

# Evidence for Complex Dynamics in Glassy Fast Ion Conductors: The Case of Sodium Thiosilicates

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 ABSTRACT:
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**ABSTRACT:** Classical molecular dynamics is used to study the dynamics of alkali ions in a promising fast ion conductor glass system, i.e.,  $Na_2S$ -SiS<sub>2</sub>. Diffusion in such thiosilicates is found to display various salient features of alkali silicates, i.e., channel-like diffusion with typical length scales emerging as the temperature is decreased to the glassy state, and Arrhenius behavior for both Na ion diffusivity and calculated conductivity. The dynamics appears, however, to be largely heterogeneous as manifested by fast and slow Na ion motion at intermediate times, both in the high-temperature liquid and in the glassy state. In the former, a diffusion-limited regime is found due to the increased motion of the network-forming species that limits the Na ion



dynamics, whereas at low temperatures, the typical dynamical heterogeneities are recovered as observed close to the glass transition.

## 1. INTRODUCTION

Fast ion-conducting batteries based on Li-ion technology are widely used in a variety of applications, such as mobile phones, electric bikes, scooters, and larger vehicles.<sup>1,2</sup> Here, the batteries consist of a Li-based oxide cathode together with an electrolyte that ensures conduction during charge and discharge cycling. Such batteries represent a safety hazard, as they contain flammable polymeric electrolytes. Specifically, shortcuts initiated by dendritic Li growth between the cathode and the anode may lead to explosion and fire upon battery failure.<sup>3</sup>

In order to improve the safety of the components, solid electrolytes have attracted increased attention.<sup>4</sup> In this context, amorphous or glassy electrolytes<sup>5</sup> are now considered as promising candidates because of the possibility to alloy components into base materials as well as superior processability and homogeneous ion transport. While, e.g., binary Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> glasses have been studied extensively,<sup>6=9</sup> silicon-based sulfides have received attention only recently,<sup>10,11</sup> largely motivated by their high ionic conduction  $(10^{-3} \Omega^{-1} \text{ cm}^{-1})$  at ambient conditions (for a review, see ref 12).

Among such disordered lithium chalcogenides, binary Li<sub>2</sub>S–SiS<sub>2</sub> glasses with varying Li content have been characterized by a variety of techniques.<sup>13–20</sup> As lithium resources are unevenly distributed and are now becoming rare and the most valuable commodity on the planet, alternative or complementary ions for battery applications are needed. In this respect, sodium appears attractive because of its abundance and comparable standard electrode potential. Compared to the Li counterparts, the corresponding Na<sub>2</sub>S–SiS<sub>2</sub> glasses have received much less attention<sup>15,16,21,22</sup> and their corresponding conductivity is somewhat smaller, e.g.,  $10^{-4} \Omega^{-1} \text{ cm}^{-1}$  and  $2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  for Li<sub>2</sub>S–SiS<sub>2</sub> and Na<sub>2</sub>S–SiS<sub>2</sub> glasses, respectively.<sup>12,23</sup>

However, the glass-forming ability appears to be better for the Na-based glasses.<sup>21</sup> It is, therefore, important to understand in more detail the features responsible for such differences and to explore how the dynamics of Na ions differ from those of other alkali ions, including Li. Molecular dynamics (MD) simulations appear helpful in this regard<sup>24</sup> and a recent ab initio and a classical study<sup>22</sup> on Na<sub>2</sub>S–SiS<sub>2</sub> glasses have made it possible to characterize the structure at selected compositions and temperatures.

Here, we explore in detail the Na dynamics for the 50:50  $Na_2S/SiS_2$  mixture, i.e.,  $Na_2S-SiS_2$  (NS) glass and its relationship with ionic conduction. We use a modified version of a previously established classical force field<sup>22</sup> (see Section 2) that has been found to fairly reproduce X-ray scattering experiments and the principal distances in this system,<sup>22,25</sup> i.e., the Si–S bond distance at 2.1 Å and that of Na–S at 2.8 Å.

Our results on ionic conduction in the NS supercooled liquids are compatible with measured data in the glassy state, although a slight change in slope (i.e., activation energy) is obtained across the glass transition region (545 K<sup>12</sup>) that is indicative of an Arrhenius crossover, in harmony with the salient phenomenology observed, e.g., in polymeric electrolytes<sup>26,27</sup> or simple oxides<sup>28</sup> or modified borosilicates.<sup>29,30</sup> The details of the dynamics, furthermore, suggest that the Na motion is decoupled from that of the network-forming species

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(Si and S) as glassy relaxation onsets and that heterogeneous dynamics takes place at intermediate times and distances below 10 Å, with complex influence from the network undergoing the glass transition phenomenon. Finally, as in other modified glasses (alkali silicates<sup>31–33</sup>), the present NS material also displays a channel-like motion that involves a typical length scale for Na–Na pair correlations.

