Ion Transport Anomalies in Glasses

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(Received 10 February 1992)

A model for ion transport in glass is presented which is based on the experimental evidence that cations in glass create and maintain their own characteristic environments. By postulating the existence of a *site memory effect*, we are able to visualize the formation of conducting pathways. We develop a quantitative theory which explains the general occurrence of the mixed cation (alkali) effect in glassy material and, in addition, shows that the anomalous dependence of conductivity on the modifier content in single alkali glasses follows a simple power-law relation.

In this paper, we present a unified theory of ion migration processes in glass. We offer a simple explanation for two long-lasting problems in the physics of glassy ionic conductors [1,2]: the anomalous dependence of conductivity on the modifier content and the mixed alkali effect.

The conductivity of single alkali glasses is usually strongly dependent on the alkali oxide content. Taking Na_2O-B_2O_3 glasses at 300 °C as an example, the conductivity actually increases approximately one millionfold as the mole fraction of Na_2O is increased from 0.15 to 0.5. Similar trends are found in binary phosphate and silicate glasses [3]. We show for the first time that in single alkali glasses there is a simple *power-law relation* between ionic conductivity and the modifier content.

The mixed alkali effect occurs in vitreous alkali conductors of the general formula $xX_2O(1-x)Y_2O$-$(SiO_2,$ B_2O_3, GeO_2, etc.) where X_2O and Y_2O are different alkali oxides. Remarkably, the ionic conductivity goes through a deep minimum as x is varied. For example, in $xK_2O(1-x)Li_2O$-$2SiO_2$ glasses at 150 °C, the minimum conductivity is 10000 times smaller than that of either single cation glass. The minimum becomes more pronounced as the temperature is lowered. Also when one alkali ion is replaced by another, the diffusion coefficient of the former always decreases [1,2]. There is an intersection of the diffusion coefficient curves, which is close to the minimum in the ionic conductivity. There are further anomalies associated with the effect, including a maximum in the Haven ratio [4] and the occurrence of additional internal friction peaks [1].

An explanation will be sought therefore which is related to some structural feature common to all ionic glasses. We focus here on the fact that the local environment of any cation *even in mixed alkali glasses* is largely unaffected by the addition of a second cation, as has been indicated by extended x-ray-absorption fine-structure (EXAFS) measurements [5] and early far-infrared spectroscopy [6]. This result points to the mobile ions creating and maintaining their own distinctive environments. Thus an A ion will be inclined to jump to a vacancy $\bar{A}$ previously occupied by an A ion (where the environment is correctly adjusted), but declines to jump to a vacant site $\bar{B}$ previously occupied by a B ion, where the environ-

ment has to relax to accommodate the A ion. This memory effect is the *leitmotif* of our model. An inevitable consequence (see below) is the emergence of (fluctuating) pathways which facilitate the migration of particular ions in glass.

Accordingly, in the same way we distinguish between two types of cations, A and B, we also distinguish between two types of sites, $\bar{A}$ and $\bar{B}$. In the model, we assume that both types of sites keep their identity for a certain time interval: If an $\bar{A}$ or $\bar{B}$ site is vacant for a period of time $\tau_{\bar{A}}$ or $\tau_{\bar{B}}$ it relaxes to some type of interstitial site (which we call a $\bar{C}$ site), which is adjusted correctly neither to an A ion nor to a B ion. Also, if a $\bar{C}$ site is occupied by an A or B ion for more than $\tau_{\bar{A}}$ or $\tau_{\bar{B}}$ time steps, it relaxes to an $\bar{A}$ or $\bar{B}$ site, respectively. We suggest that the coupling of ionic motions to these intersite conversions, and hence to structural relaxations in the glass network, is actually responsible for the internal friction peaks and other loss phenomena, which are a characteristic feature of both single and mixed alkali glasses [1,2,7].

