Molecular dynamics simulation of alkali-metal diffusion in alkali-metal disilicate glasses

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Long-timescale molecular dynamics simulations of duration 150–250 ps have been performed on alkali-metal disilicate glasses at 1400 K with the general formula $M_2Si_2O_5$ ($M = Na$, K, or an equiatomic mixture of the two). The simulations are long enough to analyse the diffusive behaviour of the alkali-metal ions in detail. The calculated diffusion coefficients show the mixed alkali-metal effect when systems having different alkali-metal contents are treated at the same pressure, but not when they are treated at the same volume (and therefore at higher pressure). There is no evidence for curvature in the time-dependent mean-square displacements of the alkali-metal ions over the 10–60 ps range, which suggests the absence of long-time memory effects. The van Hove correlation functions confirm the hopping mechanism for diffusion, though there is only partial evidence for the existence of a selection effect in the alkali-metal mobility in the mixed glass.

Alkali-metal silicate glasses have received a great deal of experimental attention in recent years[1] giving a wealth of information on their physical properties. A complementary approach to the science of glasses is afforded by molecular dynamics (MD) computer simulation.[2] Simulation studies of silica glass have been conducted for more than a decade,[3–5] but alkali-metal glasses have received close attention only recently. The studies[6–10] have broadly supported experimental interpretation, particularly regarding structure, but in general have not had much to say on the phenomena of ionic transport. This is largely due to the long relaxation times associated with glass structures, which demand long simulation times to accumulate sufficient statistical accuracy. The most recent work, however,[11–14] has begun to address this deficiency, especially in regard to the so-called mixed alkali-metal effect (MAE), according to which the electrical conductivity of a mixed alkali-metal glass is reduced considerably in comparison with the parent single alkali-metal glasses. This effect, which clearly derives from changes in the mobilities of the component ions in the mixture, is quite general and applies to other glasses and modifiers and has received much theoretical attention.[6,10,15,16] Previous studies (*e.g.* refs. 10,16) have attempted to compute the MAE by simulation, though not with fully realistic models. Only very recently has the effect been observed in realistic simulations of metasilicate glasses by Habasaki *et al.*[13] and silicate glasses by Balasubramanian and Rao.[14] In ref. 13, however, the simulations were performed at 700 K, where the diffusion was too small to provide a measurable diffusion constant. The work reported in ref. 14 complements that reported here, in that the authors have studied mixed alkali-metal glasses comprised of potassium and lithium, as opposed to potassium and sodium. In addition, however, we have examined the effect of pressure on the MAE.

The work reported here is an extension of our previous study,[12] which explored the structural and dynamical aspects of sodium disilicate glass. That work confirmed earlier studies, in particular providing clear evidence for the modified random network (MRN) model[17] and also the first quantitative determination of the alkali-metal diffusion and an associated activation energy close to the experimental value. The mechanism of alkali-metal diffusion was shown to be a 'hopping' process, involving long periods of alkali-metal atom localisation in the glass matrix punctuated by rapid moves to a new position nearby. The hops were relatively infrequent, and the timescales for the diffusion processes were very long, implying that extremely long simulations would be required to quantify the MAE. It is primarily this requirement that we have addressed in this work.

Computational details

Model potential

The model potential used in these simulations was based on our previous work,[12] where the functional forms are described in some detail. For convenience we present only a brief outline here.

The system was described by non-polarisable point ions. The alkali-metal atoms were assigned the charge of $+1e$, silicon atoms $+4e$ and oxygens $-2e$. The electrostatic interactions were calculated by the Ewald summation method,[2] with cubic periodic boundary conditions. The remaining short-range, non-bonded interactions were calculated with the empirical silica potentials of Vessal *et al.*[18] and the Na—O and K—O potentials of Parker *et al.*,[19,20] all of which are based on the Buckingham exp-6 potential which, in the case of the silica potentials, are augmented by polynomials close to the potential minimum to improve the description of the local structure.[18] No explicit non-bonded interactions were included for any combination of Si, K and Na, which therefore interacted only *via* the electrostatic terms. The Vessal silica potentials also specify three-body terms for the O—Si—O and Si—O—Si angles. These were included in our simulations, slightly modified to cater for finite cutoffs, as described in ref. 12. Inclusion of these three-body terms is essential to describe correctly the local structure around the silicon and oxygen atoms.[18] The short-range interactions were evaluated to a cutoff radius of 12.0 Å and the three-body forces were truncated after 2.6 Å.