## 2. NUMERICAL DETAILS

Classical MD simulations were conducted of the  $Na_2S-SiS_2$  system containing N = 3000 atoms [i.e.,  $N_{Na} = 1000$ ,  $N_{Si} = 500$ , and  $N_S = 1500$ , (Figure 1)]. The initial structure was made by



Figure 1. Snapshot of the simulation box of the considered system  $Na_2S$ -SiS<sub>2</sub>. Si tetrahedra are represented in light gray together with Na (blue) ions.

adding atoms randomly to a cubic simulation box of side length 41.277 Å, matching the experimental density of the glass  $(2.01 \text{ g cm}^{-3})^{22}$  while restricting the pair distance to a minimum of 1.5 Å. Forces were based on a Buckingham-Coulomb interaction potential of the form

$$V_{ij}(r) = A_{ij} \exp(-r/\rho_{ij}) - \frac{C_{ij}}{r^6} + \frac{q_i q_j}{4\pi\epsilon_0 r}$$
(1)

where *r* is the interatomic distance,  $A_{ij}$ ,  $\rho_{ij}$ , and  $C_{ij}$  are the parameters,  $q_i$  are the charges (in *e* units), and  $\epsilon_0$  is the permittivity of vacuum. *i* and *j* refer to the type of two distinct atoms. The initial potential parameters were taken from Dive et al.<sup>22</sup> However, we found that the dispersion parameter  $C_{\rm SS}$  could be optimized to offer improved reproduction of the experimental structural data. We, therefore, refined  $C_{\rm SS}$  to 4 times the value proposed in ref 22. The parameters used hereafter are given in Table 1.

The results shown in Figure 2 thus indicate a slight improvement of the structural description with a closer reproduction of the experimental structure factor,<sup>22</sup> albeit additional improvement of V(r) may be necessary to more accurately describe the correlations in Fourier space. Generally, our simulations replicate the experimental peaks, but some differences appear in intensity and, in some cases, exact peak positions. While low-*k* peaks (representing medium-range order, MRO) exhibit a slight shift with respect to the experiments, all other peaks are generally reproduced. This

Table 1. Potential Parameters as Obtained from Dive et al.,<sup>22</sup> Except for the  $C_{SS}$  Value Which Has Been Refined<sup>*a*</sup>

i	j	$A_{ij}$ (kcal mol <sup>-1</sup> )	$\rho_{ij}$ (Å)	$C_{ij}$ (kcal Å <sup>6</sup> mol <sup>-1</sup> )
Na <sup>0.6</sup>	Na <sup>0.6</sup>	175918407.400	0.080	0
Na <sup>0.6</sup>	S-1.2	7051023.133	0.180	0
Na <sup>0.6</sup>	Si <sup>2.4</sup>	137188868.400	0.076	0
Si <sup>2.4</sup>	Si <sup>2.4</sup>	52119995.520	0.072	0
Si <sup>2.4</sup>	S <sup>-1.2</sup>	2533446.376	0.178	0
S <sup>-1.2</sup>	S <sup>-1.2</sup>	482620.301	0.284	3317.512

<sup>a</sup>The superscript corresponds to the charges used in e units.



**Figure 2.** Comparison between the calculated interference function I(k) = k[S(k) - 1] using the optimized parameters of Table 1 (green), the initial parameters (red), and the experimental measurement from X-ray scattering (black) of Dive et al.<sup>22</sup> Original data have been shifted by +3 for clarity.

indicates that the MRO structure is accurately described but likely with a slight misrepresentation of distances. On the other hand, higher-*k* peaks generally exhibit a better reproduction, indicating well-reproduced short-range order. In real space, with this modified potential (Table 1), we recover (i) typical bond distances  $r_{Si-S} \simeq 2.1$  Å,  $r_{Na-S} \simeq 2.6$  Å, and  $r_{S-S} \simeq 3.3$  Å (comparable to those, e.g., found by previous ab initio simulation<sup>22</sup>) and (ii) a tetrahedral network character with SiS<sub>4/2</sub> as the base unit. Our calculated ratio  $r_{Si-S}/r_{SS}$  is indeed found to be of about 1.57, i.e., close to the value<sup>34</sup> found for a perfect tetrahedron ( $\sqrt{8/3} \simeq 1.63$ ). We, furthermore, find a S– Si–S bond angle distribution that is centered at arccos (-1/3) = 109°. Further improvement of the force field parameters for the present system is in progress.

All simulations were performed using LAMMPS,<sup>35</sup> following the procedure of ref 22. First, the fully random structure was structurally minimized before initiating a Gaussian temperature profile of 3000 K. Initial mixing at 3000 K was performed for 100 ps. Next, the glasses were quenched to 300 at 100 K ps<sup>-1</sup> and then relaxed for 1 ns. Finally, an additional 100 ps of dynamics at 300 K were accumulated for statistical averaging (for example, averaging of the scattering function of Figure 2). All simulations were performed in the *NVT* ensemble, using a Nosé–Hoover thermostat<sup>36</sup> and a time step of 1 fs. A total of five replications were performed for all quenches and subsequent dynamical simulations, and all presented data are averages of these. The diffusivity of the particles was probed in two separate simulation schemes. First, long simulations were run for 10 ns to acquire mean-square displacements (MSD) of each atom, prior to an appropriate average per species k (k = Si, Na, S)

$$\langle r_k^2(t) \rangle = \text{MSD}_k(t) = \langle \frac{1}{N} \sum_{j=1}^N |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle$$
(2)

where the sum is taken over all atoms of the type k. These long simulations were performed at fixed temperatures of T = (300, 600, 800, 1000, 1200, 1400, and 1600) K. Alternatively, the quantity MSD<sub>k</sub> can be obtained from the velocity-autocorrelation function (VACF), which is linked to the diffusivity  $D_k$  for systems at thermal equilibrium

$$D_k = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_k(0) \cdot \mathbf{v}_k(t) \rangle \mathrm{d}t \tag{3}$$

In this study, the diffusivity from eq 3 was evaluated by averaging the VACF over 20 runs each of 5 ps before taking the average of the integral in the range of 2-5 ps. The same temperatures as for the MSD calculations were evaluated.

