



Floppy mode degeneracy and decoupling of constraint predictions in super-cooled borate and silicate liquids

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The theory of temperature-dependent topological constraints has been used to successfully explain the compositional dependence of glass properties for oxide and non-oxide compositions. It relates the number of topological degrees of freedom with the glass transition temperature through the configurational entropy of the system. Based on this, we estimated the number of degrees of freedom directly from viscosity measurements of binary alkali borate and silicate glasses. Both approaches exhibit a strong decoupling, which we suggest can be traced to the presence of medium- and long-range constraints that are not taken into account by bond constraint counting. The observed variation of the energy barrier for structural rearrangement and floppy mode degeneracy also corroborate our interpretation. We provide evidence that the degeneracy of floppy modes changes with chemical composition and that the parameter $K(x)$ of the MYEGA viscosity equation could be used to assess changes in the medium-range order.

Keywords: glass, topological constraint theory, borates, silicates, viscosity

INTRODUCTION

The theory of “topological constraints” has drawn significant attention for the prediction of specific properties of glassy materials (Phillips, 1979; Phillips and Thorpe, 1985; Gupta and Mauro, 2009; Mauro et al., 2009a; Smedskjaer et al., 2010; Wondraczek et al., 2011). It relates atomistic potentials and spatial relations between constituents of the glass to the ensemble’s degrees of freedom and the average number of atomic bond constraints, respectively. An estimate of the number of constraints can be obtained via the Adam–Gibbs equation (Adam and Gibbs, 1965), which relates the viscosity of a liquid with its configurational entropy:

$$\log_{10}\eta(T, x) = \log_{10}\eta_{\infty}(x) + \frac{B(x)}{T \cdot S_c(T, x)} \quad (1)$$

where $\eta_{\infty}(x)$ is the viscosity of the liquid at infinite temperature, $B(x)$ corresponds to the energy barrier, which opposes the rearrangement of the melt structural units (Russell et al., 2003) and $S_c(T, x)$ is the configurational entropy of the melt. The configurational entropy can, in principle, be determined from calorimetric (Richet et al., 1993) or electrochemical measurements (Jordanov et al., 2012) and is calculated from Eqs 2–4 (Richet, 1984, 2009; Richet et al., 1993).

$$S_c(T, x) = S_c(T_g, x) + \int_{T_g}^T \frac{C_p^{\text{conf}}(x)}{T} dT \quad (2)$$

$$S_c(T_g, x) = \Delta S_f + \int_0^{T_m} \frac{C_p^{\text{crystal}}(x)}{T} dT + \int_{T_m}^{T_g} \frac{C_p^{\text{liquid}}(x)}{T} dT + \int_{T_g}^0 \frac{C_p^{\text{glass}}(x)}{T} dT \quad (3)$$

$$C_p^{\text{conf}}(x) = C_p^{\text{liquid}}(x) - C_p^{\text{glass}}(T_g) \quad (4)$$

where the difference in heat capacity between glassy state and super-cooled liquid state is typically taken as the configurational heat capacity $C_p^{\text{conf}}(x)$ (Richet et al., 1986). In reality, the experimental determination of $S_c(T, x)$ is problematic at best (Sipp et al., 1997). So, while the Adam–Gibbs equation successfully links the thermodynamic state of a liquid with its dynamic properties, its practical application is restricted by the difficulties arising from the experimental determination of all required calorimetric data (Richet, 2009).

Recently, Mauro et al. (2009b) proposed a new equation to describe the viscosity of liquids, which is based on the Adam–Gibbs approach, the energy landscape analysis of Naumis (2006) and the temperature-dependent constraint model of Gupta and Mauro (2009) (Mauro et al., 2009a). The model states that temperature-induced changes in the glass topology are related to changes in the number of atomic constraints relative to the number of atomic degrees of freedom. The new equation postulates a link between the configurational entropy of the liquid and its topological degrees of freedom per atom, $f(T, x)$:

$$S_c(T, x) = f(T, x) Nk \ln \Omega \quad (5)$$

where N is the number of atoms, k is Boltzmann’s constant, and Ω is the number of degenerate configurations per floppy mode (Mauro et al., 2009b). Furthermore, the authors consider that the network constraints exist in a simple two-state system: the constraints are either intact or broken. The energy difference between both states is given by $H(x)$ (Mauro et al., 2009b):

$$f(T, x) = 3 \cdot \exp\left(-\frac{H(x)}{kT}\right) \quad (6)$$

Rearranging Eq. 1 with $K(x) = B(x)/3Nk\ln\Omega$ and $C(x) = H(x)/k$, the MYEGA equation is obtained (Mauro et al., 2009b):

$$\log_{10}\eta(T, x) = \log_{10}\eta_{\infty}(x) + \frac{K(x)}{T} \cdot \exp\left(\frac{C(x)}{T}\right) \quad (7)$$

Equation 7 can be rewritten as a function of the glass transition temperature $T_g(x)$ and the fragility index $m(x)$ (Angell, 1995) assuming that $\log\eta_{\infty}(x) = -3$ [$\log(\text{Pa} \cdot \text{s})$] (Zheng et al., 2011):

$$\log_{10}\eta(T, x) = -3 + 15 \cdot \frac{T_g(x)}{T} \cdot \exp\left[\left(\frac{m(x)}{15} - 1\right) \cdot \left(\frac{T_g(x)}{T} - 1\right)\right] \quad (8)$$

