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Compressibility, diffusivity, and elasticity in relationship with ionic conduction: An atomic scale description of densified Li₂S–SiS₂ glasses

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1 | INTRODUCTION

The development of high-power rechargeable fast ion batteries with elevated energy density has attracted a broad attention because of their intensive use in mobile devices, electric bikes, scooters^{1–3} but also in distributed power-storing systems for solar energy or electric vehicles. Among such batteries, Li-based ones are the most efficient due to their high standard potential and to Li cations that are rapidly moving within a liquid electrolyte found between a Li-based oxide cathode (a lithium tran-

Abstract

We examine the dynamic and ionic properties of a typical sulfide glass electrolyte $50Li_2S-50SiS_2$ using molecular dynamics simulations and a previously parameterized force-field able to describe both the crystalline Li_2SiS_3 phase and the corresponding glass. We especially focus on the effect of moderate pressures on the glassy and supercooled state since the design of all-solid state batteries use molding conditions at moderate pressures in order to achieve contact between the electrolyte and the electrodes. The behavior of the conductivity $\sigma(P)$ with pressure permits to define an activation volume and to infer the role of compressibility and diffusivity, the latter contributing dominantly to ionic conduction, whereas temperature does not seem to impact the structural properties. These features are linked with the underlying dynamics of the Li ions as studied here by computing the longitudinal and transversal atomic species current correlations. The resulting elasticity is found to be close to experimental values.

KEYWORDS

atomistic simulation, electrolyte, glass

sition metal oxide, e.g., $LiCoO_2$) and a graphite anode. These basic features have led to the design of the popular and nowadays worldwide used Li-ion batteries launched by Sony Corp. in 1991. Since the electrolyte media is made from flammable polymeric liquids, safety hazard issues have emerged in the recent years (fires, explosions). As such, alternative solutions have to be sought.⁴ Among such solutions, the possibility to use solid electrolytes such as $Li_7P_3S_{11}$ or $Li_{10}GeP_2S_{12}$ appears attractive as these are able to exhibit high ionic conductivities at room temperature, comparable to those of liquid electrolytes in use.⁵ While



these materials attract a broad interest, glassy or glass ceramic electrolytes⁶ are also considered as promising candidates. Unlike crystalline polymorphs, glasses offer the advantage of alloving a number of components into base materials which permits to continuously improve crucial properties such as ionic conduction. While, for example, binary Li₂S-P₂S₅ glasses have now inspired numerous studies because of a high ionic conductivity,⁷⁻¹⁰ siliconbased sulfides have received a renewed attention only recently^{11,12} largely motivated by their high ionic conduction $(10^{-3} \Omega^{-1}.cm^{-1})$ at ambient conditions (for a review, see Ref. [13]). With weaker Li-S and Si-S bonds which result from the greater polarizability of the sulfide ion, sulfide glasses have, indeed, ionic conductivities higher than those of their oxide analogues.^{13,14} These weaker bonds also induce Young's moduli that are substantially lower in most sulfide electrolytes ($E = 18-25 \text{ GPa}^{15}$) when compared to oxides, and for, for example, the 50SiS₂-50Li₂S one has E = 31.0 GPa.¹⁶ Such low values permit to elastically deform the network in an increased fashion and to more easily accommodate volume changes of the electrode reactions with the lithium ions. As a result, sulfide based all-solid-state batteries usually maintain a good interface contact¹⁷ which allows for good cycle performances and long cycle lives.^{18,19}

Among lithium amorphous chalcogenides, binary Li₂S– SiS₂ glasses with varying Li content have been characterized by a variety of techniques.^{20–27} These signal that as in many other glassy conductors, conductivity depends substantially on temperature and follows an Arrhenius law of the form $\sigma \propto \exp[-E_A/(k_BT)]$, where k_B is the Boltzmann constant.

1.1 | The notion of activation volume

Pressure dependence of conductivity provides an additional insight into ionic diffusion, although rarely considered.^{28,29} Pressure and temperature control are used in order to form favorable solid-solid interfaces between the electrode and the electrolyte, and different techniques have emerged in order to increase the contact area at the interface and to reduce its contact resistance. This permits to enhance both conductivity and the utilization of electrode-active materials. Typical isostatic pressing in lithium thiosilicates involves pressures of about 300-500 MPa.^{21,30} The pressure dependence of σ is of course much smaller than the temperature dependence but its investigation permits to examine an important parameter for ionic conduction which is the activation volume. This notion is inspired by the seminal work of Barus³¹ which proposed from the viscosity (η) measurements of natural oils that $\ln \eta \propto P$. Subsequent modifications of this simple

relationship were proposed by Whalley³² and Williams,³³ and this led to the definition of the 'apparent' activation volume, ΔV^* , in:

$$X(P) = X_0^P \exp\left[\frac{P\Delta V^*}{RT}\right]$$
(1)

with $X(P) = \eta(P)$, $\tau(P)$ being the relaxation time, or $\sigma(P)$ the ionic conductivity. Here, X_0^P represents the amplitude of the corresponding property X(P). Based on Equation (1) one, thus, has $\Delta V^* = -RT(\partial \ln \sigma / \partial P)_T$. Recent measurements on compressed glassy systems^{34,35} suggest that the dynamics linked to the relaxation time $\tau(P)$ or the viscosity $\eta(P)$ obeys rather a super-Barus equation in which the activation volume is pressure dependent, and given by equation:

$$V_a(P) = \frac{RT}{P} \ln \left[\frac{\tau(P)}{\tau(0)} \right]$$
(2)

and under select thermodynamic conditions or system dependence, one has $\Delta V^* = V_a(P)$ or not. For the conductivity σ in the glassy state, one sometimes prefers³⁶:

$$\sigma(P)^{-1} = \sigma_0^{-1} \exp\left[S\frac{P\Delta V^*}{RT}\right]$$
(3)

as this modification might be linked with the fractional Stokes–Einstein relation involving a scaling parameter $S^{37,38}$ which suggests a decoupling between translational and rotational motion in supercooled liquids so that $\tau(P)^S \propto \sigma(P)^{-1}$ although Equation (1) is readily used in many experimental studies.^{28,29} These concepts (Equations 1 and 2) extracted from the transition state theory highlight the difference between volumes occupied by a molecule in an activated or non-activated state, and appear crucial for the understanding of the role of pressure on the behavior of thermalization in general. Here, $V_a(P)$ is linked with an elementary volume involved with an elementary relaxation process, and appears, therefore, central for the understanding of glassy relaxation or, alternatively, with the ion dynamics within solid electrolytes.