It is important to note that eq 3 contains a property of translational invariance over time, which is a basic property of liquids at equilibrium. At low temperatures, because of the breakdown of ergodicity which results from a limited exploration of the phase space, deep supercooled liquids (and eventually glasses) will be out of equilibrium so that the invariance fails and aging onsets.<sup>37</sup> As a result, an estimation<sup>22,38</sup> of diffusivities or conductivities in the glassy state from computer simulations is unwise, if not simply misleading. Separately, simulations of more frequent dumping were performed at 600 K for 1 ns to allow for accessing structural changes in a continuous nonlogarithmic scale.

Lastly, as an alternative to our use of *NVT*, we tested the *NPT* ensemble in two simple simulations (T = 600 K and T = 1600 K, p = 0) to find density drops of 2 and 37% for the two cases, respectively. Furthermore, we found both cases to feature a conductivity estimation  $\sim 20-25\%$  higher than that found in the fixed density case. While we are not aware of any melt density experiments of the system studied herein, compared to, e.g., oxides,<sup>39</sup> the density drop in the high *T* case is likely too excessive. Due to how the differences in the conductivity estimation between the *NPT* and *NVT* cases are not excessively high and due to the likely too significant density decrease, we thus adhere to the *NVT* ensemble for both the quenching and subsequent simulation procedures at all studied temperatures.

#### 3. RESULTS AND DISCUSSION

**3.1. Diffusivity.** Figure 3a shows the MSD of the sodium species for the different target temperatures, ranging from 300 K (blue curve) to 1600 K (red). At short times  $(t \le 0.1 \text{ ps})$ , the motion is ballistic,<sup>40</sup> i.e.,  $\langle r_k^2(t) \rangle$  scales as  $t^2$  before becoming diffusive with  $\langle r_k^2(t) \rangle \propto t$ . Depending on the temperature, for longer times, the MSD can be divided into two regimes, i.e., a cage-rattling regime usually found at low temperature (gray zone), followed by a diffusive regime which does not onset in the glass because of the computer time limitation. For higher temperatures, corresponding to the liquid or supercooled liquid still close to the melting temperature, the diffusive regime can be characterized by a diffusion constant, *D*, which in the  $t \to \infty$  limit follows Fickian diffusion. As such, the diffusion constant of some chemical



**Figure 3.** (a) Na mean-square displacement of liquid and glassy NS at different isotherms in the order of 300 (blue), 600, 800, 1000, 1200, 1400, and 1600 K (red). (b) Calculated diffusivity of Na (black), Si (blue), and S (red) atoms as a function of  $10^3/T$  (for temperatures from 600 K and up). The straight lines represent an Arrhenius fit to the data. Orange data correspond to Ag<sub>2</sub>S–GeS<sub>2</sub> (circles<sup>41</sup>), 25Na<sub>2</sub>S–75GeS<sub>2</sub> (triangles<sup>42</sup>), and 56Na<sub>2</sub>S–44SiS<sub>2</sub> (open black boxes<sup>43</sup>) and serve for comparison (see text). Errors for each point in (b) are estimated to be smaller than the size of the symbols. Colors in (a) go from low [T = 300 K (blue)] to high temperatures [T = 1600 K (red)] with black lines between blue and red corresponding to temperatures monotonically increasing from 600 to 1400 K.

species k, i.e.,  $D_k$ , is obtained directly by determining the slope of its MSD at high t

$$D_k = \frac{1}{6} \lim_{t \to \infty} \frac{\mathrm{d}\langle r_k^2(t) \rangle}{\mathrm{d}t}$$
(4)

For the considered temperatures, we can safely determine  $D_{\text{Na}}$  down to T = 600 K (Figure 3a) but not for the networkforming species (Si and S) which are already frozen  $[\langle r_k^2(t) \rangle \simeq$ 0.1-0.5 Å<sup>2</sup>] on the computer simulation time scale, as also revealed once the data are represented in an Arrhenius plot (Figure 3b), which exhibits an obvious deviation at low T. It is worth noting how the T = 300 K case in Figure 3a resembles a case where proper diffusion has not yet occurred. This ultimately questions previous estimations of diffusivity (and conductivity) using the present potential at temperatures  $T \ll$  $T_{o}^{22}$  The presented representation indicates that all species display an Arrhenius behavior of the form  $D_k \propto \exp[-E_A/k_BT]$ over an extended temperature range and reveals a dynamic of activated type. An Arrhenius fit over the temperatures 900-1600 K leads to  $E_A = 0.258$ , 0.484, and 0.472 eV for Na, Si, and S, respectively.

