Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A New Model Linking Elastic Properties and Ion Conductivity in Mixed Network Former Glasses (Wang et al.)
Supplementary Information

Derivation of the jump type probabilities

A jump type is defined by the pair of charged oxygen species at the starting site and at the ending site. Because of the symmetric arrangement of these oxygen pairs at the starting and ending sites, the activation energy for sodium jumps between such sites does not depend on the direction of the jump, which reduces the number of possible jump types. We approximate an isotropic homogeneous medium with a simple cubic lattice. Each site is associated with a pair of charged oxygen, either NBO, CBO, or a combination of the two. Accordingly, we have three types of site occupancies: NBO-NBO pairs, which we abbreviate as *A* for simplicity, CBO-CBO pairs, abbreviated as *B*, and NBO-CBO pairs, abbreviated as *X*. Accordingly, we denote by n_A, n_B, and n_X the number of sites occupied by NBO-NBO pairs, CBO-CBO pairs, and NBO-CBO thereof, respectively

Let us denote by N_{NBO}, N_{CBO}, and N_{O^-} the number of non-bridging, charged-bridging, and total charged sites, respectively. We have

$$N_{NBO} + N_{CBO} = N_{O^-} \tag{1}$$

We know N_{O^-} by design, i.e., as defined by the sodium content of the glasses, and N_{NBO} and N_{CBO} from our analysis. In fact, for NBS glasses we can express the mol fractions of NBO and CBO as

$$x_{NBO} = \frac{N_{NBO}}{N_{O^-}} = \frac{[B^{(2)}]+[S^{(3)}]}{[B^{(2)}]+[S^{(3)}]+[B^{(4)}]} \tag{2}$$

and

$$x_{CBO} = \frac{N_{CBO}}{N_{O^-}} = \frac{[B^{(4)}]}{[B^{(2)}]+[S^{(3)}]+[B^{(4)}]}, \tag{3}$$

respectively. Similarly, for NBG glasses we have

$$x_{NBO} = \frac{N_{NBO}}{N_{O^-}} = \frac{[B^{(2)}]+[Ge^{(3)}]}{[B^{(2)}]+[Ge^{(3)}]+[B^{(4)}]+2[Ge^{(6)}]} \tag{4}$$

and

$$x_{CBO} = \frac{N_{CBO}}{N_{O^-}} = \frac{[B^{(4)}]+2[Ge^{(6)}]}{[B^{(2)}]+[Ge^{(3)}]+[B^{(4)}]+2[Ge^{(6)}]}. \tag{5}$$

The probability of certain pairings on a lattice site can be derived as follows. While *A* sites account for two NBO, *X* sites are occupied by one NBO. Hence, the total number of NBO is given by

$$2n_A + n_X = N_{NBO}. \tag{6}$$

Similarly, *B* sites are occupied by two CBO, whereas *X* sites contribute only one CBO to the balance, i.e.,

$$2n_B + n_X = N_{CBO}. \tag{7}$$

Dividing both equations by 2 and adding them up yields

$$n_A + n_X + n_B = \frac{N_{NBO} + N_{CBO}}{2} = \frac{N_{O}}{2} \tag{8}$$

Dividing by $N_O/2$ results in converting the number of sites into fractions, and hence,

$$x_A = \frac{2n_A}{N_O}, \tag{9a}$$

$$x_X = \frac{2n_X}{N_O}, \tag{9b}$$

and $x_B = \dfrac{2n_B}{N_O}$. (9c)

To evaluate the number of mixed NBO-CBO site occupancies we use a mean field approach. First, we examine every NBO, of which there are N_{NBO}, and determine whether this NBO is sharing its site with a CBO. The probability for this to be the case is simply given by the mol fraction of CBO, i.e., N_{CBO}/N_O. Hence, the total count of sites with mixed-occupancy is given by the product

$$n_X = N_{NBO}\frac{N_{CBO}}{N_O}. \tag{10}$$

Note that this does not lead to double-counting sites with two NBO, because the absence of a CBO eliminates that site from the count on both occasions of scrutinizing its two NBO. As per the above definition, Eq. (9b), the fraction of mixed-occupancy sites is

$$x_X = \frac{2n_X}{N_O} = 2\frac{N_{NBO}}{N_O}\frac{N_{CBO}}{N_O} = 2x_{NBO}x_{CBO}. \tag{11}$$

Also, substituting Eq. (10) into Eq. (6) yields

$$2n_A + \frac{N_{NBO}N_{CBO}}{N_O} = N_{NBO} \tag{12}$$

or, after dividing both sides by $N_O/2$,

$$2\frac{n_A}{N_O} + \frac{N_{NBO}N_{CBO}}{N_O N_O} = \frac{N_{NBO}}{N_O} \Leftrightarrow x_A + x_{NBO}x_{CBO} = x_{NBO}, \tag{13}$$

and after rearranging, the fraction of sites occupied by two NBO is

$$x_A + x_{NBO}\left(x_{CBO} - 1\right) = 0 \Leftrightarrow x_A = x_{NBO}\left(1 - x_{CBO}\right) = x_{NBO}^2. \tag{14}$$

