

## Numerical investigation of ionic transport in glasses: the example of sodium in amorphous silica

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S1659

(<http://iopscience.iop.org/0953-8984/15/16/313>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 08:46

Please note that [terms and conditions apply](#).

# Numerical investigation of ionic transport in glasses: the example of sodium in amorphous silica

Emmanuel Sunyer<sup>1</sup>, Philippe Jund<sup>2</sup> and Rémi Jullien<sup>1</sup>

<sup>1</sup> Laboratoire des Verres—Université Montpellier 2, Place E. Bataillon, Case 069, 34095 Montpellier, France

<sup>2</sup> Laboratoire de Physicochimie de la Matière Condensée—Université Montpellier 2, Place E. Bataillon, Case 003, 34095 Montpellier, France

Received 26 March 2003

Published 14 April 2003

Online at [stacks.iop.org/JPhysCM/15/S1659](http://stacks.iop.org/JPhysCM/15/S1659)

## Abstract

We use classical molecular dynamics simulations to study the motion of sodium atoms in amorphous  $\text{Na}_2\text{O}-4\text{SiO}_2$  over a wide range of temperatures below and above the glass transition temperature  $T_g$ . We find that the region of space most visited by the sodium atoms forms a network of connected pockets that we call channels. These channels are strongly correlated with the locations of the non-bridging oxygens of the matrix and give rise to a pre-peak in the structure factor. In order to understand the physical origin of the channels we have studied the characteristics of the sodium atoms INSIDE and OUTSIDE the channels. We show that neither the potential energy nor the local environment permit us to distinguish between IN and OUT atoms. Nevertheless, our results indicate that the channels correspond to regions of higher sodium density compared to the rest of the system. Finally, as expected, we show that the mean square displacement of the sodium atoms inside the channels is significantly larger than that of the sodium atoms outside.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

It is of great importance to have a precise knowledge about the mechanisms governing the motion of ions in glasses since these transport phenomena intervene in a wide range of important physical processes, such as ion exchange, electrical and thermal conductivity, and aqueous corrosion [1–3]. Such an investigation is considerably more difficult than for regular crystals since the disorder of the glassy matrix intervenes both at short length scales (in the local motion of the ions) and at large length scales (in the global properties of the trajectories). Concerning the local motion, several models have been proposed based, for example, on a ‘forward–backward hopping mechanism’ [4] or hopping processes over random potential barriers [5]. In addition, it has been suggested that a combination of the disorder and the long-ranged Coulomb interactions between the ions gives rise to a strong backward correlation during their

motion, leading to non-Debye behaviour as observed in the dielectric response of a variety of materials [6]. Concerning the dynamics on large scales, a picture based on ‘preferential pathways’ proposed some ten years ago [7] is now generally accepted [8]. In the same spirit, recent molecular dynamics (MD) 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, 11] if the concentration of alkalis is higher than a percolation threshold.

In order to shed some light on this problem, in this paper we give a review of results obtained via MD simulations on the sodium–silicate glass  $\text{Na}_2\text{O}-4\text{SiO}_2$  (NS4). Using an adequate extension [12] of the realistic BKS potential [13] we have thoroughly analysed the dynamics of the alkali ions on short length scales as well as the properties of the trajectories at long times (2.8 ns). We have found that the ions move preferentially through a disordered network of connected pockets that we call channels [15, 16]. However, contrary to the ideas of Greaves, these channels are not due to a microsegregation of the sodium atoms but instead define a region of space most visited by uncorrelated sodium atoms during a given time. Like other authors [14], we find that the existence of these channels is reflected by a pre-peak in the structure factor at  $q = 0.95 \text{ \AA}^{-1}$  which has recently been observed experimentally [18]. We have found a strong correlation between these channels and the location of the non-bridging oxygen (NBO) atoms [19], supporting the idea that the channels are entirely defined by the underlying matrix [9, 17]. Moreover, in order to better understand the physical origin of the channels, we have analysed the characteristics of the sodium atoms according to whether they are INSIDE the channels ( $\text{Na}_{\text{In}}$ ) or OUTSIDE the channels ( $\text{Na}_{\text{Out}}$ ) [19]. By analysing the potential energy and the local pair distribution functions, we conclude that neither the potential energy nor the local environment permit us to distinguish between IN and OUT sodium atoms. We have also calculated the sodium atom density and found that it is larger inside the channels, as recently suggested [17]. Moreover, to elucidate the diffusion mechanism of the sodium atoms, we have determined a characteristic ‘residence’ time inside the channels which is shown to follow an Arrhenius temperature dependence with an activation energy slightly larger than that of all other activated processes present in the system. Finally, we have calculated the mean square displacements and found that they are significantly larger for sodium atoms inside the channels.

## 2. Simulations

We used a cubic box of edge length  $L = 20.88 \text{ \AA}$  containing  $N_{\text{Na}} = 86$  sodium, 173 silicon, and 389 oxygen atoms in order to reproduce the experimental value of the NS4 density ( $2.38 \text{ g cm}^{-3}$ ) [20]. To obtain the initial liquid configuration we considered a crystal of  $\beta$ -cristobalite in which we randomly replaced the correct number of  $\text{SiO}_4$  tetrahedra by  $\text{Na}_2\text{O}_3$  ‘molecules’ to recover the NS4 stoichiometry and melted it at 4000 K. The liquid was then left at this temperature for 70 ps (i.e. 50 000 MD steps of 1.4 fs each) in the microcanonical ensemble ( $(N, V, E) = \text{constant}$ ), a time long enough to generate a well equilibrated liquid. As stated earlier, the interaction between the ions is described by a modified version [14] of the potential proposed in [12] which is a generalization of the so-called BKS potential [13] for pure silica. This two-body potential  $U$ , which includes a coulombic part (treated by the Ewald summation method [21]) and a short-range part of the Buckingham type, has the following form:

