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Complete Identification of Alkali Sites in Ion Conducting Lithium Silicate Glasses: A Computer Study of Ion Dynamics

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The available sites for ions in a typical disordered ionic conductor are determined. For this purpose we devised a straightforward algorithm which via cluster analysis identifies these sites from long time ionic trajectories below the glass transition. This is exemplified for a lithium silicate glass $(Li_2O)_x(SiO_2)_{(1-x)}$ for $x = 0.5$ and $x = 0.1$. We find for both concentrations that the number of sites is only slightly bigger than the number of ions. This result suggests a theoretical description of the dynamics in terms of mobile vacancies as most appropriate. Furthermore, identification of the ionic sites allows one to obtain detailed characteristics of the ionic motion, e.g., quantification of correlated forward-backward jumps.

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Ion conducting glasses have been investigated by various experimental methods, including extended x-ray absorption fine structure [1,2], NMR [3–5], and conductivity spectroscopy [6,7]. Whereas quite detailed information about the local structure has become available, the mechanism of dynamics is still under debate although consensus has been reached that ion dynamics can be described as jumps of the mobile ions [8–10]. Whereas some authors stress the relevance of the disordered energy landscape [9,11] supplied by the network, others relate the complexity of ion dynamics to the Coulomb interaction among mobile ions [6]. Furthermore, it has been argued from structural considerations that the distribution of alkali ions is inhomogeneous [12].

For a closer understanding of ion dynamics microscopic information as supplied by molecular dynamics (MD) simulations is highly welcome. Jund *et al.* [13] found preferential pathways as a dynamical phenomenon by counting the number of different alkali ions that passed through subvolumes of the simulation box. The resulting subvolumes visited by the largest number of different alkali ions may be interpreted as fast areas. They form a network of conduction paths. Oviedo and Sanz have argued on a qualitative basis that for alkali concentrations lower than 10% the alkali ions are always surrounded by nonbridging oxygens (NBOs) despite the overall small number of NBOs [14]. This implies that new NBOs are formed via breaking of Si-O bonds along the alkali trajectory. In contrast, for higher concentrations hopping dynamics between so-called microchannels is proposed such that no formation of new NBOs would be necessary. Horbach *et al.* [15] showed in simulations of $(Na_2O)2(SiO_2)$ that the coherent intermediate scattering function of sodium relaxes only on the same time scale as those of the network species, proving the existence of stable alkali sites below the glass transition. Cormack *et al.* [16] have recently investigated the mechanism of sodium migration in simulations of $(Na_2O)_{0.25}(SiO_2)_{0.75}$ glasses, observing a few sequences of jumps between selected sites. He interpreted the resulting dynamics as the motion of vacancies and pointed out that the identification of *all* sites in the glass, empty or populated at a given time, would be most useful for obtaining a deeper understanding of the kinetic mechanisms.

Determination of all alkali sites in the silicate network is the purpose of this work. These sites can be defined as any regions in the network where alkali ions stay. They must correspond to local minima of the potential energy for the ions. Thus determination of the ionic sites is equivalent to determining the effective energy landscape experienced by the ions. The potential energy involves the network contribution as well as the averaged interaction with other ions.

We analyze lithium silicate glasses $(Li_2O)_x(SiO_2)_{(1-x)}$ with $x = 0.5$ and $x = 0.1$ which are common model systems for computer investigations of ion dynamics. The system size has been chosen such that for $x = 0.5$ we have 384 lithium ions and for $x = 0.1$ we have 80 lithium ions. Simulations are performed in the NVT ensemble at temperatures 640 and 920 K and simulation box lengths 22.96 and 25.28 Å, respectively. The resulting densities match experimental values [17]. The temperatures have been chosen such that the lithium diffusion constants in both systems have similar values. We use a pair potential developed by Habasaki [18]. Previous studies with this potential have shown good agreement with experimental results for static and dynamic quantities [19–21]. The molecular dynamics simulations are performed with a modified version of Moldy [22]. Since both temperatures are below the respective glass transition temperatures, we proceed in two steps. We start from a configuration which was first equilibrated just above the glass transition. It is then propagated at the selected temperature for ca. 20 ns in the NVT ensemble until the lithium subsystem is equilibrated. Afterwards we perform a production run for approximately 50 ns.

During this run, positions of all particles are recorded every 0.1 ps. More details about the simulations can be found in [21]. We checked the validity of our results for independent data of up to 10 ns duration. This time is long enough for the lithium dynamics to become diffusive, so that just the dynamics relevant for ionic transport is included.

