Channel diffusion of sodium in a silicate glass

Philippe Jund, Walter Kob, and Rémi Jullien
Laboratoire des Verres - Université Montpellier 2
Place E. Bataillon Case 069, 34095 Montpellier France
(June 11, 2001)

Abstract

We use classical molecular dynamics simulations to study the dynamics of sodium atoms in amorphous Na$_2$O-4SiO$_2$. We find that the sodium trajectories form a well connected network of pockets and channels. Inside these channels the motion of the atoms is not cooperative but rather given by independent thermally activated hops of individual atoms between the pockets. By determining the probability that an atom returns to a given starting site, we show that such events are not important for the dynamics of this system.

PACS numbers: 61.20.Ja, 61.43.Fs, 66.30.Hs
The question of ionic transport in glasses has been the topic of research for quite some time since it is linked to important transport phenomena such as electrical conductivity, ion exchange, or aqueous corrosion [1–3]. Obviously the general problem of the motion of the ions inside the glass is complex due to the inherent structural disorder of the amorphous matrix. Consequently the nature of the dynamics on short length scales, i.e. the local motion of the ions, as well as the one on large scales, i.e. the global properties of the trajectories, is understood only poorly. Concerning the local motion of the ions, models based on a “forward-backward hopping mechanism” [4] or hopping processes over random potential barriers [5] have been proposed. Furthermore it has been suggested that the combination of the disorder and the long-ranged Coulomb interactions between the ions gives rise to a strong backward correlation of the motion and is the reason for the Non-Debye behavior observed in the dielectric response of a variety of materials [6]. Regarding the dynamics on large scales, a picture based on “preferential pathways” proposed some ten years ago [7] is quite popular [8]. In that direction, recent molecular-dynamics simulations of silica glasses with different concentrations of sodium [9] have given some support to the ideas put forward by Greaves that “the clustering of alkalis in oxide glasses marks out the pathways for ionic diffusion” [10] if the concentration of alkalis is higher than a percolation limit composition. However, as stated by the authors of Ref. [9]: “these suggestions are, as yet, unconfirmed”. In this paper we therefore present the results of a classical molecular-dynamics simulation of Na$_2$O-4SiO$_2$ [NS4]. In particular we investigate in detail the dynamics of the alkali ions on short as well as long length scales to check the validity of some of the ideas described above.

Our system consists of $N_{Na}=86$ sodium, 173 silicon and 389 oxygen atoms confined in a cubic box of edge length $L = 20.88$ Å, which corresponds to the experimental value of the density (2.38 g/cm$^3$) [11]. The interaction between the ions is given by a modified version [12] of the potential proposed by Kramer et al. [13]. The potential $U(r_{ij})$ between two particles $i$ and $j$ includes a Coulombic part, and a short range part and is given by

$$U(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6} + \frac{\tilde{q}_i \tilde{q}_j e^2}{r_{ij}} [1 - (1 - \delta_{iNa})(1 - \delta_{jNa})] \Theta(r_c - r_{ij}) \quad (1)$$

with $q_{Si} = \tilde{q}_{Si} = 2.4$, $q_{O} = \tilde{q}_{O} = -1.2$, $q_{Na} = 0.6$ and $\tilde{q}_{Na} = 0.6 \ln [C (r_c - r_{ij})^2 + 1]$ ($\Theta$ is the usual Heaviside function). More details and in particular the values of the parameters can be found in Ref. [12]. In previous studies of the mixtures Na$_2$O-2SiO$_2$ [NS2] and Na$_2$O-3SiO$_2$ [NS3], this potential has been shown to reproduce reliably many structural and dynamic properties of sodium silicate melts [12]. Therefore it can be expected that it is also able to describe the salient features of the microscopic dynamics of the present system.