Simulations

The MD simulations were performed on systems comprised of 1080 ions ($240\ M^+$, $240\ Si^{4+}$, $600\ O^{2-}$), where M^+ represents Na^+, K^+, or both in an equal mixture (three compositions in all). All simulations were conducted in the Nosé–Hoover NVT ensemble[21] at a temperature of 1400 K and with a time step of 1 fs. This temperature is high enough to guarantee a reasonable diffusion rate for the alkali-metal ions[12] but does not melt the system. The initial configuration for the sodium glass was taken from our previous work[12] and represented an already well aged system. The mixed alkali-metal and potassium glasses were created from the sodium glass by substitution of sodium ions by potassium ions to a 50% or 100% level as appropriate. The new systems were simulated for a minimum of 20 ps before use.

Two sets of simulations were performed. In the first set (referred to hereafter as the 'fixed pressure' or 'FP' simulations) the mixed alkali-metal and potassium systems were simulated at the same pressure as the sodium glass at 1400 K, which was found to be 152 kbar. This was achieved by first isotropically relaxing the system volume to the required pressure using the Berendsen NPT algorithm.[22] Equilibration was established over 30 ps, followed by a further equilibration of 20 ps in the Nosé–Hoover NVT ensemble, during which the pressure was seen to remain constant. The subsequent simulations ranged from 150 to 250 ps duration, the longer simulations being preferred for the systems with low ionic mobility. In the course of these simulations, configurations were saved at intervals of 100 fs and used subsequently to calculate both structural and dynamical properties.

In the second set (referred to hereafter as the 'fixed volume' or 'FV' simulations) the sodium, potassium and mixed alkali-metal glasses were all simulated at the same volume of 14 136 $Å^3$. This volume corresponds to that of the sodium glass at ambient temperature and pressure (*i.e.* to a mass density of 2.57 g cm^{-3} in this glass). The pressures and densities of the simulated systems are presented in Table 1.

Results

We present below our results for the structure and dynamics of the glass systems studied. Our emphasis, however, is on the dynamical results and to this end the structural data are presented in order to affirm the suitability of the model for the dynamical study. Discussions of the structure of simulated alkali-metal glasses appear in several sources.[6–12]

Static structure

The total radial distribution functions (RDFs) obtained for our three systems at 1400 K and 152 kbar (weighted by the appropriate neutron scattering lengths[23]) are presented in Fig. 1, with the ambient neutron scattering result of Wright *et al.*[24] for the sodium glass. These compare closely with our earlier results for the sodium glass.[12] In all three simulated systems, the three main peaks at *ca.* 1.57 Å, *ca.* 2.55 Å and *ca.* 4.94 Å are manifest. These are generally ascribed to Si—O, O—O (first neighbour) and O—O (second neighbour) correlations respectively, though apart from the first peak they contain contributions from other correlations also. Examination of the partial RDFs shows that the second peak masks contributions from Na—Na, K—K, K—Na and, in the potassium-containing glasses, the K—O correlations also. The Na—O contribution, however, appears as a clear shoulder to the second peak, at *ca.* 2.30 Å in the sodium glass, but is much less evident in the mixed system. The first peak at 1.57 Å is slightly asymmetric, which suggests that it may split in two at lower temperature. This is in keeping with the suggestion that the bridging and non-bridging oxygen atoms maintain different Si—O bond lengths.[7]

