Sodium migration pathways in multicomponent silicate glasses: Car–Parrinello molecular dynamics simulations

Antonio Tilocca
Department of Chemistry and Thomas Young Centre for Theory and Simulations of Materials, University College London, London WC1H 0AJ, United Kingdom

(Received 23 February 2010; accepted 28 May 2010; published online 1 July 2010)

The mechanism of sodium migration in low-silica alkali-alkaline earth silicate glasses is investigated through Car–Parrinello molecular dynamics (MD) simulations. The transport of sodium to the glass surface and its subsequent release is critical for the use of these glasses in biomedical applications. The analysis of the MD trajectory, mainly through a combination of space and time correlation functions, reveals a complex mechanism, with some common features to the migration in mixed-alkali silicate glasses and several important differences. The low site selectivity of Na cations in this glass allows them to use both Na and Ca sites in the migration process. The high fragmentation and the corresponding flexibility of the silicate network enable an additional mechanism for ion migration, not favorable in the more rigid network of common higher-silica glasses, involving the creation of empty transient sites through the correlated forward-backward motion of an Na or a Ca cation. We also show that because sodium migration must involve an undercoordinated intermediate, sharing of oxygen atoms in the initial and final coordination shells is a way to reduce the energetic cost of losing favorable Na–O interactions and Na migration proceeds between corner-sharing NaOx polyhedra, where x = 5–7. For these low-silica compositions, the present simulations suggest that due to the participation of calcium in the Na migration, the latter will not be significantly hampered by extensive mixing with less mobile Ca ions, or, in any event, the effect will be less marked than for higher-silica glasses. © 2010 American Institute of Physics.

I. INTRODUCTION

Many glass properties, such as the electrical conductivity, depend on the mobility of network-modifier cations; phenomena such as the mixed alkali effect (MAE) denote a highly complex relationship between glass composition and ion mobilities, and have attracted considerable interest in recent years.1–6 The ionic transport to the surface also affects the process of dissolution of the glass in an aqueous environment, which has deep implications for advanced technological applications where the glass durability is a major issue. For instance, the rate of initial dissolution in a biological (aqueous) medium determines the possible use of soda-lime phosphosilicate glasses as implants for tissue repair and regeneration.7–9 A fast release of sodium and calcium ions, which accompanies the glass dissolution, is in fact a key requirement for the effective integration of the implant through interfacial bonding.8 There is increasing interest in identifying the complex relationships between composition and activity of a glass also for these applications and molecular dynamics (MD) simulations play a major role in this context.9 In particular, given their relevance, recent MD studies have focused on structural features of the bulk glass and of its surface, which can potentially affect dissolution.10–13

To complete this somewhat static picture, a direct investigation of the mechanism of ion migration in these glasses is highly needed. In fact, while MD simulations have thoroughly explored the mechanism of ion migration in single and mixed alkali silicate glasses, revealing several key features,1,3,4,6,14–16 not as many studies have involved mixed alkali-alkaline earth silicate glasses, and especially the highly soluble low-silica (<50 mol% SiO2) compositions most active in the biomedical field.

There is substantial evidence that, in alkali silicate glasses, the modifier cation sits in a polyhedron of coordinated oxygen atoms, and ion migration proceeds through a sequence of discontinuous, thermally activated hops between these stable sites.3,6,15,17,18 The ion spends most of the time performing local oscillations within a site, and infrequently hops to an empty adjacent site previously vacated by another ion; the initial and final coordination polyhedra typically share oxygen atoms so that direct long-range jumps of an ion between nonconnected polyhedra are unlikely.15 Instead, spatial correlations denote coordinated jumps of the order of nearest-neighbor interionic distances.6,18 Sharing of non-bridging oxygens (NBOs) between alkali ions results from high alkali-NBO coordination, when the alkali fraction is high enough: Ions then migrate along alkali-rich percolation channels that run through the glass network.14,19 Within this general picture, the MAE in alkali silicate glasses has been associated to site-specific hopping:1,3,4,6 Because the structural and energetic features of two sites hosting different ionic species are different, an ion prefers to jump to an empty site which was previously occupied by another ion of the...
same type. Mixing of different alkalis reduces the number of preferred “like” sites available; because jumps to “unlike” sites are associated with either an increased backward correlation or with an increased activation energy due to the local relaxation of the site which must adapt to the new ion, a decrease in the ionic diffusivity and the electrical conductivity is observed for mixed alkali, compared to the corresponding single-alkali glass.

