A new interpretation of the dynamic structure model of ion transport in molten and solid glasses

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We explore progress in understanding the behaviour of cation conducting glasses, within the context of an evolving "dynamic structure model" (DSM). This behaviour includes: in single cation glasses a strong dependence of ion mobility on concentration, and in mixed cation glasses a range of anomalies known collectively as the mixed alkali effect. We argue that this rich phenomenology arises from the emergence during cooling of a well-defined structure in glass melts resulting from the interplay of chemical interactions and thermally driven ionic motions. The new DSM proposes the existence of a new site relaxation process, involving the shrinkage of empty $A$ sites (thus tailored to the needs of $A^+$ ions), and the concurrent emergence of empty $C'$ sites, which interrupt the conduction pathways. This reduction of $A$ sites is responsible in the molten glass for the sharp fall in conductivity as temperature drops towards $T_g$. The $C'$ sites play an important role also in the mixed alkali effect, especially in regard to the pronounced asymmetries in diffusion behaviour of dissimilar cations.

1 Introduction

Since 1990, there has been growing interest in the mechanisms of ion transport in disordered materials including glasses. This interest has been sustained not only by a rich diversity of behaviour [1, 2, 3], but also by rapid advances in spectroscopy, notably in magic angle spinning NMR and in EXAFS [4, 5], and in the increasing sophistication of molecular dynamics (MD) and other computational techniques [6, 7, 8, 9]. Much effort has gone into accounting for "universal" aspects of glass behaviour which include the scaling properties of conductivity spectra [10, 11]. Thus, through the work of Dyre and of Funke et al [3, 12], conductivity spectra for disordered materials are well described, even though there is still active discussion of the underlying mechanisms.

The important challenge, which needs to be addressed, lies in creating a conceptual framework to enable the behaviour of different glasses to be compared and if possible, predicted from first
principles. Some years ago, a start was made in this direction by Bunde, Ingram and Maass through introduction of the dynamic structure model (DSM). The essential idea \[13, 14, 15, 16\], which was based originally on EXAFS data of Greaves et al \[5\], is that the mobile ions play a decisive role in creating the sites which they occupy (as well as the doorways to these sites) within the glassy matrix. In essence, the mobile ions shape their immediate environments to meet their own requirements and also leave behind empty sites (called \(\bar{A}\) for \(A^+\) cations, \(\bar{B}\) for \(B^+\)-cations) which act as "stepping stones" and thus define the conduction pathways. Any empty sites away from the conduction pathways, or where any memories of previous cations have been forgotten, are referred to as \(\bar{C}\) sites.

The growth of such conduction pathways \[15\] explained the steep rise in conductivity in single ionic glasses which accompanies increases in mobile ion concentration, \(c\), in many systems as a percolation phenomenon. Thus, an effective power-law behaviour often applies, where the conductivity scales as

\[
\sigma \sim c^{\alpha/kT}.
\]  

(1)

\(T\) is the temperature, \(k\) is the Boltzmann constant and \(\alpha\) is an empirically determined parameter with the units of energy. This expression was deduced first from Monte Carlo (MC) simulations and then confirmed from an extensive survey of published experimental data \[16\]. A similar steep increase in conductivity with ionic content also emerged from the calculations based on the counter-ion model \[17\] and on energy landscape models \[18\], see also \[19\].

In mixed cation glasses, discussion in terms of the DSM drew attention to the consequences of the strong competition between dissimilar mobile ions in their attempts to establish their conduction pathways. MC simulations showed how this competition led to the fragmentation of pathways, and hence to the sharp falls in conductivity that are among familiar characteristics of the mixed alkali effect (MAE). The underlying cause was attributed to dissimilar ions (\(A^+\) and \(B^+\)) being unwilling to visit each other’s (\(\bar{B}\) and \(\bar{A}\)) sites, because of a mismatch between the requirements of the ion with what the "wrong" target site and the doorway to it could offer in terms of cavity size and perhaps numbers of nearest neighbours.

