Dynamics of Sodium in Sodium Disilicate: Channel Relaxation and Sodium Diffusion

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We use molecular-dynamics computer simulations to study the dynamics of amorphous $(Na_2O)2(SiO_2)$. We find that the Na ions move in channels embedded in a SiO_2 matrix. The characteristic distance between these channels gives rise to a prepeak in the structure factor at $q \approx 0.95$ Å^{-1}. The dynamics of sodium is given by a fast process which can be seen in the incoherent scattering function and a slow process which is seen in the coherent function. The relaxation time of the latter coincides with the α-relaxation time of the matrix. The Kohlrausch exponent of the fast process for $q > 1.6$ Å^{-1} is the same as the von Schweidler exponent for the slow one. Thus the two processes are closely related.

The dynamics of mobile ions in glasses and melts is a field of great interest in geoscience, materials science, chemistry, and physics [1,2]. However, due to the experimental difficulty to probe the high temperature dynamics on a microscopic level, many details of this dynamics are not well understood. Only very recently state of the art neutron scattering experiments have started to shed some light onto the structure and dynamics of these systems and unexpected features (discussed below) have been found [3]. A very valuable tool to study the structure and dynamics of melts are molecular dynamics (MD) computer simulations and the present paper is an effort to increase our knowledge of these systems and to rationalize some of the findings of Ref. [3]. Many of the recent MD studies of alkali silicate glasses [4] have given support to the idea of Ingram [5] that alkali ions move through "preferential pathways" and that these pathways, as has been suggested by Greaves [6], are related to a microsegregation of alkali ions. Very recently Jund *et al.* [7] investigated the dynamics of the Na ions in sodium tetrasilicate (NS4) and found *no* evidence for a clustering of sodium ions in individual configuration snapshots. However, these authors did identify preferential pathways in the dynamics of the sodium ions in that the sodium trajectories form a well connected network of pockets and connecting pathways. Moreover, they gave evidence for an uncorrelated motion of the sodium ions inside these channels, contrarily to the picture of a cooperative motion proposed by Greaves [6].

What so far has been left out from the discussion is the slow relaxation dynamics of the matrix, i.e., in sodium silicates the dynamics of the silicon and oxygen atoms. This is a very important issue since most of the models for the ion transport in glasses start from a coarse-grained representation of a glassy matrix which is not derived from first principles [2]. Thus the present paper is the first investigation in which the dynamics of the fast sodium ions is compared to the slow relaxation of the matrix and below we will show that these two processes are much more closely related to each other than could naively be expected.

The system studied is $(Na_2O)2(SiO_2)$, NS2, i.e., a prototype of an ion conducting glass. The potential we use to describe the interactions between the ions in our MD simulation is a slight modification of the pair potential proposed by Kramer *et al.* which is based on *ab initio* calculations [8]. More details on this potential can be found in Ref. [9]. The simulation was done at constant volume using 8064 particles ($N_{Si} = 1792$, $N_{Na} = 1792$, and $N_O = 4480$) in a box of size $L = 48.653$ Å. This corresponds to a mass density of 2.37 g/cm^3, which is close to the experimental one [10]. The system was equilibrated at various temperatures in the range 2100 K $\leq T \leq$ 4000 K before the production runs were started. These were done in the microcanonical ensemble, using the velocity form of the Verlet algorithm with a step size of 1.6 fs. At the lowest temperatures, the temperature for which the results presented here were obtained, these runs extended over 2.5 ns (1.5×10^6 time steps) and in order to improve the statistics of the results we averaged over two independent runs.

In a recent publication we have shown that this model predicts structural and dynamical properties of NS2 which are in good agreement with experimental findings [9]. In particular we found that the static structure factor exhibits a prepeak at $q = 0.95$ Å^{-1} which corresponds to a length scale of next-nearest Na-Na or Si-Na neighbors (around 6.6 Å). This result was confirmed in a neutron scattering experiment by Meyer *et al.* [3] who found at this wave vector a pronounced shoulder in the elastic intensities. Furthermore it has been shown [9] that at temperatures $T \leq$ 2500 K the dynamics of the Na atoms is about 2 orders of magnitude faster than the one of silicon and oxygen atoms, which is in qualitative agreement with the experimental fact that this system is an ion conducting material. Hence it is reasonable to assume that the present model does indeed give a good microscopic description of real NS2.