Diffusivity data from <sup>22</sup>Na tracer diffusion on  $56Na_2S-44SiS_2$  systems (i.e., close to the present composition) have been reported for different temperatures<sup>43</sup> in the glassy state, and these appear to be compatible with the present data

obtained in the liquid with a possible marked jump in the glass transition region  $(10^3/T \simeq 2)$ . The corresponding data<sup>43</sup> and those taken from other similar sulfide systems<sup>41,42</sup> are represented in Figure 3b. All values appear to be of the same order as those calculated from the present MSDs. A recent measurement<sup>38</sup> from <sup>22</sup>Na tracer diffusion on the isochemical Na<sub>2</sub>S–GeS<sub>2</sub> glass led to a value of  $D_{\text{Na}} = 6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  for  $10^3/\text{T} = 2.23$ , i.e., somewhat smaller than our present extrapolated data. However, this can be ascribed to the facts that (i) the glass transition temperatures are different  $(10^3/T_g = 2.01 \text{ and } 1.83 \text{ for Ge}^{38} \text{ and Si-based}^{12}$  glasses, respectively) and (ii) sodium thiosilicate conductivities are usually higher than those of corresponding thiogermanates,<sup>44</sup> which underscores an increased Na mobility/diffusivity in the former. For the  $56Na_2S-44SiS_2$  system,<sup>43</sup> the Na diffusivity is  $5.83 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $10^3/\text{T} = 2.11$ , and as such, in somewhat good agreement with extrapolations of our obtained diffusivities.

We note how the diffusion coefficients of S and Si in Figure 3b change by around 4 orders of magnitude in the studied temperature span (600–1600 K), effectively representing a continuous transition from a solid to a liquid-like state as would be expected in a glass.<sup>45</sup> The latter may be realized when comparing the diffusivity of S and Si at 1600 K ( $\sim 10^{-9}$  m<sup>2</sup> S<sup>1-</sup>) with the self-diffusion coefficient of, e.g., water<sup>46</sup> ( $\sim 1.4 \times 10^{-9}$  m<sup>2</sup> S<sup>1-</sup>).

**3.2. Ionic Conduction.** Now, we estimate the ionic conductivity of the simulated system. Generally, this may be done through a similar approach as when calculating the individual diffusion coefficients through the MSD, yet now by including cross-correlation effects,<sup>47</sup> i.e.,

$$\sigma(T) = \lim_{t \to \infty} \frac{e^2}{6tVk_BT} \sum_{j,i}^N Z_j Z_j \langle [\mathbf{r}_j(t) - \mathbf{r}_j(0)] [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \rangle$$
(5)

where  $Z_i$  is the charge of the *i*th atom. Linear response theory provides a similar correlation

$$\sigma(T) = \frac{e^2}{Vk_{\rm B}T} \int_0^\infty \sum_{i,j} Z_i Z_j \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(t) \rangle \mathrm{d}t$$
(6)

Practically, eqs 5 and 6 might be split into self- and distinct parts. Rearrangement of eq 6 yields

$$\sigma(T) = \frac{e^2}{Vk_{\rm B}T} \int_0^\infty \sum_i Z_i^2 \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle dt + \frac{e^2}{Vk_{\rm B}T} \int_0^\infty \sum_{i,j,i \neq j} Z_i Z_j \langle \mathbf{v}_j(0) \cdot \mathbf{v}_i(t) \rangle dt$$
(7)

Here, the first term is the self-part where the velocity autocorrelation function is seen, similar to the self-diffusion coefficients of eq 3. The second term is the cross-correlation between different atoms. Now, the first term is a problem scaling with the number of atoms in the system, N (in this case 3000 atoms), while the double summation in the distinct term provides  $N^2-N$  parameters (~9 × 10<sup>6</sup> correlations). Practically, the distinct terms will require significantly more statistical averaging than the autocorrelation terms.<sup>47</sup> We tried to compute the averages of auto- and cross-correlations of Na atoms at 600 K (Figure S1a) and generally found the average contribution to be much smaller than the autocorrelation terms. We also tested the two separate summations of eq 7 for all auto- and cross-correlations finding the autocorrelations to quickly converge while cross-correlations converge extremely poorly, hinting toward a decoupled diffusion process (Figure S1b). For Si and S this makes sense since the displacements, especially at lower T, are negligible (see the significantly lower diffusion coefficients compared to Na in Figure 4). We also



**Figure 4.** Calculated ionic conduction as a function of  $10^3/T$  in  $Na_2S-SiS_2$  liquids (black-filled boxes, from eqs 2 and 8), compared to experimental measurements (red) from Dive et al. (open boxes<sup>22</sup>), Ribes et al. (open triangles<sup>44</sup>) and Thomas et al. for a slightly different composition ( $56Na_2S-44SiS_2$ , open circles<sup>43</sup>) in the glassy state. Data (blue circles) for the corresponding lithium thiosilicate glass system are also represented.<sup>11</sup> The gray zone represents the glass transition region.<sup>12</sup> The dashed red and solid black lines represent Arrhenius fits to the corresponding data. Errors are estimated to be smaller than the size of the symbols.

probed the displacement autocorrelations and cross-correlations of Na at 600 K to find the cross-correlations of the displacements to be fluctuating around a slope near 0 (Figure S1c), suggesting a very low contribution to overall  $\sigma$ . For this reason, and due to the significant computational effort in computing the cross-correlations, in the present work, we only consider the autocorrelations. Formally this is given by eq 7 which reduces to the Nernst–Einstein equation<sup>48</sup> in a state of uncorrelated diffusion

$$\sigma(T) = \sum_{k} \frac{N_k Z_k^2 e^2}{V k_{\rm B} T} D_k(T)$$
(8)

