Matrix-controlled channel diffusion of sodium in amorphous silica

LETTER TO THE EDITOR

Matrix-controlled channel diffusion of sodium in amorphous silica

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Abstract
To find the origin of the diffusion channels observed in sodium silicate glasses,
we have performed classical molecular dynamics simulations of Na_2O–$4SiO_2$
during which the mass of the Si and O atoms has been multiplied by a tuning
coefficient. We observe that the channels disappear and that the diffusive motion
of the sodium atoms vanishes if this coefficient is larger than a threshold value.
Above this threshold the vibrational states of the matrix are not compatible with
those of the sodium ions. We thus interpret the decrease of the diffusion by the
absence of resonance conditions.

The mechanism of ionic transport in amorphous materials [1, 2] at the atomic scale is not
completely elucidated so far and therefore it is the subject of numerous experimental [3, 4] and
numerical [5–9] studies. Among the most studied systems are the sodium silicate glasses since
they contain the essential ingredients, namely the amorphous matrix (silica) and the mobile ions
(sodium), as a first step in the simulation of more complex glasses of greater practical interest.

In previous studies [10–12], we have shown by means of classical molecular dynamics
simulations of Na_2O–$4SiO_2$ (NS4) that the sodium atoms diffuse through a well connected
network of pockets (which represents only a limited fraction of the entire available space), that
we have called 'channels' to be consistent with the literature. The existence of the channels,
which are not due to micro-segregation effects [6, 7], has been confirmed by the existence of
a pre-peak in the partial Na–Na structure factor at a wavevector $q = 0.95$ Å^{-1} [13]. This
pre-peak has also been observed experimentally [14] and numerically [15] in another study.
We have also shown that the location of the channels is strongly correlated to the positions of
the non-bridging oxygens [13] and Horbach *et al* [15] have shown that the sodium dynamics
should be related to that of the underlying silica network. This suggests that the origin of
the channels could be related to the dynamical properties of the matrix. To check this idea

we present in this letter classical molecular dynamics simulations on a series of 'toy' systems in which the atomic masses of both the oxygen and silicon atoms have been systematically changed after artificially multiplying their experimental values by a common factor μ varying from 0.5 to infinity, the usual NS4 system being recovered for $\mu = 1$.

By studying both the mean squared displacement (MSD) of the sodium atoms and the characteristics of the channels, we find a change in the sodium diffusion properties when the parameter μ is increased above a value of about 30. Above this threshold, the sodium diffusion decreases and the channels can no longer be clearly defined. Guided by the concomitant change in the short time characteristics of the velocity autocorrelation function, we have calculated the vibrational density of states (VDOS) for both the sodium atoms and the atoms of the matrix for various values of μ. We observe that the threshold corresponds to the value of μ above which the sharp VDOS of the sodium atoms starts to separate from the band of vibrational states of the matrix. Therefore we propose that the diffusive motion of the sodium atoms, i.e. their ability to escape from their local cage, is facilitated when their vibrational frequencies are compatible with those of the matrix. We argue that this mechanism is responsible for the channel diffusion of sodium in the silica matrix.

In this letter we present classical molecular dynamics calculations of a system of 648 particles (86 sodium, 173 silicon and 389 oxygen atoms) confined in a cubic box of edge length 20.88 Å with periodic boundary conditions. The density is thus the experimental density of glassy NS4, i.e. 2.38 g cm^{-3} [16]. The interactions between the particles are given by a modified version of the so-called 'BKS' potential [17, 18] which is able to reproduce the structure as well as the dynamics of several sodium silicate systems [10–13, 19] (for more details see [11]). In the present study we have generated three independent samples (in the following, all the results are averaged over these samples in order to improve the statistics) at a temperature of ∼1900 K for which the channels have been shown in our previous studies. For each sample we have performed ten different simulations in which the mass of the atoms of the matrix has been artificially multiplied by a factor μ of 0.5, 1, 2, 5, 10, 30, 10^2, 10^3, 10^4 and 10^6. We have also carried out the limiting case $\mu = \infty$ by performing simulations in which only the sodium atoms move, the atoms of the matrix being kept fixed (frozen matrix approximation). Each of these 33 samples has first been relaxed at ∼1900 K for 10^6 steps (1 step = 1.4 fs) and the following 10^6 steps were used to produce 1000 configurations recorded every 1000 time steps. These configurations have then been used to analyse the trajectories of the sodium atoms during these 1.4 ns.

