The structural relaxation of molten sodium disilicate

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Abstract
We use molecular dynamics computer simulations to study the relaxation
dynamics of $Na_2O–2(SiO_2)$ in its molten, highly viscous state. We find that at
low temperatures the incoherent intermediate-scattering function for Na relaxes
about 100 times faster than the one of the Si and O atoms. In contrast to this,
all coherent functions relax on the same timescale if the wavevector is around
$1 \, Å^{-1}$. This anomalous relaxation dynamics is traced back to the channel-like
structure for the Na atoms that have been found for this system. We find that the
relaxation dynamics for Si and O as well as the time dependence of the coherent
functions for Na can be rationalized well by means of mode-coupling theory.
In particular, we show that the diffusion constants as well as the α-relaxation
times follow the power law predicted by the theory and that in the β-relaxation
regime the correlators obey the factorization property with a master curve that
is described well by a von Schweidler law. The value of the von Schweidler
exponent b is compatible with the one found for the above-mentioned power law
of the relaxation times/diffusion constants. Finally, we study the wavevector
dependence of $f_s(q)$ and $f(q)$, the coherent and incoherent non-ergodicity
parameters. For the Si and O atoms these functions look qualitatively similar to
the ones found for simple liquids and pure silica, in that the coherent function
oscillates (in phase with the static structure factor) around the incoherent one
and in that the latter is approximated well by a Gaussian function. In contrast
to this, $f(q)$ for Na–Na is always smaller than $f_s(q)$ for Na and the latter can
be approximated by a Gaussian only for relatively large q.

1. Introduction

In the last two decades our understanding of the structural and dynamical properties of glass-
forming liquids has increased impressively [1–4]. This progress is due to significant advances in
various experimental techniques (light and neutron scattering, dielectric measurements, etc), to
the development of new theoretical approaches and concepts (mode-coupling theory (MCT),

landscapes, etc) [5–8], and, last but not least, to the extraordinary advances that computer simulations have made [9–13]. The result of all these efforts is a widely accepted picture on the relaxation dynamics of glass-forming liquids: at high temperatures this dynamics is that of a normal liquid and hence the typical time correlation functions decay exponentially in time and the T-dependence of the typical relaxation times $\tau(T)$ shows an Arrhenius law. (Note that although there is a well developed theoretical machinery to describe the *static* properties of such liquids [14], an *accurate* understanding of the *dynamics* is still lacking.) With decreasing temperature the dynamics changes in that time correlation functions are no longer exponential and the T-dependence of the relaxation times is often super-Arrhenius. In the past it has been shown that the slow dynamics observed in this temperature range can be rationalized very well by means of the so-called MCT of the glass transition, and that often this theory is able to describe this dynamics not only qualitatively but even quantitatively [5, 15–21]. If the temperature is decreased even further the relaxation times increase very quickly and typically show an Arrhenius dependence on T with an activation energy that is larger than the one found at higher temperatures. The details of the dynamics in this temperature range are not understood very well and also there exists no satisfactory theoretical description for it.

The presence of the three above-mentioned regimes in $\tau(T)$ (Arrhenius, super-Arrhenius, Arrhenius) is the typical behaviour found in the so-called 'fragile' glass-forming liquids [22], which include polymers, most molecular glass-formers, and simple liquids. In contrast to this, the so-called 'strong' glass-forming liquids (typical examples include silica and many other oxide glasses) follow over the whole accessible temperature range an Arrhenius law, i.e. no super-Arrhenius temperature dependence is found. Since it is one of the main achievements of MCT to rationalize this super-Arrhenius T-dependence, it was believed for quite some time that the theory is not very useful for such glass-formers. In recent computer simulations it was shown, however, that most models for strong glass-forming liquids exhibit at sufficiently high temperatures deviations from the Arrhenius law found at intermediate and low temperatures [23–28] and that in the temperature range in which these deviations are seen the relaxation dynamics can be described very well by MCT [25, 29, 30], in agreement with the results of some experiments [31, 32]. Therefore one can conclude that this theory is able to describe not only fragile glass-formers, but also many of the properties of intermediate and strong ones.

The results discussed so far concern systems in which the dynamics of all atomic species occurs on roughly the same timescale. There are, however, large classes of materials in which this is not the case. For example, in superionic glass-formers, such as $Na_2O–xSiO_2$ or mixed alkali glasses such as $0.5Na_2O–0.5K_2O–3SiO_2$, the alkali atoms move on a timescale which at low temperatures is many orders of magnitude faster than that for the atoms constituting the matrix (here Si and O) [33–38]. To what extent MCT is able to rationalize the very heterogeneous dynamics of these types of glass-forming system is at present unknown, although recently evidence has been found that certain aspects of the relaxation dynamics can indeed be understood by means of the theory [39]. The goal of the present paper is therefore to carry out a detailed investigation of the relaxation dynamics of a prototype of such an ion-conducting glass-former, $Na_2O–2SiO_2$, and to see to what extent the predictions of MCT regarding the dynamics of glass-forming liquids hold. Note that although so far there has been no test of MCT for these systems, computer simulations have already been used for a long time to study such ion-conducting materials. Seminal work on this goes back more than twenty years to Soules *et al* [40] who studied the structure of sodium disilicate and to Angell *et al* [41, 42] who looked at certain aspects of the diffusion dynamics. These early investigations were more recently followed up by similar studies on related systems and also many experimental investigations [43–63].

A further interesting feature of these systems is that the distribution of the alkali ions in the SiO_2 matrix is not completely uniform but instead forms an interconnected network of small pockets and filaments [34, 43, 48, 52, 61]. Although for a long time there was no *direct* experimental evidence for the presence of these structures, recent neutron scattering experiments of Meyer *et al* on $Na_2O–2SiO_2$ showed a structural feature at a wavevector $q \approx 0.9$ Å^{-1} [64], in excellent agreement with the results from computer simulations that could attribute this peak to the presence of the above-mentioned network [39, 65, 66]. How the presence of these channels affects the relaxation dynamics is, however, so far not known and therefore the present paper is also a contribution to gaining insight into this matter.

The remainder of the paper is organized as follows. In the next section we will describe the model used for the simulations as well as giving their details. The following section is then devoted to the presentation of the results and in the final section we summarize and discuss them.