The dynamical effects of the interaction between unlike ions on the ion migration in mixed alkali-alkaline earth glasses are less understood, notwithstanding the widespread use of these compositions for common (float) glass, and in the biomedical field. In principle, Ca cations, diffusing on much slower time scales, should obstruct the percolation channels and reduce Na diffusivity. In fact, the higher mobilities of sodium and calcium measured in soda-lime silicate glasses as the Na$_2$O content increases, also denote lower Na mobility when Na$_2$O is replaced by CaO. Even less is known regarding the migration mechanism of sodium in alkali-alkaline earth glasses containing a low silica fraction. Structural models of some of these compositions, characterized by the highest solubility and biological activity, highlighted a fragmented glass network, with the prevalence of chainlike silicate units and showed extensive mixing with no significant clustering of modifier cations. In order to identify the factors which affect bulk diffusion and release of modifier cations in these glasses, we need to assess whether the ion migration process is ruled by similar effects as those discussed before for mixed alkali and alkaline-earth glasses and whether the open glass matrix introduces relevant changes.

In order to explore ionic migration in these materials, we have performed ab initio (AI) MD simulations$^{26}$ of the 455S glass, probably the most representative composition among low-silica alkali-alkaline earth glasses for biomedical applications.$^{27}$ Classical MD simulations employing empirical potentials have been successfully employed to model the medium-range structure of these glasses$^{9}$ and, being computationally cheaper, are in principle better suited than AIMD to access the relatively long time scales characterizing the diffusive process. However, whereas the accuracy of the potential to reproduce structural features can be safely assessed against available experimental data, for instance, diffraction, extended x-ray absorption fine structure, and NMR measurements,$^{28–32}$ the lack of data regarding ion migration prevents a similar assessment of how well an empirical potential reproduces dynamical properties of these materials. Multicomponent phosphosilicate glasses pose a serious challenge to standard interatomic force fields; whereas the inclusion of polarizability in the potential appears necessary to fully reproduce the atomic structure,$^{33}$ an adequate representation of static structural properties is not a sufficient condition to ensure an equally accurate description of the complex dynamical rearrangements brought about by the diffusive process, such as the fast relaxation of the local mechanical and electrical strain produced by a hop into a mismatching site.

Because a full assessment of the accuracy of available potentials to model ion migration in bioglasses is not feasible at this time, parameter-free AI simulations represent the only viable alternative. AIMD has proven successful to model local, vibrational, and electronic features of these glasses,$^{34}$ as well as structure and dynamical properties of the melt precursor$^{35}$ and their surface reactivity.$^{12,13}$ Within the same computational framework, the present AIMD simulations aim at highlighting the main features of the elementary processes characterizing migration in bioactive silicate glasses. Due to the necessarily limited statistics on the long-range diffusion of the less mobile Ca ions, the analysis of the MD trajectory is mostly focused on analyzing sodium migration, and to assess the role of Ca ions in this process. We show how, and up to what extent, the general effects describing ion migration in silicate glasses, discussed before, apply to the present glasses, and highlight new features which are associated to sodium diffusion in low-silica alkali-alkaline earth compositions. The detailed description of these basic features, as highlighted by a combination of different space- and time-correlation functions, could eventually be used to evaluate and improve the performance of classical potentials to model this process.

Finally, we discuss the potential impact of the present results for applications where the glass dissolution and the release of modifier cations play a critical role.

II. COMPUTATIONAL METHODS

Car–Parrinello AIMD simulations$^{26}$ were carried out using the QUANTUM-ESPRESSO code,$^{36}$ using the Perdew-Burke-Ernzerhof exchange-correlation functional$^{37}$ to treat the electronic structure within the generalized gradient approximation to density functional theory. Core-valence electron interactions were represented using Vanderbilt ultrasoft pseudopotentials,$^{38}$ explicitly including semiconductor shells for Na and Ca. Plane-wave basis set cutoffs were set to 30 and 200 Ry for the smooth part of the wave functions and the augmented charge, respectively; $k$-sampling was restricted to the $\Gamma$ point. The MD time step $\delta t$ and fictitious electronic mass $\mu$ were 0.17 fs and 700 a.u., respectively. This computational setup has proven adequate to model local structure and dynamics of soda-lime phosphosilicate glasses and melts, as well as their surface reactivity.$^{9,12,13,34,35,39}$

The simulation was started from a glass configuration previously obtained through a full AI melt-and-quench procedure with the same computational framework.$^{35}$ The procedure involved melting a random configuration of the correct composition at 2300 K, before cooling it down to room temperature in a sequence of constant-temperature runs, at a nominal cooling rate of 20 K ps$^{-1}$. This resulted in a quite reasonable glass structure, as discussed in Ref. 35. The exact composition of the sample, 19SiO$_2$ 10Na$_2$O 11CaO P$_2$O$_5$, corresponds to the 455S bioactive glass, 46.3SiO$_2$–24.3Na$_2$O–26.8CaO–2.6P$_2$O$_5$ mol %.