Using the same type of potential for NS4 it was recently shown that the Na atoms move in preferential pathways, also called "channels," which are basically frozen in structures inside the SiO_2 matrix [7]. Furthermore, it was found that the volume of these channels is relatively low

and that they contain a large number of nonbridging oxygen atoms [11,12]. Hence it can be expected that the average density of the sodium atoms *outside* these channels is significantly lower than can be expected if the sodium atoms were distributed in the system in a uniform way; i.e., that the diffusion of the sodium atoms is strongly restricted to a small subset of the configuration space. In order to check this idea we have calculated a (coarse grained) probability of finding *no* sodium atom at a given location in space. Following the approach of Jund *et al.* [7] we calculated this probability by dividing the system into 48^3 cubes (of length $L/48 \approx 1.01$ Å). Then we calculate the probability $P(t)$ that a cube which does not contain a sodium ion at time zero is also not visited by a sodium ion until a later time t. The time dependence of $P(t)$ is shown in the inset of Fig. 1. From this graph we recognize that after 2.5 ns, i.e., after more than the α-relaxation time of the matrix [13], more than 50% of the cubes have not yet been visited by a sodium atom. [We mention that after this time the mean squared displacement of the Na atoms is more than $(45 \text{ Å})^2$, which shows that these atoms have moved a great distance. On this time scale also the local structure of the Si-O matrix is reconstructed [13].] Hence we can conclude that on this time scale the sodium free region forms a percolating structure around a network of channels, i.e., it has somewhat the structure of a Swiss cheese. In order to investigate the structure of this percolating region we define a "Swiss cheese" structure factor $S_{sc}(q,t)$ as follows: We assign to each cube which has not been visited by a sodium atom until time t a point and we compute the static structure factor of $N_{sc}(t) = P(t)(48^3 - N_{Na})$ points:

$$S_{sc}(q,t) = \frac{1}{N_{sc}(t)} \sum_{k,l=1}^{N_{sc}(t)} \exp[i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)]. \quad (1)$$
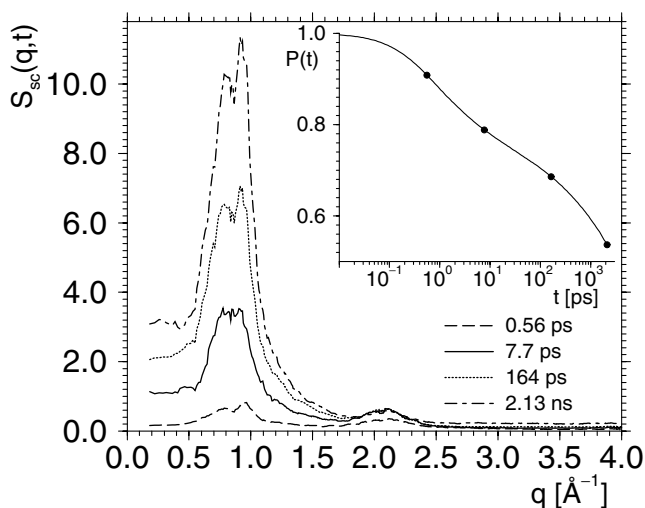
This quantity is shown in Fig. 1 for four different times: $t = 0.56$ ps, 7.7 ps, 164 ps, and 2.13 ns. We see that $S_{sc}(q,t)$ has peaks at $q_1 = 0.9$ Å^{-1} and $q_2 = 2.15$ Å^{-1} which are also the prominent features in $S_{NaNa}(q)$, the static structure factor for the Na-Na correlations [9]. Hence we can now conclude that the peak at q_1 in $S_{NaNa}(q)$, which has also been seen in n-scattering experiments [3], corresponds to the typical distance between the channels. Note that with increasing time the height of this peak increases quickly. However, it is clear that the peak at q_1 decreases again on the time scale on which the matrix starts to reconstruct itself significantly and thus rearranges the channel structure.

The peak at q_2 reflects the length scale of nearest sodium neighbors [9]. As we see in Fig. 1 its height is constant for 7.7 ps $\leq t \leq$ 2.13 ns. The fact that this peak is still present at $t = 2.13$ ns means that there are preferred sites for the sodium ions inside the channels which is reasonable because most of the sodium ions are located in the neighborhood of dangling bonds [11,12] and these bonds do not disappear until the network regions have significantly rearranged themselves. The latter finding is also in agreement with the results from Ref. [7] for the distinct part of the van Hove correlation function.