Beyond a radius of *ca.* 1.9 Å, all three systems are structurally very similar. In addition to the O—O peak at *ca.* 2.55 Å, there is clear structure at *ca.* 3.11, 3.62 and 4.17 Å. The RDFs in these systems are dominated by the oxygen components, by virtue of higher population and greater neutron weighting, hence these peaks may be assigned to Si—Si, Si—O (second neighbour) and Si—O (third neighbour), respectively. However, there are hidden contributions arising in this region from K—Si and Na—Si. It is probably these hidden contributions that affect the prominence of the peaks between 1.9 and 4.5 Å as the proportion of alkali metal increases.[24]

Table 1 Pressure (*p*) and density (*ρ*) in the simulated sodium (Na), potassium (K) and mixed (M) glasses [*p*(FP) = 152 kbar in all FP simulations]

glass	*p*(FV)/kbar	*ρ*(FV)/g cm^{-3}	*ρ*(FP)/g cm^{-3}
Na	152	2.568	2.568
M	209	2.795	2.677
K	272	3.022	2.744

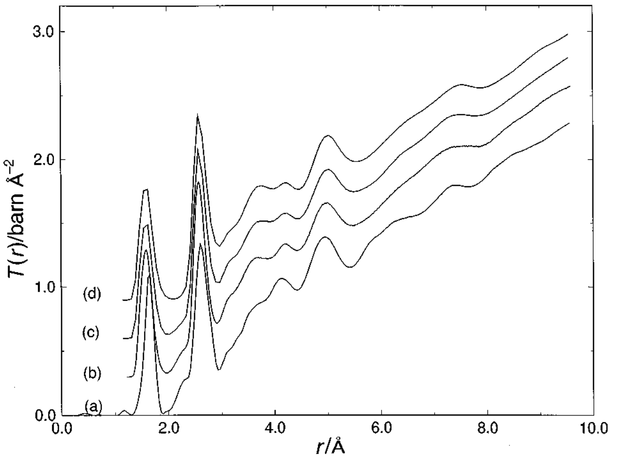

Fig. 1 The total RDF [$T(r)$] for the glasses: (a) $Na_2Si_2O_5$ (experimental); (b) $Na_2Si_2O_5$ (simulated); (c) $KNaSi_2O_5$ (simulated); and $K_2Si_2O_5$ (simulated). Note that simulation results (b)–(d) are all at 1400 K. The experimental result is obtained from neutron diffraction data (Wright *et al.*[24]) at ambient temperature and pressure. 1 barn = 10^{-28} m^2.

In addition to calculating the RDFs, we have also analysed the local environments of the constituent atoms in terms of: (i) the ratio of bridging to non-bridging oxygen atoms; (ii) the preference of alkali-metal ions for neighbouring non-bridging oxygens over bridging oxygen atoms; and (iii) the relative populations of silicon atoms with *i* bridging oxygens (the so-called Q_i populations). In the interests of brevity we do not quote the results here, but remark that they were in close agreement with our previous studies of the sodium glass.[12] These results, taken with the RDFs above, confirm the realism of the simulated glass structures and their suitability for modelling alkali-metal ion transport.

Dynamical properties

Mean square displacements. The mean square displacements of the sodium ions are presented in Fig. 2A and for potassium ions in Fig. 2B, all at 1400 K. In all cases the plots are characterised by a short initial rise followed by a region of approximately linear behaviour.[25] We have fitted the assumed linear portions of the MSD plots (over the interval 10–60 ps) using least-squares procedures and obtained the diffusion constants *via* the well known relation:

$$\langle r^2 \rangle = 6Dt + C \qquad (1)$$

where D is the diffusion coefficient and C is a constant. The results are presented in Table 2. We note that the calculated diffusion constants are of a similar magnitude to those measured previously in sodium glass over a shorter time period (5 ps).[12]

Table 2 reveals that in both the FP and FV simulations there is a marked reduction in the diffusion constant for the sodium ion in the mixed glass, when compared with the single alkali-metal sodium glass, though the reduction is greater for the FP case. Similarly, for potassium in the FP simulations, there is a marked reduction in the diffusion constant when