Similarly, we can derive the expression for the fraction of sites occupied by two CBO as

$$x_B + x_{CBO}\left(x_{NBO} - 1\right) = 0 \Leftrightarrow x_B = x_{CBO}\left(1 - x_{NBO}\right) = x_{CBO}^2. \tag{15}$$

Combining Eqs. (11), (14), and (15) we can verify that the fractions are normalized, i.e., $x_A + x_X + x_B = x_{NBO}^2 + 2x_{NBO}x_{CBO} + x_{CBO}^2 = \left(x_{NBO} + x_{CBO}\right)^2 = 1$, since $x_{NBO} + x_{CBO} = 1$.

Now we examine the jump type probabilities. The jump type is identified based on the pairing of pairs. Assuming that the forward and reverse jumps between two arbitrary type of sites are on average associated with the same activation barrier, which is to be expected or else the glass would undergo phase separation, we can distinguish between six jump types: AA, where both starting and ending cation sites involve two NBO, BB, the jump between two pairs of CBO, AB, where on site has two NBO and the other site has two CBO, AX, where one site has a pair of NBO and other site a mixture of NBO and CBO, BX, where one site has a pair of CBO and other site a mixture of NBO and CBO, and XX, where both sites have a mixture of NBO and CBO. Given the aforementioned simple cubic lattice, there are $z = 6$ choices for a sodium cation to jump from any given site to a nearest-neighbor site. This value for z represents the geometry factor in the coefficient for diffusion in an isotropic medium.

all AA-jumps are shared between two A-sites,

To derive the jump probabilities between an A-site and any other site, we count all z jump connections emanating from every A-site in the system, which covers all AA-jumps twice, and all AB-jumps and AX-jumps once. Hence,

$$zn_A = 2u_{AA} + u_{AB} + u_{AX}, \tag{16}$$

where we denote by u_{JK} the number of jump connections between J- and K-sites. Similarly,

$$zn_B = 2u_{BB} + u_{AB} + u_{BX}, \tag{17}$$

and

$$zn_X = 2n_{XX} + n_{AX} + n_{BX}. \tag{18}$$

The number of jumps connecting different types of sites can be derived using a similar argument as for obtaining Eq. (10), i.e., given an A-site as a starting point, z jumps are possible to a nearest-neighbor site. Accounting for all A-sites, there are zn_A jumps. The probability that the neighbor site is a B-, respectively, X-site is simply equal to the fraction of those sites. Hence,

$$u_{AB} = zn_A \frac{n_B}{N} = zn_A x_B \tag{19}$$

where $N = n_A + n_B + n_X$. For the same argument given above, this construct prevents over-counting of jump connections. Similarly,

$$u_{AX} = zn_A x_X, \tag{20}$$

and

$$u_{BX} = zn_B x_X \tag{21}$$

Substituting Eqs. (19)-(21) in Eqs. (16)-(17) yields

$$zn_A = 2u_{AA} + zn_A x_B + zn_A x_X \Rightarrow u_{AA} = \frac{zn_A}{2}\left(1 - x_B - x_X\right), \tag{22}$$

$$u_{BB} = \frac{zn_B}{2}\left(1 - x_A - x_X\right), \tag{23}$$

and

$$u_{XX} = \frac{zn_X}{2}\left(1 - x_A - x_B\right) . \tag{24}$$

Dividing both sides of Eqs. (19)-(24) by N yields

$$q_{AB} = zx_A x_B \tag{25}$$

$$q_{AX} = zx_A x_X \tag{26}$$

$$q_{BX} = zx_B x_X \tag{27}$$

$$q_{AA} = \frac{zx_A}{2}\left(1 - x_B - x_X\right) \tag{28}$$

$$q_{BB} = \frac{zx_B}{2}\left(1 - x_A - x_X\right) \tag{29}$$

$$q_{XX} = \frac{zx_X}{2}\left(1 - x_A - x_B\right) \tag{30}$$

While all x_K are normalized to unity, the q-quantities are not. Indeed, the sum of these six fractions is

$$\begin{aligned}
q_{AA} + q_{BB} + q_{XX} + q_{AB} + q_{AX} + q_{BX} &= \frac{zx_A}{2}\left(1 - x_B - x_X\right) + \frac{zx_B}{2}\left(1 - x_A - x_X\right) + \frac{zx_X}{2}\left(1 - x_A - x_B\right) \\
&\quad + z\left[x_A x_B + x_A x_X + x_B x_X\right] \\
&= \frac{z}{2}\left[x_A + x_B + x_X - x_A x_B - x_A x_X - x_B x_A - x_B x_X - x_X x_A - x_X x_B\right] \\
&\quad + z\left[x_A x_B + x_A x_X + x_B x_X\right] \\
&= \frac{z}{2}\left[x_A + x_B + x_X - 2x_A x_B - 2x_A x_X - 2x_B x_X\right] + z\left[x_A x_B + x_A x_X + x_B x_X\right] \\
&= \frac{z}{2}\left[x_A + x_B + x_X\right]
\end{aligned}$$