1.2 | Classical force-fields for sulfide glasses: a rapid and critical review

Atomic scale simulations such as ab initio or classical molecular dynamics (MD) simulations are useful tools for establishing features from statistical mechanical averages of microscopic atomic features all the way to estimating macroscopic physico-chemical properties. Specifically, when having to increase the system size and the timescale above few hundreds of atoms and 100 ps, classical MD is usually preferred, especially if one attempts to focus on dynamical, mechanical, or elastic properties of disordered systems, where the small systems and limited time in ab initio simulations are greatly limiting. On oxide and especially silicate glasses, besides the seminal contribution of Pedone^{39,40} and the publication of the very efficient Teter potential,⁴¹ there has been a huge literature devoted to various binary and ternary oxide compounds or to the corresponding network formers.^{42–47}

Once oxygen is replaced by the more polarizable sulfur atoms, glasses become less ionic and more covalent making the explicit treatment of the chemical bonding more challenging, even for ab initio simulations.^{48–51} Indeed, among other features, the reduced electronegativity difference leads to a breakdown of chemical order which is manifested by typical homopolar pre-peaks (Ge–Ge or S–S) in the partial pair correlation functions measured experimentally in isotope substituted neutron diffraction^{52–55} or by anomalous X-ray scattering⁵⁶ in stoichiometric network formers (GeS₂). Attempts to model the network formers using classical force-fields have not been very convincing in this respect.^{57–60} In addition, for the binary glasses incorporating an alkali modifier the conductive properties of glass electrolytes are closely related to their bonding and structure, and the present attractive sulfide systems display the same phenomenology as the archetypal Li₂O-SiO₂ silicate glasses. That is, the addition of lithium sulfide causes the depolymerization of the base network SiS₂ formed by corner- and edge-sharing tetrahedra SiS_{4/2} by transforming bridging sulfur (BS) into nonbridging sulfur atoms (NBS).²⁴ The negative charge of the latter is compensated by the Li^{\oplus} ions. Lack of extended structural data (neutron or X-ray scattering) for such thiosilicate or thiogermanate glasses has been an additional roadblock to force-fitting studies (see however^{61,62}), but a certain number of scattering data have been reported in the recent years.^{10,12,63,64} There is, therefore, an opportunity for considering a new effort in this direction.

Regarding such modified sulfide glasses, we are aware of only a select number of cases, where classical force-fields have been proposed. The Na₂S–SiS₂ thiosilicate⁶⁵ has been modeled using a Buckingham-type potential but it fails to accurately reproduce the structure factor, even in a slightly improved version.⁶⁶ For the GeS₂–Li₂S system, the structure models have been obtained from reverse Monte Carlo simulations⁶³ and a force-field for the Li ions only has been proposed for the low temperature glass,⁶⁴ although it is known that activation barriers for structural relaxation are huge in the glassy state so that a reasonable estimation of the ion dynamics is out of reach. Early investigations on the Li₂S–SiS₂ have also led to some spurious results⁶⁷ such as five-fold Si atoms in the glassy state, and recent scattering results on this system¹² completely rule out the force-field.⁶⁸ An alternative one has been proposed with some success for SiS_2-Li_2S glasses and crystals,⁶⁸ and we build on it in the present contribution. The main criteria of selecting this potential are its ability to reproduce the crystallographic data of the related crystalline Li_2SiS_3 polymorphs (cell lengths, density), experimental structure functions accessed from neutron or X-ray scattering,¹² and also realistic diffusion coefficients for a slightly different composition⁶⁹ (60 Li₂S–40 SiS₂).

1.3 | Purpose of the present contribution

In order to explore the role of properties such as compressibility and elasticity on ionic conduction in detail, we used such classical MD simulations which permits us to link the atomic scale description with calculated ensemble averaged quantities such as diffusivity and conductivity. We use a recently parameterized force-field which has shown great ability to model the structural properties of SiS_2-Li_2S glasses and crystals.⁶⁸ It is, indeed, able to correctly reproduce the structural properties of the glass (experimental structure functions such as structure factor and pair correlation functions^{12,61}), and the crystal properties^{70,71} (cell lengths, densities at zero pressure), together with other different properties.

Here, the investigation of pressure effects indicates that in the chosen (moderate, ≤ 1 GPa) pressure range, both diffusivity and conductivity tend to linearly decrease with increasing P which suggests that the activation volume is not pressure dependent so that $V_a(P) = \Delta V^*$. The huge difference in diffusivity between Li ions and the network species also signals a clear decoupling between network and ion dynamics. This leads to a dominant contribution from Li ions to the conductivity. The important increase of ΔV^* which varies from $\simeq 3.0$ Å at low temperature (700 K) to 7.0 Å at the highest liquid temperature (1 500 K) suggests an obvious softening of the network with temperature increase, and this increase is linked with more available free volume that is entirely controlled by the density variation, that is, structural changes are minimal so that the fraction of free space is almost independent of temperature. Finally, we explore the ability of the potential to describe the elastic properties and possible dynamical correlations with the structure using density correlation functions and dynamical structure factors, each separated in transversal and longitudinal components. While elastic quantities (e.g., speed of sound, Bulk modulus,...) are close to reported ones from experiments,¹⁶ our results indicate that S-Li correlations display some cooperative dynamics, and there is a well-defined correlation of Li movements for a scale of around 40 Å. A rather unusual profile for Li-Li correlations which manifests by broad

distributions over temporal and spatial frequencies suggests a possible stochastic motion for the charge carriers.

