduces rather well the neutron diffraction results [46]. Most importantly, the measured position at  $k_{FSDP} = 1.85 \text{ Å}^{-1}$  and the width  $\Delta k_{FSDP}$  of the FSDP are fairly well reproduced. With increasing pressure, the principal peak (PP) found at



**Figure 2** (online color at: www.pss-b.com) Total simulated structure factor  $S_N(k)$  of amorphous NS2 at increasing pressures. From bottom to top: 0, 3, 12, 50 GPa. The circles are experimental data by Misawa et al. [46]. The red curves are the Lorentzian fits (see text for details). The insert shows the Si–O partial structure factor at three selected pressures, together with the position  $k_{FSDP}$ .

5.3 Å<sup>-1</sup> remains nearly constant in intensity and wavevector position whereas the second PP at  $3 \text{ Å}^{-1}$  builds up and becomes dominant at elevated pressures. The FSDP is found to steadily upshift from  $k_{\text{FSDP}}$  from 1.85 to 2.3 Å<sup>-1</sup> as pressure increases to 25 GPa (Fig. 3).

The most relevant partial structure factors are represented for three selected pressures in the inset of Fig. 2. For all  $(S_N(k), S_{ij}(k))$ , a Lorentzian fit is used in order to extract the position  $k_{FSDP}$  and width  $\Delta k_{FSDP}$ . Results on the FSDP (Fig. 3) show an anomalous behavior in some of the partial structure factors. For instance, the position  $k_{FSDP}$ maximizes for the partials involving the network-forming species (Si–O, O–O, Fig. 3, left panel) with an FSDP increasing from 1.53 to 1.9 Å<sup>-1</sup> at 5 GPa for  $S_{OO}(k)$ , and then decreasing at higher pressures. The behavior contrasts with the one found for the total  $S_N(k)$ . The width of the FSDP (Fig. 3 right) also shows anomalies in the same pressure interval between approximatively 2 and 13 GPa with a pronounced minimum found for  $\Delta k_{FSDP}$  in the total  $S_N(k)$ and the partial  $S_{SiO}(k)$ .

As the position of the FSDP reflects some repetitive characteristic distance between structural units, the present findings suggest that in a certain pressure interval, a typical lengthscale of distance  $L = 7.7/k_{\text{FSDP}}$  (4.05 Å for the O–O correlations) emerges, and then decreases. Here the factor 7.7 relates to the first maximum of the spherical Bessel function  $j_0(kr)$ . Similarly, the broadening of the FSDP is indicative of a correlation length, following the well-known Scherrer equation for microcrystals which connects the width of a Bragg peak with the average size of the microcrystals. This leads to the definition of a correlation length defined by



**Figure 3** (online color at: www.pss-b.com) Left: Position  $k_{\text{FSDP}}$  of the FSDP (in Å<sup>-1</sup>) of different partial structure factors. Right: Width  $\Delta k_{\text{FSDP}}$  of the FSDP (in Å<sup>-1</sup>). The gray zones correspond to pressure regions of dynamic and rigidity anomalies (see text for details).

 $\xi = 7.7/\Delta k_{\text{FSDP}}$ . From Fig. 3, one realizes that in the pressure window all atomic pairs give rise to a typical correlation length  $\xi$ . For instance, this correlation length is equal to 8.10 and 4.97 Å for the  $S_{\text{N}}(k)$  and  $S_{\text{SiO}}(k)$ , respectively. Other partials display a  $\Delta k_{\text{FSDP}}$  with a broader minimum.

**4 Link with rigidity theory** We have shown that some of the characteristic features of the FSDP (position, width) display anomalies (minima) in a certain pressure interval. These are found to be correlated to rigidity properties as discussed next. But before we describe this correlation, there is need to recognize that constraints or rigidity are tuned by external pressure.

**4.1 A pressure window as an intermediate phase** We now analyze the rigidity of the obtained densified systems by applying recently introduced methods for computing BS and BB topological constraints [45]. Given the weak radial or angular excursions of, respectively, bonds or angles associated with the Si atoms, focus is made on the more sensitive BB constraints of bridging oxygens defined by two adjacent SiO<sub>4/2</sub> tetrahedra.

