The dynamics of melts containing mobile ions: computer simulations of sodium silicates

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Abstract

We present the results of large-scale computer simulations in order to discuss the structural and dynamic properties of sodium silicate melts with the compositions $(Na_2O)2(SiO_2)$ (NS2) and $(Na_2O)20(SiO_2)$ (NS20). We show that, compared to silica (SiO_2), these systems exhibit additional intermediate range order on intermediate length scales that stem from the tetrahedral network structure. By means of intermediate-scattering functions, we characterize the dynamics of sodium in the system under consideration. Whereas in NS2 the incoherent scattering functions for Na decay much faster to zero than the coherent ones for Na–Na, in NS20 this different behaviour of the incoherent and coherent functions is not very pronounced. On the other hand, the incoherent functions of the two systems share a very peculiar feature: their long-time decay can be described by a Kohlrausch law with a constant exponent β for $q > q_{th}$ where q_{th} is significantly below the location of the main peak in the static structure factor for the Na–Na correlations.

1. Introduction

Silicate melts and glasses are of fundamental interest for geosciences and technology, and, moreover, many of these systems are paradigms for the understanding of basic phenomena in physics and materials science such as phase separation, nucleation, ion conduction, and the glass transition. Starting with the pioneering work of Soules and Busbey [1] and Angell *et al* [2], molecular dynamics (MD) computer simulations have proved a very valuable tool for understanding structural and dynamical properties of silicates on a microscopic level [3].

In this paper we consider mixtures of SiO_2 with Na_2O, i.e. we investigate the systems $(Na_2O)2(SiO_2)$ and $(Na_2O)20(SiO_2)$ (for which we use in the following the abbreviations NS2 and NS20, respectively). Sodium silicates are paradigms of ion conductors, which is related to the fact that at low temperatures the sodium ions are much more mobile than the oxygen and silicon atoms. The structure of these systems is more complicated than that of a

pure silica melt where a disordered tetrahedral network is formed in which SiO_4 tetrahedra are connected via the oxygens at the corners. The sodium ions partially destroy the SiO_4 network structure and, as we show below, they not only modify the structure on local length scales but also introduce also new intermediate length scales that can be identified by means of the static structure factor. Very recently, extensive neutron scattering experiments on NS2 by Meyer *et al* [4] have shown that these intermediate length scales really exist and have confirmed the prediction of the simulation [5, 6] that they are important for the transport of the Na ions: the Na ions move through a network of channels in the 'Si–O matrix' and the characteristic wavevector of this channel system is equal to that of the location of the first peak in the static structure factor at $q = 0.95$ Å^{-1}. Our main aim in the following is to compare the structure and dynamics of NS2 with those of NS20, i.e. a material that has a relatively small Na_2O content of about 5 mol%.

The rest of the paper is organized as follows. In the next section we briefly give the main simulation details. The structure of NS20 and NS2 is then discussed with respect to intermediate length scales in section 3. In section 4 the results that concern the dynamics of sodium are presented. Finally we summarize the results in section 5.

2. Simulation details

The model potential that we use to compute the interaction between the atoms in sodium and aluminium silicates is the one proposed by Kramer *et al* [7]. The details of this potential as well as the necessary modifications that we have made to describe the present systems can be found in [7–9]. Our models yield predictions for structural and dynamic properties of the systems under consideration which are in good agreement with experimental findings [9]. Furthermore, Ispas *et al* [10] have shown for $(Na_2O)4(SiO_2)$ that *ab initio* simulations (Car–Parrinello MD) yield comparable results as regards the structure to those obtained with MD simulations in which our potential model is used.

The simulations have been done at constant volume: the density in NS2 as well as that in NS20 was fixed at 2.37 g cm^{-3} which is close to the value that one finds in experiments [11]. We simulated systems of 8064 particles. Since the model potential contains a long-ranged Coulomb term, a huge numerical effort is required: the longest runs for the sodium silicate systems (at the lowest temperatures) had a length of about 10 million time steps for which a time of two weeks was needed on 64 processors, thus giving a total CPU time of about 128 weeks of (single-) processor time.

The equations of motion were integrated with the velocity form of the Verlet algorithm using a time step for the integration of 1.6 fs. The temperature range investigated was 4000 K $\geqslant T \geqslant$ 2100 K in the case of NS2 and 4000 K $\geqslant T \geqslant$ 2500 K in the case of NS20. To equilibrate the systems, the temperatures were controlled by coupling the particles to a stochastic heat bath. After the system was equilibrated at the target temperature, we continued the run in the microcanonical ensemble, i.e. the heat bath was switched off. More details of the simulations can be found in [6–9].