2. Model and details of the simulation

The force field used in the present work is a modification of the one proposed by Kramer *et al* to describe zeolites [67], i.e. crystalline materials that contain also Si, O and Na. This potential had the functional form

$$\phi_{\delta\epsilon}(r) = \frac{q_\delta q_\epsilon e^2}{r} + A_{\delta\epsilon} \exp(-B_{\delta\epsilon}r) - \frac{C_{\delta\epsilon}}{r^6} \qquad \delta, \epsilon \in [\text{Si, Na, O}], \qquad (1)$$

where r is the distance between two atoms of types δ and ϵ. The parameters $A_{\delta\epsilon}$, $B_{\delta\epsilon}$, and $C_{\delta\epsilon}$ can be found in [67]. Note that q_δ is an *effective* charge with values $q_{\text{Si}} = 2.4$ and $q_{\text{O}} = -1.2$. In [67] the effective charge of the sodium atoms was chosen to be $q_{\text{Na}} = 1.0$, which has the disturbing effect that Na_2O is not neutral. Hence we changed the potential of [67] somewhat, by assigning to the Na atom an effective charge $q_{\text{Na}} = 0.6$ [66]. This change of the charge affects of course the local structure and therefore we have added to $\phi_{\delta\epsilon}(r)$ a term which compensates for this change at *short* distances. Hence the potential that we used in our simulation is given by

$$\Phi_{\delta\epsilon}(r) = \phi_{\delta\epsilon}(r) + \frac{\tilde{q}_\delta \tilde{q}_\epsilon e^2}{r}[1 - (1 - \delta_{\delta\text{Na}})(1 - \delta_{\epsilon\text{Na}})]\Theta(r_c - r) \qquad (2)$$

with $\tilde{q}_{\text{Si}} = 2.4$, $\tilde{q}_{\text{O}} = -1.2$, and $\tilde{q}_{\text{Na}} = 0.6\ln[C(r_c - r)^2 + 1]$. (Here Θ is the usual Heaviside function.) The parameters $C = 0.0926$ Å^{-2} and $r_c = 4.9$ Å were chosen such that at ambient pressure the resulting structure is in good agreement with the experimental results from neutron scattering [66]. Thus the potential $\Phi_{\delta\epsilon}(r)$ used in the present work is at short distances very similar to the one proposed by Kramer *et al* and is at large distances (where the effective charges are screened) modified such that all systems of the form $Na_2O–xSiO_2$ are neutral.

In previous studies it has been shown that this potential is able to reproduce many structural properties of $Na_2O–xSiO_2$, with $x = 2, 3, 4$, and also certain aspects of the relaxation dynamics of this model are in good qualitative agreement with experiments [39, 61, 65, 66, 68]. Although it cannot be expected that such a simple model will be able to reproduce faithfully *all* the features of the relaxation dynamics of the real material, it can be expected that the salient properties will at least be correct from a qualitative point of view.

In the present simulation we integrated the equations of motion using the velocity form of the Verlet algorithm with a time step of 1.6 fs. At each temperature we first equilibrated the system by coupling it to a stochastic heat bath. This equilibration time exceeded the structural relaxation time of the silicon atoms (measured by means of the incoherent intermediate-scattering function for a wavevector 1.7 Å^{-1}, which corresponds to the length scale of the distance between two tetrahedra; see below). Subsequently we started a production run in the

NVE ensemble using a density of 2.37 g cm^{-3} which is close to the experimental value [69]. The number of particles was 8064 ($N_{Si} = 1792$, $N_O = 4480$, $N_{Na} = 1792$) in a cubic simulation box of size $L = 48.653$ Å. So large a system size is needed if one wants to avoid finite-size effects in the relaxation dynamics [70, 71]. In addition, previous simulations have shown that sodium silicate glasses have structural features that extend over 6–8 Å [39, 52, 61] and therefore also this calls for rather large system sizes. The temperatures investigated were 4000, 3400, 3000, 2750, 2500, 2300, and 2100 K. At the lowest temperature the length of the production run was 1.5 million time steps, which corresponds to 2.5 ns. In order to improve the statistics of the results we did at each temperature two completely independent runs.

3. Results

The main quantities of interest in the present paper are $F(q, t)$ and $F_s(q, t)$, the coherent and incoherent intermediate-scattering functions for wavevector q. (Note that for isotropic systems, like the one studied here, these space-time correlation functions depend only on q, the modulus of q, i.e. there is no directional dependence. Therefore we have made use of this fact also in the analysis of our data and have averaged over all wavevectors with the same modulus.) These two observables are not only of great theoretical interest [14], but certain linear combinations can also be measured in neutron scattering experiments [72]:

$$F^{\delta\epsilon}(q, t) = \frac{1}{N} \sum_{j=1}^{N_\delta} \sum_{k=1}^{N_\epsilon} \langle \exp[iq \cdot (r_j(t) - r_k(0))] \rangle \tag{3}$$

$$F_s^\delta(q, t) = \frac{1}{N} \sum_{j=1}^{N_\delta} \langle \exp[iq \cdot (r_j(t) - r_j(0))] \rangle. \tag{4}$$

Here $r_j(t)$ is the position of particle j at time t, N_δ is the number of atoms of type δ, and N is the total number of atoms.

In [66] we have shown that in NS2 the partial structure factors $S_{SiSi}(q)$, $S_{SiO}(q)$, and $S_{OO}(q)$ have *two* pre-peaks: one at $q_1 \equiv 0.94$ Å^{-1} and a second one at $q_2 \equiv 1.7$ Å^{-1}. (The 'main' peaks, corresponding to the length scale of a nearest-neighbour pair of Si–O and Na–O, are at ≈ 2.8 and ≈ 2.1 Å^{-1}, respectively.) The peak at q_2 is related to the distance between neighbouring tetrahedra and thus corresponds to the so-called 'first sharp diffraction peak' in pure silica. The peak at q_1 has recently been shown to be related to the typical distance between the channels mentioned in the introduction [39]. Unfortunately, due to cancellation effects in the partial structure factors (weighted with the appropriate experimental neutron scattering cross-sections) it is hard to see this peak in a neutron scattering experiment done at room temperature [64, 66, 73]. However, the recent neutron scattering studies of Meyer *et al* have shown that this system shows at high temperatures, i.e. above $T \approx 1200$ K which is well above the glass transition temperature [69], a feature in the elastic signal at a wavevector around 0.9 Å^{-1}, i.e. very close to q_1 [64]. Thus we conclude that this structural feature is not only seen in the present model for NS2, but can be found in the real material as well. In the following we will demonstrate that these structural features also have a strong influence on the relaxation dynamics of the system.