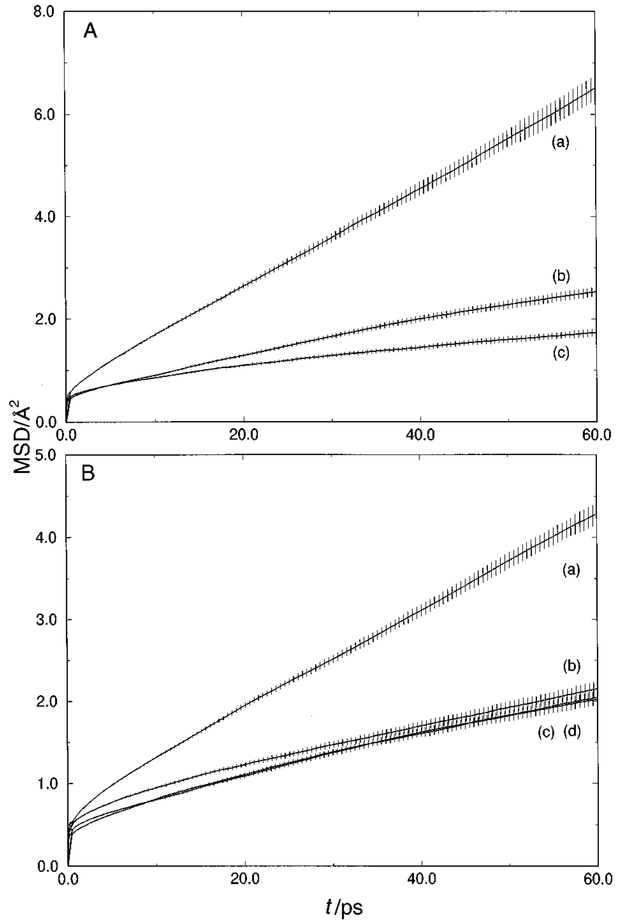

Fig. 2 Alkali-metal mean square displacements (MSDs) at 1400 K. **A**, MSD of sodium in (a) sodium glass; (b) fixed volume mixed glass; and (c) fixed pressure mixed glass. **B**, MSD of potassium in (a) fixed pressure potassium glass; (b) fixed pressure mixed glass; (c) fixed volume potassium glass; and (d) fixed volume mixed glass.

Table 2 Calculated diffusion constants of sodium ions (Na^+) and potassium ions (K^+) in the pure and mixed disilicate glasses

ion	D(FP)/10^{-10} m^2 s^{-1}	D(FV)/10^{-10} m^2 s^{-1}
Na^+	1.60 ± 0.08	1.60 ± 0.08
Na^{+a}	0.28 ± 0.06	0.54 ± 0.07
K^+	0.99 ± 0.05	0.40 ± 0.04
K^{+a}	0.39 ± 0.04	0.41 ± 0.04

[a]Mixed glass.

comparing the potassium and mixed glasses. However, in the FV case the potassium diffusion in the potassium and mixed glasses is almost identical. In all mixed glass simulations the diffusion of both alkali metals is similar in magnitude. On this evidence, the result for the potassium glass at fixed volume is anomalous.

It is seen from these results that the mixed alkali-metal effect is only present if the glass systems are allowed to relax to the same pressure. By comparison, the changes between glasses of different composition but kept at the same volume (and therefore different pressures) are complex. Though the combined alkali-metal diffusion (and therefore conductivity) is reduced in the mixed glass compared to the sodium glass at fixed volume, this is due to the fall in sodium mobility alone, and the combined mixed glass diffusion remains above that seen in the potassium glass. There is evidence, therefore, for a significant pressure effect in the mixed alkali-metal phenomenon. Unusual effects are also seen in glasses of the same composition. Diffusion in the potassium glass approximately halves between FP and FV and therefore with increasing pressure. On the other hand, in the mixed alkali-metal glass, diffusion of sodium approximately doubles as the pressure increases between FP and FV systems. This behaviour should be contrasted with earlier simulation studies of sodium in $NaAlSi_2O_6$ melts at 6000 K by Angell *et al.*[26] who found a general monotonic decrease in sodium diffusion for pressures up to 400 kbar.