3. Intermediate length scales in sodium silicates

An appropriate quantity to use to investigate the structure of atomic systems on intermediate length scales is the static structure factor. It is essentially the Fourier transform of the pair correlation function which is proportional to the probability of finding an atom at a distance r from another atom [12]. The structure factor can be directly measured in neutron
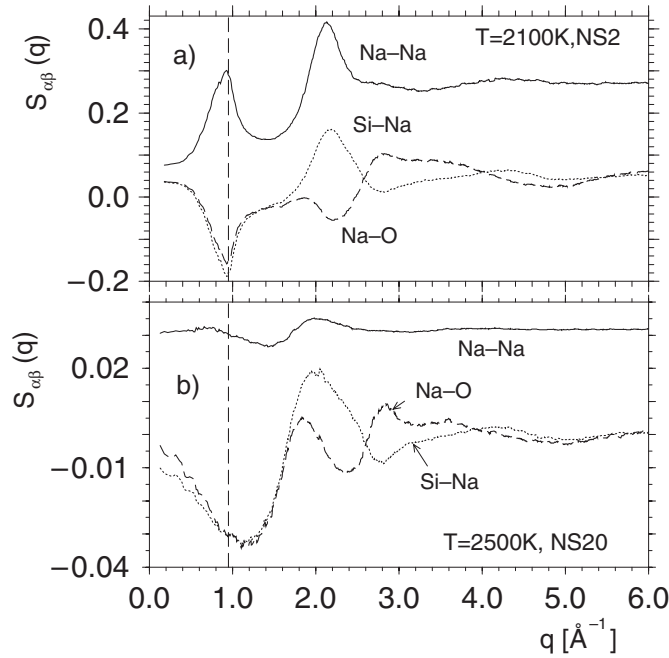
Figure 1. Partial structure factors $S_{Na-Na}(q)$ (solid curves), $S_{Si-Na}(q)$ (dotted curves), and $S_{Na-O}(q)$ (dashed curves) for (a) NS2 at $T = 2100$ K and for (b) NS20 at $T = 2500$ K. The vertical dashed line corresponds to the location of wavevector q_1 discussed in the text.

scattering experiments from the intensity of the radiation observed with a momentum transfer $\hbar q$ ($\hbar$: Planck's constant; q: the wavevector of the momentum transfer). In a three-component system one can define six different partial structure factors as [12]

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_{k=1}^{N_\alpha} \sum_{l=1}^{N_\beta} \langle \exp(\mathrm{i}q \cdot [r_k - r_l]) \rangle, \tag{1}$$

where the first sum runs over N_α particles of type α and the second one over N_β particles of type β. N is the total number of atoms and r_k is the position of atom number k.

The addition of sodium oxide to a silica melt partially destroys the SiO_4 network which can be directly recognized in the partial structure factors. Three of them, i.e. those for the Na–Na, Na–O, and Si–Na correlations, are shown in figure 1(a) for NS2 at $T = 2100$ K: in these functions a peak around 1.7 Å^{-1} is absent which is found in the structure factors of SiO_2, reflecting the tetrahedral SiO_4 network. We mention that the latter peak in S_{Si-Si}, S_{Si-O}, and S_{O-O} is also much less pronounced for NS2 than for pure SiO_2. But we observe a pronounced prepeak at smaller q, i.e. at $q_1 = 0.95$ Å^{-1}, a prepeak that is found not only in $S_{\alpha\beta}$ shown in figure 1(a) but also in all partial structure factors. This q-value is of the order of the length scale of next-nearest Na–Na or Si–Na neighbours (around 6.6 Å). As we have already suggested recently [6], it is the characteristic wavevector of a percolating network that is formed by Na_2O-rich string-like regions. For NS20 (figure 1(b)) one can still identify peaks around q_1, although they have moved to a slightly smaller q in the Na–Na correlations and to a slightly larger q for the Si–Na and the Na–O correlations. This shows that, due to the much smaller sodium concentration, there is no typical length scale of a percolating network formed by the sodium atoms any longer, since, if there was, one would expect a peak at the same q_1 for all correlations as in NS2.
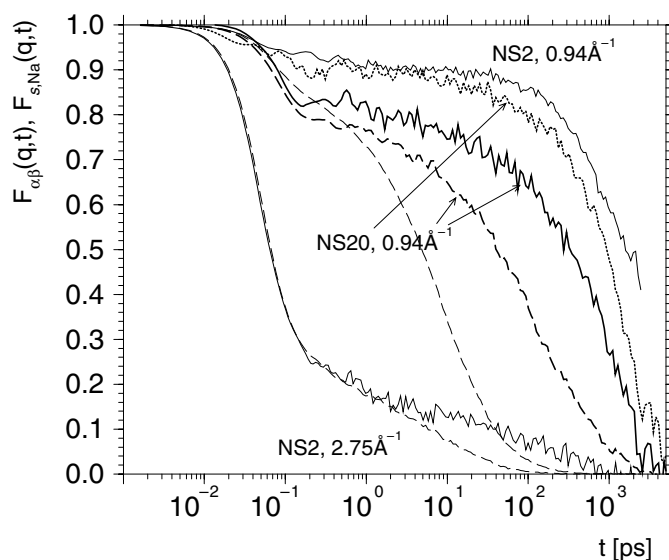
Figure 2. Coherent intermediate-scattering functions $F_{Na-Na}(q, t)$ (solid curves) and incoherent intermediate-scattering functions $F_{s,Na}(q, t)$ (dashed curves) for the values of q indicated. The bold curves correspond to NS20 at $T = 2500$ K whereas the thin curves are for NS2 at $T = 2100$ K. For NS20 at $T = 2500$ K, $F_{Si-Si}(q, t)$ at $q = 0.94$ Å^{-1} is also shown (bold dotted curve).