Because diffusive events in silicate glasses occur infrequently (with respect to typical MD time scales) at room temperature, simulations of these processes are often run at a significantly higher temperature, in an effective approach to accelerate the statistical sampling and observe a significant number of diffusive events.$^{3,6,15,31,42}$ The selected tempera-
ture is not high enough to melt the glass, thus ensuring that the diffusing ions still move in an essentially static silicate matrix, so that the observed diffusive features can be considered well representative of an ion migrating in the amorphous solid in practical conditions. For the present work, the starting configuration described above was reheated up to 1100 K using a Nosé thermostat, and a Car-Parrinello Molecular Dynamics (CPMD) trajectory of 150 ps at 1100 K was carried out, the last ~120 ps of which were used in the subsequent analysis. We checked that only thermal oscillations and no diffusion of network-forming Si, P, and O atoms occurred during the MD trajectory, confirming that no melting of the glass had occurred in the observation time.

III. RESULTS AND DISCUSSION

A. Site structure

The structural features of the sites occupied by sodium and calcium are an important issue to assess, before examining their dynamical behavior. The radial distribution functions for pairs involving Na and/or Ca are shown in Fig. 1. The Na–O and Ca–O nearest-neighbor peaks are both centered around 2.30 Å, but the Ca–O peak is significantly narrower, denoting a more rigid Ca–O than Na–O coordination shell. The Na–Na, Na–Ca, and Ca–Ca nearest-neighbor distances are around 3.3, 3.4, and 3.6 Å, respectively, again with a narrower peak involving calcium pairs, which reflects the lower mobility of calcium compared to sodium. The distributions of possible coordination numbers (CNs) in Fig. 2 show that sodium is found coordinated to six to seven oxygen atoms, four to five of which are nonbridging (NBO). Ca is found more frequently associated to seven oxygen atoms than Na, which results in a higher average Ca–O than Na–O coordination number (6.83 versus 6.46, respectively, using a 3.3 Å distance cutoff). The width of the CN distributions denotes a much more strict preference of Ca for pseudooctahedral sites containing six NBOs, whereas Na coordination appears more flexible and less biased toward NBOs, with most Na sites containing only four and five NBOs. While the higher affinity between divalent Ca cations and NBOs had been highlighted in previous simulations, the more strict requirements that Ca ions appear to impose on their coordination shell is an important factor to consider when discussing the site selectivity of Na and Ca ions in the present compositions.

The distributions of O–M–O angles (where M is Na or Ca), shown in Fig. 3, further highlight the structure of the coordination shell of the modifier cations. The individual BO

![Fig. 1. Radial distribution functions of pairs involving Na\(^+\) and/or Ca\(^{2+}\).](image1)

![Fig. 2. Distributions of the number of oxygen (O) and nonbridging oxygen (NBO) atoms in the coordination shell of Na\(^+\) and Ca\(^{2+}\).](image2)

![Fig. 3. Distributions of O–M–O angles, where M is Na (top panel) or Ca (bottom panel). The total distribution is represented as bold dark curve; the NBO–M–NBO, BO–M–NBO, and BO–M–BO components are also shown.](image3)
and NBO components show that BO-Na-BO and NBO-Na-NBO angles are about 60° and 90°, respectively, reflecting the greater repulsion between two NBOs with a higher negative charge, whereas BO-Na-NBO angles can have both values. These features also apply to the Ca coordination shell, the main difference being that the calcium distribution is dominated by the NBO-Ca-NBO component, and only very few Ca ions are found linking two BOs, reflecting the preferential Ca-NBO association. The highlighted differences between the coordination polyhedra of sodium and calcium, namely the higher flexibility of Na coordination environments and the higher NBO fraction in the calcium polyhedra, are likely related to each other: Due to the higher field strength, Ca ions are able to set tighter constraints on their environment, at the expense of sodium, whose environment will consequently (and necessarily) have a more varied character.\textsuperscript{43}

B. Mean square displacements

During the observation time of the CPMD trajectory, most Na ions show diffusive behavior (75% of them leave their initial site); the trend is reversed for Ca, with most ions localized, and only 30% performing a few jumps to neighboring sites. This should not be interpreted as a general effect, but only as an indication of the different time scale of Na and Ca diffusion in this system, with the consequence that the present simulations can provide a more accurate statistical description of the diffusive behavior of sodium, and will be mostly focused on the Na migration mechanism.