In figure 1 we show the time dependence of the incoherent intermediate-scattering function for all temperatures investigated. We see that at high temperatures the relaxation of the structure is relatively fast in that the correlation function decays, after the microscopic timescale which lasts around 0.2 ps, basically exponentially. From this graph we also recognize that at these temperatures this decay is about a factor of four faster for the sodium atoms than the one for the silicon atoms, and about a factor of three faster than the one for the oxygen atoms. This is in
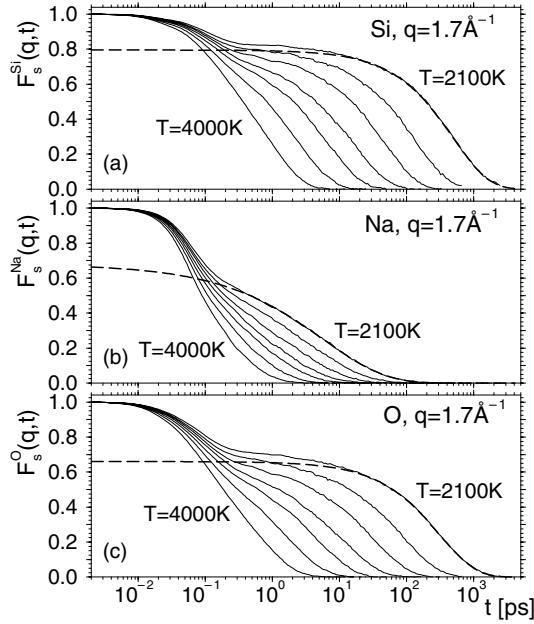
Figure 1. Time dependence of the incoherent intermediate-scattering function for Si, Na, and O (top to bottom) for all temperatures investigated and a wavevector $q = q_2 = 1.7$ Å^{-1}. The dashed curves are fits to the curve for $T = 2100$ K with a KWW law.

agreement with the values for the diffusion constants which at this temperature show the same dependence on the species [66]. At low temperatures the correlators have a time dependence that differs qualitatively from the one at high T in that they show a plateau at intermediate times. This plateau is related to the fact that on this timescale the particles are trapped by their surrounding neighbours (a behaviour which is often called a 'cage effect') and hence the time correlation function changes only slowly. Only for relatively large times are the particles able to leave this (temporary) cage and hence the correlators finally decay to zero. It is customary to call the dynamics in the time window in which the correlators are close to the plateau the 'β-relaxation' whereas the second relaxation step is called the 'α-relaxation'. From the figure we see that at low temperature, $\tau(q)$ (the timescale for the α-relaxation) for the sodium atoms is about a factor of 30 smaller than the one for the oxygen atoms and about a factor of 100 smaller than the one for silicon. Hence we conclude that the temperature dependence of τ depends on the species; this is also in agreement with the one found for the diffusion constant [66]. Below we will discuss this dependence in more detail.

Also included in the figure is a fit to the curves at the lowest temperatures with a Kohlrausch–Williams–Watts (KWW) law, i.e. $F_s^\delta(q, t) = A_\delta \exp(-(t/\tau_\delta)^\beta)$ (dashed curves). We see that this functional form is able to describe the data very well in the α-relaxation regime, as is usually the case for the relaxation dynamics of glass-forming liquids. The value of the exponent β is 0.8 for Si and O and 0.47 for Na. Thus we see that the relaxation dynamics is not very stretched for the atoms making up the matrix whereas it is very stretched for the network modifier. Below we will come back to a possible interpretation for this low value of β. (Note that a high value of β for Si and O is in agreement with the observation that in pure silica also the correlators for these length scales are not very stretched [66]. The presence of sodium does, however, indeed lower the value of β somewhat.)
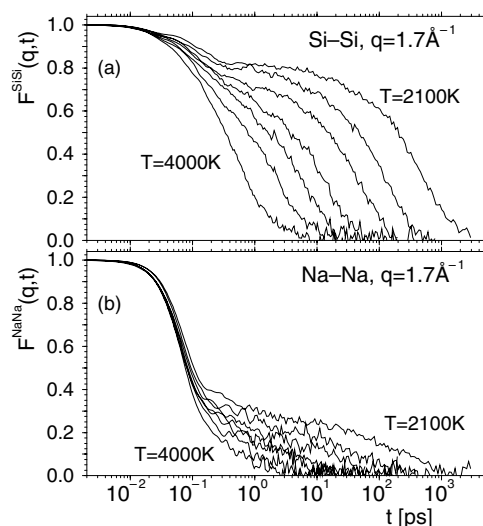
Figure 2. Time dependence of the coherent intermediate-scattering function for the Si–Si (a) and Na–Na (b) correlations for all temperatures investigated.

Having discussed the species and temperature dependence of $F_s^\delta(q, t)$ we now focus on the coherent function $F^{\delta\epsilon}(q, t)$, defined in equation (3), since that gives information on how the overall structure of the system relaxes. The time and temperature dependence of $F^{SiSi}(q, t)$ and $F^{NaNa}(q, t)$ is shown in figure 2 (the result for the O–O correlation is similar to that for Si–Si). A comparison of the curves in this figure with the incoherent functions, figure 1, shows that for the case of silicon the coherent and incoherent functions are very similar in that the height of the plateau at intermediate times and the typical relaxation times for the α-relaxation are quite comparable. This is the usual behaviour found for glass-forming systems such as pure silica, water, or simple liquids [30, 75, 76]. In contrast to this, the time dependence of $F_s^{Na}(q, t)$ for sodium differs strongly for the coherent function $F^{NaNa}(q, t)$ in that the relaxation time of the former is about a factor of ten smaller than that of the latter. This shows that the relaxation dynamics of the sodium atoms has unusual features. In fact it has been shown in [39, 61] that the motion of a tagged Na atom is relatively fast in that the particles hop between certain preferential sites (generated by the Si–O matrix). However, the *relative* spatial arrangement of the Na particles (i.e. their global structure) does not change under this type of motion and hence the coherent function decays much more slowly than the incoherent one.