The DSM continues to influence research in glassy ionics. Thus, although there are some researchers, see for example \[20\], who discuss the origin of mixed cation effects without invoking site recognition or percolation effects, there is a growing consensus that this is the right approach. Thus, evidence for the existence of distinguishable \(\bar{A}\) and \(\bar{B}\) sites comes from both MD and molecular orbital simulations \[5, 21, 22, 23\]. Recently, Swenson et al \[24\] have shown by reverse Monte Carlo (RMC) and bond-valence calculations how \(Li^+\) and \(Rb^+\) ions in mixed-cation phosphate glasses find themselves on pathways containing mixtures of \(\bar{Li}\) and \(\bar{Rb}\) sites. They too attribute the loss of ion mobility to a mismatch energy along the lines previously proposed by some of us \[15\].

As a consequence of this activity, new questions continue to arise. First and foremost, there is the role of the network. How much does the matrix participate in inter-site conversions (\(\bar{A}\) to \(\bar{C}\), etc.)? Do these processes occur above and below \(T_g\), or only above \(T_g\) as suggested recently by Maass \[25\]? How closely linked are the chemical and physical processes which lie behind the behaviours observed in molten and glassy materials? Are we yet in a position to say that we have a theory of the mixed alkali effect? The present paper is an attempt to see how far these questions can be answered in the light of an updated dynamic structure model.
2 Single cation systems

2.1 Different temperature regimes

Figure 1 contains Arrhenius plots showing how the conductivity varies exponentially with reciprocal temperature for $Na_2O - 2SiO_2$, $K_2O - 2SiO_2$ and $0.7AgI - 0.3Ag_2MoO_4$ glasses in both the molten and glassy states [26]. Characteristically, the plots are curved above $T_g$ and linear below. For convenience, we identify three regions of interest. First, there is the high temperature regime, where conductivities approach those of typical molten salts (ca. $1 \Omega^{-1}cm^{-1}$). Second, there is a region of under cooling which extends right down to $T_g$. This region is associated with huge increases in melt viscosity (from about $10^1$ to $10^{13} Pa.s$) and by comparison a rather smaller decrease (only two to three orders of magnitude), in the ionic conductivity. Third, there is the region below $T_g$ in which ion transport proceeds with a constant activation within an apparently rigid solid. The conductivity decreases comparatively rapidly with $1/T$ in the middle region, while it decreases comparably slower in the first and third regimes.

At temperatures far above $T_g$, (region 1), all ionic motions are coupled to processes involved in viscous flow. These microscopic processes include the switching of non-bridging oxygens (nBOs) between neighbouring silicon atoms and temporary changes in the coordination number of Si from 4 to 5 or even to 6 [27]. The sites created by the mobile ions may be of limited duration, but they will be precisely determined by the interplay of forces representing the chemical requirements of both mobile ions and the various silicate or other anionic species present in the melt.

However, it is known from the work of Moynihan and Angell [28, 29] that undercooling leads to progressive decoupling of cation motions from the host matrix, with an associated increase in the ratio of relaxation times for viscous flow to those for conductivity, i.e. of $\tau_{\text{shear}}/\tau_{\text{sigma}}$. 
The value of this ratio at $T_g$ is called the decoupling index, $R_\tau$, and reaches values around $10^{11}$ in typical silicate glasses. In practice, this means that since structural relaxation times are approximately $100 \text{ s}$ at $T_g$, (as measured, for example, in a typical differential scanning calorimetry (DSC) experiment), the corresponding electrical relaxation time ($\tau = RC$) is about $10^{-9} \text{ s}$. In simple terms, this gives an indication of how long ions are remaining in their sites at the glass transition temperature. The inverse of $\tau$ is the average effective hopping rate.

On further cooling below $T_g$, the structure changes much less, but ions spend increasingly longer times in their sites. At room temperature, a sodium ion in a typical silicate glass might sit for approximately $1 \text{ s}$ in its site before moving on. The corresponding relaxation time for viscous flow is so long it would better be expressed on geological time scales \[30\].