Here,  $N_k$  is the number of atoms of type k, and  $Z_k$  is the corresponding charge (here taken as +0.6e, -1.2e, and +2.4e for Na, S, and Si, respectively), V is the volume of the simulation box, and  $k_B$  is the Boltzmann constant. This is a very common assumption in other related works on solid-state electrolytes.<sup>49,50</sup>

Using the calculated ion diffusivities from either eq 3 or 4 (we find these to be close at  $T \ge 600$  K as presented for Na in Figure S2 in the Supporting Information), the ionic conductivity ( $\sigma$ ) as a function of temperature T can be obtained from eq 8. This is similar to defining ionic conduction from the charge autocorrelation function with a charge flux  $\mathbf{j}(t) = Z \cdot \mathbf{e} \cdot \mathbf{v}(t)$ , provided that the system is at thermodynamic equilibrium

$$\sigma(T) = \sum_{k} \frac{N_{k}}{3Vk_{\rm B}T} \int_{0}^{\infty} \langle \mathbf{j}_{k}(t) \cdot \mathbf{j}_{k}(0) \rangle \mathrm{d}t$$
(9)

Figure 4 shows the calculated (self) ionic conductivities (black symbols computed from eq 8 using diffusion coefficients from eq 4) together with published data (red symbols) in the glassy state.<sup>22,44</sup> Both sets of data display an Arrhenius-like behavior of the form

$$\sigma T = \sigma_0 \exp(-\Delta/k_{\rm B}T) \tag{10}$$

with an activation energy  $\Delta$  that usually contains both a Coulombic and a mobility part,<sup>51</sup> the latter being linked to diffusion. Here, a fit to our calculated data leads to  $\Delta = 0.38$ eV, i.e., a value that differs slightly from the one determined in the glassy state by Barrau et al.<sup>44</sup> to be  $\Delta = 0.43$  eV (0.44 eV from the data of Thomas et al.<sup>43</sup>). This can be simply explained by the fact that in the glass, activation barriers for sodium diffusion are substantially larger, typically of the order of 0.20-0.60 eV at room temperature, <sup>22,52</sup> as also reflected in an increased shear modulus with decreasing temperature. In addition, a moderate change in slope is observable across the glass transition region (gray zone in Figure 4, 545  $K^{12}$ ) that is indicative of an Arrhenius crossover. As in other glass-forming systems such as polymer electrolytes,<sup>26,27</sup> simple oxides,<sup>28</sup> or multicomponent silicates,<sup>29,30</sup> conductivity is enhanced as the underlying network softens across  $T_g$ . Given the set of experimental conductivity data<sup>22,43,44</sup> which displays some differences, it is difficult to conclude on a possible increase of  $\sigma$ by at least 1 order of magnitude across the glass transition region, as observed in certain borosilicates<sup>29</sup> ( $\Delta \sigma \simeq 10^3 - 10^4$  $\Omega^{-1}$  cm<sup>-1</sup>), binary CaO-SiO<sub>2</sub><sup>53</sup> or, to a smaller extent, germanosilicates.<sup>54</sup> There are clear composition effects which might explain the differences since such experimental sets focus either on  $50Na_2S-50SiS_2^{22,44}$  or  $56Na_2S-44SiS_2^{43}$  but the increase of  $\sigma$  at a fixed temperature is usually found to be moderate for this range of composition.<sup>44</sup>

**3.3. Evidence for Sodium Ordering and Channel Dynamics.** Using our atomic scale trajectories, we now analyze in more detail some characteristic features of the  $Na_2S-SiS_2$  system. Given the close analogy with oxides, it is tempting to investigate if there is a possibility of detecting channel dynamics and dynamical heterogeneity of the studied diffusive species.

In modified silicates, mobility of the ions has shown to be the result of preferential pathways<sup>55,56</sup> for Na diffusion<sup>31,33,57,58</sup> (i.e., channels). These lead to an obvious signature in quasielastic neutron scattering experiments<sup>32,59</sup> by a prepeak in the partial Na–Na structure factor  $S_{\text{NaNa}}(k)$  at  $k_{\text{PP}} = 0.9$  Å<sup>-1</sup>. Indeed, such sodium-rich regions with a characteristic length scale of  $\simeq 7$  Å are considered to be found within a nearly frozen silica matrix. These features have been documented for different compositions, and since alkali ions break the intertetrahedral Si–O–Si bond and depolymerize the structure,<sup>60</sup> Na clustering emerges and leads to percolating channels<sup>61</sup> that are already present<sup>58</sup> for 20% Na<sub>2</sub>O in binary sodium silicate glasses. The question is then whether such channels are also present in the sodium thiosilicate system.