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

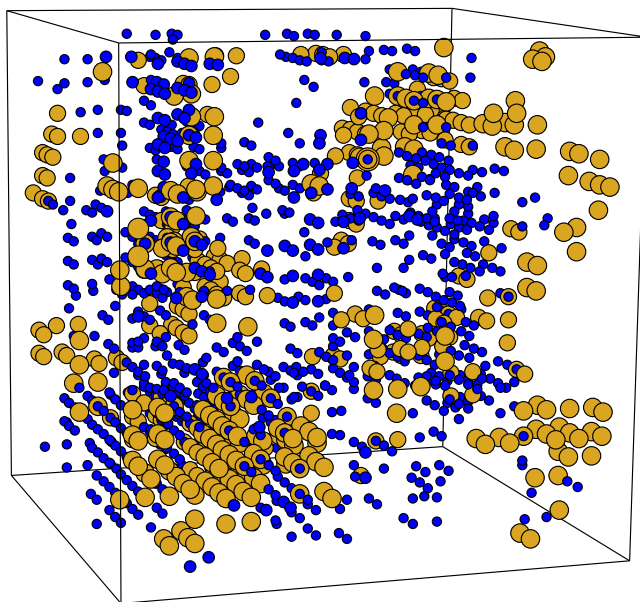
where  $\Theta$  is the usual Heaviside function and  $q_{\text{Si}} = \tilde{q}_{\text{Si}} = 2.4$ ,  $q_{\text{O}} = \tilde{q}_{\text{O}} = -1.2$ ,  $q_{\text{Na}} = 0.6$ , and  $\tilde{q}_{\text{Na}} = 0.6 \ln[C(r_c - r_{ij})^2 + 1]$ . More details, including the values for these particular parameters, can be found in [16]. In previous studies of the mixtures  $\text{Na}_2\text{O}-2\text{SiO}_2$  (NS2) and  $\text{Na}_2\text{O}-3\text{SiO}_2$  (NS3), this potential was shown to reliably reproduce many structural and dynamical properties of sodium–silicate melts [14–16]. It is therefore expected to be able to describe the salient features of the microscopic dynamics of the present system.

After equilibrating the liquid at 4000 K, we cooled it to 300 K using a linear cooling procedure with a quench rate of  $2.3 \times 10^{14} \text{ K s}^{-1}$ . During this quenching process we saved the configurations (positions and velocities) at several temperatures ( $T = 4000, 3100, 2700, 2300, 1900, 1700 \text{ K}$ ) and subsequently used them as starting configurations for production runs of 2.8 ns (i.e. two million MD steps). In order to improve the statistics, we generated at each temperature three independent samples.

### 3. Evidence for channel diffusion of the sodium atoms

Since it has already been shown [14] that the diffusion constant for the sodium atoms is considerably larger (by about two orders of magnitude) than that for the oxygen or silicon atoms in the analogous but more concentrated systems NS2 and NS3, it can be assumed that the sodium atoms in NS4 diffuse inside a quasi-frozen  $\text{SiO}_2$  matrix at sufficiently low temperatures. Although the atoms of this matrix vibrate around equilibrium positions, they do not show a substantial structural relaxation on the timescale of a few nanoseconds. To determine the preferential pathways of the sodium atoms through the matrix we have followed their trajectories. We divided the simulation box into  $N_{\text{tot}} = 20^3$  distinct cubes (each with the same volume of  $\approx 1 \text{ \AA}^3$ ) and determined the number density of sodium atoms in each of these small cubes as a function of time. This discrete distribution is thus a coarse-grained approximation to a continuous one but we have made sure, by varying the mesh dimensions, that the results obtained do not depend qualitatively on our choice of cube size.

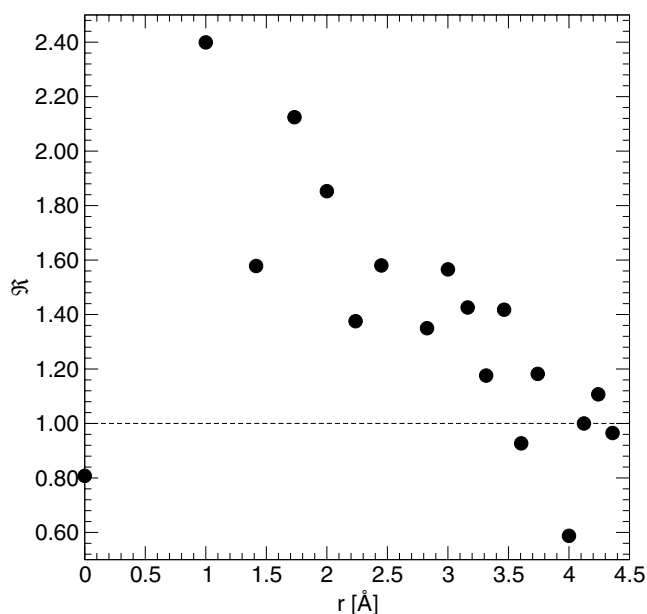
In figure 1 we show by large grey spheres those cubes which have been visited by at least  $\xi = 11$  *different* Na atoms during a 1.4 ns run at 2000 K. The number of these cubes represents the upper 10% of all cubes visited by at least one sodium atom. Therefore the grey spheres outline that region of space through which relatively many *different* sodium atoms pass (note that it is important to consider only different Na atoms to avoid taking 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 atom motion occurs in a relatively small subset ( $\approx 6\%$ ) of the total available space; i.e. that the Na atom trajectories do not uniformly fill the space. This subset is itself composed of several blobs or pockets which are connected to each other by rather loose structures. These pockets have a typical size of around 3–6  $\text{\AA}$ , although larger ones can also be found. This size has to be compared with the typical cage size seen by a sodium atom on the timescale of the  $\beta$ -relaxation which is of the order of 2–3  $\text{\AA}$  [14]. Hence we conclude that these pockets are comparable in size to the local cages in which the atoms rattle back and forth at short times. The distance between these pockets is typically 5–8  $\text{\AA}$ , which compares with a typical distance between two sodium atoms of about 3.4  $\text{\AA}$  (estimated from MD simulations [19]) and with a hopping distance of 1–2  $\text{\AA}$  (this distance has been estimated from experiment using the assumptions that all ions are mobile (strong electrolyte) and that the Haven ratio equals one [23]). We also mention that from figure 1 we can see that these pockets are relatively well connected and, as we will show below, this is reflected in the dynamics of the sodium atoms. We have checked that other samples show a qualitatively similar spatial distribution, although the details are of course different. Furthermore, we have checked that when defining the channels over a