In Fig. 1 we report the mean square displacement of oxygen and lithium. The dynamics of the lithium ions becomes diffusive for $t_{\mathrm{diff}} \approx 1$ ns for $x = 0.5$ and $t_{\mathrm{diff}} \approx 10$ ns for $x = 0.1$, as obtained from longer simulations. Evidently, the oxygen ions are localized on the ns time scale. The network of silicon and oxygen atoms and, with this, the lithium sites can therefore be considered as static. As a consequence, the ionic sites are basically unmodified during our run. Interestingly, as shown recently [23,24] the remaining local fluctuations of the network are nevertheless essential in promoting the ionic jumps.

Based on the lithium trajectories we have devised a straightforward algorithm to identify ionic sites. As a basic idea we let the ions decide via their dynamics where good sites are rather than determining the potential energy, as done, e.g., in [25]. First the simulation box is divided into cubic cells with size approximately $(0.3\ \text{Å})^3$. They are small enough to enable resolution of the shape of the ionic sites. During our MD run we count how many time steps a cell is visited by a lithium ion. The cells with nonzero counts describe the portion of the system that has been visited by lithium ions. These cells include the lithium sites as well as the connecting paths between them. To identify the ionic sites and to eliminate the paths between the sites, cells with less than a minimum value M of counts are dismissed. With the remaining cells a cluster analysis is performed. Cells which share a face are grouped into one cluster. Cells that are not directly or indirectly connected over common faces form different clusters. The value of M has been determined by the condition that the number of distinct ionic clusters be a maximum. For a smaller threshold some lower populated clusters would not have been detected, and for a larger threshold distinct clusters would be connected to single clusters because the transition path would be included. With M chosen according to this condition, 2.9% and 1.3% of all cells are included for $x = 0.5$ and $x = 0.1$, which contain $\approx 90\%$ of all lithium positions in both cases. The precise value of M is of no relevance for the latter analysis.

For $x = 0.5$ and $x = 0.1$, respectively, 378 and 76 clusters are found. The result is illustrated in Fig. 2, showing a snapshot of a slice through each system. The silicate network is shown as tubes, with silicon bright and oxygens dark. Lithium ions are depicted as large spheres. The white objects are the clusters obtained from the analysis described above, with each small white sphere representing one of the cells. It can be seen that the clusters are, in fact, discrete objects of compact shape. Most of the lithium ions reside inside one of these clusters, and most of the clusters are occupied by exactly one lithium ion. As

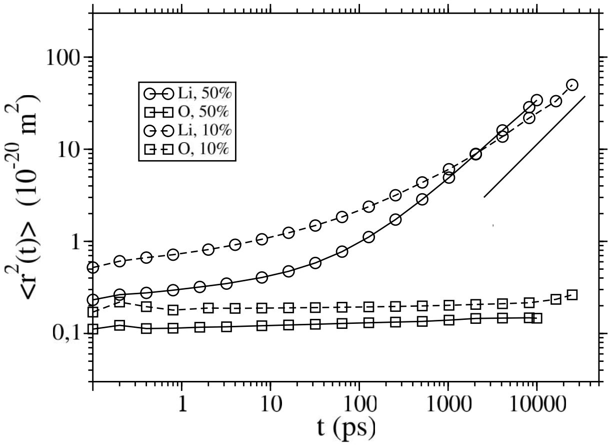

FIG. 1. Mean square displacements of lithium and oxygen in the simulations. Included is a line with slope 1.

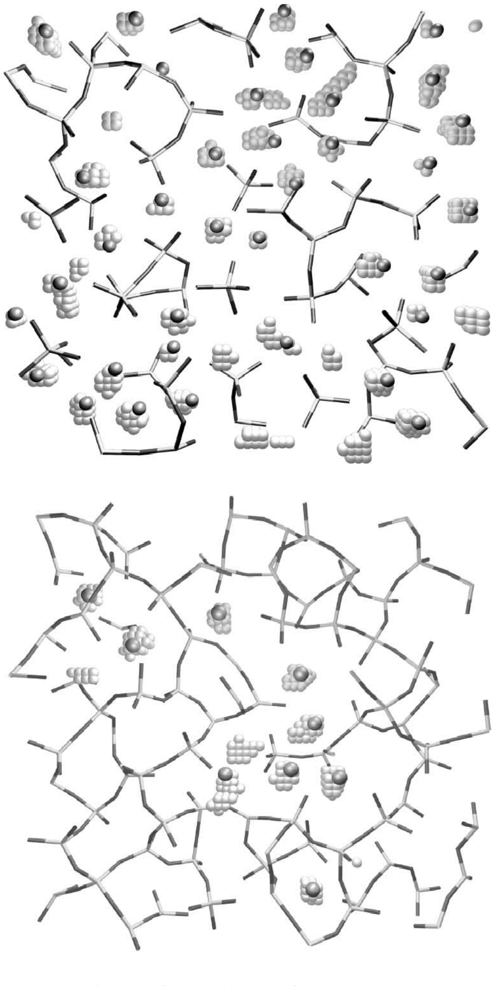

FIG. 2. Rendering of a slice of the simulation box for $(\mathrm{Li_2O})_x(\mathrm{SiO_2})_{1-x}$ with $x = 0.5$ (top) and $x = 0.1$ (bottom), together with clusters of cells with high average lithium occupation. (Created with the software vmd [26].)

will be quantified further below some clusters can accommodate up to three lithium ions.