To investigate this aspect, we follow the analysis performed by Meyer et al.,<sup>32</sup> i.e., we focus on the Na–Na partial structure factor  $S_{\text{NaNa}}(k)$  (Figure 5a), which we find to exhibit a welldefined prepeak at  $k \simeq 1.0$  Å<sup>-1</sup>. The existence of this peak is almost temperature independent as in the parent oxides,<sup>32</sup> albeit its intensity might slightly decrease with increasing temperature. The existence of this prepeak is the signature that some ordering of Na ions takes place and involves a typical length scale<sup>62</sup> of  $7.7/k_{\text{PP}} \simeq 7-8$  Å (specifically we relate the





**Figure 5.** (a) Calculated Na–Na correlations  $S_{\text{NaNa}}(k)$  in the reciprocal space for the different target temperatures. The light-red zone highlights the prepeak region around  $k_{\text{PP}} = 1.0 \text{ Å}^{-1}$ . (b) Sodium atoms (blue) are shown together with the trajectories of 1 ns of dynamics at 600 K (gray lines). Silicon and sulfur atoms are omitted for clarity.

position *r* of the peak in real space to the position *k* of the corresponding peak in Fourier space by using the relation  $kr \simeq$  7.7), which identifies the location of the first maximum of the spherical Bessel function  $j_0(kr)$ .

To further study the dynamical ordering and channel-like dynamics, we visualized the trajectories every 5 ps during a 1 ns simulation at 600 K (see Figure 5b). Here, a web-like pattern is obtained which shows clear preferential pathways in which Na atoms move, that is, channel dynamics. We also plotted the trajectories for two higher temperature cases (T = 1000 and T = 1600 K) in Figure S3 in the Supporting Information, showing what is likely the slight remains of channel dynamics at 1000 K, but random sodium diffusion at T = 1600 K. This transition from ordered channels to random diffusion is to be expected, given the transitioning of the S–Si network into the molten state (as described by their diffusion coefficients, Figure 3b). Nonetheless, from Figure 5a, it is clear that Na–Na ordering remains even in the melt.

**3.4. Evidence for Dynamic Heterogeneities.** *3.4.1. Characterization of Ion Hopping.* While Na atoms do indeed seem to have some ordered structure (Figure 5), this does not imply that all Na atoms behave similarly. A good example of this is presented in Figure 6 displaying a selection



**Figure 6.** Selection of Na jumps (colored curves) as evidenced by the individual MSD evolution with a simulation time at 600 K. The solid black line is the average Na MSD of the present sample.

of Na MSDs with time, allowing the detection of specific motions which are not revealed in the average MSD (black solid line in Figure 3). We find that, as expected, the motion is not homogeneous and ions move by jumps (of about  $\Delta$ MSD  $\simeq 200 \text{ Å}^2$ ), followed by more or less limited spatial extension of the time trajectories, i.e., cages. These are typical features of the dynamics of particles moving between traps.<sup>63</sup>

To study the per-atom dynamics in greater detail, we calculate the self-part of the Van Hove  $[G_s(\mathbf{r}, t)]$  correlation function. Here, we examine the sodium atoms over the course of 10 ns of simulation at temperatures varying from 600 to 1600 K in intervals of 200 K. Specifically,  $G_s(\mathbf{r}, t)$  is calculated as

$$G_{\rm s}(\mathbf{r},t) = \frac{1}{N} \langle \sum_{j=1}^{N} \delta(\mathbf{r} + \mathbf{r}_{j}(0) - \mathbf{r}_{j}(t)) \rangle \tag{11}$$

The self-part of the Van Hove correlation (eq 11) function essentially provides the probability  $4\pi r^2 G_s(r, t)$  of finding a particle *j* at a distance **r** from its original position after a time *t*. For very short times,  $G_s(r, t)$  nearly reduces to the Dirac function as expected,<sup>64</sup> given the definition of  $G_s(r, t)$  (eq 11). For times on the order of 30 ps (Figure 7a), the function  $G_s(r,$ t) for Na atoms displays a broad distribution with probabilities extending up to, e.g., 5 Å at 600 K (cyan distributions), whereas such a distribution is, of course, shifted to larger distances at elevated temperatures (1600 K,  $r \simeq 2-20$  Å) because of the increased thermal activation. We note to the reader how the area under the curve in Figure 7 does not proportionally reflect the number of atoms. Combined with the vast heterogeneity shown in Figure 6, the logarithmic plotting procedure is the reason why, from the MSD in Figure 3a (which is an average metric for all atoms), it seems that all Na atoms move diffusively, while the actual behavior is governed by significant heterogeneity.

For longer times (t = 100 ps and 10 ns as presented in Figure 7b,c, respectively), the ions experience larger distances, including those typical of second nearest neighbor distances (4–5 Å). For intermediate time intervals (100 ps), a bimodal distribution for the Van Hove correlation function develops at 600 K and seems to be specific to temperatures close to the





**Figure 7.** Self-Van Hove correlation function  $G_s(r, t)$  for Na atoms at different times as a function of jump distance *r* for the isotherms T = 600-1600 K (blue: 600 K; red: 1600 K) at simulation times of (a) 30, (b) 100, and (c) 10 ns, respectively. Notice the logarithmic *x*-axis. Snapshot in panel (c) represents the Na ions colored according to their MSD value after 10 ns at 600 K. In all panels, the red-shaded distribution corresponds to 1600 K while the blue-shaded distribution corresponds to the 600 K case. Black lines between blue and red correspond to temperatures monotonically increasing from 800 to 1400 K.