Finally, we note that no discernible diffusion occurred in the oxygen or silicon atoms at this temperature, confirming that the network, which comprises the majority of atoms in the system, had not melted.

Curvature of the MSD plots

The question of curvature in the MSD of alkali-metal glasses is a subject of current debate as it is believed to indicate the presence of cooperative relaxation processes in the glass.[25] To shed light on this matter we have estimated the statistical error in the MSD using the eqn. (2)

$$\sigma = \sqrt{\left(\frac{2}{3NN_0}\right)} \langle r^2(t) \rangle \qquad (2)$$

which assumes the underlying atomic motion is a three-dimensional random walk. In this equation, $\langle r^2(t) \rangle$ represents the MSD, N the number of diffusant atoms and N_o the number of statistically independent time origins, which is given by the integer part of the ratio: N_{conf}/n, with N_{conf} being the number of configurations sampled and n the index of the nth point on the MSD plot (*i.e.* $n = t/\Delta t$, with Δt the time interval between sampled configurations.)

The plots in Fig. 2 show that it is possible to draw a straight line through the MSD that lies almost entirely within the estimated error bars over the time region 10–60 ps (and entirely so over the time region 20–60 ps). We conclude from this that the underlying diffusion mechanism is consistent with a three-dimensional random walk model in the long-time region and that the assumption of linearity is reasonable. Clearly this conclusion does not apply to the 0–10 ps region.

Van Hove correlation functions

Van Hove correlation functions are known to provide valuable insight into molecular behaviour in time-dependent phenomena in condensed phase systems.[13,27] In order to study the diffusion process we have calculated the van Hove self- [$G_s(r,t)$] and distinct- [$G_d(r,t)$] correlation functions. The self-correlation function is formally defined by eqn. (3)

$$G_s(r, t) = \frac{1}{N} \left\langle \sum_{i}^{N} \delta[r + r_i(0) - r_i(t)] \right\rangle \qquad (3)$$

and describes the probability density of finding an ion at a position $r(t)$ after a time t, given its initial position $r(0)$ at time $t = 0$; it is thus closely related to the diffusion of the same ion.

In Fig. 3 the van Hove self-correlation functions [plotted as $G_s(r,t)4\pi r^2$] for the alkali-metal ions in the sodium and potassium glasses over a period of 10–60 ps in the FP system are shown. In both cases the function is characterised by two peaks: the first at small r diminishing with time and the second at larger r increasing with time. This clearly indicates a hopping process, whereby ions originally at the origin are displaced to a nearby location. A rough estimate of the hopping distance can be obtained from these plots, which is *ca.* 3.0 Å for sodium ions and *ca.* 2.8 Å for potassium ions.

The distinct correlation function is formally defined by eqn. (4)

$$G_d(r, t) = \frac{1}{N} \left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \delta[r + r_i(0) - r_j(t)] \right\rangle \qquad (4)$$