We address now the question how the sodium ions relax inside the channels. An appropriate quantity to investigate this point are time dependent density-density correlation functions, i.e., the coherent intermediate scattering function $F(q,t)$ and its self part, the incoherent intermediate scattering function $F_s(q,t)$ [14]. In Fig. 2 we show $F(q,t)$ for the Na-Na correlations (solid lines) as well as $F_s(q,t)$ for the sodium atoms (dashed lines) for three different wave vectors: $q = 0.94$ Å^{-1}, 2.0 Å^{-1}, and 2.75 Å^{-1}. From this figure we infer immediately a surprising result: At $q = 0.94$ Å^{-1}, i.e., at the characteristic

FIG. 1.   "Swiss cheese" structure factor $S_{sc}(q,t)$ for the sodium free regions at $T = 2100$ K for $t = 0.56$ ps, 7.7 ps, 164 ps, and 2.13 ns. The inset shows the probability $P(t)$ that a cube which is sodium free at time zero remains sodium free until time t. The circles on the curve for $P(t)$ are at the times at which $S_{sc}(q,t)$ is shown.
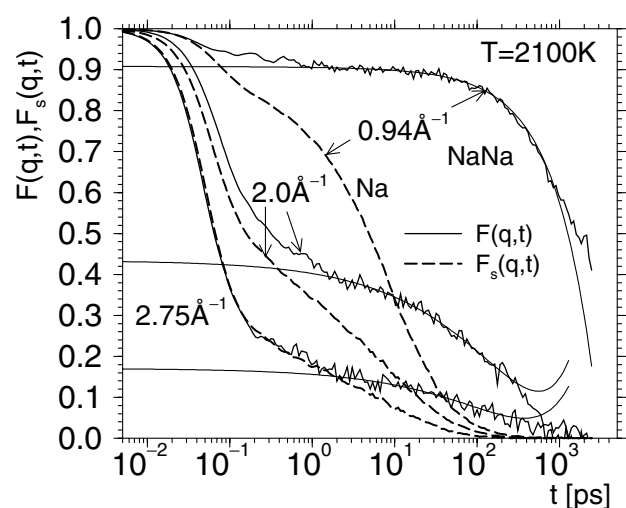

FIG. 2.   Coherent intermediate scattering functions $F(q,t)$ for the sodium-sodium correlations (bold solid lines) and incoherent intermediate scattering functions $F_s(q,t)$ (dashed lines) at $T = 2100$ K for the indicated values of q. The thin solid lines are fits with Eq. (2) (see text for details).

q value of the sodium channel structure, $F(q,t)$ decays on a time scale which is 2 orders of magnitude larger than the one for $F_s(q,t)$. Such a strong difference cannot be explained by a de Gennes narrowing argument [14]. Instead this result can be rationalized by the idea that the sodium atoms move quickly between preferential sites, since this type of motion gives rise to a fast decorrelation of the incoherent function, whereas it does not affect the coherent one. Only on the time scale of the relaxation of the SiO_2 matrix also the coherent function starts to decay (see also Fig. 3, discussed below). Note that the slow decay of $F(q,t)$ is found only for wave vectors around 0.95 $Å^{-1}$. For different q the function decays significantly faster as can be seen from the other curves shown in Fig. 2.

In order to quantify the typical relaxation time of the two mentioned processes we define the α-relaxation times τ and τ_s as the times at which $F(q,t)$ and $F_s(q,t)$, respectively, have decayed to 0.1. In Fig. 3 we show $\tau(q)$ for the Si-Si and O-O correlation, i.e., the relaxation time of the matrix for wave vector q (open symbols). Also included is $\tau(q)$ for the Na-Na correlation and we see that for wave vectors larger than ≈ 1.5 $Å^{-1}$ it is smaller than the characteristic relaxation time of the network. In contrast to this we find that for $q \lesssim q_1$ the relaxation time for Na-Na is close to the one of the matrix. Moreover, we see that $\tau(q)$ for the Na-Na correlation is in phase with the corresponding partial structure factor $S_{NaNa}(q)$ which is also shown in the figure. Furthermore, we recognize from this figure that the relaxation time of *all* coherent correlators is largest at q_1, in agreement with the discussion of Fig. 2. Also included in the figure is τ_s for the sodium atoms and we see that it is indeed much smaller than the one of $F(q,t)$, which shows that there are indeed two different processes.