One of the important predictions of MCT is that close to the critical temperature of the theory the shape of the time correlation functions does not depend on temperature. This means that a correlator $\phi(t, T)$ can be written as

$$\phi(t, T) = \hat{\phi}(t/\tau(T)), \tag{5}$$

where $\tau(T)$ is the α-relaxation time at temperature T. To what extent this prediction, which is often called the time–temperature superposition principle (TTSP), holds can easily be tested by plotting the correlators versus t/τ. For this we have defined the α-relaxation time τ as the time that it takes the correlator to decay to 0.1. Although this definition (and the value 0.1) is somewhat arbitrary, it is easy to see that *if the TTSP holds*, the details of the definition do not matter. In figure 3 we show the correlators as a function of t/τ for all temperatures investigated. We see that for silicon and oxygen the TTSP holds basically for the whole T-range if F_s is smaller than ≈ 0.3. This is in qualitative agreement with a MCT calculation for a hard-sphere
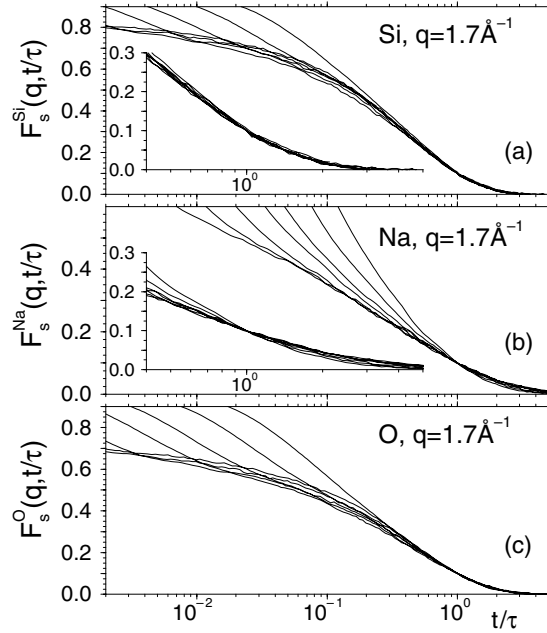
Figure 3. The incoherent function $F_s(q, t)$ versus $t/\tau(T)$ for Si, Na, and O (top to bottom). The α-relaxation time $\tau(T)$ has been defined via $F_s(q, \tau) = 0.1$. The insets in (a) and (b) show the same functions at large rescaled times.

system [74]: also in that case the TTSP holds only for values of the intermediate-scattering function that are smaller than about 0.3 (for a q that is at the structure factor maximum). For larger values of the correlators one observes systematic deviations from the (asymptotic) TTSP scaling, the formulae of which can also be calculated within MCT [74].

In the case of sodium we have already shown that its dynamics is very different from that of Si and O in that, e.g., for $F_s^{Na}(q, t)$ one obtains a very different stretching exponent β from that for F_s^{Si} and F_s^{O} at a given q. However, for $F_s^{Na}(q, t)$ the TTSP also works for low temperatures, $T \leqslant 2500$ K. That for this species the TTSP does not hold for higher temperatures is reasonable, since for $T \geqslant 2750$ K the typical α-relaxation times are still of the order of a few picoseconds only (see figure 1(b)) and thus the α-relaxation regime is not well separated from the microscopic dynamics. Note that if one were able to equilibrate the system at even lower temperatures, the TTSP could be expected to start to break down, since at low T the dynamics is likely to be dominated by a simple diffusive motion in which the single step is the breaking of a Si–O bond, a behaviour which has been found in *pure* silica [25]. Hence one can expect this to affect also the sodium dynamics and thus the breaking down of the TTSP.

The correlators discussed so far were for $q = 1.7$ Å^{-1}, the length scale corresponding to the typical distance between two neighbouring tetrahedra. We now investigate how the α-relaxation time depends on the wavevector as well as on the particle species. In figure 4 we show the q-dependence of τ as determined from the incoherent correlators as well as some of the coherent ones. The temperature is $T = 2100$ K—thus the lowest temperature at which we were able to fully equilibrate the system. Since for the case of a diffusive motion the relaxation time $\tau(q)$ of the incoherent function is equal to $(Dq^2)^{-1}$ (D is the diffusion constant), we plot directly $\tau(q)q^2$ which can be understood as an inverse q-dependent diffusion constant. We first start with the particles forming the matrix, i.e. Si and O. We see that for these elements $\tau(q)q^2$
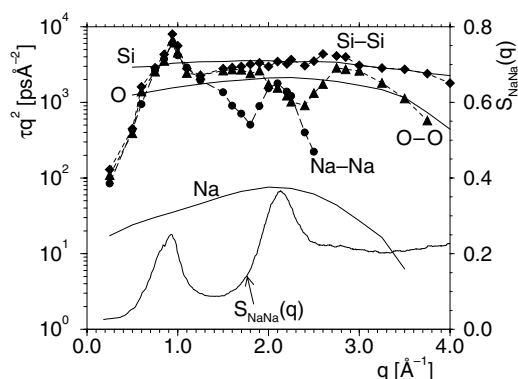
Figure 4. Wavevector dependence of τq^2 for various coherent and incoherent correlators (see the labels of the curves) at $T = 2100$ K. Right-hand scale: q-dependence of the partial structure factor for the sodium atoms.

from the incoherent functions increases weakly with increasing q, goes through a maximum, and then decreases again at large q. The location of this maximum is around 2.8 Å^{-1}, i.e. at the wavevector at which the static structure factor has the peak that corresponds to the distance between neighbouring Si–O. The same type of q-dependence has also been found in the case of pure SiO$_2$ [30] and it reflects the fact that on this length scale the system is particularly rigid. The relaxation times of the coherent functions have a more complex q-dependence in that they oscillate around the τ for the incoherent function. This oscillation is in phase with the corresponding static structure factor, a feature that is found also in simple liquids [76] as well as in systems such as pure silica [30] or water [75]. This effect is similar to the so-called de Gennes narrowing [14], but it has to be emphasized that it appears here in the α-relaxation regime of a two-step relaxation process and, thus one cannot expect it on the basis of de Gennes' simple argumentation that uses sum rules of the short-time expansion of the coherent intermediate-scattering function.