2 | MOLECULAR DYNAMICS

The considered systems are made of 3 000 atoms with initial configurations fulfilling the stoichiometry of the Li_2SiS_3 system⁶⁸: $N_{\text{Li}} = 1\,000$, $N_{\text{Si}} = 500$, and $N_{\text{S}} = 1\,500$ and a starting density of $\rho_0 = 0.051$ Å⁻³ = 1.82 g cm⁻³ (similar to experiments, see ref. 12) corresponding to L = 38.87 Å. Classical MD simulations with a parameterized Buckingham-type potential have been used, together with a Verlet algorithm with a 1 fs time step for the integration of the equations of motion in different ensembles. Specifically, the atomic interactions were modeled as follows:

$$V_{ij}(r) = A_{ij} \exp\left(-r/\rho_{ij}\right) - \frac{C_{ij}}{r^6} + \frac{z_i z_j}{4\pi\epsilon_0 r},$$
 (4)

where *r* is the interatomic distance, A_{ij} , ρ_{ij} , and C_{ij} are parameters, z_i are the charges (in *e* units), and ϵ_0 is the permittivity of vacuum.⁶⁸ *i* and *j* refer to the type of two distinct atoms. The used parameters can be found in ref. 68.

For the investigation of the dynamics and the ionic properties, we limited ourselves to the liquid and supercooled state ($T \ge 700$ K) as this temperature range allows the systems to be equilibrated on the computer timescale (1 ns). At fixed temperatures (1 500, 1 300, 1 100, 900, and 700 K), we first equilibrated the systems in the NPT ensemble at a fixed pressure of $P \le 1$ GPa, prior to longer runs in NVT used for the statistical averages. For most of the dynamics, runs were performed over 100 ps $\le t \le 1$ ns simulation time but in order to extract diffusivities for the network species at low temperature (900 K), additional runs with t > 1 ns have been undertaken. For the calculation of the liquid compressibilities, we applied larger pressure ranges (0– 10 GPa) so that a Birch–Murnhagan fit^{72,73} to the numerical data could be applied with confidence.

3 | RESULTS

Our first interest is to determine the pressure effect on transport and ionic properties in relationship to structural changes.

3.1 | Diffusivity

To do so, we investigate the dynamics of the targeted liquids by focusing on the mean square displacement (msd)



FIGURE 1 Calculated mean square displacement of Li (red) and S (black) atoms in the supercooled state at different temperatures (1 300, 900, and 700 K) and at P = 0 GPa. The inset shows the evolution of the potential energy $E_p(T)$ across the glass transition for a cooling rate of 1 K/ps.

of the atoms, defined from the positions $\mathbf{r}_i(t)$ at time t:

$$\langle r_k^2(t) \rangle = \left\langle \frac{1}{N_k} \sum_{j=1}^{N_k} |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \right\rangle$$
(5)

where the sum is taken over all atoms of type k (k = Si, S, Li). The self-diffusion D_k constant in the long-time limit is defined from the Einstein equation:

$$D_k = \frac{1}{6} \lim_{t \to \infty} \frac{d\langle r_k^2(t) \rangle}{dt}.$$
 (6)

Note that for all temperatures, we can safely determine the Li diffusivities as the different $\langle r_k^2(t) \rangle$ display a welldefined diffusive regime that sets in for t > 10 ps to 1 ns (Figure 1) and which manifests by a linear evolution of $\langle r_k^2(t) \rangle$ with slope one in a log-log plot after a shorttime ballistic regime $(\langle r_k^2(t) \rangle \propto t^2)$ and a possible cage-like dynamics ($\langle r_k^2(t) \rangle \simeq \text{const.}$) at low temperature. For the lowest temperature (700 K), there is already a substantial reduction of the (Si, S) motion which appears to be of the cage-like type but the Li diffusive regime can be clearly acknowledged at higher t (Figure 1). Diffusivity results are presented in Figure 2 in an Arrhenius representation for the Li₂SiS₃ liquids. We are not aware of any Li tracer diffusion measurements in such glasses/liquids, but the obtained values are compatible with those measured in similar modified sulfide glasses^{74–76} using Na or Ag. We note that the species obviously do not follow the



FIGURE 2 Calculated diffusivity of Li (red), Si (green), and S (black) atoms in the liquid state at ambient pressure (P = 0, filled circles) and at P = 1 GPa (open boxes), and compared to data of related sulfide glasses: Ag₂S-GeS₂⁷⁴ and 56Na₂S-44SiS₂.⁷⁶ The inset shows the activation energies $E_A(P)$ for Li diffusivity (red) and conductivity (black) obtained from an Arrhenius fit to the data.

same dynamics since the network species (S, Si) display diffusivities that are about a factor of about 50 smaller than $D_{\rm Li}$, this being valid for all considered temperatures, and at the lowest temperatures the motion is made of still fast moving Li ions within a frozen (glassy) network. These features are linked with the energy evolution across the glass transition (inset) which shows that at zero pressure, a progressive deviation of the high-temperature liquid behavior occurs at 900 K. Conversely, the low temperature (glass) behavior departs at $\simeq 500$ K which defines for the given cooling rate a numerical glass transition region 500 K \leq $T_g \leq 900$ K. In this temperature range, the lower temperature corresponds to the one at which the Li subnetwork melts, whereas network species enter only into the liquid state at higher temperatures.

We find the diffusivity to obviously follow an activated (Arrhenius) type as evidenced from the representation (semi-log in 1/T, Figure 2). The corresponding activation energy for the Li is $E_A = 0.44$ eV at zero pressure, that is, exactly the same value as the one reported for the isochemical sodium glass.⁷⁶ The application of pressure leads to small changes in D_{Li} as also evidenced from the evolution of the corresponding activation energy $E_A(P)$ which remains nearly constant, and in the range of 0.4-0.5 eV (see the inset of Figure 2).