Having discussed the relaxation dynamics of the SiO_2 matrix and the sodium atoms on a qualitative level, we proceed now to investigate this dynamics in more detail.
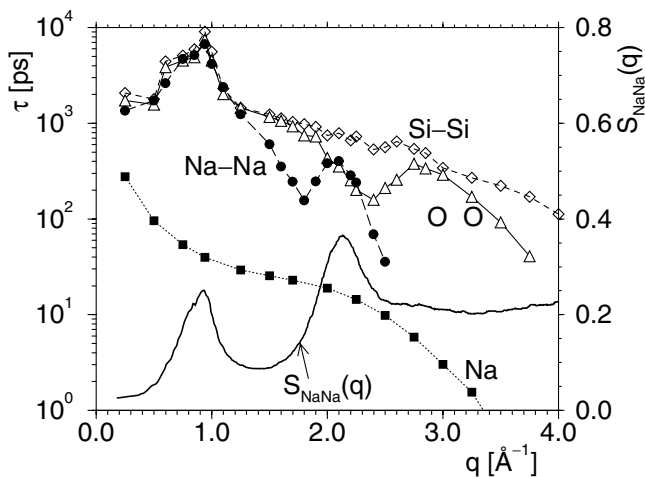

FIG. 3. τ from $F(q,t)$ for the Si-Si (diamonds), O-O (triangles), and Na-Na (filled circles) correlations and τ_s from $F_s(q,t)$ for Na (filled squares). The labels for the y axis on the right-hand side are for the partial static structure factor $S_{NaNa}(q)$ (bold solid line).

In this context it is of interest that a calculation of Bosse and Kaneko within the mode coupling theory (MCT) [15] found that in a binary system of hard spheres with large size ratio the coherent and incoherent scattering functions decay on very different time scales [16]. This similarity suggests to test whether MCT might be able to give a reliable *qualitative* description of the relaxation dynamics of the present system. Indeed we show elsewhere [13] that the incoherent and coherent dynamics of silicon and oxygen in NS2 can be nicely described by the universal predictions of MCT. In particular the time-temperature superposition principle for the α-relaxation regime holds and the late β-relaxation regime, i.e., the time window in which a correlation function $\Phi_q(t)$ starts to fall below the plateau at intermediate times, can be described very well by the expression predicted by MCT,

$$\Phi_q(t) = f_q^c + h_q t^b + h_q^{(2)} t^{2b}. \tag{2}$$

Here f_q^c is the height of the mentioned plateau in $\Phi_q(t)$ [$= F(q,t)$ or $F_s(q,t)$], and h_q and $h_q^{(2)}$ are constants. The second term on the right hand side is called von Schweidler law and according to MCT the exponent b in Eq. (2) should be a system universal constant, i.e., be independent of the correlator or q. From Fig. 2 we see that a fit with Eq. (2) describes our data at 2100 K over 2 orders of magnitude in time if we fix the exponent b to 0.47. If we increase the temperature the regime where the fit works decreases whereas the shape of the correlators at long times remains unchanged, in agreement with MCT. Because of the decay of $F_s(q,t)$ for sodium on much faster time scales these correlators do not exhibit a pronounced von Schweidler regime also at $T = 2100$ K.

In the following we will relate this result with the relaxation dynamics of the sodium atoms as measured by $F_s(q,t)$. The long time decay of these functions can be well described by Kohlrausch laws,

$$\Phi_q(t) = A_q \exp\{-[t/\tau_{KWW}(q)]^{\beta(q)}\}. \tag{3}$$

The q dependence of the exponent β is shown in the inset of Fig. 4. Very surprisingly we see that, for $q > 1.6$ $Å^{-1}$, β seems to become independent of q and is around $\beta_\infty = 0.47$. That β really becomes independent of q is demonstrated in Fig. 4 where we plot $F_s(q,t)/A_q$ versus the rescaled time t/τ_{KWW} for 1.7 $Å^{-1} \leq q \leq 4$ $Å^{-1}$. [Note that for $q \gtrsim 1.7$ $Å^{-1}$ A_q and τ_{KWW} have been obtained from fits to $F_s(q,t)$ in which β was fixed to β_∞.] If $\beta = \beta_\infty$ really holds the curves for the different q should fall onto a master curve in the α-relaxation regime and they do so for $t/\tau_{KWW} > 0.1$. That this result does not hold for all q is demonstrated by the curve for $q = 0.5$ $Å^{-1}$ which is included in the figure as well.