In figure 1 we show $R^2(t)$, the MSD of the sodium atoms, for various values of μ. While these curves have the characteristic long-time shape of strong diffusion for small values of μ, they flatten out as μ increases. In the limiting case $\mu = \infty$ (frozen matrix) the curve even becomes completely flat, at least within the period of time covered by our simulations. In order to give a quantitative idea of how the ionic diffusion properties decrease with increasing μ, we have determined a characteristic time τ_{MSD} necessary for $R^2(t)$ to be equal to 4 Å^2. This corresponds to an average travel distance of 2 Å which is the *minimum* distance between two Na neighbours (as determined from the Na–Na radial pair distribution function [12]). In the inset of figure 1 we give the variation of τ_{MSD} with μ. While τ_{MSD} is almost independent of μ for small μ, it starts to increase for values of μ larger than a value of about 30.

Since we have previously shown that the diffusive motion of the sodium atoms takes place within channels [10–13], it is worth studying how these channels are modified when the mass of the atoms of the matrix is changed. Therefore, for all our values of μ, we have determined the channels, in the same manner as previously [10]: using a three-dimensional mesh we determine the number of *different* sodium atoms that have visited each cube of the mesh during the total simulation time. Then we define ξ, which is the minimal occupation
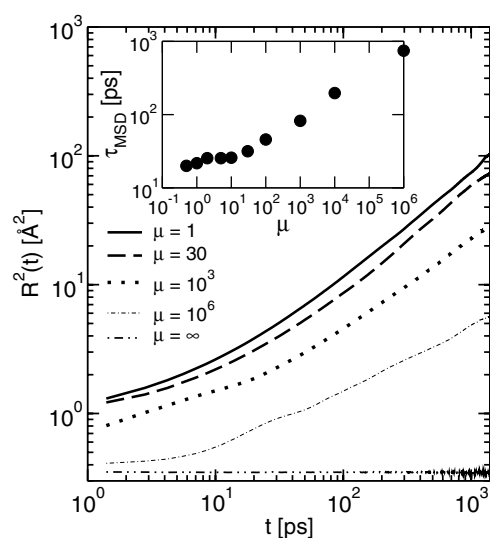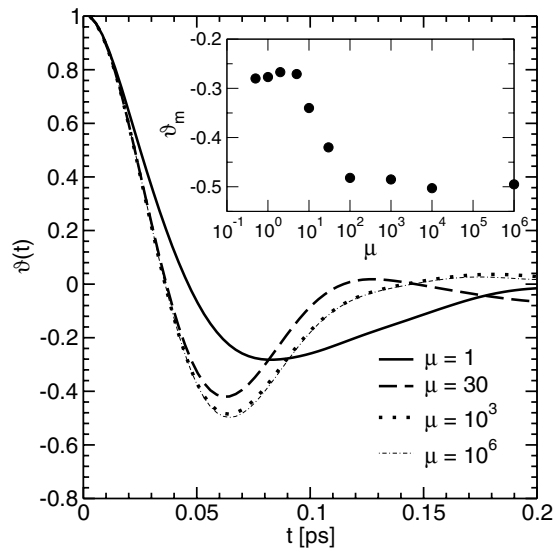
Figure 1. Plot of the MSD $R^2(t)$ of the sodium atoms for different values of μ. Inset: plot of the characteristic diffusion time τ_{MSD} (see the text for a definition) as a function of μ.
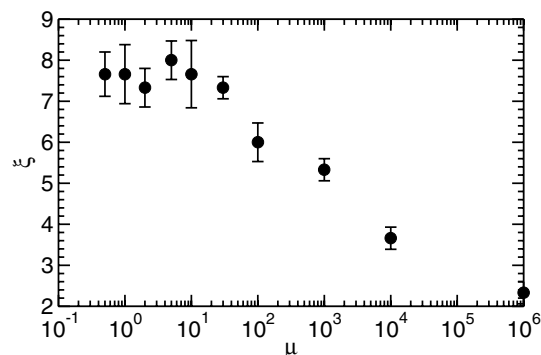
Figure 2. Plot of ξ, the quantity used to define the channels (see the text for further details) as a function of μ.

number such that the cubes visited more than ξ times represent the upper 10% of all the visited cubes (for more details see [10]). In previous studies we have shown that at $T \sim 1900$ K a cube needed to be visited by at least $\xi = 8$ different sodium atoms during a 1.4 ns simulation in order to be part of the channel structure.