The logarithmic and linear plots of the mean square displacement (MSD) of all the atomic species, plotted in Fig. 4, confirm that during the MD run at 1100 K, only local oscillations are performed by the atoms forming the glass network (Si, O, and P), whereas the modifier cations show diffusive behavior. The markedly different behavior of modifier cations compared to the network-forming species is more evident in the linear inset, although one can also note how the logarithmic MSD curves of Si, P, and O all follow a common pattern, different from that of Na and Ca, denoting that the motion of the modifier ions and of the network formers are decoupled, and the modifier ions diffuse into a frozen silicate matrix which does not significantly relax during the dynamics.\textsuperscript{23} The initial free ballistic regime rapidly decays into an oscillatory local motion for Si, P, and O, whereas for Na and Ca is followed by a relatively slow transition to diffusive motion. This transitional regime is characterized by local, rattling motions within the coordination cage,\textsuperscript{44} preceding escape and hop to an adjacent site (see also the discussion on the self van Hove correlation function below). The logarithmic curves denote a transition to diffusive regime after approximately 10 ps for Na, and significantly longer for Ca ions. Due to the highly heterogeneous dynamics in these systems,\textsuperscript{45,46} characterized by a distribution of hopping rates, the onset time for the diffusive regime does not reflect a constant hopping frequency, but could be regarded as an approximate lower limit. The longer onset time for Ca partially reflects its more marked site selectivity.\textsuperscript{6,42}

C. Dynamic correlations: van Hove functions

Further insight into the correlation between ionic displacements can be obtained through the self- and distinct parts of the van Hove correlation functions, defined by\textsuperscript{47}

\[
G_s^\alpha(r,t) = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle \tag{1}
\]

and

\[
G_\beta^\alpha(r,t) = \frac{V}{4\pi r^2 N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_j(0)|) \rangle \tag{2}
\]

where \(N_\alpha\) and \(N_\beta\) are the total numbers of atoms of species \(\alpha\) and \(\beta\), respectively, \(V\) is the volume of the simulation box, and the primed summation excludes the \(i=j\) case when \(\alpha = \beta\). \(G_s^\alpha(r,t)\) is then the probability that an atom initially at the origin at \(t=0\) is found at a distance \(r\) after a time \(t\); \(G_\beta^\alpha(r,t)\) is the probability that, after a time \(t\), a different atom of species \(\beta\) is found at a distance \(r\) from the location occupied by an atom of type \(\alpha\) at time \(t=0\). The latter essentially is a time-dependent radial distribution function, with \(G_\beta^\alpha(r,0) = g_{\beta\alpha}(r)\).

The self-part of the van Hove correlation function for Na and Ca is shown in Fig. 5 for selected times. After 1 ps, a Na ion still occupies the initial site (where it started at \(t=0\)); a second peak, corresponding to the ion leaving the original site, starts to form already after 10 ps, consistently with the onset of diffusive regime in the MSD(Na) plot in Fig. 4. The position of the second peak, around 3.4 Å, roughly matches the nearest-neighbor Na–Na and Na–Ca distances in the corresponding radial distribution function (Fig. 1). This confirms that, also for the present compositions, long-range diffusion of Na proceeds through a sequence of hops between adjacent cation sites. The slower migration dynamics of Ca ions is evident in the bottom panel of Fig. 5: The probability that a Ca ion initially at the origin has escaped its coordination shell, represented by the density beyond the first peak in the \(G_s^\text{Ca}(r,t)\) function, is still very low after 10 ps, and after 30 ps remains about an order of magnitude lower compared to sodium. In agreement with the end of the local transitional regime discussed before, a well-defined peak around 3.4 Å in
G_{Ca}^{Ca}(r, t) only forms after 60 ps, when a small fraction of the Ca ions have managed to escape the original site.

The cumulative sum $\Sigma(R \cdot t) = \sum_{t=0}^{t=80 \text{ps}} G(r, t)$, superimposed to the figure for the $t = 80 \text{ps}$ curves, represents the fraction of ions which have moved by $R_c$ in 80 ps. Taking $R_c = 2.15 \text{ Å}$, corresponding to the first minimum in $G_s^{Ca}(r, t)$, the position of the peak at $r = 3.5 \text{ Å}$ in the same panel must then result from Ca ions moving into one of the neighbor sites that was occupied by a Ca ion at $t = 0$, and thus reducing the “distinct” Ca density there. The increasing density at the origin in the $G_{CaCa}^{Ca}(r, t)$ function (bottom panel) does confirm that Na ions frequently occupy Ca sites, even though this process is much slower compared to that involving Na ions occupying Na sites.