Does one see the peaks at q_1 also in experiments? In experiments such as neutron scattering studies, one does not have access to the partial structure factors for systems such as NS2 or AS2, since one measures a sum of the partial structure factors, $S_n(q)$, where the different contributions are weighted by the neutron scattering lengths. As we have found recently, our simulations predict for $S_n(q)$, under normal pressure conditions, that the prepeak at q_1 is only a weakly pronounced shoulder at room temperature, whereas it becomes much more prominent for the melt. This behaviour is due to a cancellation effect of negative and positive contributions in $S_{\alpha\beta}(q)$ (the negative contributions stem from $S_{\alpha\beta}(q)$ with $\alpha \neq \beta$; see figure 1(a)). And indeed, very recent neutron scattering experiments by Meyer *et al* [4] do find the feature at q_1 for NS2. Meyer *et al* have measured for the first time the temperature dependence of the structure factor, or more precisely the elastic signal, from $T = 300$ K (where the system is in a glass state) to $T = 1600$ K (where one has a melt). They find that the feature at q_1 becomes more and more pronounced on increasing the temperature and one can clearly identify it at $T = 1600$ K—i.e., a behaviour which is similar to what we see in our simulations.

4. The dynamics of sodium in sodium silicates

In a recent simulation of a NS2 melt [6] we have demonstrated that at low temperatures the sodium ions move through channels in the SiO$_2$ matrix, which confirms the picture for ion conducting materials that the alkali ion trajectories can be characterized by preferential paths in the system [13] (note that this had already been demonstrated for NS4 [5]). Thereby, the characteristic wavevector of the latter system of channels is at $q_1 = 0.95$ Å^{-1}, i.e. the location of the first prepeak in the static structure factor. The transport of the sodium ions through the channels is accompanied by two processes: the fast motion of the sodium ions itself and the slow rearrangement of the channel structure. A consequence of this can be
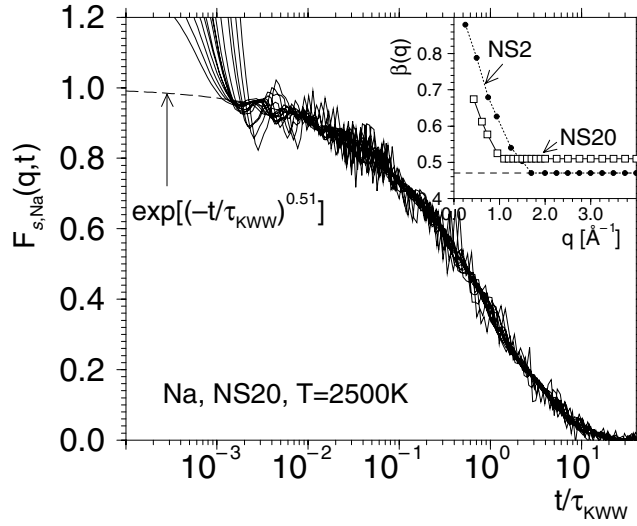
Figure 3. The solid lines show $F_s[q, t/\tau_{KWW}(q)]/A_q$ for NS20 for $q = 1.1, 1.2, 1.3, 1.4, 1.5,$ 1.6, 1.7, 1.8, 1.9, 2.0, 2.25, 2.5, 2.75, 3.0, 3.25 Å^{-1} (from left to right). The dashed curve is the Kohlrausch law indicated. The inset shows the Kohlrausch exponent β as a function of q for NS20 and NS2 (the data for NS2 are taken from [6]).