In the present context, it is noteworthy that Binder et al \[31\] also draw attention to the second temperature region described above, which they identify as falling between the critical temperature $T_c$ of mode coupling theory (MCT) where the system undergoes some "structural arrest" and the "solidification temperature" (i.e. the experimental $T_g$). They also point out that the time scale for viscous flow at $T_c$ is about ten orders of magnitude shorter than it is at $T_g$, and suggest that it is unlikely that significant changes will not occur as a liquid is cooled between $T_c$ and $T_g$. This is precisely the region of melt behaviour where the decoupling ratio is increasing from values close to unity to much larger values. Indeed, within the framework of MCT it seems likely that near $T_c$ the dynamics of the network forming species will be dominated by mutual blocking effects, and their diffusion will be drastically reduced. In effect, the network structure is forming around $T_c$, and already a pattern of behaviour is being established which continues on cooling even into the solid glass.

### 2.2 The mechanism of ion transport

Evidence from recent NMR studies \[32\] shows that cations in glass will typically find sites near at least one nBO. More generally, in glasses where nBOs may be absent, e.g. in aluminosilicate glasses, the cations will be found in regions close to where negative charge resides in the network. The increasing values of $\tau_{\text{shear}}/\tau_{\text{sigma}}$, see above, show that even in the melt the local network structure persists for much longer times than the ions reside in their sites. We are looking at a hopping process which is well established in the molten state.

But what kinds of site do the ions hop into? What distinguishes an $\bar{A}$ from a $\bar{C}$ site has not so far been rigorously defined. It was assumed \[15\] that $\bar{A}$ character expresses a "goodness of fit", and combines a number of factors that determine the accessibility of the site to an $A^+$ ion, including cavity size, coordination number, and the availability of negative charge as indicated often by the presence of nBOs.

We now propose to distinguish two kinds of $\bar{C}$ sites. First, there are $\bar{C}$ sites, which in silicate melts would be remote from nBOs. These can only become $\bar{A}$ sites with the active assistance of chemical rearrangements occurring in the silicate matrix. It is likely that such rearrangements occur readily only at high temperatures (possibly in the vicinity of the $T_c$ of MCT), and that they occur less and less frequently as the melt is cooled towards $T_g$.

The second kind of $\bar{C}$ site has very different origins. Let us suppose that a freshly vacated $\bar{A}$ site looks just like a filled site, but with the cation missing. As long as it stays like that, we shall call it an $A$ site. However, after being vacated, the $\bar{A}$ site may start to relax in such a way as to minimise the (now largely uncompensated) repulsions between negatively charged oxygens in what was previously the primary coordination sphere of the cation. This relaxation might be envisaged, for the purpose of illustration, as the reorientation of $Si - O$ bonds to
Figure 2: Site relaxation, showing the collapse of an empty $\bar{A}$ site, either during cooling of molten glass or when glass is subjected to external pressure, with the consequent creation of a new $C'$ site and the resulting disappearance of some free volume at the same time.

avoid pointing the oxygens directly at each other (as will be the case in the newly emptied $\bar{A}$ site) but instead towards neighbouring silicon atoms which (because of differences in chemical electronegativity) will carry small positive charges. Whatever the actual (microscopic) details of this relaxation process, we call this new site a $C'$ site.

The processes of site relaxation occur in the molten state, but because melts are relatively rich in "free volume", the $C'$ and $\bar{A}$ sites may not differ too much from each other. However, the melt contracts on cooling and so some free volume must disappear. We suggest that this contraction occurs most readily by the conversion of empty $\bar{A}$ into smaller $C'$ sites, as illustrated in Fig. 2. Below $T_g$, the total number of $\bar{A}$ and $C'$ sites will remain constant and further shrinkage of the $C'$ sites will be less important.

Below $T_g$, two alternative scenarios may in fact be envisaged. In the first, the structure may be completely frozen, with all sites retaining their $\bar{A}$, $C'$, and $C$ identities as they were defined at $T_g$. Such a situation would be consistent with many contemporary views of glass behaviour [17, 25].

The alternative would be that minor structural fluctuations such as those involved in converting $C'$ into $\bar{A}$ sites or vice versa, would still occur, since changes in network topology would not be involved. The main difference between $C'$ and $\bar{A}$ sites would thus be related to local density fluctuations. In this way, it would still be possible to refer to a dynamic energy landscape, which is attributed to the network structure, even below $T_g$.