and ultimately,

$$q_{AA} + q_{BB} + q_{XX} + q_{AB} + q_{AX} + q_{BX} = \frac{z}{2}, \tag{31}$$

which, as expected, is the number of jump connections per cation site (i.e., counting jumps in one direction only). Hence, dividing each q-quantity by $z/2$ yields the normalized probabilities for each jump type,

$$p_{AA} = x_A\left(1 - x_B - x_X\right), \tag{32}$$

$$p_{BB} = x_B\left(1 - x_A - x_X\right), \tag{33}$$

$$p_{XX} = x_X\left(1 - x_A - x_B\right), \tag{34}$$

$$p_{AB} = 2x_A x_B, \tag{35}$$

$$p_{AX} = 2x_A x_X\ , \tag{36}$$

$$p_{BX} = 2x_B x_X \ . \qquad (37)$$

In these expressions we substitute the x_K variable using Eqs. (11), (14), and (15), and in turn Eqs. (2)-(5) to substitute x_{NBO} and x_{CBO} in these equations.

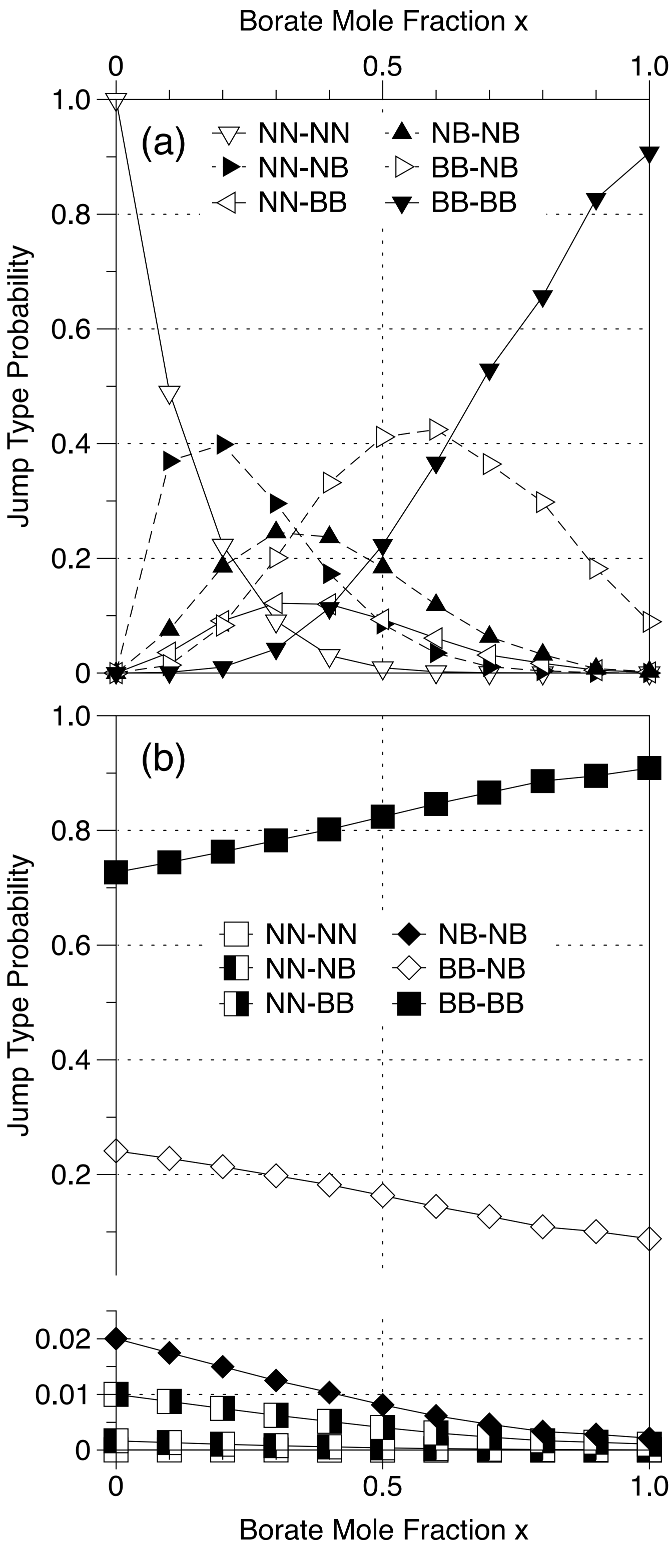

Fig. 6 Jump type probabilities for (a) sodium borosilicate glasses and (b) sodium borogermanate glasses. Each jump type is identified by the pair of charged oxygen atoms at the starting site and that at the ending site, separated by a hyphen, where the letter N represents a non-bridiging oxygen and the letter B represents a charged bridging oxygen.