3.2 Conductivity

The conductivity (σ) as a function of temperature *T* can be obtained from the Nernst-Einstein equation⁷⁷ using the



Calculated conductivity (black filled circles) and Li FIGURE 3 (red filled circles) and network contributions (blue filled circles) at zero pressure in the liquid state, compared to experimental data in the glass from Ahn and Huggins,⁷⁸ Morimoto et al.,⁷⁹ and Mori et al.¹² The activation energy for conductivity and the experimental glass transition region¹³ is indicated.

positions of the atoms:

$$\sigma(T) = \lim_{t \to \infty} \frac{e^2}{6tVk_BT} \sum_{i,j} z_i z_j \left\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)][\mathbf{r}_j(t) - \mathbf{r}_j(0)] \right\rangle$$
(7)

where V is the volume of the simulation box, e is the elementary charge, z_i and z_j are the fractional charges of ions *i* and *j* of the interaction potential, respectively. Here, $\mathbf{r}_i(t)$ is the position of atom *i*, and the brackets $\langle \rangle$ denote ensemble averages. We note that cross (distinct) correlations ($i \neq i$ *j*) between the motions of the different atoms are negligible compared to self-contributions so that only diagonal contributions (i = i) contribute. In this case, Equation (7) may be rewritten⁷⁷ as:

$$\sigma = \frac{\rho_0 e^2}{k_B T} \sum_k x_k z_k^2 D_k \tag{8}$$

with x_k being the atomic fraction of species k and ρ_0 the atomic number density. Corresponding data for $\sigma(T)$ (Equation 8) are represented in Figure 3 in the liquid state where the simulated systems can be safely equilibrated, and can be compared to experimental measurements in the glassy state.^{12,78,79} We are not aware of any conductivity measurement across T_g as it is the case for some silicate systems^{80,81} but we note that the data calculated in the liquid state are compatible with those measured^{12,78,79} in the glass at $10^3/T > 1.7$ since the trends of the low- (experimental) and high-temperature (theoretical) can eventually connect together in the glass transition region. Both display an obvious Arrhenius behavior, and we found for the liquid state $E_A = 0.34(9)$ eV at zero

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FIGURE 4 Calculated conductivity σ along different isotherms as a function of pressure *P* (A) or system density (B). (C) Calculated activation volume ΔV^* for conductance as a function of temperature.

pressure (inset of Figure 2). Second, an inspection of the different contributions appearing in Equation (8) leads to the conclusion that Li conductivity dominates $\sigma(T)$ and network (S, Si) contributions are about 8–9 times smaller for all temperatures so that one can approximate the conductivity (Equation 8) by $\sigma \simeq 3\rho_0 e^2 D_{Li}/25k_BT$ given that $z_{Li} = 6/10$ from the parameters of the force-field.⁶⁸

The evolution with pressure is now displayed in Figure 4A for the various isotherms involved, and this permits to investigate the behavior of the activation volume. At fixed temperature, the trend obviously indicates that $\ln \sigma$ scales linearly with pressure (solid lines), and this suggests that the activation volume does not depend on pressure as it is the case in the super-Barus equation.³⁵ The behavior of $\sigma(P)$, furthermore, indicates a global reduction of ionic conductivity although molding experiments dedicated to the battery production sometimes lead to a moderate increase in σ with applied pressure, prior to a near saturation (plateau-like behavior³⁰) and a possible decrease. Note that a similar trend is obtained when the isothermal conductivity is calculated as a function of system density (Figure 4B). The slope $\sigma(P)$ finally permits to have the evolution of the activation volume as a function of temperature (Figure 4C). This signals a rather important jump of ΔV^* appearing at around 1 000 K. Specifically a jump from 3–4 Å³ at low temperatures to about 7.0 Å³ at 1 500 K is found. This jump reflects important changes involved in the ion dynamics happening as temperature increases.



FIGURE 5 Calculated equation of state (EOS) $V/V_0(P)$ of liquid and glassy 50Li₂S–50SiS₂ for different isotherms (symbols). The solid curves correspond to a BM fit (Equation 10).

4 | DISCUSSION

4.1 Compressibility versus diffusivity

Given the constant value for ΔV^* (or $V_a(P)$) determined from the trend $\sigma(P)$ of Figure 4, applying $\Delta V^* = -RT(\partial \ln \sigma / \partial P)_T$ to Equations (7) and (8) leads to:

$$\Delta V^* = -RT\kappa_T - \frac{e\mathcal{F}\rho_0}{\sigma} \sum_k x_k z_k^2 \left(\frac{\partial D_k}{\partial P}\right)_T \tag{9}$$

where \mathcal{F} is the Faraday constant and κ_T is the isothermal compressibility. Expression (9) contains two terms, the first one being related to the activation volume mediated by the possible compressibility of the system, whereas the second one essentially contains the pressure evolution of the diffusivity.

In order to estimate the weight of the two factors appearing in Equation (9), access to the isothermal compressibility κ_T is needed. To this end, we explore the equation of state of Li₂SiS₃ at different target temperatures in the range of 300 K $\leq T \leq 1$ 500 K and by varying the system pressures up to 10 GPa. Results are displayed in Figure 5, highlighting the usual behavior of a compressed liquid/glass, that is, we find a monotonic decrease of the liquid volume $V(P)/V(0) = V/V_0$ upon compression. Such data are conveniently fitted using a second-order Birch–Murnhagan equation of state^{72,73} which contains two parameters, the Bulk modulus *B* and its derivative with

TABLE 1 Birch–Murnhagan fit to the data of Equation (10): Bulk modulus K_0 , derivative K'_0 with pressure, and correlation coefficient *r* to the fit.