We define $w_{A\bar{A}} = v_{A\bar{A}}\exp(-E_{A\bar{A}}/k_BT)$ as the jump probability of cation A to a vacant nearest-neighbor site $\bar{A}$. Similarly, $w_{A\bar{B}} = v_{A\bar{B}}\exp(-E_{A\bar{B}}/k_BT)$ and $w_{A\bar{C}} = v_{A\bar{C}}\exp(-E_{A\bar{C}}/k_BT)$ define the jump probabilities of cation A to a neighboring site $\bar{B}$ or $\bar{C}$. Since the environment of $\bar{B}$ must distort in order to accommodate the arrival of alkali A and the lattice distortion requires appropriate elastic (or chemical) energy $\Delta E_{A\bar{B}}$, we can write $E_{A\bar{B}} = E_{A\bar{A}} + \Delta E_{A\bar{B}}$, with $\Delta E_{A\bar{B}} > 0$ [8]. The jump to the interstitial site $\bar{C}$ naturally requires a larger activation energy $E_{A\bar{C}} = E_{A\bar{A}} + \Delta E_{A\bar{C}}$ than the jump to the $\bar{A}$ site; hence $\Delta E_{A\bar{C}} > 0$. Similar arguments apply to the motion of cation B, with $E_{B\bar{A}} = E_{B\bar{B}} + \Delta E_{B\bar{A}}$ and $E_{B\bar{C}} = E_{B\bar{B}} + \Delta E_{B\bar{C}}$. Similarly to the above, we assume that also the relaxation times can be written as $\tau_{\bar{A}} = v_{\bar{A}}^{-1}\exp(E_{\bar{A}}/k_BT)$ and $\tau_{\bar{B}} = v_{\bar{B}}^{-1}\exp(E_{\bar{B}}/k_BT)$.

For simplicity and to reduce the large number of parameters involved we shall concentrate here on a symmetric situation where $E_{A\bar{A}} = E_{B\bar{B}}$, $\Delta E_{A\bar{B}} = \Delta E_{B\bar{A}} \equiv k_BT_0$, $\Delta E_{A\bar{C}} = \Delta E_{B\bar{C}} \equiv k_BT_1$, and all prefactors of the jump probabilities are the same. Similarly we can assume $\tau_{\bar{A}} = \tau_{\bar{B}} \equiv \tau$. Taking $w_{A\bar{A}}^{-1}$ as a unit of time (without loss of generality), we arrive at the following set of parame-

ters:

$$w_{A\bar{A}} = w_{B\bar{B}} = 1, \quad w_{A\bar{B}} = w_{B\bar{A}} = e^{-T_0/T},$$ (1a)

$$w_{A\bar{C}} = w_{B\bar{C}} = e^{-T_1/T}, \quad \tau_{\bar{A}} = \tau_{\bar{B}} \equiv \tau = \tau_0 e^{T_\tau/T}.$$ (1b)

In (1b), $\tau_0 = v_{A\bar{A}}/v_{\bar{A}}$, and $k_B T_\tau = E_{\bar{A}} - E_{A\bar{A}}$.

We have performed Monte Carlo simulations [9] to explore the consequences of this model. First the sites of a (usually simple cubic) lattice are randomly occupied by N cations A and B with concentrations c_A and c_B sitting on $\bar{A}$ and $\bar{B}$ sites, respectively. The remaining sites are $\bar{C}$ sites. Next, an ion is chosen randomly, and a nearest-neighbor site is also chosen, to which the ion attempts to jump. If the neighboring site is occupied by another ion, the jump is rejected. If the neighboring site is empty, the ion jumps to it with the corresponding jump probability that depends on the chosen ion and the history of that site. After each trial, time is incremented by $1/N$. Those sites $\bar{A}$ and $\bar{B}$ that are vacant for a period of time τ change into $\bar{C}$ sites, and those $\bar{C}$ sites that are occupied by an A or B ion for a period of time τ change into $\bar{A}$ or $\bar{B}$ sites. Next a new particle is chosen at random and the process is repeated again and again, until thermal equilibrium is reached and then the relevant quantities are determined. The calculations are made at different temperatures and different ionic concentrations.