**Figure 1.** A snapshot of the simulation box. The grey spheres represent the regions where at least eleven different sodium atoms have passed during a 1.4 ns run at 2000 K. The black spheres indicate the regions where, during the same time, at least three different non-bridging oxygen atoms have passed.

different simulation time (in particular 2.8 ns which is the time over which the results of the next section have been calculated), their characteristics (mean pocket size and mean distance between pockets) are almost the same as when they are defined as being the 10% of boxes most visited by different sodium atoms. Only the threshold value  $\xi$  defined above depends on the simulation time (it is roughly proportional to it). Hence we confirm the idea proposed earlier [7] that the trajectories of the sodium atoms lie in channels that go through the  $\text{SiO}_2$  matrix. We emphasize, however, that the percolating structure that we see in figure 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 by contrast with a *static* picture in which at *any* instant the sodium atoms form some sort of percolating cluster [5]. In figure 1 we also show the locations of the non-bridging oxygens by black spheres. More precisely, the black spheres indicate the cubes that have been visited by more than three different non-bridging oxygens during the simulation time. One can see in this figure a spatial correlation between the grey and black spheres.

In order to be more quantitative, we have calculated, for a given distance  $r$  between two cube centres (which can only be a discrete number: 0, 1,  $\sqrt{2}$ ,  $\sqrt{3}$ , 2, ... times the individual cube edge length  $\delta = 1.044 \text{ \AA}$ ), the number  $\aleph(r)$  of grey-black distances effectively seen in figure 1. After averaging over three independent runs, the quantity  $\langle \aleph(r) \rangle$  has been divided by its value for  $N_{\text{Na}}$  grey cubes and  $N_{\text{NBO}}$  black cubes randomly chosen (without exclusion); that is,  $\aleph_{\text{ran}}(r) = N_{\text{Na}} N_{\text{NBO}} n_{\text{d}(r)} / N_{\text{tot}}$  where  $n_{\text{d}(r)}$  is the ‘degeneracy’ of the distance  $r$ , i.e. the number of independent realizations of this distance from a given cube (1 for  $r = 0$ , 6 for  $r = \delta$ , 12 for  $r = \delta\sqrt{2}$ , 8 for  $r = \delta\sqrt{3}$  ...). In figure 2 the ratio  $\aleph(r) = \langle \aleph(r) \rangle / \aleph_{\text{ran}}(r)$  has been plotted as a function of  $r$ . The fact that this ratio is significantly larger than unity for distances between 1 and 2  $\text{\AA}$  indicates that there are strong short-range correlations between

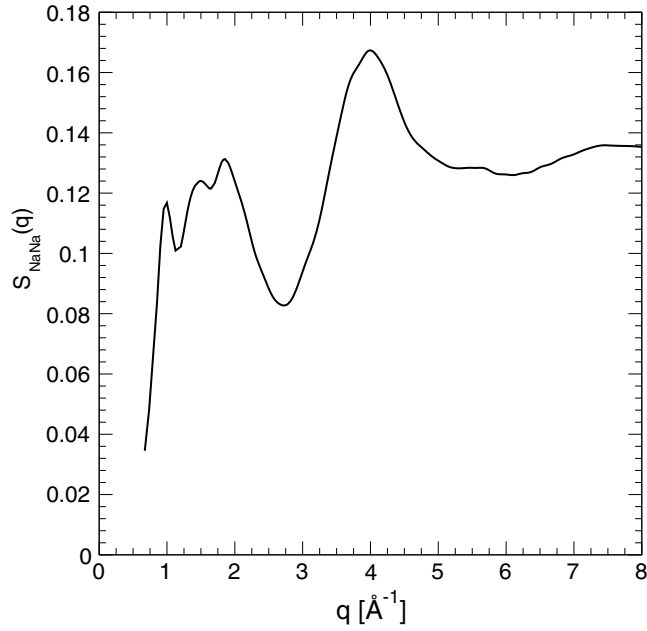


**Figure 2.** A plot of  $\mathfrak{R}(r)$  which gives a quantitative measure of the spatial correlation between cubes defining the channels and cubes containing the NBOs, normalized by the result obtained for randomly chosen cubes (see the text for a definition).

the positions of the cubes defining the channels and the cubes containing the NBOs. Since the matrix is not totally frozen at 2000 K, the Na atoms moving inside the channels and some NBO atoms can visit the same cube during the length of the simulation: this explains why  $\mathfrak{R}(0) \neq 0$ . Note, however, that  $\mathfrak{R}(0)$  is smaller than  $\mathfrak{R}(\delta)$  indicating that the maximum correlation could occur for distances smaller than or close to 1 Å. The existence of this maximum at a non-zero  $r$ -value indicates that the NBOs are probably located on the border of the pockets defining the sodium diffusion channels. Quantitative evidence for such a correlation between the location of the NBOs and the location of the pockets confirms the idea that the channels are closely related to the structure of the silica matrix [9, 19].