T (K)	B (GPa)	K'_0	r
300	48.1 ± 1.2	6.87	0.99
600	42.3 ± 2.0	8.1	0.99
900	37.8 ± 2.0	8.9	0.99
1 100	32.3 ± 2.3	9.1	0.99
1 300	26.5 ± 2.7	9.2	0.99
1 500	22.8 ± 2.6	9.9	0.99
600 900 1 100 1 300 1 500	42.3 ± 2.0 37.8 ± 2.0 32.3 ± 2.3 26.5 ± 2.7 22.8 ± 2.6	8.1 8.9 9.1 9.2 9.9	0.9 0.9 0.9 0.9

respect to pressure (K'_0) .

$$P = \frac{3}{2}B\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right]$$
(10)

$$\times \left[1 + \frac{3}{4}(K'_0 - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right]$$

The resulting compressibilities $\kappa_T = B^{-1}$ increase with temperature, and we find for, for example, 300 K $\kappa_T = 2.08(2) \times 10^{-11} \text{ Pa}^{-1}$ and $\kappa_T = 4.48(4) \times 10^{-11} \text{ Pa}^{-1}$ at 1 500 K. Note that the value obtained for the glassy state is very close to the one determined from an ultrasonic pulse-echo technique¹⁶: $\kappa_T = 3.83 \times 10^{-11} \text{ Pa}^{-1}$ or B = 26.1 GPa for the Bulk modulus, to be compared with our B = 48.1 GPa (Table 1), the latter quantity being also evaluated independently from the calculated elasticity (see below). The obtained values of $\kappa_T(T)$ now permits us to evaluate the compressibility contribution to the activation volume (Equation 9) which is presented in Figure 6, and shows how the contribution ($RT\kappa_T$) increases monotonically with temperature.

Altogether, it now appears (inset of Figure 6) that this contribution $RT\kappa_T/\Delta V^*$ grows substantially across the same temperature interval (1 100–1 300 K), where we have previously observed the evolution of the activation volume ΔV^* (Figure 4), and at 1 500 K the contribution of the ease to bulk compression (i.e., compressibility) represents about 25% of the activation volume. The important growth in the compressibility is obviously linked with the glass-liquid glass transition (inset of Figure 1) during which the number of possible dynamic processes (i.e., the activation volume) increases dramatically.

4.2 | Free and activated volume

Since ion dynamics is intimately linked with free space,⁶ it is interesting to explore the link between the free volume V_f for ion conduction and the activation volume



FIGURE 6 Factor $RT\kappa_T$ as a function temperature in liquid Li₂SiS₃. The inset shows the ratio $RT\kappa_T/\Delta V^*$ which provides an estimate of the contribution of the compressibility to ionic conduction.

of the system. It is important to emphasize that the former (V_f) is associated with particle occupation, whereas the latter is the volume required for a given process, for instance a jump between neighboring sites. Recently, such features have been analyzed for the similar thiogermanate system.⁸² The volume occupied by the network $V-V_f$ can be determined for each (Si,S) particle from a Voronoi cell defined from the region of space closer to a given atom than any other particle. This is mathematically defined by requesting that for a given metric space (M, d) and a discrete set of atomic positions $\{s_1, s_2, \ldots\} \subset M$, the Voronoi cell of an atom fulfills

$$V(s_i) = \{x \in M \mid d(x, s_i) \le d(x, s_j)\} \ \forall i \ne j$$

Resulting distributions $h(V_f^i)$ of the free volume V_f are displayed for various temperatures in Figure 7. As for glassy relaxation⁸³ where the notion of free volume has been used in the popular Cohen–Turnbull theory of glass transition,⁸⁴ here one acknowledges $V_f > \Delta V^*$ as we found for the average free volume at 700 K and zero pressure $\langle V_f \rangle \simeq 21$ Å³ and $\Delta V^* = 3-4$ Å³. The former corresponds to a radius 1.69 Å for a spheric volume, and it is close to the size $L = \sqrt{\langle r_{Li}^2(t) \rangle}$ of the cage for Li motion, visible from the msd plateau value (Figure 1). With temperature increase, the average free volume increases (inset), remains systematically larger than ΔV^* , and its distribution broadens as the network deformation is made easier. Although the average free volume increases with *T*, the fraction of free space $\eta = V_f/V$ remains almost constant as we find $\eta = 34.0\%$ and 34.6% for 700 K and 1 500 K,



FIGURE 7 Free volume distribution $h(V_f^i)$ for different temperatures in liquid Li_2SiS_3 with indication of the fraction η of free space left for Li motion for the two end temperatures (700 and 1 500 K). The inset shows the average $\langle V_f \rangle$ of the distribution as a function of temperature. The right axis of the inset the liquid density at zero pressure (red symbols).

respectively, and this underscores the absence of an important structural modification upon temperature increase (see below). Noteworthy is the fact that the respective occupation of S and Si atoms represent 53.3% and 12.7%, respectively (700 K), that is, silicon does not occupy much of the system volume and is associated with a rather sharp distribution $h(V_f^i)$ (not shown), whereas the sulfur distribution has a similar profile as Li. With η is almost constant, it is, finally important to stress that the free volume increase that leads to an increased motion for the Li particles is entirely driven by the density evolution of the liquids, as shown in the inset (right axis) of Figure 7.

4.3 | Link with structure

Since there is a small evolution of the structure functions (pair correlation function g(r) and structure factor S(k)) with temperature or pressure, we focus here only on the population of species using the Q^n terminology,⁸⁵ that is, the population of Si tetrahedra having *n* BS. Such a statistics can be accessed by solid-state nuclear magnetic resonance (²⁹Si NMR^{13,24,86}) but appears to be hard to establish experimentally because of the small number of reference crystalline phases (Li₂SiS₃ and Li₄SiS₄) which serve for the NMR chemical shift identification. This is a serious drawback with respect to corresponding oxides (silicates⁸⁷). Furthermore, the addition of Li₂S into SiS₂ leads only to small variations in the ²⁹Si chemical shift,⁸⁸ so that the Q^n distribution with composition or temperature is almost unknown.

We provide in Table 2 the Q^n statistics of the liquid systems, together with the 300 K temperature one.⁶⁸ As for the glassy system, the distribution covers all accessible Q^n structures, ranging from a small fraction of remaining Q^4

TABLE 2 Calculated fraction of Q^n distribution (in %)) in liquid 50 SiS₂-50 Li₂S at 700 K and 1 500 K, and compared to results at 300 K,⁶⁸ and to models from the literature.

	Q^4	Q^3	Q^2	Q^1	Q^0
1 500 K	4.4	18.3	37.0	29.3	11.0
700 K	4.6	18.4	35.8	30.3	10.9
300 K ⁶⁸	5.8	20.7	35.4	30.6	7.5
Topological model ⁸⁹	8.6	19.2	35.2	36.8	
²⁹ Si NMR ²⁴	50.0		50.0		
Silicate (²⁹ Si NMR) ⁸⁷	16.0	57.0	25.0		

Note: Statistical error of the fraction is about $\simeq 1.0\%$. Note that the NMR data on silicates⁸⁷ apply on 40% modified silica (no Li₂SiO₃ data available).