glass transition (Figure 7b). Such a distribution is also vaguely visible at smaller simulation times (Figure 7a). However, such features are absent for larger temperatures, indicating that once the system is partially frozen, i.e., when atomic motion between network-forming species (S and Si with  $D_{\rm Si} \simeq 10^{-8} {\rm ~cm}^2 {\rm ~s}^{-1}$ ) and cation motion  $(D_{\rm Na} \simeq 10^{-5} {\rm cm}^2 {\rm s}^{-1})$  is basically decoupled, a two-step process sets in. This process consists of greatly limited Na motion (1 Å) due to constraints by the surrounding thiosilicate network, i.e., trap-induced cage-like motions. This happens in-between and prior to dynamics over longer distances (2-10 Å). For longer times (10 ns, Figure 7c), such cage-like features are absent because of the generalized diffusive regime at all considered temperatures, although a nonhomogeneous distribution of MSDs is acknowledged (colored snapshot in Figure 7c). The bimodal distribution of the Van Hove function thus contains the statistical signature of the jumps and reduced motion depicted from individual particles as showcased in Figure 6.

3.4.2. Non-Fickian Dynamics. For long times and in an ordinary liquid for which relaxation phenomena are negligible,<sup>64</sup> the Van Hove function behaves as

$$G_{\rm s}(r,t) = \frac{\exp\left[-\frac{r^2}{4Dt}\right]}{(4\pi Dt)^{3/2}}$$
(12)

where *D* is the diffusivity of the particle. Here, the calculated function  $G_s(r, t)$  appears to be much more complex with, e.g.,

bimodal distributions (Figure 7b) or tails in the long time limit (Figure 7c). Such behavior has previously been found in other glass-forming liquids.<sup>33,65,66</sup>

The probability distribution of displacements (such as the histograms represented in Figure 7) has been found to contain information on dynamic heterogeneity, as manifested in computer simulations by a non-Gaussian distribution of particle displacements.<sup>67</sup> However, for short times and in the absence of glassy dynamics (e.g., 0.03 ns in Figure 7a), the Van Hove function is made of a single Gaussian distribution that is shifted to longer distances with increasing time (Figure 8), and the location of the maximum evolves as  $t^2$ , which arises from the ballistic behavior of the MSD (Figure 3a).



**Figure 8.** Self-Van Hove correlation function at T = 600 K for Na atoms at different simulation times (same data as in Figure 7). The arrow indicates a departure from Gaussian behavior (eq 12, dashed red area).

This characteristic does not apply at intermediate times but is recovered at very long times, for which  $G_s(r, t)$  is again given by a Gaussian. In the present system, we observe a clear departure from a Gaussian behavior at, e.g., 0.1 ns (Figure 8), as manifested by a tail at long distances (r > 10 Å, corresponding to a jump probability of 78.0%). The departure from this Gaussian behavior represents that some Na ions move farther than expected from a Gaussian approximation, a result that has been previously found in, e.g., fragile viscous liquids.<sup>68</sup>

A convenient way to characterize the departure from such distributions (Figure 8) is given by the so-called non-Gaussian parameter  $(NGP)^{69}$  containing the second and fourth moments of the displacement distribution

$$\alpha_{2}(t) = \frac{3\langle r_{Na}^{4}(t) \rangle}{5\langle r_{Na}^{2}(t) \rangle^{2}} - 1$$
(13)

The NGP becomes nonzero at intermediate times (Figure 9) when  $\langle r_{\text{Na}}^2(t) \rangle$  starts to exhibit a plateau-like behavior (Figure 3a). This behavior is directly related to the cage effect and dynamic heterogeneities when, for example, the network species (Si and S) and neighboring Na act as traps for moving Na cations.

Figure 9 now represents the NGP  $\alpha(t)$  for the Na particles in the studied thiosilicate system. As in other systems, 37,67,69 $\alpha(t)$  features the salient phenomenology observed during glassy relaxation, i.e.,  $\alpha(t)$  displays a maximum value at intermediate times. In addition, the position  $\tau^*$  of the maximum and the maximum value  $\alpha(\tau^*)$  increase with decreasing temperature. Both quantities can be described by



**Figure 9.** NGP  $\alpha(t)$  of Na atoms for the isotherms T = 300-1600 K (blue: 300 K; red: 1600 K). The inset represents the temperature dependence of the maximum  $\tau^*$  value of  $\alpha(t)$ . We note to the reader how the time axis in the main plot as well as both axes in the inset are logarithmic. Deviations in the inset are standard deviations of the five repetitions. Colors in the main plot go from low [T = 300 K (blue)] to high temperatures [T = 1600 K (red)], with black lines between blue and red corresponding to temperatures monotonically increasing from 600 to 1400 K.

an Arrhenius-like behavior, i.e., an exponential growth with 1/T (see inset of Figure 9).

We furthermore note that at low *T*, the NGP of the (Si and S) atoms is smaller when compared to the NGP of the Na ions and shifts to longer times (not shown). This indicates that dynamic heterogeneity is less pronounced for the network species at lower temperatures and increased relaxation times. At higher temperatures, the NGP of all species seems to follow a similar tendency of decaying toward 0, however, with somewhat slower decays for the network forming (S and Si)-species. The nonzero NGP for S and Si reflects the heterogeneity of the network-building Si–S network, likely caused by differences in the rigidity of functional groups of the network.