After having equilibrated the liquid at 4000K for 50000 time steps (35ps) we have cooled the system to 300K, with a linear cooling schedule at a quench rate of $2.3 \times 10^{14}$ Ks$^{-1}$. During this quenching process we have saved the configurations (positions and velocities) at several temperatures ($T = 4000, 3000, 2500, 2000, 1500$ and 300 K), and subsequently used them as starting configurations of production runs of 1 million steps (with a time step of 1.4 fs), giving thus for each temperature a total production time of 1.4 ns. Similarly to a previous study on pure silica [14] a plot of the potential energy vs $T$ shows a change of slope around 2400 K which gives a rough estimate of the glass transition temperature in our system. In order to improve the statistics we have used, at 2000 K and 1500 K, three and
two independent samples, respectively.

We first study the properties of the Na-trajectories at long times. In Ref. [12] it was shown that, for NS2 and NS3, the diffusion constant for the sodium atoms is around two orders of magnitude higher than the one of the silicon and oxygen atoms, if $T \leq 2500 K$. Hence it was concluded, in qualitative agreement with experiment, that the sodium atoms are diffusing inside a frozen matrix of $\text{SiO}_2$. Although the atoms of this matrix vibrate around an equilibrium position they do not show a structural relaxation on the time scale of many ns. In the present work we therefore study the details of the dynamics of the Na atoms through this frozen matrix. For this we investigate the space dependence of the distribution of the number density of the sodium atoms. To determine this distribution we divided the simulation box in $N_{\text{tot}} = 20^3$ distinct cubes (hence each has a volume of $\approx 1 \, \text{Å}^3$) and determined the number density of the sodium atoms in each of these small boxes. Thus this discrete distribution is a coarse grained approximation to the continuous one, the latter one being not accessible in a simulation. By varying the size of this mesh between 0.5 Å and 2 Å we made sure that the results obtained do not depend qualitatively on this size.

In Fig. 1 we show those boxes which have been visited by at least $\xi = 11$ different Na atoms during a 1.4ns run at 2000 K (grey spheres). The number of these boxes represents approximately 10% of all the boxes visited by at least one sodium atom. Therefore these spheres line out that region of space in which relatively many different sodium atoms passed. (Note that it is important to consider only different Na atoms; else one might also take into account regions in which one sodium atom just oscillates around its equilibrium position.) From this figure we recognize immediately that most of the Na-motion occurs in a relatively small subset ($\approx 6\%$) of the total available space, i.e. that their trajectories do not fill the space uniformly. This subset is itself composed of several blobs which are connected to each other by rather loose structures. These pockets have a typical size of around 3–6 Å, but also larger ones can be found. This size has to be compared with the typical cage which is seen by a sodium atom on the time scale of the $\beta-$relaxation and which is on the order of 1 Å [12]. Hence we conclude that these pockets are somewhat larger than the size of the local cages in which the atoms rattle back and forth at short times. The distance between these pockets is typically 5–8 Å, which has to be compared with the typical distance between two sodium atoms (3.4 Å, see Fig. 4 below) and an experimental estimate for this quantity (1–2 Å) [13]. (Note that this estimate has been obtained by using a very crude model, under the “strong electrolyte assumption” i.e. all the charge carriers are mobile, and neglecting cross correlations between the ions. If some of the assumptions of this model are changed slightly, an estimate for the distance of 5 Å is obtained [13], in reasonable good agreement with the value found here). In order to check for finite size effects, we analyzed a NS3 sample containing 8192 atoms and found basically the same characteristic dimensions of the blobs and connecting structures. We also mention that from Fig. 1 we see that these pockets are relatively well connected, which, as we will show below, is also reflected in the dynamics of the sodium atoms.