While revealing some of the hopping features of an individual ion, the self-part of the van Hove function does not provide insight into the correlation between the motion of different cations. For instance, the self-part of the function does not allow us to say whether a site had been vacated immediately or relatively long before being occupied by another ion, or it clarifies the average identity (Na or Ca) or the migrating cation. These complex correlation effects can be quantitatively assessed by looking at the $G_{d}^{\alpha \beta}(r, t)$ functions, shown in Fig. 6, with $\alpha$ and $\beta$ covering Na–Na, Ca–Ca, and mixed pairs. The increase with $t$ of the $t=0$ peak corresponds to the increasing probability of finding a different ion $I'$ in a site initially occupied by ion I. The decrease of the peak at $r = 3.4–3.5 \text{ Å}$ is generally due to the atom initially at the origin which after a certain time has moved into one of the nearest-neighbor sites, replacing the ion originally there. The distinct part of the Na–Na van Hove function in the top panel of Fig. 6 denotes a significant probability that a Na ion initially at the origin is replaced by a different Na already after 10 ps. On the other hand, the absence of density at $t = 0$ in the $G_{CaCa}^{Ca}(r, t)$ (central panel of the figure) denotes that no Ca ions moved into sites previously occupied by another Ca, during the MD trajectory: The decrease in $G_{d}^{CaCa}(r, t)$ at $r = 3.5 \text{ Å}$ in the same panel must then result from Na ions moving into one of the neighbor sites that was occupied by a Ca ion at $t = 0$, and thus reducing the “distinct” Ca density there. The increasing density at the origin in the $G_{d}^{CaNa}(r, t)$ function (bottom panel) does confirm that Na ions frequently occupy Ca sites, even though this process is much slower compared to that involving Na ions occupying Na sites.

The analysis of the van Hove functions shows that, for this glass composition, correlated jumps involve two Na, or a Na and a Ca, but not two Ca ions. Given the slow Ca dynamics, the absence of correlations in which a Ca ion occupies a site vacated by another Ca during the observation time does not rule out this possibility, but it does denote a higher correlation of Ca displacements with those of Na ions.

**D. Ion migration mechanism**

Direct inspection of the MD trajectory highlights instances of the correlated jumps, some of which are shown in Figs. 7 and 8. In Fig. 7, the sodium atom labeled “0” (Na0) jumps to the site vacated by Na2, while Na1 enters the site originally occupied by Na0 original site. Thereafter, following further displacements of Na2 and Na4, Na0 continues its migration, vacating a site that is occupied by Na5. The overall sequence of correlated jumps is rather rapid, the time separation between each snapshot being about 3 ps; in particular, direct visualization of the MD trajectory allows one to identify separate jumps as fast, discrete displacements well distinct from local oscillations in a site, consistently with a hopping mechanism.

Figure 8 illustrates the role of a Ca ion in a correlated jump: While Na1 occupies the site vacated by Na0, the latter moves close to Ca3, which is temporarily displaced. This is
followed by a further jump of Na0 into the site vacated by Na4, while Ca3 returns to its original position. This suggests that a forward-backward displacement of another cation, which temporarily vacates a site before returning to it shortly afterwards, can assist ion migration by opening a pathway which would otherwise be unavailable. The participation of transient sites which are occupied only temporarily during a jump sequence, had been proposed by Cormack et al.\textsuperscript{15,48} for alkali silicate glasses. In the present case, the low connectivity of the silica network (\textasciitilde{}2 for the 45S5 glass\textsuperscript{8}) could provide a favorable route for the creation of these transient sites. In higher-silica compositions the rigid silicate network does not easily distort to accommodate a modifier ion in a metastable position; however, a more flexible network can reduce the energy cost of temporarily hosting a cation in a nonfavorable location,\textsuperscript{49,50} and thus make additional migration pathways available. In other words, the temporary displacement of a cation to create an empty transient site can be achieved more easily in low-silica compositions, as in some cases a cation could temporarily vacate a site without having to find another empty site, through a forward-backward shift. In practice, empty transient sites created in this way would reduce the waiting time for subsequent Na hops.

This mechanism is exemplified in the traces of the MD trajectory in Fig. 9: Besides the Ca ion (cyan) mentioned above, two Na ions (yellow) highlighted by dark arrows also appear to move “aside” to create a transient passage for the diffusive Na at the center (red) before returning to their initial positions. A transient site can thus be created by a temporary shift of either another Na or of a Ca ion. The latter possibility, in particular, could be related to the higher selectivity of Ca ions for their environment, discussed before, which may prevent an ion to find a matching new site, thus prompting it to return to the original site whenever possible. On the other hand, Na ions can easily be accommodated in Ca sites so they can use both Na and Ca sites for migrating in the bulk. This supports the idea that, in these compositions, mixing with the less mobile Ca ions does not necessarily hinder Na migration, which can occasionally proceed through temporary displacement of Ca ions.