For each individual atom k, the angular motion over the time trajectory leads to a single bond angle distribution  $P_k(\theta)$  characterized by a mean  $\overline{\theta}_k$  (the first moment of the distribution), and a second moment (or standard deviation  $\sigma_{\theta_k}$ ). The latter represents a measure of the strength of the underlying BB interaction. In fact, if  $\sigma_{\theta_k}$  is large (one has



usually  $\sigma_{\theta_k} > 15-20^{\circ}$  [45]), it suggests that the BB restoring force which maintains the angle fixed around its mean value  $\overline{\theta}_k$  is ineffective. Consequently, the corresponding BB topological constraint should be broken, and does not contribute to network rigidity. The opposite reasoning can be applied for low values of  $\sigma_{\theta_k}$  which will give rise to an intact BB constraint and contribute to  $n_c$ . Finally, the average over the whole system leads to a distribution  $f(\sigma)$  of standard deviations which can be analyzed and tracked with pressure or temperature.

Figure 4 shows the distribution of angular standard deviations for the bridging oxygen in a 2000 K liquid for increasing pressures (0 < P < 20 GPa). At ambient pressure, a bimodal distribution is found, similarly to Ref. [45]. The high and low contributions ( $\sigma_b$  and  $\sigma_i$ , respectively) are assigned to broken and intact constraints. This assignement is rather obvious: at ambient pressure and at elevated temperatures (4000 K, [45]), all constraints must be broken because of thermal activation whereas at low temperature (300 K) the standard deviations are found inside a sharp distribution centered at low  $\sigma$  (<10°). In the intermediate temperature interval (e.g., 2000 K), both contributions vary, and lead to the displayed bimodal distribution (Fig. 4). From the latter, the fraction of intact BB constraints can be computed and is equal to q(2000 K) = 0.77. As observed in the figure, the main feature is the progressive vanishing of the peak centered at  $\sigma_b$  which suggests that the thermally activated broken constraints are restored with applied pressure.

The fraction q(P) of intact constraints can be computed along the isotherm T = 2000 K (Fig. 4 insert), and a clear minimum is found in a pressure window approximatively located over the interval 2 < P < 13 GPa. The present anomaly in q(P) results from an interplay between the



**Figure 4** Standard deviation distributions  $f(\sigma)$  (right axis) of liquid (2000 K) NS2 at increasing pressures showing a bimodal distribution centered at  $\sigma_i$  and  $\sigma_b$ . The insert shows the corresponding computed fraction of intact constraints q(P) with pressure, defining a pressure interval (gray zone). See text for details.

increase of connectivity (and thus of stress) due to the pressure-induced tetrahedral to octahedral coordination change [10], and the softening of the oxygen BB constraints which reduces rigidity. It is found that at P = 0, the NS2 glass and liquid are flexible ( $n_c = 2.56$  at low temperature [47]). Since the average silicon and oxygen coordination numbers  $\overline{r}_{Si}$  and  $\overline{r}_{O}$  increase with pressure because of the growth of Si<sup>V</sup>, Si<sup>VI</sup>, and O<sup>III</sup> species [22], the number of constraints per atom increases by  $\Delta n_c = 0.50$  at P = 10 GPa. However, this global increase of  $n_c$  can be reduced during a certain pressure interval by breaking the softer BB constraints, resulting in a decrease of q(P) at low pressure. With growing pressure (and increasing  $\overline{r}_{Si}$  and  $\overline{r}_{O}$ ), the adaptive behavior can hold only up to a certain threshold pressure ( $\simeq 13$  GPa at 2000 K). For P > 13 GPa, no accomodation is possible any more and q(P) now increases steadily. This behavior not only defines a pressure window (gray zone in the insert of Fig. 4), but also bears large similarities with the self-organized Boolchand IP where growing stress induced by composition is released by network adaptation in self-organized networks [19, 20, 31] which maintains  $n_c \simeq 3$  as long as possible, once the network has undergone the flexible to rigid transition (identified here at  $P = P_c$  (1)  $\simeq 2$  GPa) but not the rigid to stress transition at  $P = P_c$  (2)  $\simeq$  13 GPa.