From the figure we recognize that the largest relaxation time is at a wavevector $q \approx 0.95$ Å^{-1}, which corresponds to the length scale of the network of channels discussed in [39, 61]. The different chemical ordering of silicon and sodium leads to the presence of an additional intermediate length scale which is reflected in the dynamics of sodium in that the trajectories of the sodium atoms are restricted to a network of channels in a Si–O matrix. This network of channels is reflected in the collective correlations by the slowest relaxation process of our system, the rearrangement of the channel structure. Finally we remark that for wavevectors below 0.95 Å$^{-1}\tau(q)q^2$ exhibits a very steep increase: we see that in this range of q-values the curves are very much compatible with a straight line which corresponds to a growth of the relaxation times like $\tau(q) \propto q^{-2}\exp(Aq)$, where A is a positive constant. Although we are not aware of any theoretical reason for such a dependence, it seems to describe our data remarkably well over two decades in τ.

For the sodium atoms the q-dependence of τ is more complicated than that for Si and O. For the coherent correlators this function is qualitatively similar to the one found for Si–Si and O–O. In particular we find again a pronounced peak at $q \approx 0.95$ Å^{-1}, i.e. the length scale of the channels. Note that close to this peak also the absolute value of τ is close to the ones for Si and O, which shows that on this length scale the spatial arrangement of the Na atoms can only relax if the Si–O matrix relaxes. The relaxation time for the incoherent Na function behaves very differently. First of all we see that it is significantly smaller than that of the

coherent function, in agreement with our conclusions from figures 1 and 2. Also this function increases for small and intermediate wavevectors, shows a maximum at the location of the corresponding peak in the partial structure factor (included in the figure as well), and then decreases for even larger q. It is not possible to determine the relaxation times of $F^{NaNa}(q, t)$ for $q > 2.5$ Å^{-1} with our definition $F^{\delta\epsilon}(q, t = \tau) = 0.1$ because for large wavevectors, $F^{NaNa}(q, t)$ has already decayed to values around or lower than 0.1 before the α-relaxation starts to develop (see figure 8 below). In contrast to that we can determine the relaxation times for $F_s^{Na}(q, t)$ also for relatively large wavevectors. Since for sufficiently large q one has $F_s^{\delta}(q, t) \approx F^{\delta\delta}(q, t)$, we know that in this limit the relaxation times for $F^{\delta\delta}(q, t)$ have to approach the ones for $F_s^{\delta}(q, t)$. This implies that the curve $\tau(q)$ for the Na–Na correlation must start to decrease quickly in order to approach the one for the Na correlation. Hence we expect for large wavevectors the relaxation times for the Na–Na correlation to become significantly smaller than that of the matrix. An inspection of the correlation functions shows, however, that this is not yet the case for wavevectors smaller than 3.5 Å^{-1}.

In an earlier study of pure silica, the paradigm of a 'strong' glass-former, we found the surprising result that the temperature dependence of the diffusion constant as well as the viscosity show at high temperatures a significant deviation from the expected Arrhenius law [25]. In that paper it was argued that this deviation can be rationalized by MCT which predicts the existence of a 'critical temperature' T_c close to which the transport coefficients show a non-Arrhenius behaviour [5]. Since significant deviations from an Arrhenius law have been observed also for the sodium silicate system investigated here [66], it is reasonable to investigate to what extent MCT is able to rationalize the relaxation dynamics. The theory predicts that close to T_c the temperature dependence of the diffusion constants or α-relaxation times is given by a power law:

$$D(T) \propto (T - T_c)^\gamma \qquad \text{and} \qquad \tau(T) \propto (T - T_c)^{-\gamma}. \tag{6}$$

Here γ is a system-universal constant, i.e. it does not depend on what species or wavevector one considers. In addition, MCT predicts that the value of the exponent γ has a one-to-one correspondence with the exponent b of the so-called von Schweidler law that is discussed below. This connection is given by

$$\gamma = \frac{1}{2a} + \frac{1}{2b} \qquad \text{with} \frac{[\Gamma(1 - a)]^2}{\Gamma(1 - 2a)} = \frac{[\Gamma(1 + 2b)]^2}{\Gamma(1 + 2b)}, \tag{7}$$

i.e. the second equation can be used to determine the value of a from b and then the first equation can be used to calculate γ (here $\Gamma(x)$ is the usual Γ-function). In [39] we have shown that the value of b is around 0.47 (see also figure 6). Hence equations (7) give a value of $\gamma = 2.87$, which can be considered as the theoretical estimate of MCT for the exponent. If the prediction of the theory for the power law and the value of the exponent is correct, a plot of $\tau^{-1/\gamma}$ (or $D^{1/\gamma}$) versus T should give a straight line. A plot of this type is shown in figure 5 for the relaxation times $\tau(q)$ for the wavevectors $q = 0.94$ and 1.7 Å^{-1} as well as the diffusion constants (which were determined from the long-time limit of the mean squared displacement of a tagged particle [66]). Note that we have not included the data for Na, since, as shown in [66], the diffusion constant for Na follows an Arrhenius law in the whole temperature range, and hence the power laws given by equation (6) certainly do not hold for this species. We see that all the curves do indeed show a straight line in a temperature interval that is quite substantial. Linear fits in this region are included in the graph as well (solid lines). It is quite remarkable that this type of plot rectifies the data for the diffusion constant for the Si as well as those for O, since for binary systems it is often found that the more mobile species has an exponent γ that is smaller than the one for the less mobile species (see, e.g., [76, 84]). This
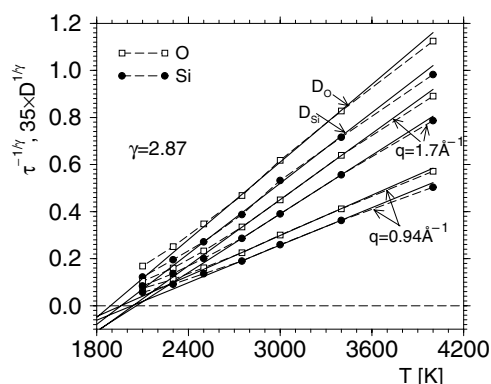
Figure 5. A test for the presence of a power law for the relaxation times $\tau(q)$ for Si and O and two wavevectors. Also included are the data for the diffusion constants D_{Si} and D_O, which for the sake of producing a clearer presentation have been multiplied by 35. The bold straight lines are linear fits show the prediction of MCT.
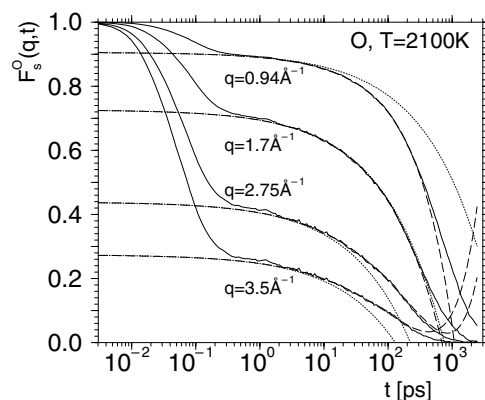