(typical of the base network SiS_2) to the isolated Q^0 motif (an isolated $Li_4^{\oplus}SiS_4^{\ominus}$ molecule). We note a close statistics with respect to the glassy state and a small effect due to temperature since the difference between the 700 K and the 1 500 K analysis is very small.

A variety of other motifs are present, including Q^2 species (35.8%–37.0%) which represent the unique geometry in the crystalline phase and in an ideal chemical model of the glassy state (100%). As for the glassy state, the calculated statistics appears to be somewhat different from the proposed NMR statistics,²⁴ but one has, once again, to remind that he distinction from NMR between the various Q^n species is difficult to establish in Li₂S–SiS_S glasses given the close chemical shifts between reference Q^2 and other crystalline reference compounds. We finally note that a broad distribution of Q^n species is usually found in modified oxides with cations of small sizes,^{85,87} and this situation seems to be met in the present glasses as well, as also confirmed by a topological model.⁸⁹



FIGURE 8 Distribution of Si–BS (red) and Si–NBS bonds (blue) in liquid Li_2SiS_3 at 700 K (solid curves) and 1 500 K (broken curves).

Since the effect of the Q^n statistics with temperature is weak, we can argue that structural effects do not contribute substantially to the important growth of the ionic conduction with *T*, and is essentially linked with steric effects which manifests by an overall increase of free volume that is driven by the decrease of the liquid density (inset of Figure 7).

Figure 8 represents the Si–BS and Si–NBS bond distance distribution. As in the glassy state,⁶⁸ in other sulfide^{82,90} or silicate glasses lithium silicates,⁹¹ we do obtain a bond length which is different between BS and NBS environments as we find, for example, an average Si–BS and Si–NBS bond distance of 2.15 Å and 2.09 Å at 700 K, respectively. As for other systems, the physical origin of Si-bridging atom (O,S) versus Si-nonbridging atom (O,S) bond distance difference is linked with the influence of the lithium ions on the neighboring charges and the Si–NBS iono-covalent character.

The presence of positive charges in the vicinity of sulfur atoms impacts the electronic structure of next neighbor Group IV atoms, as recently determined from an ab initio analysis in thiogermanates.⁸² It was recognized that the non-directional character of the NBS–alkali bond induces an electronic density of NBS atoms that points essentially toward the close Group IV atom with a rather well-defined depletion of the valence charge. Conversely, the electronic and bonding characteristics obtained for the BS atoms involve p orbitals which display deformation the deformation of the valence charge, and involve an obvious reduced depletion. The difference in bond length obviously underscores a delicate balance between electron localization on the atomic sites involved in ionic bonding and electronic elocalization, that is, covalent effects.

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The ion diffusion dynamics and its behavior with pressure can be further decoded by looking at dynamical correlations like density and charge current correlations. It is of special interest to separate such correlations into longitudinal and transverse currents as recently performed on liquid Te.⁹² Longitudinal currents are associated with diffusion and longitudinal phonons while the transverse part is associated with transverse phonons. Note that the latter serves as a hallmark of system rigidity in certain systems,^{93–95} and in liquids, the transverse current presents a dynamic gap associated with viscoelasticity.96 In addition, early theories (Anderson-Stuart model⁹⁷) and more recent approaches98,99 have emphasized the link between elasticity and ion conduction in glasses with, for example, the activation energy for ion conduction being proportional to the shear modulus.¹⁰⁰ It is, therefore, tempting to investigate in detail the link between such properties in this archetypal amorphous electrolyte.

The transversal current density correlation $C_T(k, t)$ is defined by [101, 102],

$$C_T(k,t) = \langle \langle \boldsymbol{j}_T^*(\boldsymbol{k},t) \cdot \boldsymbol{j}_T(\boldsymbol{k},0) \rangle_{\boldsymbol{k}} \rangle, \qquad (12)$$

where the brackets $\langle \langle ... \rangle_{k} \rangle$ indicates an ensemble average taken after a previous average over all wave vectors k with norm $k = |\mathbf{k}|$. The function $\mathbf{j}_{T}(\mathbf{k}, t)$ is the transversal density current obtained by summing all projections of the atomic velocities into a perpendicular direction to a given wave vector^{101,102} \mathbf{k} ,

$$\boldsymbol{j}_{T}(\boldsymbol{k},t) = \frac{1}{\sqrt{2N}} \sum_{j=1}^{N} \hat{\boldsymbol{k}} \times \boldsymbol{v}_{j}(t) \exp\left(i\boldsymbol{k} \cdot \boldsymbol{r}_{j}(t)\right) . \quad (13)$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$ and $\mathbf{v}_j(t)$ is the velocity of atom *j* at time *t*. By performing a Fourier transform in time, one obtains the transversal current correlation as a function of \mathbf{k} and ω ,

$$C_T(k,\omega) = \int_0^\infty J_T(k,t) \mathrm{e}^{-i\omega t} dt \,. \tag{14}$$

From Equation (14), it is then possible to calculate the transverse dynamical structure factor ($S_T(k, \omega)$), related with the transversal current correlation by [101]:

$$C_T(k,\omega) = \frac{\omega^2}{k^2} S_T(k,\omega).$$
(15)

Proceeding is a similar way, the longitudinal current is obtained by projecting the velocities on a given wave vector k,

$$\boldsymbol{j}_{L}(\boldsymbol{k},t) = \frac{1}{\sqrt{2N}} \sum_{j=1}^{N} \left[\hat{\boldsymbol{k}} \cdot \boldsymbol{v}_{j}(t) \right] \hat{\boldsymbol{k}} \exp\left(i \boldsymbol{k} \cdot \boldsymbol{r}_{j}(t) \right) , \quad (16)$$

from where the longitudinal correlation $C_L(k, t) = \langle \langle \mathbf{j}_L^*(\mathbf{k}, t) \cdot \mathbf{j}_L(\mathbf{k}, 0) \rangle_k \rangle$ and the longitudinal dynamic factor $S_L(k, \omega)$ is obtained. The total currents and dynamical structure factor are obtained by summing the transversal and longitudinal parts. Additionally, to gain more insight, we can further separate the contribution of the currents due to the different pairs of atomic species.