For $x = 0.5$ ($x = 0.1$) in total 29 (14) additional small clusters have been excluded. They are set apart by a conspicuous drop in the effective radius plot; see Fig. 3. Detailed analysis characterized most of them as simple satellites of bigger clusters. The remaining ones serve as short-lived saddlelike states during transitions between bigger clusters. The small clusters thus need not be considered as sites themselves.

On the basis of the clusters, the dynamics of a lithium ion can be expressed as successive residences in clusters separated by shorter time intervals where the lithium ion is outside any cluster. When a lithium ion leaves one cluster and moves into a different one, this sequence of events is recorded as a jump. In contrast, if an ion explores part of the volume outside a cluster without entering a second one and comes back to the original cluster, it is regarded as occupying the same cluster during the whole time. Consequently, the residence time of a lithium ion in a cluster is defined as the time between its jump into this cluster and the subsequent jump to another cluster. With this definition on average a lithium ion in the system with $x = 0.5$ belongs to a cluster at 99.5% of all times. The remaining 0.5% correspond to jumps between different sites. For $x = 0.1$, the portion of times corresponding to jumps is 1.1%. The typical distance traveled by the lithium ions during a jump coincides well with the first maximum of the radial distribution function of the clusters in both cases. For $x = 0.5$, 93% of all jumps are inside the first neighbor shell (94% for $x = 0.1$) as defined by the first minimum of the radial distribution function. Thus the ion dynamics can be described as jumps between adjacent clusters.

Having defined the residence times, the mean number of lithium ions occupying each cluster can easily be evaluated. It is plotted in Fig. 3 for $x = 0.5$, with the clusters ordered from left to right by decreasing volume V [the effective radius $r_{\mathrm{eff}} \equiv (3V/4\pi)^{1/3}$ of the individual clusters is plotted in the inset]. The occupation data confirm the impression gained from Fig. 2. For most clusters the value is close to unity. These clusters are occupied by a single ion during the largest part of the simulation. Their effective radius $r_{\mathrm{eff}} \approx 0.6$ Å is very similar. Only the largest clusters offer space for more than one lithium ion; i.e., they contain more than one site, and often they are indeed multiply occupied.

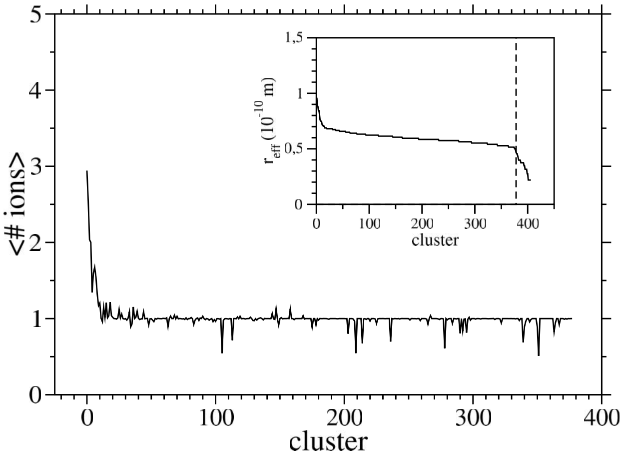

FIG. 3. Mean occupation of clusters. Inset: effective radius $r_{\mathrm{eff}} \equiv (3V/4\pi)^{1/3}$ of clusters, including the small clusters excluded from further analysis (see text).