Figure 6. Time dependence of the incoherent intermediate-scattering function for oxygen at $T = 2100$ K. The solid curves are $F_s^O(q, t)$ for different wavevectors (see the labels). The dotted curves are fits with a von Schweidler law, the first term in equation (8), with an exponent $b = 0.47$. The dashed curves are fits with the von Schweidler law including the leading-order corrections (see equation (8)).

observation might tentatively be taken as evidence that the relaxation dynamics of the present system (as measured by the Si and O atoms) is quite homogeneous.

Furthermore, we see from the graph that the extrapolation of these straight lines to lower temperatures intersects the T-axis at a point, the critical temperature T_c, which depends only weakly on the quantity considered, and which is around 2000 K. Hence we conclude from this figure that the relaxation times and diffusion constants for Si and O do indeed show the predicted power-law dependence with a common exponent γ and a common critical temperature T_c. Finally, we note that in the temperature interval in which τ and D show this power law these quantities change by about two orders of magnitude and hence the existence of the power laws is not just a trivial matter. Note that although MCT predicts that at T_c the relaxation times should diverge, in reality this is not found. The reason for this is that once the relaxation times have increased beyond a certain value, for atomic systems, usually times of the order of 10 ns, the system starts to relax via processes that currently can be taken into account by

the theory only in a schematic way. Despite the presence of these processes, usually called 'hopping processes', the theory is still able to make predictions on the relaxation dynamics on the timescale of the β-relaxation. For more details we refer the reader to [5, 77]. The presence of these hopping processes for the present system can be inferred from figure 5, in that the data points for $T \leqslant 2600$ K are above the theoretical straight lines, i.e. the relaxation is faster than predicted from the power law.

Having discussed the relaxation dynamics of the system in the α-regime, we now turn our attention to the β-regime, i.e. the time window in which the correlators are close to the plateau (see figure 1). The late β-regime can be understood as the short-time regime of the α-relaxation, i.e. the regime where the density correlator starts to decay from the plateau value to zero. Within MCT the short-time expansion of the α-relaxation master function in equation (5) is known and yields the following formula for the intermediate-scattering functions [74]:

$$\Phi(q, t) = f_c(q) - h_c(q)(t/\tau)^b + h_2(q)(t/\tau)^{2b}. \tag{8}$$

Here $\Phi(q, t)$ stands for the different coherent and incoherent intermediate-scattering functions. $f_c(q)$ is the height of the plateau, also called the non-ergodicity parameter, and $h_c(q)$ is the so-called critical amplitude that depends, like the amplitude $h_2(q)$, only on q (as well as on the species). The first power law of equation (8) is often called the 'von Schweidler law' and the exponent b the 'von Schweidler exponent'. Note that the theory predicts that the value of b should be the same for all correlators (i.e. independent of the value of q). In figure 6 we show the time dependence of the incoherent intermediate-scattering function for the oxygen atoms for various wavevectors (at $T = 2100$ K). Also included are fits with the functional form given by equations (8) using the height of the plateau as a fit parameter. The dotted curves correspond to a fit in which only the first term on the RHS of equation (8), the von Schweidler law, is used, whereas the dashed curve is the case where the second term in equation (8) is also taken into account. In these fits $h_c(q)$ and $h_2(q)$ were fit parameters that were allowed to depend on q, whereas the exponent b was a global fit parameter. From the figure we conclude that the von Schweidler law is indeed able to describe well the dynamics close to the plateau. Furthermore, we see that the inclusion of the correction term increases the time window for which this law holds by about a factor of ten in qualitative agreement with the results of such an analysis for other glass-forming liquids [5, 30, 75, 76]. We also mention that a similar good fit is obtained for the case of $F_s(q, t)$ for Si. In [39] we showed fits of the same type for the coherent functions of Si and O and found that for these correlators the late β-regime is also described very well by the functional form given in equation (8).

We emphasize that a universal exponent b exists only in the late β-relaxation (or short-time α-relaxation) regime and not for the late α-relaxation. For the latter one finds that the stretching exponent β, and therefore the shape of the correlator, depends on the species or the wavevector. In particular, we have discussed in [39] the wavevector dependence of β for the Na atoms and have shown that for small and intermediate q, $q \leqslant 1.5$ Å^{-1}, β changes significantly, thus showing that the α-relaxation is indeed not universal from this point of view.

In this context it is, however, very interesting that $\beta(q)$ for the Na atoms becomes independent of q for $q \geqslant 1.6$ Å^{-1} [39], *although* in this q-range the structure factor $S_{NaNa}(q)$ still shows pronounced features, i.e., it is not a constant. Such a behaviour was predicted some time ago by Fuchs, who used MCT to show that $\lim_{q \to \infty} \beta(q) = b$, i.e. for large wavevectors β should converge to the von Schweidler exponent b [79]. We have found that in our case this is indeed the case, i.e. that for large q the stretching exponent is indeed compatible with $b = 0.47$ [39]. Hence this nice agreement between our results and the prediction of MCT shows that the theory is indeed also able to describe this feature of the relaxation dynamics of the present system. We also mention that for the case of a hard-sphere system the MCT prediction

for the independence of β of q holds only for wavevectors that are much larger than the location of the first peak in the structure factor. The fact that for the present system this asymptotic value is reached already for quite small wavevectors is thus rather surprising. We note, however, that a closer inspection of $F_s^{Na}(q, t)$ for $q \geqslant 1.6$ Å^{-1} shows that the α-relaxation regime of these correlators falls into the late β-relaxation regime of all the other (slow) correlators in which the von Schweidler law holds. Thus, it seems that the relaxation processes in the β-regime of the slow correlators that correspond to the universal von Schweidler decay are impressed onto the dynamical behaviour of the single-particle motion of the sodium atoms which leads to stretched-exponential decay of $F_s^{Na}(q, t)$ with $\beta = b$. For smaller wavevectors this is not the case, since there the α-relaxation of $F_s^{Na}(q, t)$ overlaps essentially only with the *plateau* of the slow correlators.