We note that the value of β_∞ coincides with the value of the von Schweidler exponent b from Eq. (2). This important observation can be rationalized by the prediction of Fuchs, obtained within a MCT calculation, that the Kohlrausch law becomes exact for $q \to \infty$ in which case
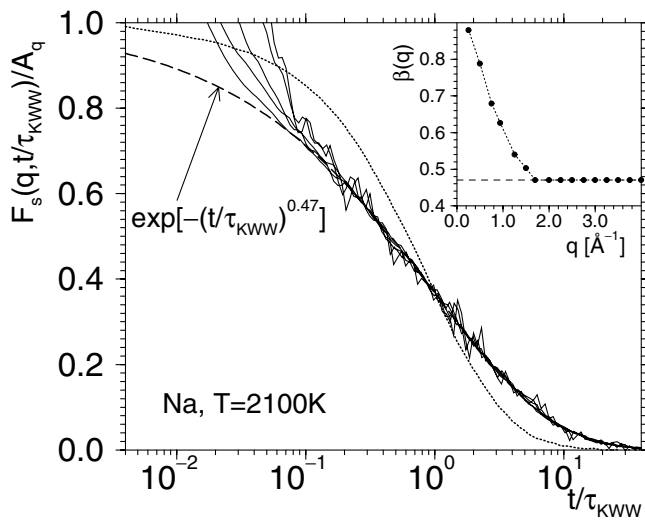
FIG. 4. The solid lines show $F_s[q, t/\tau_{KWW}(q)]/A_q$ for $q = 1.7$ Å^{-1}, 2.0 Å^{-1}, 2.75 Å^{-1}, 3.5 Å^{-1}, and 4.0 Å^{-1} (from left to right). (See text for the determination of A_q and τ_{KWW}.) The dotted line shows the same quantity for $q = 0.5$ Å^{-1}. The dashed line is the Kohlrausch law $\Phi(\hat{t}) = \exp[-(t/\tau_{KWW})^{0.47}]$. The inset shows the Kohlrausch exponent β as a function of q.

β_∞ is equal to the von Schweidler exponent b [17]. Fuchs has argued that this result can be interpreted using Levy's generalization of the central limit theorem [18]: For large q the α relaxation of the correlators is the result of a sum of many independent terms, each of which follows the von Schweidler law Eq. (2). According to Levy's central limit theorem this sum is the characteristic function of a stable distribution and the latter is exactly the Kohlrausch law with exponent b.

If we apply this probabilistic interpretation of $F_s(q, t)$ for sodium we obtain two important results: First, Levy's central limit theorem can already be applied for $q > 1.6$ Å^{-1}, i.e., deviations become important only on length scales which are larger than the nearest neighbor distance between sodium atoms. Second, the α processes for the self-motion of sodium ions and the relaxation of sodium channels have—although appearing on completely different time scales—the same short-time behavior given by a von Schweidler law with exponent $b = 0.47$. So it seems that the fast diffusion of sodium ions through the channels has its slow counterpart in the relaxation of the matrix, i.e., the rearrangement of the channels at long times.

In summary, we have found that the sodium trajectories in NS2 form channels in the SiO$_2$ network, in agreement with recent results for NS4 [7]. The characteristic distance between these channels is of the order of 6.6 Å, and is reflected in the static structure factor as a prepeak at $q = 0.95$ Å^{-1}. Structural relaxation in NS2 is dominated by two processes: the fast sodium diffusion through the channels and the rearrangement of these channels on the time scale of the relaxation of the SiO$_2$ matrix. The von Schweidler exponent b for the system can also be found in

the incoherent intermediate scattering function for sodium in that for $q > 1.6$ Å^{-1} its long time decay is given by a Kohlrausch law with $\beta_\infty = b$. This shows that the relaxation of channels at long times and the fast sodium diffusion inside these channels are intimately connected to each other. Note that we expect that this connection is present for all temperatures in which the Na dynamics is significantly faster than the one of the network and hence should be observable also at temperatures at which current experiments can be done.

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