Whichever scenario is adopted, this new description has several advantages. As one example, it allows one to visualise what is happening in the Arrhenius plots (see Fig. 1) in different temperature regimes. Above $T_g$, the progressive increase in slope seen during cooling, is a consequence of the decreasing number of empty $\bar{A}$ sites as they are converted into smaller $C'$ sites. The arrest at $T_g$ signals the effective end of this process. Below $T_g$, the energy landscape is determined by the distribution of empty $\bar{A}$ and $C'$ sites.

We can go on further to consider that the number of $C'$ sites is significantly greater than the number of empty $\bar{A}$ sites. The situation in glass has some resemblance to the "vacancy-like" models proposed recently by several authors [12, 33, 34]. Under the influence of external pressure it may even be possible to convert some of the remaining empty $\bar{A}$ into smaller $C'$ sites.

Elsewhere, one of us [35] argues that the apparent "activation volume" for charge transport in cation-conducting glasses can be interpreted in this way, and indeed is equal to the volume difference between empty $C'$ and $\bar{A}$ sites.

Regarding the existence of preferred pathways or conducting channels [36, 37, 38]: In a recent paper, Meyer et al. [37] identify a prepeak observed in both neutron scattering data and
molecular dynamics simulations with the emergence of Na\textsuperscript{+} ion channels in sodium silicate melts and glasses. In terms of the new DSM, we expect that $\bar{Na}$ and $C'$ sites close to the nBOs form these channels. Hence, suppression of the formation of nBOs, e.g. by addition of Al\textsubscript{2}O\textsubscript{3} to sodium silicate glasses should disrupt the pathway structure, in agreement with very recent experiments by Kargl et al. \cite{38}.

3 Mixed cation glasses

3.1 The mixed alkali effect (MAE)

The mixed alkali effect \cite{39,40,41} embraces a wide range of phenomena. Some of these, such as diffusivity crossovers and conductivity minima are directly related to changes in ion mobility, and are associated with maxima in activation energies and entropies, and in the activation volume \cite{42}. There are, however, other anomalies, which only indirectly involve ion transport. These include minima in $T_g$ \cite{40,43}, large internal friction peaks \cite{40,44} and volumetric relaxations \cite{40,45} observed below $T_g$, and viscosity minima observed in molten glass \cite{46}.

Figure 3(a) shows the diffusivity crossover in Na\textendashCs silicate glasses reported by Jain and coworkers \cite{47}. The behaviour of Na differs markedly from that of Cs. While the self-diffusion coefficient of the latter decreases exponentially with decreasing Cs content, the corresponding coefficient for Na levels off at low Na contents. This asymmetry is disguised in conductivity...
plots, which tend to be rather U or V-shaped in appearance. The conductivity is, however, always dominated by the more mobile and numerous (majority) cations; the significant differences in behaviour between large and small ions tend to show up more clearly only when the ions in question are in the minority.

On the other hand it is possible to overstate the degree of asymmetry. Measurements of activation volumes \( V_A = -RTd\ln \sigma/dP \), with the pressure \( P \) and the gas constant \( R \) in mixed cation glasses reveal increases in \( V_A \) occurring at both ends of the composition range, when larger ions are diluted by smaller ones or vice versa [42, 48]. This evidence for some degree of symmetry has suggested some degree of coupling between the local motions of the ions, involving \( A^+ \) ions moving into \( \bar{B} \) sites and \( B^+ \) ions moving into \( \bar{A} \) sites [42, 43].

In the dynamic structure model, the asymmetry was expressed in terms of different jump rates of \( A^+ \) and \( B^+ \) cations. In the published simulations [15], for simplicity and for revealing the crucial effect of mismatch between unlike ions, a hypothetical case was considered of a glass containing a mixture of cations, \( A^+ \) and \( B^+ \), alike in all respects except that a mismatch energy appeared whenever either ion entered sites belonging to the other. Figure 3(b) shows the crossover in diffusivities predicted by the quantitative model [15]. This figure correctly reveals the steep falls in ion mobility found in the dilute foreign alkali region, but of course it could not replicate the contrasting behaviours of \( Na \) and \( Cs \) shown in Figure 3(a).