In figure 3 we show the sodium–sodium atom partial structure factor obtained from our simulation. As already found for the NS2 and NS3 systems [14, 17], the structure factor exhibits a pre-peak at about  $q_{\max} = 0.95 \text{ \AA}^{-1}$  which corresponds in real space to the characteristic distance between pockets. This pre-peak has recently been observed experimentally [18]. Moreover, Horbach *et al* [17] have performed similar work using a larger simulation box and have found a pre-peak at about the same position. This result gives more confidence in the existence of channels. In [15] we have shown that the location of the channels remains practically independent of time (over a simulation time of 1.4 ns) for temperatures below 2000 K. It is reasonable to argue that channel diffusion exists only inside the solid glassy phase of the matrix (in that regime where the sodium atoms explore only a fraction of the total available space) whereas in the liquid phase, because of the diffusive motion of the silicon and oxygen atoms themselves, the channels can no longer be defined (the sodium atoms explore the total available space).

So far we have shown that at low  $T$ , the sodium atoms diffuse within a subspace of the total available space. Also of interest is an understanding of how the Na atoms move inside these channels. To address this point we have studied a quantity that we have called  $G_{\text{dB}}^{\text{NaNa}}(t)$  by



**Figure 3.** A plot of the sodium–sodium atom partial structure factor,  $S_{\text{NaNa}}(q)$ , as a function of the modulus  $q$  of the wavevector.

analogy with the distinct part of the van Hove correlation function [15, 22]. It is proportional to the probability of finding a new sodium atom in a small cube at time  $t$  if a different sodium atom was inside the same cube at time  $t = 0$ , and is given by

$$G_{\text{dB}}^{\text{NaNa}}(t) = \frac{N_{\text{tot}}}{N_{\text{Na}}(N_{\text{Na}} - 1)} \sum_{i=1}^{N_{\text{Na}}} \sum_{j=1}^{N_{\text{Na}}} \delta[\mathbf{m}_i(t) - \mathbf{m}_j(0)] \quad (2)$$

where  $\mathbf{m}_i(t)$  is the vector made by the integer coordinates of the small cube containing particle  $i$  at time  $t$ . In figure 4 we show  $G_{\text{dB}}^{\text{NaNa}}(t)$  at different temperatures as a function of time  $t$ . We see that with increasing time the curves for each temperature reach a maximum before decreasing and finally converging towards unity, which is the expected long-time limit. The maximum probability is reached after time  $t = \tau_{\text{max}}(T)$ . In figure 5 we have plotted  $\tau_{\text{max}}$  versus  $1/T$  and one can verify that  $\tau_{\text{max}}$  exhibits an Arrhenius behaviour with an activation energy of about 1.3 eV. This value is consistent with those found for the activation energy of the diffusion coefficient in NS2 (0.93 eV) and NS3 (1.26 eV) [14]. Hence we can conclude that the sodium atoms move by thermally activated jumps between sites previously occupied by other sodium atoms, in agreement with the suggestion of Greaves and Ngai [2]. We emphasize, however, that  $\tau_{\text{max}}(T)$  is *not* the time that an atom takes between jumps from one site to a neighbouring site, which would be related to the diffusion constant, but is the time that it takes for a site that has been freed to be occupied by a new Na atom (which is not necessarily a nearest neighbour).

This result does *not*, however, 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, then it is expected that the increase of this distance,  $\Delta(t, \delta_0)$ , will be slower if the initial separation between the two atoms,  $\delta_0$ , is small rather than large. In figure 6 we show from top to bottom the time

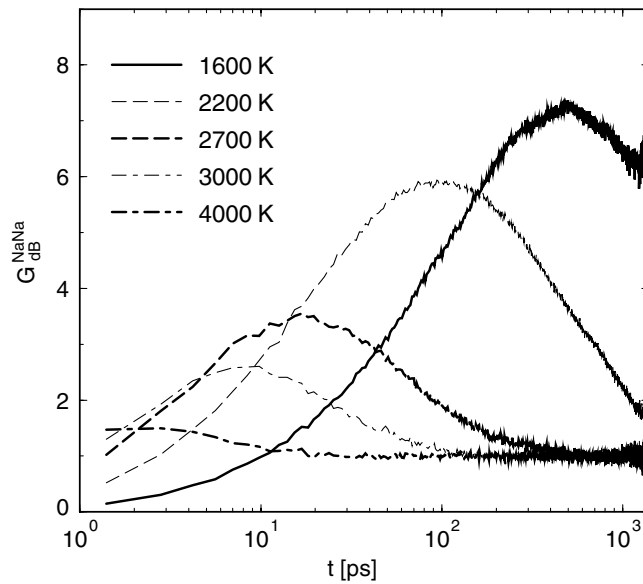


Figure 4. A plot of  $G_{dB}^{NaNa}(t)$  at different temperatures (see the text for a definition).