and in the context of this work describes how the radial

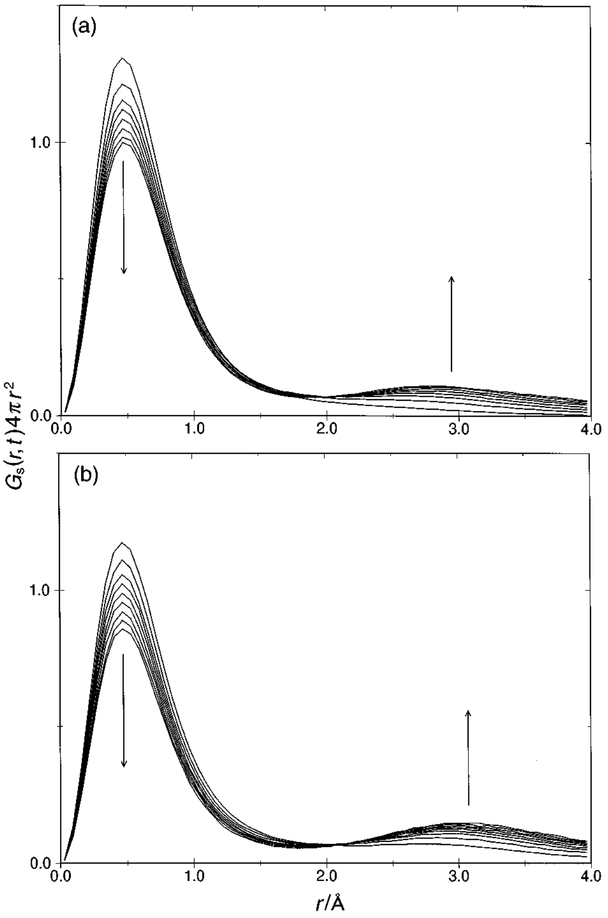

Fig. 3 Van Hove self-correlation functions for potassium (a) and sodium (b) glasses at fixed pressure and 1400 K over a period of 0–60 ps showing fall in density at *ca.* 0.5 Å and rise at *ca.* 2.8 Å (K^+) and *ca.* 3.0 Å (Na^+) with increasing time (as indicated by the arrows)