It is now appropriate to look again at the MAE in the light of the newly “updated” dynamic structure model.

### 3.2 The MAE in molten glass

There have been several reports in the literature of the MAE found in molten glass [49, 50]. Baucke and Werner have shown, that for a series of \( Na_2O - K_2O - CaO - SiO_2 \) glasses, there are significant deviations from additivity in ionic conductivity, and especially in the activation energy well above \( T_g \) (see Fig. 4(a) and (b), respectively). The effect is thus still apparent in melts of relatively modest viscosity, arguably close to the critical temperature, \( T_c \), of mode coupling theory. The persistence of the MAE up to such high temperatures is strong evidence that distinctions between \( \bar{A} \) and \( \bar{B} \) sites can still be made.

According to our updated dynamic structure model, the sites are formed in the melt between \( T_c \) and \( T_g \) where the volumes of the \( \bar{A} \) and the \( C' \) sites do not differ very much. In mixed alkali melts, the situation is further complicated owing to the different sizes of the \( A^+ \) and the \( B^+ \) ions. When the smaller \( A^+ \) ions are in the overwhelming majority, the \( C' \) sites are on average smaller than when the larger \( B^+ \) ions are in the majority. Close to the conduction minimum, where nearly the same numbers of \( A^+ \) and \( B^+ \) ions are present, we would expect a broad distribution of \( C' \) sites, including sites to be found in each of the single alkali melts. Under such conditions, ion transport involves continual melt rearrangement, and this gives rise to the maximum in activation energy which is so evident in Baucke and Werner’s data.

### 3.3 The MAE in solid glasses

The starting point, as in earlier discussions [15], is to recognise the mismatch effect which arises whenever ions enter "wrong sites". It is clear that larger (\( B^+ \)) ions will find it harder (as a natural consequence of electron repulsions) to enter smaller (\( \bar{A} \)) sites than vice versa. Also, because of the broad distribution of \( C' \) sites which formed in the melt, there are many more \( C' \) sites available to \( A^+ \) ions than there are to \( B^+ \) ions. Accordingly, in \( Na/Cs \) glasses (see
Figure 4: (a) Conductivity as a function of the potassium mole fraction \( x \) in the molten mixed-alkali system \((1 - x)Na_2O \cdot xK_2O \cdot 0.7CaO \cdot 4.8SiO_2\) at various temperatures. (b) The corresponding activation energies at various temperatures taken from curved Arrhenius plots. (Redrawn after [50]).

Fig. 3(a)), \(Cs\) ions will be expected to suffer much larger losses in mobility than \(Na\) ions, which indeed is the experimental result. This explains also why \(Na\) ion mobilities level off at low \(Na\) contents, but to a value lower than that of the majority \(Cs\) ions (if ions jump into sites which are too large for them, they will tend to "roll back" into their original sites.) If cations do not differ too much in size, as in \(Li/Na\) and \(Na/K\) mixtures for example, the \(A^+\) cations may find themselves entering \(\bar{B}\) sites in preference to less attractive \(C'\) sites. In this way, \(A^+\) ions and \(\bar{A}\) sites become randomly mixed up with \(B^+\) ions and \(\bar{B}\) sites (as indeed is indicated both by infrared and NMR spectroscopies [4, 51]. The frequent entry of \(A^+\) ions into \(\bar{B}\) sites and vice versa leads to a loosening of the structure. This loosening was seen by Ingram and Roling as being the underlying cause of minima in \(T_g\) [43] and of melt viscosity [46], as interpreted with the concept of matrix mediated coupling (CMMC).

Remarkably, these indirect effects may be smaller when cations differ more markedly from each other. This was found in internal friction experiments [40]. Very small loss peaks were reported in \(Li/Cs\) silicate glasses, compared with much larger ones in \(Li/Na\) glasses. We now understand this additional anomaly (i.e. the suppression of an important aspect of the mixed alkali effect) in terms of \(Li^+\) and \(Cs^+\) ion simply differing too much from each other to enter each other's sites.