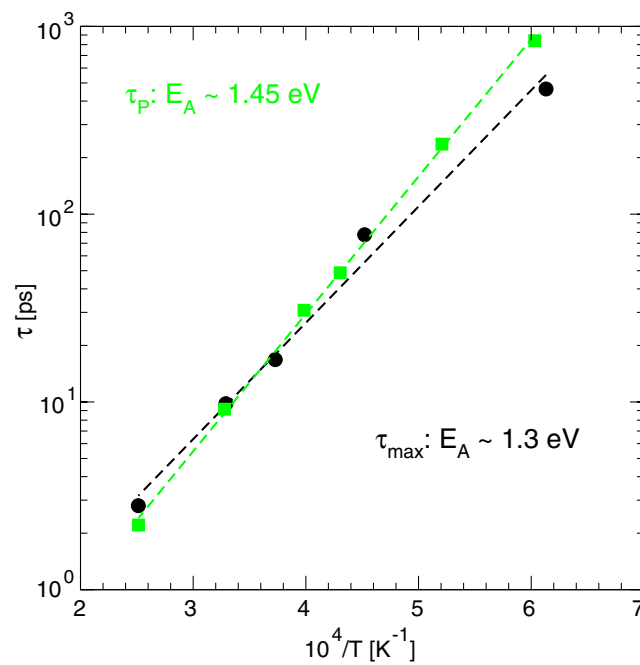
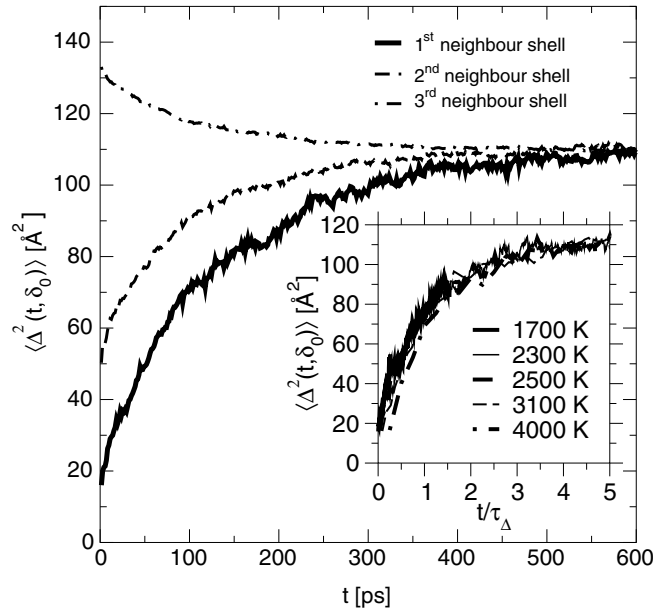


Figure 5. A plot of  $\tau_{max}$ , the location of the maximum of the  $G_{dB}^{NaNa}(t)$  curve, versus  $1/T$ . In the same figure we have also plotted the time constant  $\tau_p(T)$  obtained from an exponential fit of the quantity  $P(0, t)$  represented in figure 8.

dependence of  $\Delta^2(t, \delta_0)$  for sodium pairs that at time zero were nearest, next-nearest, or third-nearest neighbours (the sorting of the atoms is done by examining the radial pair distribution





**Figure 6.** The 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  $T = 2000$  K. The three curves correspond to distances  $\delta_0$  to the first-, second-, or third-nearest-neighbour shell (bottom to top). Inset:  $\Delta^2(t, \delta_0)$  for the first-nearest-neighbour shell, at different temperatures, versus rescaled time.

function  $g_{\text{NaNa}}(r)$ ). From this figure we recognize that all three curves converge towards the long-time limit  $L^2/4$  with the *same* time constant (the same general result is obtained by studying the evolution of the Na–Na distance in ‘real space’, i.e. without taking into account the periodic boundary conditions in which case the squared distance is not bounded by  $L^2/4$ ). Since there is no dependence on  $\delta_0$  we can conclude that the motion of the atoms is *not* cooperative, by contrast to suggestions made in the literature [8]. In view of the fact that the snapshot in figure 1 shows that each pocket has several connections (pathways) to other pockets, such a quick decorrelation is, *a posteriori*, not surprising (note that the connectivity between the pockets is even higher than suggested in figure 1 since all of the connections cannot be seen due to the periodic boundary conditions).

We also note that the decay of the correlations can be well approximated by an exponential function with a time constant  $\tau_\Delta$  independent of  $\delta_0$ . In the inset of figure 6, we plot  $\Delta^2(t, \delta_0)$  for the first-nearest-neighbour shell, for all temperatures investigated, versus  $t/\tau_\Delta(T)$ . Since these curves collapse onto a master curve within the accuracy of the data at low  $T$ , we conclude that the mechanism for the decorrelation, and hence the motion, is independent of  $T$ . Finally we mention that  $\tau_\Delta(T)$  also shows an Arrhenius dependence with an activation energy around 1.3 eV, in agreement with the other timescales for sodium atom motion.

Certain models for the sodium atom dynamics assume that after the jump of an atom there is an enhanced probability for it jumping back to its original site [4]. Therefore we have calculated the probability that a sodium atom in a site at time zero moves, for  $t > 0$ , over a distance which is larger than the beginning of its first-nearest-neighbour shell ( $2 \text{ \AA}$  as determined from  $g_{\text{NaNa}}(r)$ ) and then back to its original site. We found that the maximum value for this probability is around 26% at 2000 K. This result has to be compared with the ‘trivial’ one which is obtained by noting that each sodium atom in NS4 has about five other sodium

atom nearest neighbours, thus giving a probability for jumping back of  $1/5 = 20\%$ . Hence we conclude that the atoms do not show a significant tendency for jumping back (backward correlations), at least not in the temperature range studied here.

#### 4. Differences between sodium atoms inside and outside the channels

Once the channels are defined as being the upper 10% of the cubes visited by different sodium atoms during a given period of time (2.8 ns in what follows), we can go back and distinguish for every time  $t$  those sodium atoms which are inside ( $\text{Na}_{\text{In}}$ ) and those which are outside ( $\text{Na}_{\text{Out}}$ ) the channels and calculate the physical quantities characteristic for each of them.