The result in figure 6 shows that the time dependence of the correlation functions for the time regime in which they start to fall below the plateau is compatible with the functional form given in equation (8). However, there is a more general prediction of MCT for the whole β-relaxation regime that should hold, as equation (8), close to T_c: the so-called factorization property. This property is expressed in the following formula:

$$\phi(t) = f_c + h_\phi G(t). \tag{9}$$

In this equation $\phi(t)$ denotes any time correlation function that couples to density fluctuations. Equation (9) is called the factorization property because $\phi(t) - f_c$ factors into a system-universal time-dependent function $G(t)$ and a ϕ-dependent function. (Note that this factorization property holds also for the case where hopping processes are present [5, 77].) The time dependence of $G(t)$ is given by the solution of a non-linear equation which can be solved numerically [5]. A way to check to what extent the factorization property holds, without making use of the explicit form of $G(t)$, is to calculate the following quantity:

$$R_\phi(t) = \frac{\phi(t) - \phi(t')}{\phi(t'') - \phi(t')}. \tag{10}$$

Here t' and t'' are two arbitrary times in the β-regime. It follows immediately that *if* equation (9) holds, R_ϕ is independent of ϕ, since it is just the system-universal function $G(t)$. In figure 7 we show the time dependence of R_ϕ at $T = 2100$ K. The correlators ϕ used are $F_s(q, t)$ for Si and O at $q = 0.94$ Å^{-1}, $q = 1.7$ Å^{-1}, $q = 2.0$ Å^{-1}, and $q = 3.0$ Å^{-1}, as well as the coherent functions $F(q, t)$ for Si–Si, Na–Na, and O–O at the same values of q. The times t'' and t' from equation (10) are 2.9 and 10.3 ps, respectively. From the figure, we recognize that in the β-regime the $R_\phi(t)$ for all these correlators collapse nicely onto a master function, which is the function $G(t)$. Hence we conclude that the factorization property predicted by MCT holds for the present system. Finally, we mention that we find for higher temperatures the same type of collapse, but that the time window in which the master curve is observed shrinks rapidly, in qualitative agreement with the prediction of MCT.

The last quantity that we will discuss is $f_c(q)$ from equation (8). Since f_c is just the height of the plateau of the correlator at intermediate times, this parameter is often also called the 'non-ergodicity parameter' (NEP) since it reflects how much memory the system has of its state at $t = 0$. In the following we will focus on the wavevector dependence of $f^{\delta\epsilon}(q)$ and $f_s^\delta(q)$, the NEP for the coherent and incoherent scattering functions. (Note that $f^{\delta\epsilon}(q)$ and $f_s^\delta(q)$ are often also called the Debye–Waller factor and Lamb–Mössbauer factor, respectively.) We have determined $f^{\delta\epsilon}(q)$ and $f_s^\delta(q)$ by using equation (8) to fit the correlators. The q-dependences of $f^{\delta\epsilon}(q)$ and $f_s^\delta(q)$ for the cases of silicon and oxygen are shown in figure 8. We see that in both cases $f_s^\delta(q)$ (open symbols) decays quickly with increasing q and that this dependence can be described very well by a Gaussian (bold solid curves). Such a behaviour has already been found for the case of pure silica [66] and is in qualitative agreement with the prediction
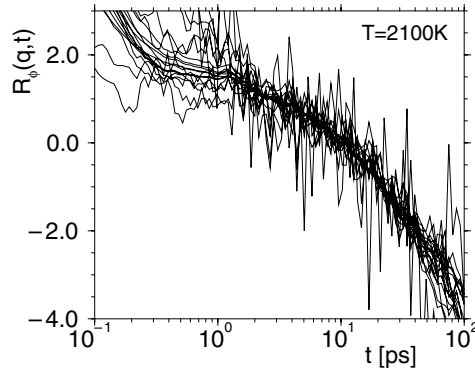
Figure 7. Time dependence of the function $R_\phi(t)$, defined in equation (10), at $T = 2100$ K. The correlators used to make this plot are $F_s^{Si}(q, t)$ and $F_s^O(q, t)$ for $q = 0.94, 1.7, 2.0, 3.0$ Å^{-1} and $F^{\delta\delta}(q, t)$ with $\delta \in \{Si, O, Na\}$ at the same wavevectors.
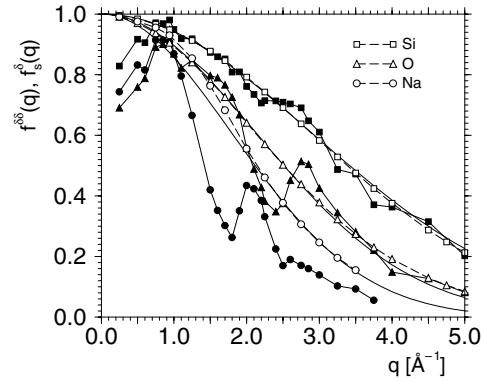

Figure 8. Wavevector dependence of the NEPs $f_s^\delta(q)$ and $f^{\delta\delta}(q)$ (curves with open and closed symbols, respectively) for $\delta \in \{Si, O, Na\}$. The bold curves are Gaussian fits to the NEP for the incoherent functions.

of MCT [5]. The widths q_s of these Gaussians are 4.1 and 3.0 Å^{-1} for Si and O, respectively. This means that in the timescale of the β-relaxation the particles are trapped in a cage with radius $r_s = 1/q_s = 0.24$ Å (Si) and 0.33 Å (O). For the case of pure SiO$_2$ the corresponding values are 0.23 and 0.29 Å [66]. Hence we see that the presence of sodium slightly increases the size of the cage and that this increase is more pronounced for the case of oxygen than for silicon. This result is reasonable since some of the oxygen atoms are in the immediate vicinity of the sodium atoms but are bound to them less strongly than they are to the silicon atoms (and of course there is no Si–Na bond). In addition, the presence of dangling bonds (i.e. non-bridging oxygens) will also lead to an increase of the size of the cage for oxygen.