E. Relationship between ion coordination and mobility

Because the migration of a modifier cation in the static silicate matrix involves a change in its coordination, during the move to a new site, where at least a fraction of the coordinated oxygen atoms has been replaced, the cation will have to temporarily either reduce or increase its coordination number. In principle both mechanisms are possible. In order to shed light on this issue, we have focused on two distinct subsets of “diffusive” Na ions, which had the highest MSDs, and “nondiffusive” Na ions, which essentially remained in
their initial sites for the whole length of the simulation, and calculated specific radial distribution function for each sub-set, plotted in Fig. 10. The comparison should allow us to identify how the coordination affects the diffusive behavior of Na ions. Nondiffusive (Na\textsuperscript{ND}) ions have on average 7.1 oxygen atoms in their coordination shell, whereas the Na–O coordination number decreases to 6.2 for diffusive (Na\textsuperscript{D}) ones: In other words, Na\textsuperscript{ND} and Na\textsuperscript{D} are characterized by a higher and lower than average oxygen coordination number, respectively. This supports the mechanism in which the coordination of an Na cation temporarily decreases during a jump from a site to another; note that if the Na-NBO coordination, rather than Na–O, was considered, the coordination numbers would be 4.9 and 4.5 for nondiffusive and diffusive Na, respectively.

Direct inspection of the trajectories of diffusive Na ions confirms this finding: Fig. 11 shows that the number of O coordinated to the migrating Na cation decreases from six (initial state A) to four (state B), before increasing to six again (C). Three (one) Na–O links are broken (formed) in the A→B interchange; the B→C process, on the other hand, involves breaking two Na–O links and forming four new ones. These interchanges obviously require that some of the oxygen atoms in the initial coordination polyhedron are retained in the new shell, that is, some O are common to the initial and final coordination shells of a Na ion: In particular, A and B share three oxygens, B and C share two, whereas A and C only share one. The sharing of oxygen atoms is clearly an important way to reduce the number of Na–O links to be broken and therefore the energy cost involved in the elementary migration events.\textsuperscript{15} This suggests again that direct long-range jumps, where an ion reaches a completely new coordination shell, are less likely, and long-range diffusion must occur by subsequent smaller jumps where the coordination shell is only partially renewed.\textsuperscript{6}

Another interesting effect also emerges from Fig. 10: Whereas the number of Ca neighbors of diffusive and nondiffusive Na is not significantly different, on average a higher number of sodium atoms (4.6 versus 3.5) is found close to Na\textsuperscript{D} than to Na\textsuperscript{ND}. This further confirms the role of Na–Na correlations in triggering Na migration, likely through the coordinated jumps discussed before.

F. Hopping statistics

In order to analyze the migration process of sodium atoms in a more quantitative way, we have examined the hopping statistics in the individual trajectory of each Na ion. A jump can be defined as the dynamical event in which the identity of most of the oxygen atoms coordinated to a Na ion changes.\textsuperscript{15} When the coordination shell of an ion changes, an
event \( j \) is recorded: We record the time of the event \( t_j \), the identity of all oxygen atoms forming the new shell, and the coordinates of the Na ion in the new site. In order to assign event \( j \) to a jump, two conditions must be fulfilled:

(i) in order to check that the ion had left its previous site, the length of the jump, measured as the distance between the current \( j \) and previous \( (j-1) \) site coordinates, must be larger than a threshold, which is taken equal to the first minimum in the van Hove self-correlation function (Fig. 5).

(ii) in order to verify that the ion has jumped forward, and not back to the site \( j-2 \) whence it came from, the new coordination shell \( j \) must be different not only from the previous \((j-1)\) site, but also from the site \( j-2 \), visited before \( j-1 \).