Here we study how ξ changes with μ and the results (averaged over three samples) are reported in figure 2. While for $\mu < 30$, ξ remains almost constant between 7 and 8 within the error bars, it starts to decrease dramatically for $\mu > 30$. Obviously, as explained in [10–13], one can no longer speak of 'channels' if ξ becomes as small as 1. Therefore one can interpret the results in figure 2 by assuming that the channels disappear progressively as soon as $\mu > 30$. Then one can argue that the increase of the characteristic time for the diffusion observed in figure 1 is intimately correlated with the disappearance of the channels shown in figure 2. It should be noticed that the plateau observed in the inset of figure 1 and in figure 2 for $\mu < 30$ is consistent with the standard theory of diffusion, which predicts that the diffusion characteristics of the ions are only weakly dependent on the mass of the atoms of the matrix.

Figure 3. Plot of the velocity autocorrelation function $\vartheta(t)$ of the sodium atoms for different values of μ. Inset: plot of the intensity of the first minimum ϑ_m as a function of μ.

In order to know if the observed change in the long-time diffusive behaviour of the sodium atoms is accompanied by a change in their short-time dynamical properties, we have calculated the Na velocity autocorrelation function $\vartheta(t) = \langle \vec{v}(t_0)\vec{v}(t_0+t)\rangle / \langle v^2(t_0)\rangle$ and studied its short-time behaviour. As seen in figure 3 the short-time part of $\vartheta(t)$ is characterized by a first minimum at τ_ϑ, typical of the time for a sodium atom to bounce back and forth against the internal boundaries of the cage in which it vibrates (well before being eventually able to jump towards another cage). In the inset of figure 3 the intensity of the minimum $\vartheta_m = \vartheta(\tau_\vartheta)$ has been plotted as a function of μ. $\vartheta_m \simeq -0.28$ for $\mu < 10$ while ϑ_m drops down to -0.5 for $\mu > 30$. This increasing depth can be interpreted as an increasing stiffness of the internal cage boundaries when μ is increased. In a classical mechanics picture, due to this increased stiffness, the probability for a sodium atom to escape from its cage becomes weaker and this is consistent with the vanishing diffusion observed in figure 1.

To go further in our microscopical analysis, and to understand the changes occurring around $\mu \sim 30$, we have calculated the VDOS of the sodium atoms and the atoms of the matrix, by Fourier transforming the corresponding velocity autocorrelation functions. It is known that such a method reproduces only approximately the VDOS, since at finite temperature (here $T \sim 1900$ K), the harmonic hypothesis does not fully hold but this approximation will not be crucial for our arguments. In figure 4(a) the VDOS of the oxygen atoms for different values of μ are represented (a similar picture could be drawn for the Si atoms). The VDOS for $\mu = 1$ is, of course, close to that of amorphous silica obtained experimentally, except that it is less structured, which is a known drawback of the BKS potential [20]. Such a VDOS is typical of a broad band of vibrational states, extending from $\nu = 0$ up to $\nu_1 \simeq 35$ THz, as a result of the coupling between neighbouring oxygen and silicon atoms forming a strong random covalent network. When increasing the mass of the atoms of the matrix, one observes a shrinkage of the VDOS towards low frequencies. The top of the oxygen band, ν_{max}^O, has been plotted versus μ in figure 4(c): as expected from standard solid state physics ν_{max}^O varies like $\nu_1 \mu^{-1/2}$. The situation is quite different for the Na VDOS represented in figure 4(b) for three typical values
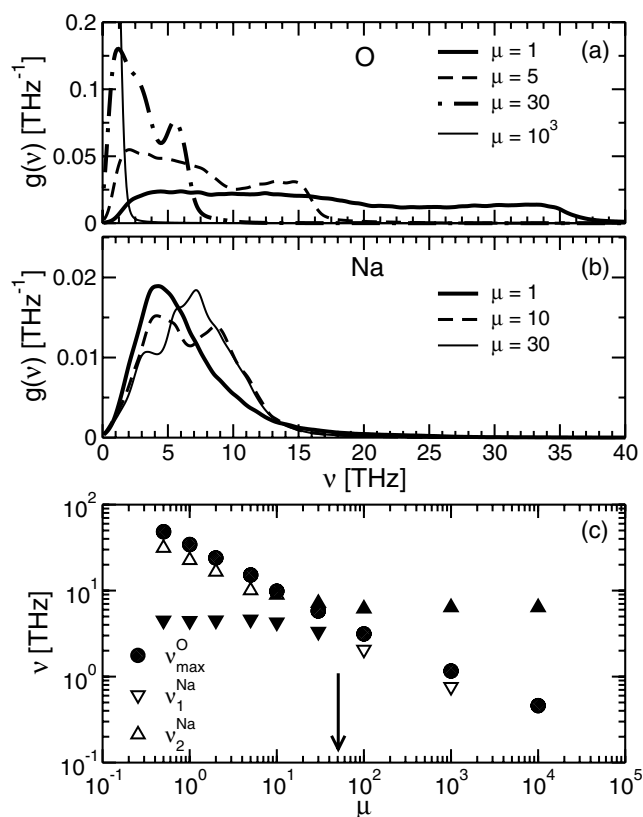
Figure 4. (a) Plot of the VDOS of the oxygen atoms for different values of μ. (b) Plot of the VDOS of the sodium atoms for $\mu = 1$, 10 and 30. (c) Plot of the highest frequency of the oxygen VDOS ($\bullet$), the frequency of the first peak ($\triangledown$) and the second peak ($\triangle$) of the sodium VDOS as a function of μ. Full symbols ($\blacktriangledown$ and $\blacktriangle$) indicate the principal peak in the Na VDOS as μ changes.