Note that the result presented in Fig. 1 is typical in the sense that other samples show a qualitatively similar distribution of the density, although of course all the details are different. Hence we confirm the idea proposed earlier [2] that the trajectories of the sodium atoms lie in channels that go through the $\text{SiO}_2$ matrix. We emphasize, however, that the structure that we see in Fig. 1 is a “dynamic” one in the sense that it can only be found by
averaging over the trajectories of all the Na atoms and over a sufficiently long time. This is thus in contrast to a static picture in which at any instant the sodium atoms form some sort of percolating cluster. Therefore a typical single snapshot of all the sodium atoms in the system, like the one presented in Fig. 2, does not show any significant indication for the presence of these channels. We also mention that we find a strong correlation between the location of these pockets and the location of the non-bridging oxygen (NBO) atoms, which thus relates these pockets to the structure of the silica matrix. When comparing the mean square displacement of the NBOs with the one of the bridging oxygens, we find that they are very similar and therefore that all the oxygen atoms are in an almost frozen state at 2000K.

Also shown in Fig. 1 are the trajectories of two sodium atoms (black spheres: the most mobile Na atom; white spheres: an arbitrary Na atom chosen at random). From these trajectories we see that individual atoms explore a substantial fraction of the channels. Hence we conclude that the structure seen in the figure is not just an agglomerate of the trajectory of many different atoms, but that most atoms visit a large fraction of this structure.

The above chosen value of $\xi = 11$ used to define the channels is somewhat arbitrary in that decreasing or increasing $\xi$ will make the channels broader or thinner, respectively. Furthermore it is clear that if one increases sufficiently the time over which the density distribution is measured, at the end the Na atoms will have visited all the boxes at least a few times, since even energetically very unfavorable configurations will have a non-zero Boltzmann weight. Thus if one wants to investigate the properties of the channels in more detail it is necessary to determine where they have the largest Boltzmann weight, since this will correspond to their core. This can be done as follows: For every time $t$ we measure $n_i(t)$, the number of different sodium atoms that have visited box $i$ in the time $t$ since the start of the production run. Using $n_i(t)$ we therefore can define for every time $t$ a distribution $P(k)$, which is the number of boxes that have been visited exactly $k$ times. (Note that for short times the maximum of $P(k)$ is at $k = 0$, since most of the boxes have not been visited at all). We now search for the boxes with high $n_i(t)$ i.e. those who have been visited most frequently and hence contribute to the tail of $P(k)$. For this we define the quantity $\xi(t)$ as the largest integer such that the sum $N(t) = \sum_{k=\xi(t)}^{\infty} P(k)$ is at least 10% of the total sum, i.e. of $\sum_{k=1}^{\infty} P(k)$ (with this definition, one recovers the value of $\xi = 11$ used in Fig. 1). Hence the boxes whose value of $n_i(t)$ is larger than $\xi(t)$ will be at the core of the channels and therefore can be used to study them in more detail.

Equipped with these definitions we can now investigate the important question of how the structure of the channels depends on time, i.e. whether with time the sodium atoms explore more and more space in the matrix (by finding new pockets or pathways between pockets) or whether after a relatively short time they have explored most of the available space. To address this point, we define $N_c(t)$ which is the number of different boxes that have been (at any time) at the core of the channels (as defined above) after a time $t$ since the beginning of the simulation. In Fig. 3 we show how the fraction $N_c(t)/N_{tot}$ evolves with increasing time for different temperatures. At very short times ($t < 10\text{ps}$) this fraction increases rapidly with $t$. Then this increase slows down and we see that for $T = 1500 \text{ K}$ the curve becomes relatively flat for times larger than around 50ps (a closer examination of the curve in this time regime shows that $N_c(t)$ increases logarithmically in $t$), which shows that at this temperature the channels are independent of time. Although at $T = 2000 \text{ K}$, the increase of $N_c(t)/N_{tot}$ after
50ps is more important, the channels fill nevertheless only 17% of the total available volume after 1.4ns. Therefore we conclude that at sufficiently low temperatures the structure of the channels is practically independent of time. We note a clear change of behavior for the curves obtained at higher temperatures \((T \geq 2500 \text{ K})\) both for the fraction of space visited after 1.4ns (55% at 4000 K) as well as for the increase at long time. This indicates that at these temperatures it is no longer reasonable to refer to channels since the sodium atoms can explore more and more new boxes as a consequence of the diffusing motion of the Si and O matrix atoms. A special case is the curve for \(T = 300 \text{ K}\): For this low temperature the curve is still rising even at the end of the 1.4ns run. This indicates that the sodium atoms have not yet managed to explore the whole network of channels in this time. We have found that also this increase is proportional to \(\log(t)\), with the same prefactor of the logarithm as the one found for the curve at \(T = 1500 \text{ K}\) at long times. This shows that the mechanism how the sodium atoms explore the network is, at long times, independent of \(T\), if the temperature is sufficiently low. Hence we conclude that the results studied here should also be valid in the temperature range and time range probed in real experiments. Note that this slow exploration of the network immediately rationalizes the experimental observation that the diffusion of the ions at low temperatures is anomalous and that the conductivity shows a dispersion.