The NEP for the coherent functions of Si and O oscillate around the ones for the incoherent functions. This oscillation is in phase with the corresponding structure factor, a behaviour which is in qualitative agreement with the theoretical expectation [5, 78]. In particular, we see that the amplitude of this oscillation is smaller for the case of silicon than for oxygen, in agreement with the findings for pure SiO$_2$ [30] and binary mixtures of particles [76]. This finding can be rationalized by the fact that in a binary system with strong asymmetry in the concentration, the coherent correlation functions for the minority species are in general very similar to the incoherent functions.

Also included in the figure is $f^\delta(q)$ as determined from the Na correlator. (Note that $F_s^{\mathrm{Na}}(q,t)$ does not show a well defined plateau for $q \geqslant 1.5$ Å^{-1} (see, e.g., figure 2 in [39]). Hence a fit with the functional form given by equation (8) is rather difficult if q is large, and thus the height of the plateau cannot be determined with high accuracy. However, for $q \leqslant 1.2$ Å^{-1} one does indeed find a well developed plateau and thus it is possible to determine $f_s^\delta(q)$ with good accuracy.) From figure 8 we see that $f_s^\delta(q)$ for Na decays significantly faster than the ones for Si and O. This can be interpreted by saying that the cage for the sodium atoms is wider than the one for Si and O. However, care must be taken in drawing this conclusion since, as just mentioned, at the temperatures investigated neither the intermediate-scattering functions for intermediate and large q nor the mean squared displacement of the Na atoms show a well defined plateau at intermediate times. Hence one cannot really say that on this timescale the particles are caged, and hence also the interpretation of $f_s^\delta(q)$ as the Fourier transform of the shape of the cage is not quite appropriate. What is remarkable with $f_s^\delta(q)$ for Na is the fact that it is *not* possible to fit it well with a Gaussian. If one fits the data for $q \geqslant 2.2$ Å^{-1} with such a functional form it is possible to obtain a very good fit (bold solid curve). (The width of this Gaussian is 2.52 Å^{-1}, which corresponds to a 'cage' of size 0.39 Å.) However, this fit gives a very poor representation of the data for smaller wavevectors. This result, which is in contrast to the findings for Si and O, shows that the dynamics of Na is indeed rather unusual. Roughly speaking, one can thus say that for small length scales, i.e. large q, the cage is relatively soft and therefore the $f_s^{\mathrm{Na}}(q)$ decays quickly. However, on the length scales of the typical distances between the channels (small q) the 'cage' is relatively rigid, since on this length scale, as we have mentioned before, the dynamics of Na is strongly coupled to relaxation processes in the matrix. But of course this is just a hand-waving explanation of the finding and it would be nice to find support for it by means of a more thorough theoretical calculation. We also mention that it is *not* possible to describe the q-dependence of the Na data as the simple sum of two Gaussians, which shows that this dependence is indeed non-trivial.

Also included in the figure is the NEP for the Na–Na correlation. Qualitatively, this $f^{\delta\epsilon}(q)$ looks similar to that for the Si–Si or O–O correlation and, in particular, it shows a pronounced peak at around 2.0 Å^{-1}, which corresponds to the nearest-neighbour distance between two Na atoms ($=3.3$ Å) [66]. However, we notice an important difference in that this NEP does not oscillate around the NEP for the incoherent function, but instead stays systematically below it. Also, for this behaviour we are not aware of any theoretical prediction or experimental result.

4. Summary

In this paper we have studied by means of molecular dynamics computer simulations the relaxation dynamics of a melt of Na$_2$O–2SiO$_2$, one of the prototypes of an ion-conducting glass-former. In particular we investigated the temperature and wavevector dependence of the coherent and incoherent scattering functions. Due to the very different timescale of the dynamics of Na compared with that of the species forming the matrix, the q-dependence of these correlators for the sodium atoms shows features that are neither found in simple liquids nor in network-forming liquids such as pure silica, i.e. systems in which the dynamics of the individual species takes place on a comparable timescale. For example, we find that the time and temperature dependence of the incoherent function for Na is very different from that for the coherent function. This is related to the fact that in this system the sodium atoms have the tendency to populate a relatively small subregion of space, so-called channels, and that the dynamics of the atoms in these channels is relatively quick and occurs by (activated) single-particle hops. In contrast to this, the overall structure of the channel, and hence the coherent function for the Na atoms, relaxes only on the timescale of the α-relaxation time of the Si–O

matrix. The temperature dependence of the relaxation times for the matrix and $F^{NaNa}(q, t)$ shows a strong deviation from an Arrhenius law in agreement with experimental findings for this system [80, 81]. In the past such deviations have been found for simple liquids [76, 82–84] and their existence has been rationalized by means of MCT. However, finding them in systems such as silica [25, 26] or in the present sodium silicate system is rather surprising. In this paper we have shown that in the temperature regime where these deviations are seen, many of the features of the relaxation dynamics can again be rationalized by means of MCT, thus showing that with respect to this there is no difference from the results found for the so-called fragile glass-formers. Hence we conclude that the main difference between strong and fragile glass-formers is that the presence of the hopping processes leads to a shrinking of the dynamical range in which the T-dependence of the relaxation times follows the power law predicted by MCT (as compared to the range found in fragile systems). Nevertheless, despite this reduced range, the time correlation functions still show a behaviour that can be rationalized remarkably well by the theory.

Of course one has to wonder to what extent the results presented in this paper can be found also for real Na_2O–$2SiO_2$, or similar systems. Although it must be expected that the potential used is not sufficiently accurate to reproduce all the properties of the real material on a quantitative level, the surprisingly good agreement of the results of the present model with the neutron scattering results of Meyer *et al* [64] shows that the potential is quite realistic. Therefore, it can be hoped that the results presented here will be found also in appropriate coherent and incoherent neutron scattering experiments and we hope that the present work helps to motivate such experiments.

Acknowledgments

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