In Figure 9, we present the typical currents $C_L(k,t)$ and $C_T(k, t)$ at the smallest studied value of k, separated on each possible correlation of atomic species, obtained at T = 300 K and zero pressure for the Li₂SiS₃ system, together with their Fourier transform $C_L(k,\omega)$ and $C_T(k,\omega)$, all of them being obtained¹⁰³ from the atomic trajectories. An inspection of the different panels shows typical behaviors previously encountered in, for example, tellurium.⁹² Namely, all correlations exhibit typical low-frequency oscillations that reflect in peaks at $\omega \approx 6$ meV and $\omega \approx 3$ meV. Such peaks are associated with the transverse and longitudinal acoustic phonon branches, respectively, with some degree of mixing between them. Figure 9 shows that all species contribute to the acoustic phonons as expected for an effective elastic medium. However, the relevant feature here is the different behavior of the Li-Li correlations. Although the Li-Li current correlations do have an acoustic phonon contribution, there are also present many other higher order frequencies. Moreover, there are two well-defined peaks in the highfrequency region; one in the transversal current at $\omega \approx 47$ meV (11.2 THz) and the other in the longitudinal current $\omega \approx 41 \text{ meV}$ (9.8 THz). Such maxima are not observed in the transverse current.

To further elucidate the differences between the Li-Li and the other correlations, we proceed to study the currents at different values of k. In Figure 10, we present surface plots as functions of k and ω for all possible atomic pairs. In this plot, the contribution of Li-Li current to the acoustic phonon branch appears weakest among all correlations. Moreover, its content of high frequencies is evident across the entire range of k. Specifically at $\omega \approx 50$ meV, $k = 1.6 \text{ nm}^{-1}$, there is a peak reminiscent of an optical phonon branch. The S-Li correlation also exhibits a faint signal of such an optical phonon, suggesting some cooperative dynamics between both species. Silicon atoms do not participate in such dynamics. Although the origin of this kind of optical branch is not completely clear, it means that there is a well-defined correlation of Li movements for a scale of around $\lambda = (2\pi/1.6) = 3.927$ nm $\simeq 40.0$ Å. In some

glasses, optical branches have been proposed to be related to the boson peak. $^{104}\,$

The maximal Li–Li correlation is observed at $k = 5.6 \text{ nm}^{-1}$, corresponding to $\omega \approx 21$ and 47 meV. Similarly, this correlation suggests the presence of a significant lengthscale of approximately 10.0 Å. In other systems like in Li doped silicates, it has been proposed that diffusion takes place by exchange of two Li ions.¹⁰⁵ This kind of mechanism can also be in play here resulting in a coherent current if we observe that the radius of the Li cages and the radius of the average free volume is around $L \approx 1.69$ Å. The faint correlation with S can be understood as a possible path for ion mobility. A somewhat similar effect has been recently extracted from molecular simulations of sodium silicate glasses, where Na mobility is anticorrelated with the local density of defect oxygen neighbors.¹⁰⁶

The previous analysis based on current correlations supports the idea that Li diffuse over a nearly frozen (Si,S) matrix. To be more specific, the broad distribution over spatial and temporal frequencies of Li–Li ion correlations indicates that the process is reminiscent of an stochastic motion with memory and colored by the collective modes of the frozen matrix. From this analysis of Li–Li correlations, we also conclude the existence of dynamic characteristic lengthscales and of a nearly optical phonon branch.

The accuracy of the previous calculation can be checked by focusing on the low-frequency acoustic branch region, in which the dispersion relation of phonons is linear with a coefficient given by the speed of sound $\omega = v_{T(L)}|\mathbf{k}|$ for transversal modes and (*L*) longitudinal modes. These are determined from the maximum position ω_i of their corresponding dynamic structure factors. In Figure 11, we present the evolution of both v_L and v_T at 300 K and at a more elevated temperature (583 K), showcasing a convergence to a linear dispersion relationship at lower $|\mathbf{k}|$ values. A fit to this data leads to v_L and v_T , then with these values, it is possible to obtain the elastic moduli in an isotropic system like,¹⁶

$$G = \rho_0 v_T \tag{17}$$

$$v = \left(v_L^2 - 2v_T^2\right) / \left(2\left(v_L^2 - v_T^2\right)\right)$$
(18)

$$E = 2G(1+v) \tag{19}$$

$$B = E/(3(1-2v)),$$
 (20)

where ρ_0 is the density, *G* is the shear modulus, ν is the Poisson's ratio, *E* and *B* are the Young's and Bulk



FIGURE 9 Transversal (Tv) and longitudinal (Ln) correlations in time and in the frequency domain for different pairs of atomic species at $|\mathbf{k}| = 1.6027$ nm⁻¹ and T = 300 K and zero pressure. Observe the prominent peaks of the longitudinal and transversal currents due to phonons in the acoustic region $\omega < 10$ meV. All species contribute to such phonons. The Li–Li correlation is different from others. In the time domain, $C_T(k, t)$ and $C_L(k, t)$ present the same low-frequency phonon oscillation, but there is also an over imposed high-frequency dynamics. This is confirmed by looking at $C_T(k, \omega)$ and $C_L(k, \omega)$, where we can see a significant spectral content for $\omega > 15$ meV. Moreover, two peaks $\omega \approx 41$ meV and $\omega \approx 47$ meV are seen, indicative of a possible optical phonon branch.

modulus, respectively. Table 3 summarized the values obtained for the speeds of sound and the elastic moduli. Note that the obtained Bulk moduli B (68.42 and 42.33 GPa at 300 and 583 K, respectively) are close

to those determined from the Birch-Murnhagan fit (Equation 10) as we previously obtained, for example, 42.3 GPa at 600 K (Table 1). From Table 3, it is observed that $v_L \simeq 6.740 \pm$ and $v_T \simeq 2.630 \pm 272$ m s⁻¹ at 300 K,