Our aim in this section is to understand why, at low temperatures, the Na atoms visit more frequently a particular fraction of the total available space (some of the results contained in this section are already published in [19]). The first possible explanation is that the Na atoms visit sites that are more energetically favourable. To check this idea, we have calculated the individual potential energy distributions of the sodium atoms at 1700 K (over 2000 configurations and three samples) when they are inside or outside a channel. We find that there is no significant difference between the distributions for  $\text{Na}_{\text{In}}$  and  $\text{Na}_{\text{Out}}$  since they are both Gaussians centred approximately at  $-3.8$  eV with the same half-width at half-maximum of  $\approx 0.6$  eV. Therefore it appears that the energy is not the driving force for explaining why the Na atoms form channels. Nevertheless, one may argue that the time average can smear out the effect but, as we have shown in section 3, the sodium atoms visit sites previously occupied by other sodium atoms [15, 16] and therefore if these sites were energetically more favourable we should have been able to distinguish them.

Nonetheless, if there exists a structural difference at short range for  $\text{Na}_{\text{In}}$  and  $\text{Na}_{\text{Out}}$ , it would not be detectable in the two distributions, since they reflect the whole environment of the Na atoms, including the long-range arrangement of the surrounding particles. Therefore we decided to analyse the local environment of the sodium atoms (at 1700 K) via the radial pair distribution function and the integrated number of neighbours [19]. The major difference is that a  $\text{Na}_{\text{In}}$  atom is surrounded on average by one more Na neighbour compared to a  $\text{Na}_{\text{Out}}$  atom and this goes together with a decrease in the number of nearest Si neighbours. In contrast, the local oxygen environment remains identical for the sodium atoms inside and outside the channels. Finally, concerning the nearest-neighbour distances to other species, there is no significant change between  $\text{Na}_{\text{In}}$  and  $\text{Na}_{\text{Out}}$  except a slight decrease (0.1 Å) of the  $\text{Na}_{\text{In}}\text{-Na}$  distance compared to the distance between a  $\text{Na}_{\text{Out}}$  and other sodium atoms. Given these results, it is clear that the local structure of the sodium atoms inside and outside the channels is not significantly different enough to explain the existence of the channels.

It appears, nevertheless, from the last paragraph that the  $\text{Na}_{\text{In}}$  atoms have on average more Na neighbours than the  $\text{Na}_{\text{Out}}$  atoms. It is hence justifiable to calculate the sodium density  $\rho_{\text{Na}}$  inside and outside the channels (which is simply  $N_{\text{Na}}^{\text{In}}/V_{\text{chan}}$  or  $N_{\text{Na}}^{\text{Out}}/(V_{\text{vis}} - V_{\text{chan}})$  where  $V_{\text{vis}}$  is the *total* volume visited by the sodium atoms and  $V_{\text{chan}}$  is the volume of the channels) as a function of  $T$ . In figure 7, one can see immediately that the sodium density inside the channels is higher than that outside, particularly at low temperatures (below  $T_g$ ). The channels have been defined as a subspace highly visited by the sodium atoms, but we can now assert that they also form a subspace of *high sodium density*. We emphasize that a higher sodium concentration does not necessarily imply a clustering of alkalis [2, 10, 11, 24, 25]. Actually we have previously shown that no clustering can be observed in a single snapshot of the simulation box [15]. Finally, the fact that the two curves converge towards the limit of uniform density at high temperatures is evidence that channels do not exist when the system is completely melted.

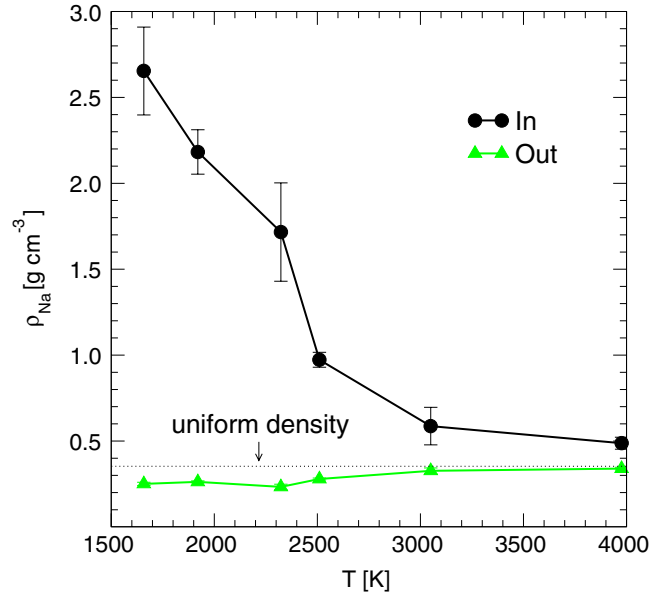


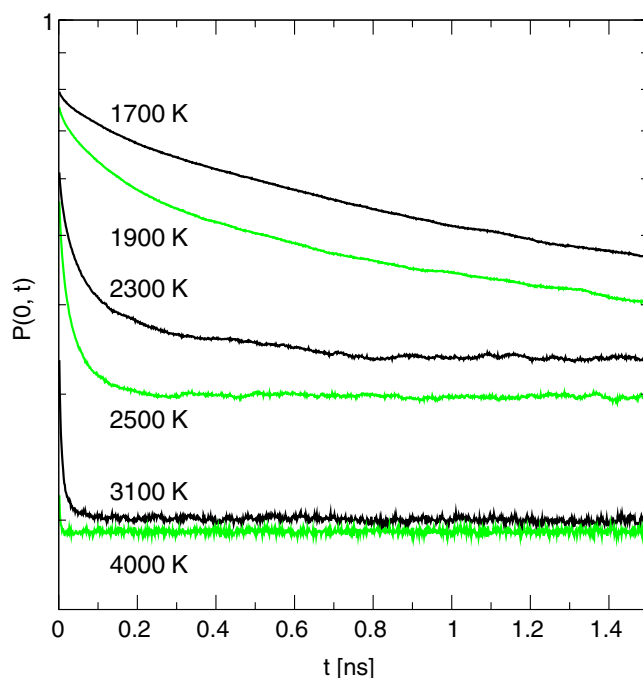
Figure 7. Sodium density  $\rho_{\text{Na}}$  inside and outside the channels versus temperature.