First we consider single ionic glasses, where only one species of ions (A) is present. Equations (1a) and (1b) reduce to $w_{A\bar{A}} = 1$, $w_{A\bar{C}} = \exp(-T_1/T)$, and $\tau_{\bar{A}} = \tau_0 \exp(T_\tau/T)$. For illustration we show, in Fig. 1, the $\bar{A}$ sites in a two-dimensional system occurring at a certain instant of time for $T_\tau/T_1 = \frac{1}{2}$, $\tau_0 = 3$, and temperature $T_1/T = 2\ln(10)$, i.e., when $w_{A\bar{C}}$ is 100 times less then $w_{A\bar{A}}$ and $\tau_{\bar{A}} = 30/w_{A\bar{A}}$. The $\bar{A}$ sites, marked by filled squares in the figure, represent the pathways for the A ions in the glassy network; the rest of the lattice consists of $\bar{C}$ sites. At small A concentrations [$c_A = 0.2$ in Fig. 1(a)], only small isolated clusters of $\bar{A}$ sites exist. Diffusion is dominated by the small jump probability $w_{A\bar{C}}$ and we expect a low conductivity. As c_A increases, the size of the clusters increases, and at $c_A = 0.4$ an infinite A path exists [Fig. 1(b)]. We have a "percolation phenomenon," but the
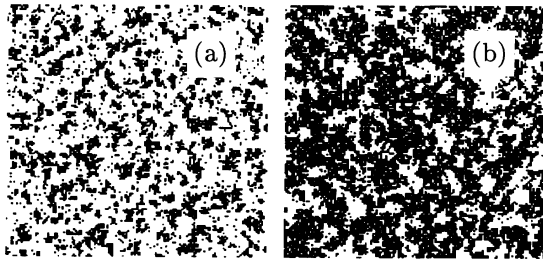
(fluctuating) structures seem to be more compact than in ordinary percolation [10]. At low temperatures, the concentration of $\bar{C}$ sites depends only very weakly on temperature.

Figure 2 shows, for three temperatures, the diffusion coefficient D_A multiplied with c_A, which roughly behaves as the dc conductivity σ. The results shown here are for the simple cubic lattice. The data which are plotted in a new log-log presentation showing the combined effects of temperature and composition, highlight a power-law dependence, $\sigma \sim c_A^\gamma$, where $\gamma \sim 1/T$. (An equivalent statement is to say that the activation energy has a logarithmic dependence upon the concentration c_A.) This relation is not derived analytically, but it does emerge with equal clarity from both the simulated data and from Martin's experimental data [11] for sodium aluminoborate glasses taken at two temperatures (50 and 150 °C) [12]. Thus the "simulated" and "real" glasses show, in effect, the same dependence on glass composition and temperature, indicative of the underlying soundness of the model.

Next we consider the more general case of mixed ionic glasses, where two types of ions A and B are present with a total concentration $c_{tot} \equiv c_A + c_B$. We define by $x \equiv c_A/c_{tot}$ the relative concentration of A ions. In all simulations we choose $c_{tot} = 0.25$, $T_1/T_0 = 2$, $T_\tau/T_0 = 1$, and $\tau_0 = 3$, and investigate how the transport properties change if x or the temperature T_0/T is varied. We have found that in the temperature range considered, the $\bar{C}$

FIG. 1. Fluctuating A paths (■) for $T_1/T = 2\ln(10)$, $\tau = 30$ and the concentrations (a) $c_A = 0.2$ and (b) $c_A = 0.4$. The empty regions in the figure denote the $\bar{C}$ sites.
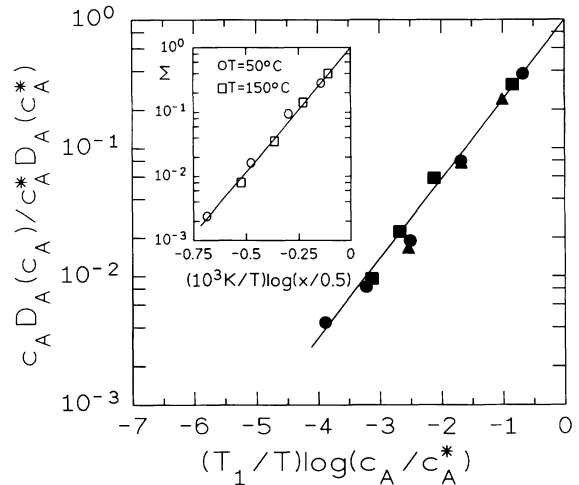

FIG. 2. Diffusion coefficient D_A times c_A normalized to the value at $c_A^* = 0.35$ as a function of $(T_1/T)\log_{10}(c_A/c_A^*)$ for $\tau_0 = 3$, $T_\tau/T_1 = \frac{1}{2}$, and temperatures $T_1/T = 2\ln(10)$ (●), $2.5\ln(10)$ (■), and $3\ln(10)$ (▲). Inset: Experimental data for the normalized dc conductivity $\Sigma \equiv \sigma(x)/\sigma(0.5)$ of xNa$_2$O$(1-x)$[4B$_2$O$_3$-Al$_2$O$_3$] as a function of $(10^3$ K$/T)\log(x/0.5)$ at two different temperatures $T = 50$ and 150 °C (redrawn from [12]). Both the simulated and the experimental data show a power-law dependence of c or x with an exponent proportional to the inverse temperature.