If only condition (i) was verified, but not (ii), because the new coordination shell matched the one visited just before the previous, then a backward jump (recrossing) was recorded, rather than a forward jump. A caveat exists for the definition, namely that one must arbitrarily select the extent of the change in the coordination shell required to assign the ion to a new site. Given a specified matching fraction \( f_m \), we record a forward jump when the identity of the oxygen atoms in the new \( j \) shell differs by more than \( f_m \% \) with respect to the oxygen atoms in \((j-1)\) and \((j-2)\) shells, and a backward jump when the new shell differs by more than \( f_m \% \) from \((j-1)\), but also matches shell \((j-2)\) by the same fraction. Table I lists the average features of jump and recrossing events of sodium for three different values of \( f_m \). By comparison to a direct check of the trajectory, which allows one to roughly identify (through a very tedious and time-consuming visual inspection) the number of diffusive events performed by selected atoms, it turns out that the \( f_m = 1 \) case corresponds to an exceedingly coarse-grained description of the dynamics. Figure 12 shows the projection in the \( xy \) plane of the trajectory of a sodium atom, with arrows denoting the main jumps identified by the algorithm. Whereas the algorithm with \( f_m = 1 \) successfully locates the main sites visited during the observation time, it also misses some important excursions to neighbor sites, which do contribute to the migration mechanism. Using \( f_m = 0.75 \), a more detailed description of the actual trajectory is obtained, including a few jumps which escaped detection using \( f_m = 1 \).

In practice, using \( f_m = 1 \) one separates the dynamics into forward jumps (almost no backward jumps are found with this matching fraction) which occur on a longer time scale (approximately 26 ps elapse between two consecutive forward jumps), compared to what actually seems to be the mechanism in action (see also Sec. III C), involving a combination of shorter forward and backward jumps. Therefore, a more consistent description is obtained by setting \( f_m = 0.75 \) (bottom panel of Fig. 12): The diffusion parameters in Table I denote in fact shorter (2.9 ± 0.3 Å on average, roughly matching the first peak of \( G_{Na}(r,t) \) for \( t > 10 \) ps) and more frequent (on average every 11 ps) jumps, with significant backward correlations. A further decrease of \( f_m \) to

---

**Table I. Jump and recrossing statistics for Na ions.** \( f_m \) is the matching fraction (see text), \( N_j \), \( \tau \), and \( N_s \) are the average number of jumps per ion, the mean jump length, the mean jump duration, and the average number of shared oxygen atoms. The last column \( p_r \) is the recrossing probability, calculated as \( N_r/(N_r+N_j) \).

<table>
<thead>
<tr>
<th>( f_m )</th>
<th>( N_j )</th>
<th>( \tau ) ( (\text{Å}) )</th>
<th>( \tau ) ( (\text{ps}) )</th>
<th>( N_s )</th>
<th>( N_r )</th>
<th>( \tau ) ( (\text{Å}) )</th>
<th>( \tau ) ( (\text{ps}) )</th>
<th>( N_s )</th>
<th>( p_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>3.8(2)</td>
<td>3.6(0.5)</td>
<td>26(15)</td>
<td>0</td>
<td>0.2(0.5)</td>
<td>3.1(0.2)</td>
<td>5.7(3.5)</td>
<td>⋯</td>
<td>0.05</td>
</tr>
<tr>
<td>0.75</td>
<td>6.5(4)</td>
<td>2.9(0.3)</td>
<td>11(7)</td>
<td>1(0.1)</td>
<td>4.4(4.8)</td>
<td>2.6(0.4)</td>
<td>7(5.5)</td>
<td>1(0.1)</td>
<td>0.40</td>
</tr>
<tr>
<td>0.50</td>
<td>8.3(5)</td>
<td>2.2(0.07)</td>
<td>10(9)</td>
<td>2.7(0.3)</td>
<td>14.1(7.7)</td>
<td>2.2(0.03)</td>
<td>5.5(3.4)</td>
<td>2.7(0.3)</td>
<td>0.63</td>
</tr>
</tbody>
</table>

**Figure 12.** Projection in the \( xy \) plane of the trajectory of a sodium cation (black continuous line). The elementary forward (backward) jumps are shown as green (red) arrows, for the analysis performed with matching fraction \( f_m = 0.75 \) and \( f_m = 1 \).
0.5 tends to overestimate the number of jumps per ion, with an average jump length of 2.2 Å which is now inconsistent with \( G_r(r,t) \).

Despite the strong dependence on the \( f_m \) parameter, the data in Table I allow us to confirm that, for Na, an averaged description of the diffusive process involves elementary steps with \( l=2.9\pm0.3 \text{ Å} \) and \( \tau=11\pm7 \text{ ps} \); whereas the mean hopping length confirms that diffusion of mobile ions mainly proceeds along nearest-neighbor sites, the relatively broad distribution of hopping times reflects the heterogeneity of the dynamics.