Once we know the position of the Na atoms at every time  $t$  with respect to the channels, it is of great interest to calculate a mean ‘residence’ time of the Na atoms within the channels. This can be done by determining the probability  $P(0, t)$  that a sodium atom inside a channel at  $t = 0$  is still inside a channel after a time  $t$ .  $P(0, t)$  is given by

$$P(0, t) = \frac{1}{N_{\text{Na}}^{\text{In}}(0)} \sum_{i=1}^{N_{\text{Na}}^{\text{In}}(0)} n_i(t), \quad \text{with } n_i = \begin{cases} 0 & \text{outside a channel,} \\ 1 & \text{inside a channel.} \end{cases} \quad (3)$$

This probability is represented in figure 8 at different temperatures. The expected fast decay from unity at shorter times cannot be seen in figure 8 due to the fact that we save the configurations every 1.4 ps (1000 MD steps). But since the channels have been determined with this ‘time step’ we have decided to calculate our probability under the same conditions. Consequently,  $P(0, t)$  is slightly overestimated since we do not take into account the short-time dynamics. In figure 8 we see that  $P(0, t)$  decreases and converges towards the long-time limit  $N_{\text{Na}}^{\text{In}}/N_{\text{Na}}$  very rapidly at high temperatures while at low temperatures ( $T \leq 2300$  K) this limit is not reached until after 1.5 ns. Each of these curves can be fitted reasonably well, after subtracting the asymptotic limit, by an exponential function with a time constant  $\tau_P$ . The  $1/T$  dependence of the latter is shown by a linear–log plot in figure 5 where it is compared with  $\tau_{\text{max}}$  defined earlier. It is remarkable that the typical residence time  $\tau_P(T)$  exhibits an Arrhenius behaviour with an activation energy around 1.45 eV. This value is larger than the activation energy of 1.3 eV found earlier which is characteristic of the diffusive motion of the whole assembly of sodium atoms. This probably indicates that, from an energetic point of view, the mechanism governing the expulsion of Na ions from a channel is more costly than other mechanisms which control the mean displacement of the ions.

Finally, we have decided to quantify the influence of the location of the sodium atoms on their diffusion. Therefore we have calculated the mean square displacements (MSD),  $R_{\text{In/Out}}^2(t) = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ , of the atoms that are *continuously* inside/outside of the channels with a discretization time of 1.4 ps. In figure 9 we see that at low temperatures

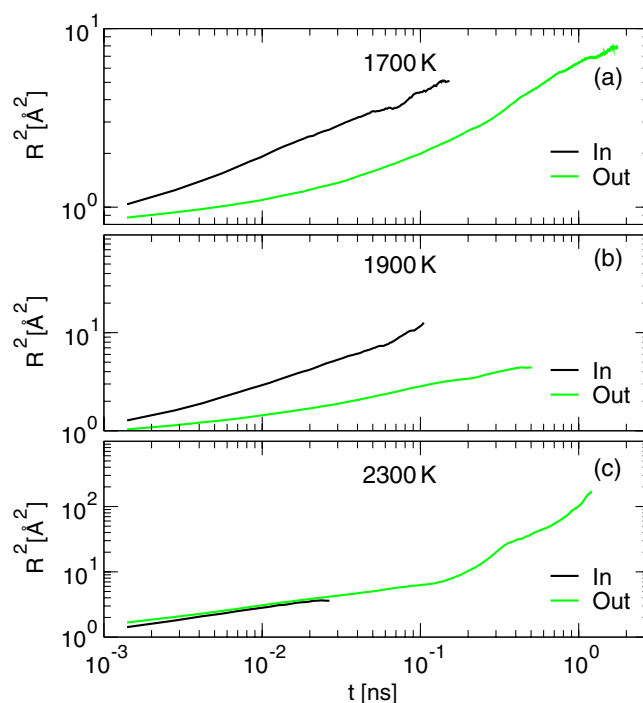


**Figure 8.** The probability  $P(0, t)$  that a sodium atom is inside a channel between time  $t = 0$  and time  $t \neq 0$  for different temperatures.

( $T = 1700, 1900$  K)  $R_{\text{In}}^2$  is always larger than  $R_{\text{Out}}^2$  with a maximum difference after  $\approx 0.1$  ns when  $R_{\text{In}}^2$  is twice as large as  $R_{\text{Out}}^2$ . One can hence assert that the Na atoms are more mobile inside the channels. This result is consistent with the findings of Horbach *et al* [17] who state that the ‘sodium atoms move quickly between preferential sites’ but has never before been directly quantified. On the other hand, no distinction can be seen between the two mean square displacements at  $T = 2300$  K (figure 9(c)). This originates from the fact that when the temperature increases, the channels are no longer static and are less and less well defined (the discrimination between IN and OUT becomes therefore more difficult) such that they no longer influence the diffusion of the Na atoms (this is of course also true at even higher temperatures). We can hence conclude that at low temperatures when static channels are formed, the diffusion coefficient of the sodium atoms is higher when they are inside the channels.