**4.2 Evidence for dynamic anomalies** The trend in pressure of the fraction of intact constraints q(P), the position  $k_{\text{FSDP}}$  and the width  $\Delta k_{\text{FSDP}}$  of the FSDP for some partial structure factors appears to be correlated with a certain number of transport anomalies in the liquid state. Figure 5 shows that in the same pressure window where BB constraints soften and reduce from q(P) = 0.82 to 0.72 at 10 GPa (Fig. 4) in order to lower rigidity induced by pressure, diffusion, and viscosity are found to be maximum and minimum, respectively. Other related quantities display anomalies as well. In fact, the Arrhenius plot of the viscosity (insert of Fig. 5) shows a linear behavior indicative of a function of the form  $\eta = \eta_0 \exp[E_A/k_BT]$  where  $E_A$  is the activation energy for viscous flow. Note that the same kind of behavior is obtained for the diffusion constants of the network forming species (Si,O). When the corresponding activation energies  $E_A$  for viscous flow or oxygen diffusion are plotted as a function of pressure, they also exhibit a minimum in the same pressure window as q(P) or  $k_{\text{FSDP}}$ .

Taken together, Figs. 3, 4, and 5 underscore the fact that there is a link between structural, dynamical, and rigidity properties, which manifest in a certain pressure window where most of these properties display an anomalous behavior.

**5 Establishing correlations** Having calculated these various structural, dynamic, and rigidity properties, can more correlations be sketched on a general ground ?

**5.1 Optimal glass formation and fragility** The fact that at fixed temperature, the system is able to show a minimum in melt viscosity, indicates that this pressure



**Figure 5** (online color at: www.pss-b.com) Top: Activation energy  $E_A$  for viscosity (filled circles) and oxygen diffusion (open boxes) as a function of pressure. The former is extracted from the insert which shows the viscosity as a function of  $10^4 \text{ T}^{-1}$ for three selected pressures (0, 6, and 22 GPa) together with experimental data from Bockris et al. at ambient pressure [48]. Bottom: Viscosity (filled circles) and diffusion (open squares, right axis) as a function of pressure at 2000 K.

window may well be the location of optimal glass formation which is one of the salient features of the IP. Richet has observed [49] that glass-forming tendency is in fact increased for systems that are able to increase their melt viscosity down to lower temperatures. At eutectics where freezing-point depressions exist, glasses form more easily as these depressions bring the liquid to lower temperatures and higher viscosities. Such observations correlate rather well with observed minima in the critical cooling rate that is needed in order to avoid crystallization [50]. Following this reasoning, it is therefore expected that along an isotherm (*e.g.*, the one shown in Fig. 5, bottom), glass-formation will be optimized for systems having a lower melt viscosity in the pressure window.

The evolution of the numerical glass transition temperature  $T_g$  with pressure has not been computed. Therefore, it is not possible to rescale the behavior of the viscosity from  $\eta(1/T)$  to  $\eta(T_g/T)$  at fixed pressure in order to estimate the liquid fragility defined by  $\mathcal{M} = \partial \log_{10} \eta/\partial(T_g/T)$ at  $T = T_g$ . However, recalling that for an Arrhenius behavior of the viscosity, one has the known formula [51]:  $\mathcal{M} = E_{\rm A} \ln_{10} 2/k_{\rm B}T_{\rm g}$ , and assuming that  $T_{\rm g}$  does not depend too much on pressure, one can expect that in the present system the intermediate pressure phase coincides with a minimum in fragility. This conclusion is consistent the one obtained from a simplified Kirkwood–Keating model of the glass transition [51] showing that glass-forming liquids in the IP are strong (with a low  $\mathcal{M}$ ), and that activation energy for viscosity or relaxation time are minimum when  $n_c \simeq 3$ .

The present results indicate a general correlation between paramaters characterizing the FSDP in partial structure factors, fragility, and ease of glass formation. In fact, intermediate range order which contributes to  $k_{\rm FSDP}$  or  $\Delta k_{\rm FSDP}$  is strongly affected by the thermal history leading to glass formation, and keeps track of the anomalies taking place in the liquid at selected pressures.

5.2 Low frequency modes and typical lengthscales It has also been suggested that a lengthscale associated with low-frequency excitations [52] can contribute to the FSDP. Specifically, it has been shown that for several glasses  $\Delta k_{\text{FSDP}}$  can be correlated to the boson peak maximum found in the low frequency part of the vibrational density of states, and that  $k_{\text{FSDP}}/\Delta k_{\text{FSDP}}$  is nearly a constant. Given our results displayed in Fig. 3, the latter situation obviously does not seem to be fulfilled for the NS2 system. However, floppy modes which contribute to the boson peak in chalcogenides [21], do exist in NS2 at ambient pressure and disappear as the rigidity of system is changed [53]. One may therefore anticipate a correlation between the calculated structural, dynamic and rigidity properties, and low-frequency vibrational properties [22]. Work in this direction is in progress.