site concentration increases only very slowly with decrease in temperature. For fixed temperature it varies between 0.64 ($x=0$ or 1) and 0.68 ($x=0.5$) if x is changed. Thus the simulated "structures" contain the ingredient of *structural stability* which identifies these as glassy (as opposed to molten) materials. Again, the ionic transport can be discussed qualitatively by considering the connectivity of the structural A and B pathways in the system.

For small x only small clusters of $\overline{A}$ sites exist, while the $\overline{B}$ sites form a percolating structural pathway. Diffusion of the B ions is dominated by the large jump probability $w_{B\overline{B}}$, while diffusion of the A ions is dominated by the small probabilities $w_{A\overline{B}}$ and $w_{A\overline{C}}$. Hence we expect a small diffusion constant D_A for the A ions, a large diffusion constant D_B for the B ions, and consequently a large dc conductivity. At $x=\frac{1}{2}$, $c_{\overline{A}}=c_{\overline{B}}\cong0.16$, and neither a percolating A nor a percolating B path exists. For both A and B ions diffusion is dominated by the small jump probabilities $w_{A\overline{B}},w_{A\overline{C}}$ and $w_{B\overline{A}},w_{B\overline{C}}$, and we expect that both diffusion coefficients and the dc conductivity are small. For x close to 1, the B clusters are small and the A path percolates through the lattice. Accordingly, we expect a small diffusion constant D_B, a large diffusion constant D_A, and a large dc conductivity.

Figure 3 shows the diffusion coefficients for three temperatures, $T_0/T=\ln(10)$, $T_0/T=1.25\ln(10)$, and $T_0/T=1.5\ln(10)$. By substituting ions of one type by dissimilar ions of the second type, the diffusion coefficient of the remaining primary ions always decreases. This effect becomes more pronounced at smaller temperatures or larger T_0, i.e., when the mismatch between the two cations is increased, in full agreement with the experimental situation [1].
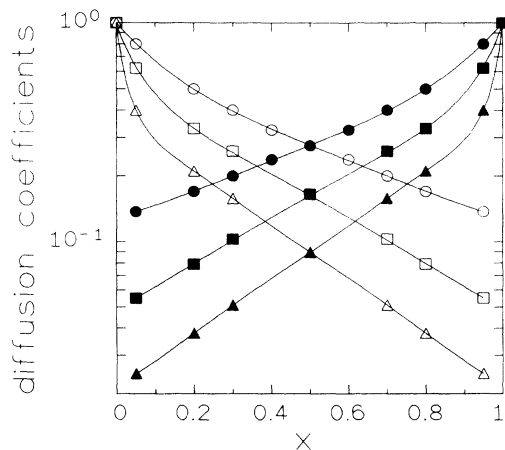
Figure 4 shows the conductivity obtained from the current response to an external sinusoidal field of frequency ω, as a function of x, for fixed (small) frequency $\omega=0.001$ and three temperatures, $T_0/T=\ln(10)$, 1.25 $\times\ln(10)$, 1.5$\ln(10)$. For the lowest temperature we show also the results for two larger frequencies, $\omega=0.1$ and 0.01. According to the time unit defined above, a particle performs on the average $2\pi/\omega$ jump trials during one period of the external field. As expected, the curves show a broad minimum at $x=0.5$ which is deeper at lower temperatures (reflecting a maximum of the activation energy at $x=0.5$) and lower frequencies, in apparently good agreement with the experiments [13]. The disappearance of the mixed alkali effect at high frequencies highlights a key feature of this model, namely, that *all* cations in mixed-cation glasses possess *local* mobility (because of the continuing proximity of $\overline{A}$ sites to A ions and $\overline{B}$ sites to B ions). Only the long-range ionic mobilities are strongly composition dependent.