Generally an empty site must be available for a jump of a lithium ion. The total number of sites can now be estimated from the occupation data in Fig. 3. For the larger clusters with cluster index <19 we have taken the next higher integer number to estimate the number of available sites. In this way we find three clusters with three sites and nine clusters with two sites. Starting from cluster index 14 one finds a few clusters with occupation number $1 + \epsilon$ with $\epsilon < 0.2$. Here it would be rather unphysical to attribute two sites to this cluster. Rather a more detailed analysis of explicit ion trajectories has revealed the following scenario. At most time instances a single ion stayed in this cluster. During the short times during which this ion explored the immediate neighborhood of this cluster without entering a new cluster (typical excursion length scales are 2 Å from the center of the cluster) a second ion may briefly enter this cluster and immediately leave this cluster again. Thus one may either say that these clusters contain only a single site or, to be more conservative with respect to finding an upper bound of the total number of sites, attribute $1 + \epsilon$ sites to this cluster. With the latter variant we obtain 395 sites for our 384 lithium ions. Analogously, 86 sites were found for the 80 ions for $x = 0.1$. These results shed new light on the mechanism of ion dynamics. Rather than speaking of individual ions jumping between accessible sites, it is more appropriate to speak to first approximation of vacancy dynamics, i.e., the dynamics of the noninteracting unoccupied sites in the energy landscape.

Actually, Dyre [27] has recently suggested this type of scenario based on general reasoning. He relates the possible near equality of sites and ions to the effect that during network formation at the glass transition only a minimum number of sites will be formed due to energetic reasons. This scenario is also compatible with the counterion model, proposed by Dieterich and co-workers [28], but is at variance with single-particle approaches.

In the remaining part of this Letter we characterize the ion dynamics in terms of the individual clusters. Figure 4 shows the cumulative distribution function $S(\tau)$ of residence times. Thus $S(\tau)$ denotes the fraction of clusters with an average residence time less than τ. Its median τ_{median}, defined by $S(\tau_{\mathrm{median}}) = 0.5$, is close to 1 ns for $x = 0.5$ and 250 ps for $x = 0.1$. These numbers have to be compared with the median of the transition time for a

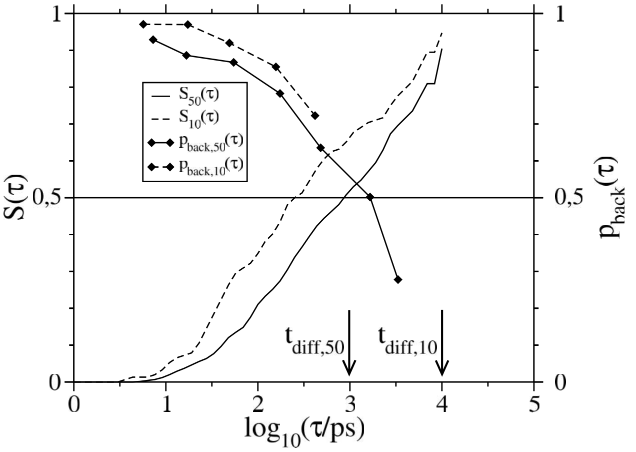

FIG. 4. Cumulative distribution function $S(\tau)$ of residence times and time dependence of the back-jump probability $p_{\text{back}}(\tau)$ for systems with $x = 0.5$ and $x = 0.1$. Arrows mark the times at which the diffusive regime is reached.

jump between two clusters, which is 500 fs for $x = 0.5$ and 200 fs for $x = 0.1$. This dramatic time scale separation clearly justifies the hopping picture in this kind of materials, as known from previous simulations [29]. The lithium dynamics on long time scales can thus be mapped to jumps between the clusters. The generally higher frequency and lower duration of jumps at $x = 0.1$ can be traced to the higher temperature that was chosen for this system to achieve similar diffusivities.

The effectiveness of jumps for diffusive transport is strongly decreased by correlated forward-backward motion. We determined the probability p_{back} that a jump from a cluster A to another cluster B is followed by a direct backjump to the cluster A. The result is also shown in Fig. 4. One can clearly see that clusters with short residence times show a stronger tendency for a correlated forward-backward jump. For the fastest clusters, p_{back} reaches more than 0.9, which is several times higher than the statistical value given by the inverse number of nearest neighbors ($\approx 0.2 \ldots 0.3$). The difference in $p_{\text{back}}(\tau_{\text{median}})$, which is ≈ 0.8 for $x = 0.1$ compared to ≈ 0.55 for $x = 0.5$, may explain why the former system becomes diffusive only after most ions have performed several jumps, as shown by the ratio $\tau_{\text{median}}/t_{\text{diff}} \gg 1$. In contrast, one finds $\tau_{\text{median}}/t_{\text{diff}} \approx 1$ for $x = 0.5$, meaning that only half of the ions have jumped at least once at the onset of diffusion. The dispersive regime at shorter times is thus dominated by the fastest lithium ions.

Beyond the results shown in Fig. 4, a detailed analysis of the dynamics, i.e., in terms of cooperativity, becomes feasible. Our approach may easily be generalized to more complex systems, and important questions concerning, e.g., the character and the lifetime of the individual sites, may be analyzed.

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