So far we have shown that at low \(T\) the sodium atoms diffuse within a sub-space of the total available space. Of interest is also how the Na atoms move inside these channels. One possibility to address this point is to investigate the distinct part of the van Hove function defined by \[G_{d}^{\text{NaNa}}(r, t) = \left(L^3 / 4\pi r^2 N_{\text{Na}}^2\right) \sum_{i=1}^{N_{\text{Na}}} \sum_{j=1}^{N_{\text{Na}}} \langle \delta(r - |r_i(t) - r_j(0)|) \rangle. \tag{2}\]

Thus, e.g., if at time \(t = 0\) there is a sodium atom at the origin, the function \(G_{d}^{\text{NaNa}}(r = 0, t)\) is proportional to the probability to find at time \(t\) a different sodium atom at the origin. For \(t = 0\) this function is proportional to the usual radial distribution function \(g_{\text{NaNa}}(r)\). In Fig. 4 we show \(G_{d}^{\text{NaNa}}(r, t)\) for various times. We see that with increasing time the correlation hole at \(r = 0\) is quickly filled up and that a large peak grows at this distance. The height of this peak attains a maximum after a time \(\tau_{\text{max}}\) and then decreases again. Hence we conclude that once a sodium particle has moved from its location it had at \(t = 0\), there is a very high probability that a different Na atom will take up its place and that this probability is highest after the time \(\tau_{\text{max}}(T)\). In the inset of Fig. 4 we show \(G_{d}^{\text{NaNa}}(r, \tau_{\text{max}}(T))\) for different temperatures and we recognize that the maximum height of the peak increases quickly with decreasing temperature. This increase shows that with decreasing \(T\) the matrix becomes more and more rigid and hence maintains the memory of the locations of the sodium atoms, even if they have moved away since a long time. The time \(\tau_{\text{max}}\) shows an Arrhenius dependence with an activation energy around 1.3 eV. This value is very well in line with those found in the study of the diffusion coefficient of NS2 (0.93 eV) and NS3 (1.26 eV) \[12\]. The results shown in Fig. 4 indicate that the sodium atoms move by thermally activated jumps between sites previously occupied by other sodium atoms, in agreement with the proposition of Greaves and Ngai \[2\]. We emphasize, however, that \(\tau_{\text{max}}(T)\) is not the time that an atom takes between a jump from one site to a neighbor site, which thus is related
to the diffusion constant, but the time it takes until a site that has been freed is occupied by a new Na atom (which is not necessarily a nearest neighbor).

Note, however, that this result does not necessarily imply that the motion of the sodium atoms is collective. To investigate this point we have calculated how the distance between two sodium atoms changes with time. If the motion of the atoms is collective, it can be expected that the increase of this distance $\Delta(t, \delta_0)$ is slower if $\delta_0$, the initial separation between the two atoms, is small, than if $\delta_0$ is large. In Fig. 5 we show the time dependence of $\Delta^2(t, \delta_0)$ for sodium pairs that at time zero were nearest, next nearest, or third nearest neighbors (bottom to top). (For this classification we used the radial distribution function shown in Fig. 4.) From this figure we recognize that all three curves converge to the long time limit $L^2/4$ with the same time constant. Thus since there is no dependence on $\delta_0$ we conclude that the motion of the atoms is not cooperative, in contrast to what has been suggested in the literature [8] and in agreement with (indirect) experimental evidence [15].