**6** Concluding remarks In summary, this study links for the first time characteristic features of the FSDP with transport properties in a liquid silicate. We have investigated the structural, dynamical, and rigidity properties of densified sodium silicates using MD simulations. It has been found that some of the parameters characterizing the FSDP were displaying an anomalous behavior in a certain pressure interval which coincides with the interval where anomalies in transport properties take place. An analysis using MDbased topological constraint counting shows that BB (angular) constraints involving the bridging oxygen between two tetrahedra soften in the same pressure interval. This leads to the definition of a pressure window where obviously the network-forming liquid self-organizes and lowers the number of BB constraints in order to reduce the rigidity induced by the increasing pressure. In this respect, the present findings can be seen as the pressure analog of the Boolchand IP found in rigidity driven by composition. More generally, these numerical results on the FSDP suggest that structural signatures for the IP should be found, and these should come from a detailed analysis of neutron diffraction experiments involving the partial structure factors. Up to now, only calorimetric, optical, and thermodynamic signatures of the IP have been found.

Acknowledgements The authors thank C. Bichara, P. Boolchand, O. Laurent, M. Malki, C. Massobrio, N. Mousseau, J. C. Phillips, P. Simon for useful discussions. The present paper is dedicated to Professor Stephen Elliott for his 60th anniversary. On the issue of the IP, he has been oscillating between support and skepticism, but has remained always intrigued. Support from Agence Nationale de la Recherche (ANR) (Grant No. 09-BLAN-0109-01) is gratefully acknowledged.

## References

- [1] S. R. Elliott, Nature **354**, 445 (1991).
- [2] S. R. Elliott, Phys. Rev. Lett. 67, 711 (1991).
- [3] S. R. Elliott, J. Phys.: Condens. Matter 4, 7661 (1992).
- [4] S. R. Elliott, J. Non-Cryst. Solids 182, 40 (1995).
- [5] L. E. Busse, Phys. Rev. B 29, 3639 (1981).
- [6] P. H. Gaskell and S. J. Wallis, Phys. Rev. Lett. 76, 66 (1996).
- [7] P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips, and J. P. Remeika, Phys. Rev. B 20, 4140 (1979).
- [8] C. Von Dittmer and H. Schäeffer, Acta Crystallogr. B 32, 2726 (1976).
- [9] C. M. Massobrio and A. Pasquarello, J. Chem. Phys. 114, 7976 (2001).
- [10] M. Bauchy and M. Micoulaut, Phys. Rev. B 83, 184118 (2011).
- [11] J. Du and R. Corrales, Phys. Rev. B 72, 092201 (2005).
- [12] M. Wilson and P. A. Madden, Phys. Rev. Lett. 80, 532 (1998).
- [13] E. Bychkov, C. J. Benmore, and D. L. Price, Phys. Rev. B 72, 172107 (2005).
- [14] J. M. Zaug, A. L. Soper, and S. M. Clark, Nature Mater. 7, 890 (2008).
- [15] G. d'Angelo, C. Crupi, M. A. Gonzalez, E. Basile, V. C. Nibali, and C. Mondelli, J. Phys. Chem. B 114, 12565 (2010).
- [16] J. H. Lee, A. Pradel, G. Taillades, M. Ribes, and S. R. Elliott, Phys. Rev. B 56, 10934 (1997).
- [17] M. Bauchy and M. Micoulaut, submitted (2013).
- [18] M. Bauchy, M. Micoulaut, N. Sator, and B. Guillot, Chem. Geol. 2012, http://dx.doi.org/10.1016/j.chemgeo.2012.08.035.
- [19] M. Micoulaut and J. C. Phillips, Phys. Rev. B 67, 104204 (2003).
- [20] M. Micoulaut, Phys. Rev. B 74, 184208 (2006).
- [21] P. Chen, C. Holbrook, P. Boolchand, D. G. Georgiev, and M. Micoulaut, Phys. Rev. B 78, 224208 (2008).
- [22] M. Bauchy, J. Chem. Phys. 137, 044510 (2012).
- [23] M. T. M. Shatnawi, C. L. Farrow, P. Chen, P. Boolchand, A. Sartbaeva, M. F. Thorpe, and S. J. L. Billinge, Phys. Rev. B 77, 094134 (2008).
- [24] S. Hosokawa, I. Oh, M. Sakurai, W.-C. Pilgrim, N. Boudet, J.-F. Bérar, and S. Kohara, Phys. Rev. B 84, 014201 (2011).
- [25] G. Chen, F. Inam, and D. Drabold, Appl. Phys. Lett. 97, 131901 (2010).