If we consider the additional diffusion parameters produced by the analysis with \( f_m=0.75 \), the initial and final coordination shells share approximately one oxygen, on average. The backward jumps are always faster compared to forward jumps, as it would be expected for an activated process when the product state is not rapidly thermalized, but also for a temporary displacement to a metastable position, discussed above. The probability \( p_f \) that a forward jump is followed by a backward jump, reported in the last column of Table I, confirms that backward correlations of Na ions are an important feature of this glass composition, with a 0.40 probability. This is higher than the statistical probability \( p_f^{\text{stat}} \) given by the inverse number of mobile nearest neighbors to sodium, which yields \( p_f^{\text{stat}}=0.14–0.22 \), depending on whether the less mobile calcium ions are counted or not. Enhanced backward correlations in mixed-alkali silicate glasses have been associated to inefficient relaxation, for instance after a jump into a mismatching site, besides this mechanism, Na atoms temporarily moving to “interstitial” positions before returning to their original site also contribute to an increased \( p_f \).

**IV. CONCLUSIONS**

The present simulations have concerned the elementary steps characterizing ion migration in a mixed alkali-alkaline earth glass composition of high practical relevance, but not well understood at a fundamental level. In particular, we have focused on the sodium migration mechanism and on the role played by the less mobile calcium ions in the same process.

Notwithstanding the highly heterogeneous dynamics of these systems, which entails a distribution of hopping events with different features, one can still describe the migration process through the information extracted from extensive space-and-time averaging of the MD trajectory, as long as the results obtained by a combination of different tools are employed, and carefully checked for consistency. In this work, a thorough analysis was based on radial distribution functions, MSDs and van Hove correlation functions, as well as an algorithm to decompose the trajectory in terms of individual hops.

The emerging picture of Na migration in this composition shares some features with single- and mixed-alkali glasses, but introduces some important differences, related to the low-silica fraction and to the significant fraction of calcium. As for alkali-silicate glasses, ion migration in this glass can be described as a hopping process, where the ion moves in rapid, discrete jumps between sites previously vacated by another ion. Na jumps appear strongly correlated with the displacement of other Na, and filling of Ca sites by Na cations is also an important process, although slower than Na–Na. Ca–Ca dynamical correlations appear less relevant for this system. Na is thus able to use both Na and Ca sites for migrating: We have linked this effect to the less selective nature of Na ions regarding the number and type of oxygen atoms in their coordination shell, compared to Ca.

Na migration can be assisted by correlated forward-backward motion of another ion (either Na or Ca), which creates a transient empty site by moving to an intermediate position and then returns to its original site after the passage of the migrating ion. We propose that the high fragmentation of the silicate matrix in the present compositions can promote this mechanism, by stabilizing temporary sites with interstitial (rather than vacancy) character, through local distortion of the network which is not as favorable in the more rigid matrix of higher-silica glasses.

The analysis also shows that the sodium diffusive process involves undercoordinated intermediate Na species, with a lower than average Na–O coordination number. The number of favorable Na–O interactions to be lost, and the corresponding energetic cost to form the intermediate, are reduced if the initial and final coordination shell share oxygen atoms. While the absence of direct long-range jumps confirms that oxygens are indeed shared, detailed analysis shows that only one oxygen is common to the initial and final shell, on average: In other words, sodium transport in this glass occurs along corner-sharing coordination polyhedra. This could also reflect the low stability of edge- or face-sharing coordination polyhedra.

The transport of sodium to the glass surface and its release are key steps leading to the biological activity of this composition; calcium release, needed for the later stages of interfacial bonding, takes place only after most Na ions have been released. Therefore, the Na:Ca ratio and their mutual interaction play a central role in the properties of these glasses related to the ionic solubility. In general, mixing with the heavier and much less mobile Ca ions could be expected to slow down Na migration because Ca ions would occupy sodium sites and partially block the Na migration pathways. Whereas this picture seems to fit to higher-silica compositions, the present simulations suggest that a different situation may arise in low-silica bioactive glasses. Here, the low site selectivity of Na and the high flexibility of the glass network (compared to the more rigid higher-silica glasses) allow sodium to move through Ca (as well as Na) sites, temporarily vacated by the hosted cation: Therefore the sodium mobility may not be negatively affected by the mixing with Ca. Further models of different compositions are needed to assess how this effect depends on the Na:Ca ratio; this kind of insight could be very useful in order to control the transport properties of these glasses and to achieve release rate of active ions tailored to specific applications.

**ACKNOWLEDGMENTS**

The author would like to thank the U.K.’s Royal Society for the award of an University Research Fellowship, and
52. In the present algorithm, when an ion returns to its original site after visiting a neighbor one, the residence in the original site is restarted from zero, and we do not allow the possibility that an ion leaves a site without visiting another one, which would require the residence in the original site not being interrupted (Ref. 6).