In view of the fact that the snapshot in Fig. 1 shows that each pocket has several connections (pathways) to other pockets, such a quick decorrelation is, a posteriori, not surprising [18].

We also note that the decay of the correlation can be approximated well by an exponential function with a time constant $\tau_\Delta$ independent of $\delta_0$. In the inset of Fig. 5 we plot $\Delta^2(t, \delta_0)$ for the first neighbor shell, for all temperatures investigated, versus $t/\tau_\Delta(T)$. Since, within the accuracy of the data, at low $T$ these curves collapse onto a master curve, we conclude that the mechanism for the decorrelation, and hence the motion, is independent of $T$. Finally we mention, that also $\tau_\Delta(T)$ shows an Arrhenius dependence with an activation energy around 1.3 eV, in agreement with the other time scales of the sodium motion.

Certain models of the sodium dynamics assume that after a jump of an atom, there is an enhanced probability that it jumps back to its original site [4]. Therefore we have calculated the probability that a sodium atom that was at the origin at time zero, moves for $t > 0$ over a distance which is larger than the beginning of its first nearest neighbor shell (2 Å, determined from $g_{NaNa}(r)$) and then back to its original site. We have found that the maximum value for this probability is, at 2000K, around 26%. This value has to be compared with the “trivial” one which is obtained if one considers that in this system each sodium atom has around 5 other sodium atoms as nearest neighbors, thus giving a probability to jump back of 1/5=20%. Hence we conclude that the atoms do not show a significant trend to jump back (backward correlations), at least not in the temperature range studied here.

In summary we have shown that at low temperatures the long time trajectories of the sodium atoms in the silica matrix occupy only a relatively small fraction of the total space. This subset forms a well connected network of channels and pockets which is explored very quickly by each sodium atom. We emphasize that from individual snapshots the existence of these channels can hardly be seen [16], at least for the sodium concentration studied here, which is in contrast to the popular picture proposed by Greaves [10]. The motion inside these channels is not cooperative since nearby atoms decorrelate quickly and this is also in distinction to common belief. Furthermore we find that in this system the “forward-backward jumps” are not important. However, it cannot be excluded that at higher concentrations of sodium such a mechanism becomes relevant.

Part of the numerical calculations were done at CINES in Montpellier.
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[18] Note that the connectivity between the pockets is even higher than suggested in Fig. 1, since due to the periodic boundary conditions not all connections can directly be seen.
FIG. 1. Snapshot of the simulation box. The grey spheres represent the regions where at least seven different sodium atoms have passed during a 1.4 ns run at 2000 K. The black and white spheres show the trajectory of two individual sodium atoms.

FIG. 2. Single snapshot of the positions of the Na atoms in the simulation box along the x-direction (similar snapshots are obtained along the y and z directions) after 700 ps at 2000 K.
FIG. 3. Time dependence of the fraction of cubes in the core (see text for definition) of the channels for different temperatures.

FIG. 4. Plot of the distinct part of the van Hove function at 2000K for $t = 0$ (solid bold), 7ps (long dashed), 28ps (dotted), 70ps (dot-dashed), 105ps (dashed), and 140ps (thin solid). Inset: $G_d^{NaNa}(r, \tau_{\text{max}}(T))$ at different temperatures, where $\tau_{\text{max}}(T)$ corresponds to the time for which $G_d^{NaNa}(0, t)$ is maximum.
FIG. 5. Time dependence of \( \Delta^2(t, \delta_0) \), the squared distance between two sodium atoms that at time zero were separated by a distance \( \delta_0 \), at \( T=2000K \). The three curves correspond to \( \delta_0 \) in the first, second, third nearest neighbor shell (bottom to top). Inset: \( \Delta(t, \delta_0) \) for the first nearest neighbor shell, at different temperatures, versus rescaled time.