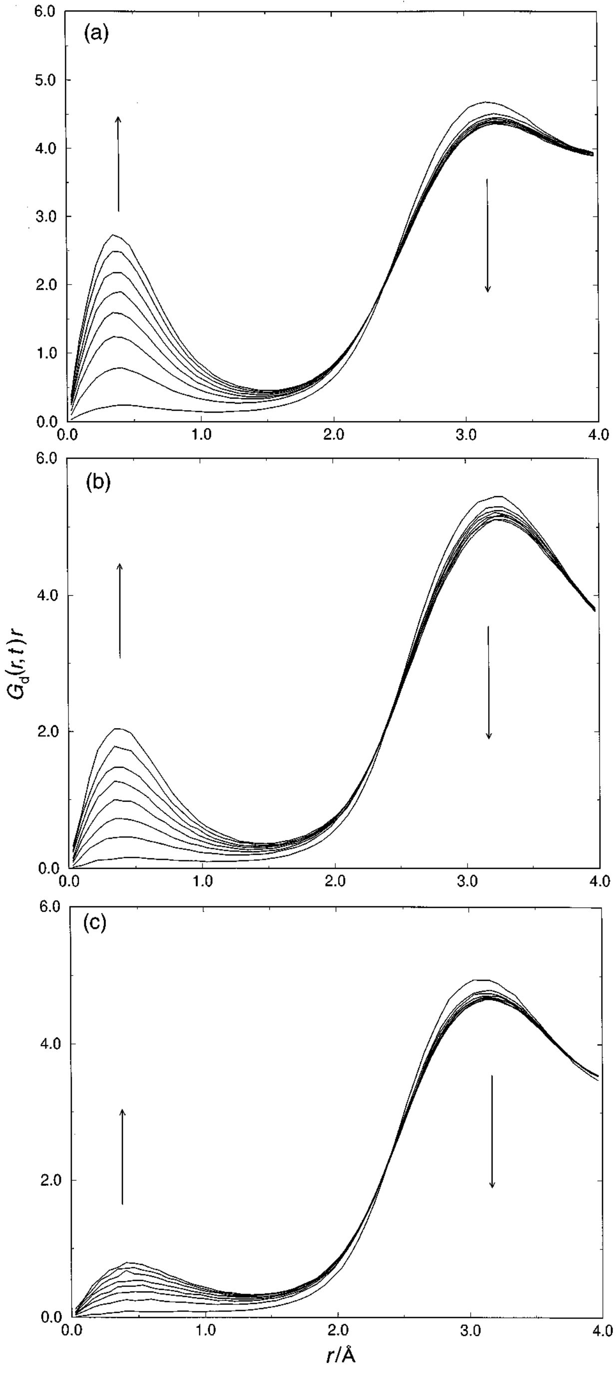

Fig. 4 Van Hove distinct correlation functions at fixed pressure over a period of 0–60 ps for (a) potassium vacancy and potassium ions in potassium glass; (b) potassium vacancy and potassium ions in mixed glass; and (c) sodium vacancy and potassium ions in mixed glass. All functions show a rise in density near the origin and a diminution of density at the first neighbour shell at *ca.* 3.0 Å with increasing time (as indicated by the arrows).

distribution function $g(r)$ changes in response to the displacement of the ion at the centre as a result of the hopping process.

The van Hove distinct correlation functions [examples of which are shown in Fig. 4; plotted as $G_d(r,t)r$] also show two changing peaks. However, in this case it is the peak at small r that grows at the expense of that at larger r. This behaviour is entirely consistent with the ions from the first shell of the pair distribution function migrating into the vacancy left by the departing ion.

By the radial integration of the functions $G_d(r,t)$ it is possible in principle to calculate the quantity of ions entering a vacancy in a given time interval, though it must be emphasised that these calculations are subject to considerable statistical uncertainty. Table 3 shows the results of the integration, presented as the fraction of an ion of a given type entering within a radius of 1.5 Å of a vacancy of a given type in a 60 ps period for all the systems studied. A reduction in the total fraction of a given ion entering all vacancy types in comparison with the corresponding single alkali-metal glass is clearly evident for sodium in both FV and FP simulations *i.e.* 0.097 (0.049 + 0.048) *vs.* 0.346 for FP and 0.186 (0.104 + 0.082) *vs.* 0.346 for FV. However, for potassium in the FP simulations a significant difference is recovered between the mixed system and potassium glass (*viz.* 0.146 *vs.* 0.229), while in the FV simulation there is only a small difference (*viz.* 0.158 *vs.* 0.176). These results crudely mirror the differences in alkali-metal diffusion in these simulations (Table 2) and point to a weakening of the mixed alkali-metal effect with pressure.

Table 3 also provides an opportunity to observe the ease with which ions move into the vacancies left by dissimilar ions compared to vacancies of a similar kind. In the mixed glass FP simulation there is positive evidence for mobility selectivity operating on potassium ions diffusing into potassium in preference to sodium vacancies (*ca.* 9 : 5) that can be seen clearly in Fig. 4. The evidence is only slight for this kind of selectivity in the FV mixed glass simulation though, where there is a small preference (*ca.* 5 : 4) for a sodium ion entering a sodium vacancy over a potassium vacancy. In either case it is not obvious on the timescale of these simulations whether the identity of the vacancy for a particular type of alkali metal is permanent or temporary. It is interesting to observe, however, that the apparent reduction in site selectivity with increasing pressure

Table 3 Fraction of sodium (Na^+) or potassium (K^+) ions entering a sodium ($Na^{+\prime}$) or potassium ($K^{+\prime}$) vacancy in the single and mixed alkali-metal glasses in a 60 ps period at 1400 K (radius of integration 1.5 Å)

vacancy, ion	fixed P	fixed V
$Na^{+\prime}$, Na^+	0.346	0.346
$K^{+\prime}$, K^+	0.229	0.176
$Na^{+\prime a}$, Na^+	0.049	0.104
$K^{+\prime a}$, Na^+	0.048	0.082
$K^{+\prime a}$, K^+	0.094	0.078
$Na^{+\prime a}$, K^+	0.052	0.080

[a] Mixed glass.

mirrors the weakening of the mixed alkali-metal effect (Table 2).