of μ: it looks like a well defined peak centred at a frequency ν_1^{Na} close to 5 THz for small values of μ. Such a peak can be interpreted as being mostly due to the vibrations of the sodium atoms in their cage. Using the approximate formula for such a motion, $R^{-1}\sqrt{kT/m_{Na}}$, where $R = 1$ Å is a typical size of the cage deduced from the MSD and m_{Na} is the mass of a sodium atom, one finds a frequency of about 8 THz, in reasonable agreement with ν_1^{Na}. The broadening of the peak is then certainly due to the polydispersity of the R values as well as to the coupling of the sodium atoms with other species. With increasing μ a second peak at ν_2^{Na} grows out of the high frequency part and increases while the peak at ν_1^{Na} decreases and shifts towards low frequencies. The variation of ν_1^{Na} and ν_2^{Na} with μ is represented in figure 4(c) where the main peak of the Na VDOS is represented by the full symbols. One sees that, up to $\mu = 30$, the peak at ν_1^{Na} is the main peak while for higher values of μ the peak at ν_2^{Na} becomes the main peak. Once the transition is fulfilled, the secondary Na peak (ν_1^{Na}) follows the variation of ν_{max}^O with μ while the principal peak (ν_2^{Na}) remains at a constant frequency. Such a behaviour is typical of hybridization effects as commonly seen in electronic and vibrational systems. It is due to the coupling between the sodium atoms and the atoms of the matrix. The characteristic value μ_0, for which the principal peak in the Na VDOS starts to escape from the broad oxygen band, can be estimated by equating the top of the band $\nu_1 \mu_0^{-1/2}$ and the typical sodium frequency,

5 THz. This gives $\mu_0 \simeq 50$ (indicated by the arrow in figure 4(c)), which is remarkably close to the value of 30 above which we have observed the change in the diffusive properties of the Na atoms.

Therefore the above analysis of the VDOS provides a very simple explanation of the predominance of channel diffusion for μ smaller than μ_0. In that case the sodium frequency peak lies within the limits of the vibrational band of the matrix, as shown in figure 4(c). Therefore there always exists a vibrational mode of the matrix with the same frequency as that of the sodium atoms. Using a simple picture in direct space, the vibrational amplitudes of the sodium atoms can become very large due to 'resonance conditions', giving them the possibility to escape from their cage and to jump to a neighbouring cage, as is expected in a local picture of the diffusive motion. Moreover, at the location where a sodium atom is connected to an oxygen atom via a covalent-like bond, it is clear that the local hybridization is important and this explains why the location of the channels, i.e. the preferential pathways for the sodium diffusive motion, is strongly correlated to the position of the non-bridging oxygen atoms. On the contrary, for $\mu > \mu_0$, the vibrational peak of the sodium atoms is located outside the VDOS of the matrix (figure 4(c)) and the resonance conditions are more difficult to be fulfilled. As a consequence, the sodium atoms stay much longer confined in their cages. This picture is consistent with our interpretation of the increasing depth of the first minimum of the Na velocity autocorrelation function as being due to an increasing stiffness of the internal cage boundaries when μ is increased above μ_0.

In conclusion, we have demonstrated the essential role played by the vibrations of the atoms of the matrix in the existence of the channel diffusion of sodium inside an amorphous silica matrix. In a sense this is close to the concept of 'matrix-mediated-coupling' recently used to interpret the mixed cation effect in glasses [21] except that we show here that the *direct* hybridization between the ionic modes and the modes of the matrix is necessary to ensure a fast diffusion process of the ions. This result is also coherent with previous studies showing indirectly that the sodium dynamics should be intimately linked to that of the matrix [15]. Of course, it would be extremely interesting to extend the present study to other kinds of ions, such as Li, H, etc, to test the generality of our interpretation (according to preliminary results it appears indeed that a similar behaviour is observed for Li in SiO_2 [22]). This would constitute a real improvement in the understanding of the mechanisms of ionic transport in random media.

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