## 5. Conclusions

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 pockets which is explored very quickly by each sodium atom. We emphasize that in individual snapshots the existence of these channels can hardly be seen, at least for the sodium concentration studied here, which is in contrast with the popular picture proposed by Greaves [10, 11]. The motion inside the channels is not cooperative since nearby atoms decorrelate, quickly which is also distinct from common belief. Moreover, we have investigated the properties of the sodium atoms according to whether they are INside or OUTside a channel. We have first shown that, contrary to a naive picture, the distribution of



**Figure 9.**  $R_{\text{in}}^2(t)$  and  $R_{\text{out}}^2(t)$ , the mean square displacements of Na atoms which are continuously inside or outside the channels respectively, at (a) 1700 K, (b) 1900 K, and (c) 2300 K.

the potential energy of the individual  $\text{Na}_{\text{In}}$  atoms does not differ from that of the  $\text{Na}_{\text{Out}}$  atoms. Presumably the existence of the channels has to be looked for more in terms of free energy and may be connected to entropic effects. In fact, it is reasonable to think that the creation of the channels is related to the vibrational characteristics of the  $\text{SiO}_2$  matrix. To address this point it is possible to modify these characteristics and measure their influence on the sodium dynamics, an investigation which is currently under way [26]. In addition, from a study of the environment of the  $\text{Na}_{\text{In}}$  and  $\text{Na}_{\text{Out}}$  atoms, we have found only a slight increase in the Na coordination number for sodium atoms inside the channels which is nevertheless consistent with the fact that at low temperatures ( $T \leq 3000$  K) the concentration of Na atoms is higher inside than outside the channels. This is no longer true at high temperatures since the matrix completely melts and channels no longer exist. In addition, by calculating the probability  $P(0, t)$  that a Na atom is inside a channel between times 0 and  $t$ , we have defined a characteristic residence time inside the channels,  $\tau_P(T)$ , that exhibits an Arrhenius dependence with an activation energy around 1.45 eV. The comparison of this energy with that of the other activated processes present in the system seems to indicate that the mechanism governing the expulsion of Na ions from a channel is energetically more costly than the mechanism for global diffusion of the ions. Finally, we have shown that at low temperatures when the channels are well defined, the Na atoms are more mobile inside the channels than outside and, in this sense, one can really speak about channel diffusion.

### Acknowledgment

Parts of the numerical calculations were done at CINES in Montpellier.

## References

- [1] Day D E 1976 *J. Non-Cryst. Solids* **21** 343  
Jonscher A K 1977 *Nature* **267** 673  
Ingram M D 1987 *Phys. Chem. Glasses* **28** 215  
Maass P, Bunde A and Ingram M D 1992 *Phys. Rev. Lett.* **68** 3064  
Elliott S R 1994 *Solid State Ion.* **70/71** 27
- [2] Greaves G N and Ngai K L 1995 *Phys. Rev. B* **52** 6358
- [3] Sen S, George A M and Stebbins J F 1996 *J. Non-Cryst. Solids* **197** 53  
Funke K and Cramer C 1997 *Curr. Opin. Solid State Mater. Sci.* **2** 483  
Sen S and Stebbins J F 1997 *Phys. Rev. B* **55** 3512
- [4] Funke K and Hoppe R 1990 *Solid State Ion.* **40/41** 200
- [5] Roling B 2000 *Phys. Rev. B* **61** 5993
- [6] Maass P, Petersen J, Bunde A, Dieterich W and Roman H E 1991 *Phys. Rev. Lett.* **66** 52
- [7] Ingram M D 1989 *Phil. Mag.* **60** 729
- [8] Kahnt H 1996 *J. Non-Cryst. Solids* **203** 225 and references therein
- [9] Oviedo J and Sanz J F 1998 *Phys. Rev. B* **58** 9047
- [10] Greaves G N 1985 *J. Non-Cryst. Solids* **71** 203
- [11] Greaves G N 2000 *Mineral. Mag.* **64** 441 and references therein
- [12] Kramer G J, de Man A J M and van Santen R A 1991 *J. Am. Chem. Soc.* **64** 6435
- [13] van Beest B W H, Kramer G J and van Santen R A 1990 *Phys. Rev. Lett.* **64** 1955
- [14] Horbach J, Kob W and Binder K 1999 *Phil. Mag.* **79** 1981  
Horbach J, Kob W and Binder K 2001 *Chem. Geol.* **174** 87
- [15] Jund P, Kob W and Jullien R 2001 *Phys. Rev. B* **54** 134303
- [16] Sunyer E, Jund P, Kob W and Jullien R 2002 *J. Non-Cryst. Solids* **307–310** 939
- [17] Horbach J, Kob W and Binder K 2002 *Phys. Rev. Lett.* **88** 125502
- [18] Meyer A, Schober H and Dingwell D B 2002 *Eur. Phys. Lett.* **59** 708
- [19] Sunyer E, Jund P and Jullien R 2002 *Phys. Rev. B* **65** 214203
- [20] Bansal N and Doremus R 1986 *Handbook of Glass Properties* (London: Academic)
- [21] Allen M P and Tildesley D J 1990 *Computer Simulations of Liquids* (Oxford: Oxford Science Publications)
- [22] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
- [23] Sidebottom D L 1999 *Phys. Rev. Lett.* **83** 983
- [24] Vessal B, Greaves G N, Marten T P, Chadwick A V, Mole R and Houde-Walter S 1992 *Nature* **356** 504
- [25] Huang C and Cormack A N 1993 *J. Chem. Phys.* **93** 8180
- [26] Sunyer E, Jund P and Jullien R 2002 *Preprint cond-mat/0212058*