- [26] M. Micoulaut and M. Popescu (eds.), Rigidity and Boolchand Intermediate Phases in Nanomaterials (INOE Publishing House, Bucarest, 2009).
- [27] J. C. Phillips, J. Non-Cryst. Solids 34, 155 (1979).
- [28] M. F. Thorpe, J. Non-Cryst. Solids 55, (1983).
- [29] Y. Cai and M. F. Thorpe, Phys. Rev. B 40, 10535 (1989).
- [30] X. Feng, W. J. Bresser, and P. Boolchand, Phys. Rev. Lett. 78, 4422 (1997).
- [31] M.-A. Brière, M. V. Chubynsky, and N. Mousseau, Phys. Rev. E 75, 056108 (2007).
- [32] X. Guoa, J. C. Mauro, D. C. Allan, and Y. Yue, J. Non-Cryst. Solids 358, 1710 (2012).
- [33] N. O. Birge and S. R. Nagel, Phys. Rev. Lett. 54, 2674 (1985).
- [34] S. Bhosle, P. Boolchand, M. Micoulaut, and C. Massobrio, Solid State Commun. 151, 1851 (2011).
- [35] S. Bhosle, K. Gunasekera, P. Boolchand, and M. Micoulaut, Int. J. Appl. Glass Sci. 3, 205 (2012).
- [36] S. Bhosle, K. Gunasekera, P. Boolchand, and M. Micoulaut, Int. J. Appl. Glass Sci. 3, 189 (2012).
- [37] F. Wang, S. Mamedov, P. Boolchand, B. Goodman, and M. Chandrasekhar, Phys. Rev. B 71, 174201 (2005).
- [38] M. Micoulaut, M. Malki, D. I. Novita, and P. Boolchand, Phys. Rev. B 80, 184205 (2009).
- [39] R. Rompicharla, D. I. Novita, P. Chen, P. Boolchand, M. Micoulaut, and W. Huff, J. Phys.: Condens. Matter 20, 202101 (2008).
- [40] M. Micoulaut and M. Malki, Phys. Rev. Lett. 105, 235504 (2010).
- [41] A. N. Cormack, J. Du, and T. R. Zeitler, J. Non-Cryst. Solids 323, 147 (2003).
- [42] J. Du and A. N. Cormack, J. Non-Cryst. Solids 349, 66 (2004).
- [43] J. Horbach, W. Kob, and K. Binder, Chem. Geol. 174, 87 (2001).
- [44] Y. Vaills, Y. Luspin, and G. Hauret, J. Non-Cryst. Solids 286, 224 (2001).
- [45] M. Bauchy and M. Micoulaut, J. Non-Cryst. Solids 357, 2530 (2011).
- [46] M. Misawa, D. L. Price, and K. Suzuki, J. Non-Cryst. Solids 37, 85 (1980).
- [47] Y. Vaills, T. Qu, M. Micoulaut, F. Chaimbault, and P. Boolchand, J. Phys.: Condens. Matter 17, 4889 (2005).
- [48] J. O. M. Bockris, J. D. Mackenzie, and J. A. Kitchener, Trans. Faraday Soc. 51, 1734 (1955).
- [49] P. Richet, M. Roskosz, and J. Roux, Chem. Geol. 225, 388 (2006).
- [50] C. Y. Fang, H. Yinnon, and D. R. Uhlmann, J. Non-Cryst. Solids 57, 465 (1983).
- [51] M. Micoulaut, J. Phys.: Condens. Matter 22, 285101 (2010).
- [52] A. P. Sokolov, A. Kisliuk, M. Soltwitsch, and D. Quitmann, Phys. Rev. Lett. 69, 1540 (1992).
- [53] H. M. Flores-Ruiz and G. G. Naumis, Phys. Rev. B 83, 184204 (2011).