3.4.3. Fast and Slow Na Dynamics. The results in Figure 9 indicate that since there are signatures of heterogeneous dynamics, there must be both fast- and slow-moving particles; however, it provides no further information on the differences between these species.

To understand the local structural signature of fast and slow Na atoms in the near-glassy state, we calculated the MSD of all Na atoms after 100 ps of simulation time in a pure dynamic simulation at 600 K (same simulations used for Figure 6). From this information, we identify the IDs of atoms with the 25% highest and lowest MSDs and denote these atoms as fast and slow, respectively. This categorization enables us to calculate the partial pair distribution functions (at t = 0, i.e., at the initiation of dynamics) of three cases, i.e., (i) the correlation between fast and other fast atoms, (ii) the correlation between fast and slow atoms. The results are presented in Figure 10.

Interestingly, significant differences in the three studied correlations are observed, i.e., while fast-fast and slow-slow correlations are as expected [clear shell-like ordering above randomicity for nearest neighbors as depicted by g(r) > 1], the correlation between fast and slow atoms show clear depletion [g(r) < 1] at nearest neighbor distances. This indicates dynamical heterogeneity not just between different chemical



**Figure 10.** Na–Na pair correlation of the 25% fastest and slowest Na atoms (fast and slow, respectively). The fast–fast correlation represents the correlation between fast and other fast Na atoms, the slow–slow correlation represents the correlation between slow and other slow Na atoms, and finally, the fast–slow correlation represents the correlation between fast and slow Na atoms.

species<sup>67,69</sup> but also for the different Na atoms in the presently studied system. That is, fast Na atoms tend to move in the vicinity of other fast Na atoms, while slow Na atoms are "trapped" together with other slow Na atoms. Notably, by comparing Figure 10 with the self-Van Hove correlation in Figure 8, the average diffusion distance is seen to be on the order of  $\sim$ 7 Å. This corresponds to around two molecular "shells" as depicted from the Na–Na Resource Description Framework (Figure 10). This supports the idea of the collective movement of Na atoms, where two or more sodium atoms tend to move faster collectively.

The next question is whether it is possible to identify some distinct structural characteristics for slow and fast Na atoms, respectively. To this end, we have computed the paircorrelation function at the initiation of the simulation based on an evaluation between fast and slow Na atoms against either all Na atoms or all S atoms. These analyses show that fast Na atoms appear to have slightly more Na atoms and slightly fewer S atoms in their vicinity compared to slow Na atoms (Figure S4 in the Supporting Information). As Na atoms are significantly more mobile than S and Si atoms, a collective effect of increased mobility when many Na atoms move in each other's vicinity arises. This supports the idea of collective Na channels, where the ions may move and collectively enhance the diffusivity. In contrast, being near more S atoms means that the Na atom is closer to the rigid S/Si network, experiencing less enhancement of collective Na jumps.

Finally, we have computed the coordination numbers of the nearest neighbor S atoms of fast and slow Na atoms (as identified by Na–S separations below 4 Å), respectively. The S atoms near fast Na atoms are found to have an average S–Si coordination of 1.34, while the average S–Si coordination of S atoms near slow Na atoms is 1.48. This observation is interesting, as the results indicate that fast Na atoms tend to be situated near S atoms of lower atomic rigidity, while slow Na atoms are in the vicinity of S atoms of relatively higher atomic rigidity. This agrees with recent simulation work on lithium thiophosphate glasses, suggesting that lithium atoms are more mobile in the vicinity of smaller thiophosphate groups as opposed to larger and more rigid functional groups.<sup>70</sup> We note how more complex combined structural/dynamical metrics

may provide more details on distinguishing fast and slow Na ions in future studies.

## 4. SUMMARY AND CONCLUSIONS

In this study, we investigated the dynamics of a glassy electrolyte  $Na_2S$ -SiS<sub>2</sub> that serves as a base material for alloying possibilities to increase the ionic conductivity. We have first slightly improved the parametrization of a classical potential and then used it to study the ion dynamics in relationship with ionic conduction. The results show the salient phenomenology of modified network glasses with Arrhenius-like diffusion for all (S, Si, and Na) species, yet a progressive decoupling between network species (Si and S) diffusivity and cation (Na) diffusivity in a fashion similar to the archetypal sodium silicates.<sup>33</sup> In addition, when compared with experimental data in the glassy state, the Na conductivity appears to display a jump at the glass transition temperature, as observed in other glassy electrolytes.

The atomic scale description reveals that above  $T_{g}$ , the Na dynamics occurs within channels and involves fast- and slowmoving particles. These display either jumps or spatially reduced cage-like motion, the latter being imposed by the disordered environment of the network-forming species that are thought to play a critical role in ion transport. Finally, we show evidence of how fast and slow Na atoms move separately, i.e., fast Na atoms tend to move together with other fast Na atoms, while slow Na atoms move together with other slow Na atoms. These fast Na atoms tend to have slightly more Na neighbors and slightly fewer S neighbors than do the slower Na atoms. In addition, the S atoms close to fast Na atoms tend to have a Si-S coordination number lower than that of the S atoms in the vicinity of slow Na atoms. This highlights how the local rigidity of the network directly impacts the movement of adjacent mobile cations.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.3c02909.

Estimated cross-correlations, Green–Kubo results of diffusivity, and estimations of structural descriptors of fast and slow atoms (PDF)

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#### Notes

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