4 Conclusions

We introduce an updated dynamic structure model for explaining the complex behaviour of single and mixed cation glasses. As in the original version [14, 15], we distinguish between \(\bar{A}\), \(\bar{B}\) and \(C\) sites. However, in contrast to the old DSM, we assume that \(\bar{A}\) and \(\bar{B}\) sites can only be generated close to the countercharges (which often are non-bridging oxygens). When an \(\bar{A}\) site is vacated, it relaxes to a \(C'\) site whose size is determined largely by the host matrix, but it is better suited to accommodate mobile ions than are the \(C\) sites, which are remote from the localized countercharges. In a single cation glass, the \(\bar{A}\) and \(C'\) sites found close to the countercharges, form "stepping stones" for the mobile \(A^+\) ions.

As in the recent papers [36, 37, 38], we expect that these pathways will appear in the melt, perhaps at a temperature close to \(T_c\) of mode coupling theory, when the diffusion of the network
forming units is blocked, and viscosity becomes very temperature dependent. These pathways constitute an integral part of glass structure below $T_g$. The pathways become interrupted when the stepping stones are too far apart, i.e. when the countercharge concentrations are too small. The pathways may be "frozen in" at $T_g$ or they may be allowed to fluctuate in the glassy state as a result of localised density fluctuations. In both cases, the loss of good pathways leads to the abnormal decreases in conductivity with decreasing ion content, an effect which is especially severe in certain systems such as alkali borate glasses.

In a mixed ionic glass, it is much more difficult to find separate pathways for the $A^{+}$ and the $B^{+}$ ions, made up of $\bar{A}$ and $C'$ and of $\bar{B}$ and $C'$ sites, respectively. This appears to be the underlying cause of many of the observed anomalies. As in the old DSM, we envisage that there will be a mismatch whenever a (small) $A^{+}$ ion enters a (large) $B$ site or vice versa. We now recognise that this mismatch is greater if a larger cation is trying to enter a smaller site, and in this way we can account for the observed asymmetries in diffusion behaviour, these being especially significant with cations of markedly different sizes, as in the $Na-Cs$ system for example. By contrast, the smaller of the two ions ($A^{+}$) will make use of available $C'$ sites, when the supply of ($\bar{A}$) sites is insufficient to provide extended diffusion pathways. This comment is consistent with the "levelling off" in the diffusion coefficient of $Na^{+}$ ions at low concentrations, as seen in the $Na-Cs$ system.

However, in molten glass, the $A^{+}$ and $B^{+}$ ions will have sufficient energy to visit each other's sites, and regularly disturb the local structure. This could possibly explain the strong reduction of $T_g$ and of melt viscosity reported in many mixed alkali systems. When the ions do not differ too much in size, these site exchange effects may persist below $T_g$. In this way, we could account for the large internal friction peaks seen in $Li/Na$ silicate glasses and for the anomalous increases in activation volume which point to some coupling between the motions of the $A^{+}$ and the $B^{+}$ cations.

What is urgently needed is more information about empty sites in glass, and how the nature of these sites depends on glass composition and temperature. In the related field of polymer electrolytes, diagnostic information is coming from positron annihilation lifetime spectroscopy or PALS. This technique exploits the variable lifetimes of the ortho-positronium species in order to determine the size of available cavities within the host matrix. Such information, together with activation volumes determined from variable pressure measurements, might enable $\bar{A}$ and $\bar{B}$ sites to be distinguished from each other and from the possibly more numerous $C'$ sites. Comparisons made between fast quenched and slow cooled glasses would provide information not only on structural dynamics but also on the growth and consolidation of percolation pathways.

Finally, it is interesting to note previous comments in the literature to the effect that the concentration dependence of conductivity in mixed cation glasses is closely related to those encountered in single cation systems. If this rule applies quite generally, it would imply that the $C'$ sites encountered in single cation glasses must be very similar to those encountered in mixed cation systems. This may or may not be the case. Further consideration of the MAE in such glass forming systems as the aluminosilicates, where the conductivity dependence in single cation glasses is weak, should be highly informative.

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