seen in time-dependent density–density correlation functions, i.e. the coherent intermediate-scattering function $F_{\alpha\beta}(q, t)$ and its self-part $F_{s,\alpha}(q, t)$: as can be inferred from figure 2, at $q = 0.94$ Å^{-1}, $F_{Na-Na}(q, t)$ decays on a two-orders-of-magnitude larger timescale than the incoherent function $F_{s,Na}(q, t)$. This is because correlations between different sodium ions cannot decay as long as the channel network and thus the slow components Si and O have rearranged themselves. With increasing q one expects $F_{\alpha\beta}(q, t)$ to become more and more similar to its self-part $F_{s,\alpha}(q, t)$. However, at a value as high as $q = 2.75$ Å^{-1} the slow relaxation of channels is still present, in that the coherent function decays on a much slower timescale for $t > 2$ ps than the incoherent function.

As we can recognize also from figure 2, for NS20 at q_1 (the temperature is $T = 2500$ K) the timescale on which the incoherent and the coherent function decay to zero (the α-relaxation time) differs only by a factor of 2–3. At the same time, at q_1, F_{Na-Na} is much more stretched than, e.g., F_{Si-Si}, and the height of the plateau is at 0.82 for F_{Na-Na} whereas it is at 0.9 for F_{Si-Si} (corresponding to a more localized process in the case of Si–Si). This behaviour is very different from that in NS2, where at q_1 all coherent correlators lie essentially on top of each other (see [6, 9]). The latter behaviour in NS2 corresponds to the relaxation process of the channel network which has its characteristic value of q around q_1. A similar process does not occur in NS20 due to the small Na$_2$O concentration: in this system channels may still exist but they are not forming a network structure any longer.

For NS2 we have shown in [6] that the long-time decay, i.e. the α-relaxation, of $F_{s,Na}(q, t)$ can be well described by a Kohlrausch law, $\Phi_q(t) = A_q \exp\{-[t/\tau_{KWW}(q)]^{\beta(q)}\}$. Very surprisingly, for $q > 1.6$ Å^{-1} the exponent β is independent of q and is around $\beta_\infty = 0.47$ (see the inset of figure 3), a value that is equal to the von Schweidler exponent of our NS2 model [9]. Such a behaviour is predicted by the mode coupling theory of the glass transition for $q \to \infty$ and Fuchs has shown that this can be interpreted using Levy's central limit theorem [14]: for large q the α-relaxation of the correlators is the result of many independent terms each of which follows a power law $\Phi_q(t) = A_q[1 - (t/\tau_{KWW})^b]$ (the von Schweidler law), and

Levy's theorem says that this sum is the characteristic function of a stable distribution whose functional form is the Kohlrausch law with exponent b.

The question arises of whether in NS20 also the long-time decay of $F_{s,Na}(q, t)$ can be described by a Kohlrausch law with constant β for $q > q_{th}$. And indeed figure 3 shows that this is the case with $\beta = 0.51$ for $q > 1.0$ Å^{-1}. Thus, we find an exponent β_∞ which is very similar to the one for NS2, and moreover for NS20, β becomes constant at even smaller values of q than for NS2, which is probably related to the fact that the prepeak at q_1 in $S_{Na-Na}(q)$ for NS20 has moved to smaller wavevectors. Since the structure of the sodium trajectories in NS20 cannot be described by a network of channels, this means that the description of $F_{s,Na}(q, t)$ by a Kohlrausch law with an exponent β around 0.5 for $q > q_{th}$ is related to the local environment of the sodium atoms and is therefore rather independent of the sodium concentration.

5. Summary

MD computer simulations were used to study the structure and dynamics of the sodium silicate melts NS20 and NS2. Whereas in NS2 the sodium ions move through a network of channels in the Si–O matrix, in NS20, due to the small content of sodium, such a network with its characteristic dynamic features does not exist any longer. However, the one-particle dynamics on the local length scale are very similar in the two systems: for $q > q_{th}$, with q_{th} being below the location of the first main peak in the static structure factor, the long-time decay of the incoherent intermediate-scattering function $F_{s,Na}(q, t)$ can be well described by a Kohlrausch law with an exponent β around 0.5. Further investigations to gain a more detailed understanding of these findings are in progress.

Acknowledgment

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