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FIGURE 10 Surface plot of $C_L(k, \omega)$ for all possible atomic species pairs at T = 300 K and zero pressure. The acoustic longitudinal phonon branch is observed in the region $k < 3 \text{ nm}^{-1}$, $\omega < 15 \text{ meV}$. Except for Li–Li, all maximal correlations are seen for the lowest computed value of k. Notice that the region $k < 1.6 \text{ nm}^{-1}$ is not accessible for the used system size. The Li–Li current contributes, as do all other species, to the acoustic phonon branch, but the signal is weaker. In particular, observe the peak at $\omega \approx 50$ meV for k = 1.6 nm⁻¹ reminiscent of an optical phonon branch. The S-Li correlation also displays traces of such an optical phonon, indicating some cooperative dynamics in which Si does not participate. Yet, the maximal Li–Li correlation is observed as two yellow spots located at k = 5.6 nm⁻¹, corresponding to $\omega \approx 21$ and 47 meV, defining a characteristic dynamical lengthscale.



FIGURE 11 Evolution in frequency ω and wave vector k of the dynamic structure factor maxima of the longitudinal and transversal acoustic branches. These symbols were obtained from the MD simulation and the lines through them are guides to the eye. The two lines in green and yellow are the linear phonon dispersions with slopes given by performing a linear regression for the first six |k| values.

meanwhile $v_L \simeq 6540 \pm 371$ and $v_T \simeq 3909 \pm 403$ m s⁻¹ at 583 K. These velocities are higher than the reported experimental values¹⁶ of $v_L = 4\,770 \text{ m s}^{-1}$ and $v_T = 2\,540 \text{ m s}^{-1}$, although the ratio between the longitudinal and transversal velocities are close, that is, we obtain $v_L/v_T \simeq 2.56$ at 300 K and $v_L/v_T \simeq 1.67$ at 583 K, while the experimental one is $\simeq 1.88$. From Table 3, it is possible to note that the elastic moduli obtained from the MD simulations at 300 K are closer to the experimental ones,¹⁶ however at 583 K the discrepancy between the MD results and the experiment is bigger, which is essentially due to the overestimation of v_T in the model. The results, thus, indicate that the potential (4) provides a reasonable description of the elastic properties at long wavelengths but as in other glassy systems¹⁰⁴ some overestimation of v_i (i = L, T) is acknowledged. Larger systems and longer time simulations are needed to refine the value of the speed of sound, as the slope is still not completely well converged. With temperature increase, the longitudinal speed of sound decreases as expected¹⁰⁷ from the progressive softening of the network and reduction of the relaxation time.

TABLE 3 Longitudinal and transversal velocities v_L and v_T respectively, correlation coefficient to the fit r, Shear modulus G, Poisson's ratio v, Young's modulus E, and Bulk modulus B.

T (K)	\boldsymbol{v}_L (m.s ⁻¹)	r	\boldsymbol{v}_T (m.s ⁻¹)	r	G (GPa)	ν Poisson	E (GPa)	B (GPa)
300	$6\ 740 \pm 273$	0.99	$2\ 630 \pm 272$	0.99	13.70	0.410	36.87	68.42
583	6 540 ± 371	0.99	3 909 <u>±</u> 403	0.98	28.87	0.220	70.58	42.33
583 ¹⁶	4 770	_	2540	_	11.90	0.302	31.00	26.10

Note: The elastic moduli were obtained from the speeds of sound calculated from the MD simulations (see Equations 17, 19, and 20). MD, Molecular dynamics.

5 | SUMMARY AND CONCLUSIONS

Modified sulfide glasses containing a network former (SiS₂, GeS₂, As₂S₃,...) and a modifier (Ag₂S, Li₂S,...) have attracted a growing interest in glass science, due to their promising properties for all-solid-state batteries and high-density power sources. Among such properties, the conductivity ($10^{-3} \Omega^{-1}$.cm⁻¹) of certain glasses at room temperature is now of the same level as those obtained in popular crystalline sulfides which makes them attractive. The advantages of using glasses for such applications are known and well documented: infinite compositional space, stability, deformability, increased surface contact with the electrodes, etc.

In order to improve such performances, the usefulness of models and especially atomic scale models is central to the understanding of structure–property relationships. Here, we have explored the dynamic, ionic, and elastic properties of a promising candidate for such applications, 50 SiS₂–50 Li₂S (or Li₂SiS₃) glass, using MD simulations and a previously parameterized force-field able to describe accurately a certain number of properties of the crystalline and glassy phases.⁶⁸ Here, one furthermore acknowledges that the force-field is capable of providing an estimate of (i) ionic conductivity that is compatible with low-temperature experimental measurements, and (ii) a reasonable reproduction of elastic properties (compressibility, sound velocities).

Our results reveal that the dynamics and conductivity is mainly controlled by the lithium ions, and of activated (Arrhenius) type, whereas at low temperature an obvious decoupling emerges that leads to the motion of charge carriers within a frozen (Si,S) matrix. The evolution of such properties with pressure permits to define an activation volume for the processes which is found to be substantially smaller that the occupation volume (free volume) of the ions, and to be sensitive to the softening of the (Si,S) network at the glass transition. For larger temperatures, the compressibility contribution increases substantially and represents up to 25% of the activation volume. These changes involve small effects due to structure and free volume ratio, the available volume for ion motion with increasing temperature being essentially driven by the density variation.

The study of the elastic properties of 50 SiS_2 –50 Li_2S permits a direct comparison with experimental data but also reveals a well-defined correlation of Li movements for a scale of around 10 Å that leads to a radically different profile for Li–Li correlations in dynamic structure factors. This central result is of particular interest and has not been detected before and might be used to correlate elastic properties with ion motion in order to enhance conductivity for applications in fast-ion batteries.

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Taken together, these investigations exemplify the importance of computational techniques for the analysis and characterization of amorphous fast ion conductors. In this respect, it might be interesting to focus on other promising binary or ternary systems such as SiS_2-Li_2S-LiI or $P_2S_5-Li_2S$.

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