From Figs. 3 and 4 we can compare the relative decrease of the total diffusion coefficient $D_{\text{tot}}\equiv xD_A+(1-x)D_B$ ($D_{\text{tot}}=D_B$ at $x=0$ and $D_{\text{tot}}=D_A=D_B$ at $x=0.5$) with the relative decrease of the conductivity at $\omega=0.001$. One sees that the decrease of the conductivity is slightly larger than the decrease of the total diffusion coefficient at the temperatures $T_0/T=1.25\ln(10)$ and $T_0/T=1.5\ln(10)$. Since the conductivity decreases monotonously with decreasing frequency, this effect will become stronger in the limit $\omega\to0$. Accordingly, at low temperatures the Haven ratio $H_R(x)$, which is proportional to $D_{\text{tot}}(x)/\sigma_{\text{dc}}(x)$, must go through a maximum near to the conductivity minimum at $x=0.5$. Also this feature, which can be seen as indicating a decrease in forward-correlated $A\overline{A}$ and $B\overline{B}$ hops, is in accordance

FIG. 3. Normalized diffusion coefficients $D_A(x)/D_A(1)$ and $D_B(x)/D_B(0)$ of cations A and B as a function of the mixed alkali concentration $x=c_A/c_{\text{tot}}$ for $c_{\text{tot}}=0.25$, $T_1/T_0=2$, $T_r/T_0=1$, $\tau_0=3$ and temperatures $T_0/T=\ln(10)$ (●,○), 1.25$\ln(10)$ (■,□), $T_0/T=1.5\ln(10)$ (▲,△). The solid symbols refer to the A ions, the open symbols to the B ions.
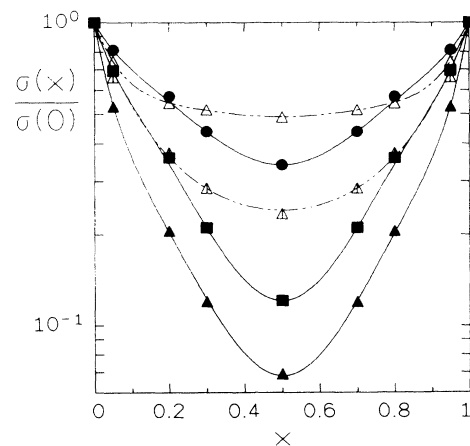

FIG. 4. Normalized real part of the ac conductivity $\sigma(x)/\sigma(0)$ as a function of x for the same parameters as in Fig. 3 for fixed frequency $\omega=0.001$ and three temperatures $T_0/T=\ln(10)$ (●), 1.25$\ln(10)$ (■), and 1.5$\ln(10)$ (▲). The open triangles are for $T_0/T=1.5\ln(10)$ and two larger frequencies $\omega=0.01$ (▲) and 0.1 (△).

with previous experimental data [4].

In summary, we have presented a unified model which explains the ionic transport in single and mixed ionic glasses, including the newly identified power-law behavior seen in single ionic glasses. This behavior emerged naturally from the computer simulations based on the model and seems equally to be a feature of experimental data. It is remarkable that we can describe the compositional dependence of conductivity, and also the main features of the mixed alkali effect, without requiring information on either *chemical speciation* (e.g., the nature of borate anions in borate glasses), the existence of chemically or structural microheterogeneity in the glass [14], or long-range ion-ion interactions [15]. The site memory effect provides a "universal" mechanism for creating conducting pathways in all glasses and thus explains why many aspects of the ion transport behavior show universal features. It may also provide a simple explanation for the emergence of long-range structures in glass, e.g., the "connective tissue" for which there is some evidence from vibrational spectroscopy [16]. We hope our results provide a stimulus to further experimentation, and to the ongoing discussion of mechanisms of ionic mobility in glass.

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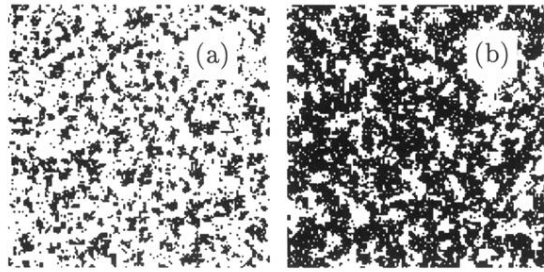[16] M. D. Ingram, G. D. Chryssikos, and E. I. Kamitsos, J. Non-Cryst. Solids **131-133**, 1089 (1991).

FIG. 1. Fluctuating A paths (■) for $T_1/T = 2\ln(10)$, $\tau = 30$ and the concentrations (a) $c_A = 0.2$ and (b) $c_A = 0.4$. The empty regions in the figure denote the $\bar{C}$ sites.