Discussion and Conclusions

We have performed long-timescale MD simulations of alkali-metal disilicate glasses $Na_2Si_2O_5$, $K_2Si_2O_5$ and $KNaSi_2O_5$ at 1400 K, fixing either the pressure (FP) or volume (FV) to that of the sodium glass. The structures of the glasses are very reasonable approximations to the experimental structures. The diffusion of the alkali-metal ions has been measured over the interval 0–60 ps and shown to be linear over 10–60 ps. We find that in the FP simulations the diffusion in the mixed glass is considerably less than those of the single alkali-metal glasses, while the mixed glass FV simulations display a diffusion rate that is intermediate between those of the sodium and potassium glasses. The so-called mixed alkali-metal effect has therefore been demonstrated for the FP system, whilst trends in diffusion with mixed alkali-metal composition in the FV systems are less obvious. The van Hove self-correlation functions fully confirm the hopping diffusion mechanism in both FP and FV systems, but the corresponding distinct correlation functions provide only partial evidence for alkali metals in mixed glasses preferentially hopping to sites previously occupied by the same type of alkali metal.

The possibility of hopping selectivity raises interesting questions, however, regarding the nature of the mixed alkali-metal effect. This clearly results from interference between the transport of individual alkali metals when both are present in the same glass. There is now much evidence from the changing atomic environments of alkali metals in mixed glasses determined by XAFS[28,29] that the different alkali metals are structurally intimate and randomly mixed as predicted by the MRN.[7,17] The idea that each alkali metal in a mixed alkali-metal glass might hop preferentially to sites vacated by the same alkali-metal type, even though both alkali metals are stochastically mixed in the mixed glass structure, is not intuitive. Nevertheless, in a phenomenological approach to the MAE,[30] structure-dependent expressions based on this notion have been used to demonstrate agreement between the local structure of alkali metals and the measured transport properties in disilicate glasses. The principle of hopping selectivity was first proposed by Maass and co-workers[16,31] in their simple Monte Carlo model, with the *caveat* that the identity of a vacancy with a particular type of alkali metal only persisted for a short duration. In their recent MD simulations of mixed alkali-metal glasses Habasaki *et al.*[13] and Balasubramanian and Rao[14] reproduced site-selective mobility but, as in the present study, do not provide direct evidence for an ephemeral memory effect.

Our semi-quantitative analysis of the van Hove correlation functions in mixed alkali-metal glasses (Table 3) provides firm evidence for selective alkali-metal hopping only in simulations at 152 kbar (Fig. 4). Taking the results of FP and FV simulations together introduces uncertainties in the hypothesis that there is always a preference in mixed alkali-metal glasses for a vacancy to accept the ion type that it was previously occupied by, particularly if the pressure is increased. It is therefore not possible to confirm from these results the existence of this mechanism as the cause of the MAE, though the results are suggestive. It is interesting to note that Balasubramanian and Rao[14] report clear evidence of selectivity in the lithium/potassium glasses by essentially the same method, a result which probably indicates the importance of the relative ionic radii of the alkali-metal ions. Habasaki *et al.* have also reported confirmation of such a mechanism[13] at 700 K, though somewhat less convincingly; while it is feasible that at a lower temperature the selection process is more marked, it is harder to satisfy the requirement of statistical accuracy when the diffusion is so low. Taking all studies into account, however, there now seems little doubt that the mechanism is real, though further investigation is desirable. In particular, we note that in our investigation there are changes in the mobilities of particular alkali metals between single and mixed compositions (for instance sodium in the FP simulations and potassium in the FV simulations) that owe nothing to the selection effect. This may indicate a more general dependence of mixed alkali-metal transport in glasses on system pressure and volume.

This research was performed with an allocation of computer time on the Cray T3D parallel computer at Edinburgh from the Materials Consortium of the High Performance Computing Initiative. Daresbury Laboratory provided additional computer time on the IBM SP-2. T.R.F. is supported by a grant from the EPSRC.

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Paper 6/06185K; *Received 9th September*, 1996