This equation provides a versatile tool, which allows for the determination of the glass transition temperature, the kinetic fragility of the melt and the viscosity parameters $K(x)$ and $C(x)$ from viscosity data. Substituting $C(x)$ in Eq. 6 one can calculate the number of degrees of freedom per atom from viscosity:

$$f_{\text{visc}}(T, x) = 3 \cdot \exp\left(-\frac{C(x)}{T}\right) \quad (9)$$

NUMBER OF TOPOLOGICAL DEGREES OF FREEDOM

The temperature-dependent constraint theory of Gupta and Mauro (2009) provides another way of calculating the number of atomic degrees of freedom from experimental data (Mauro et al., 2009a). Starting with the Adam–Gibbs equation (Eq. 1), for two different but similar systems x and w at their glass transition temperature, the equilibrium viscosity should be equal to $10^{12} \text{ Pa} \cdot \text{s}$, resulting in the following equality:

$$\frac{B(x)}{T_g(x) \cdot S_c(T_g(x), x)} = \frac{B(w)}{T_g(w) \cdot S_c(T_g(w), w)} \quad (10)$$

Assuming that the variation of the energy barrier is independent on chemical composition, $B(x) \approx B(w)$, and using Eq. 5 one gets:

$$\frac{T_g(w)}{T_g(x)} = \frac{S_c(T_g(x), x)}{S_c(T_g(w), w)} = \frac{f(T_g(x), x)}{f(T_g(w), w)} \quad (11)$$

In order to test if the number of atomic degrees of freedom calculated from viscosity (Eq. 9) and the Bond Constraint Theory (Eq. 11) coincide, we took viscosity data for B_2O_3 , $x\text{Na}_2\text{O} \times (1-x)\text{B}_2\text{O}_3$, and $x\text{Li}_2\text{O} \times (1-x)\text{B}_2\text{O}_3$ glasses and fitted with Eqs 7 and 8 assuming $\log\eta_{\infty}(T, x) = -3$. The results are shown in **Table 1**.

Considering that the relative number of degrees of freedom [given by $f(T_g(x), x)/f(T_g(w), w)$] is the same for both approaches, Eqs 9 and 11 can then be combined as:

$$\frac{f(T_g(x), x)}{f(T_g(w), w)} = \frac{T_g(w)}{T_g(x)} = \frac{\exp\left(-\frac{C(x)}{T_g(x)}\right)}{\exp\left(-\frac{C(w)}{T_g(w)}\right)} \quad (12)$$

Taking vitreous B_2O_3 as a reference composition, $T_g(w) = 522.9 \text{ K}$ [see **Table 1**; this temperature is somewhat lower than the one reported by Mauro et al. (2009a)], $C(w) = 557 \text{ K}$ from **Table 1** and $f(T_g(w), w) = 3/5$ (Mauro et al., 2009a), then the comparison with the binary alkali glasses becomes straightforward and the results are found in **Figures 1** and **2**.

Interestingly, in **Figure 1**, we see that the number of floppy modes calculated from viscosity measurements has a stronger dependence on the chemical composition than the one calculated from glass transition temperature data. **Figure 2** illustrates this mismatch very well and we see that both alkali borate glasses follow the same trend.

DEGENERACY AND DECOUPLING OF CONSTRAINT PREDICTIONS

From **Figures 1** and **2**, the experimental data suggest that the number of degrees of freedom from viscosity and the BCT diverge significantly. Recalling Eq. 5, we see that the configurational entropy is a function of the atomic degrees of freedom, the number of atoms and the degeneracy of each floppy mode. Equation 11 assumes that the size of the system and the floppy mode degeneracy can be considered constant as the chemical composition changes. While the number of atoms in the system may vary slowly enough to be considered constant [as the molar volume of sodium borate glasses does not exhibit a strong compositional variation (Berke-meier et al., 2005)], the floppy mode degeneracy has to be analyzed more carefully. As stated above, Mauro et al. (2009a) modeled the bond constraints as a simple two-state system with the energy difference between the broken and intact constraints given by $H(x)$ and the number of topological degrees of freedom given by Eq. 6. This simple system is represented schematically in **Figure 3A**.

The fraction of bond constraints that are either broken or intact can then be calculated through the Boltzmann distribution (Landau and Lifshitz, 1980):

$$\frac{N_i}{N} = \frac{g_i \exp\left(-\frac{E_i}{kT}\right)}{Z(T)} \quad (13)$$

where N_i is the number of bond constraints with energy E_i , N is the total number of bond constraints, g_i is the degeneracy of the state of energy E_i (or, in other words, the number of different states with the same energy E_i), and $Z(T)$ is the partition function, given by:

$$Z(T) = \sum_i g_i \exp\left(-\frac{E_i}{kT}\right) \quad (14)$$

It is important to note that this calculation of the fractions of intact and broken constraints requires that the constraint breakage to not be a step-function of the temperature, which is in line with recent MD simulations (Bauchy and Micoulaut, 2011). From **Figure 3A**, we have that the intact bond constraints have ground energy $E_g(x)$ and the broken constraints have an energy of $E_g(x) + H(x)$. Thus, the relation between the number of broken and intact constraints is given by:

$$\frac{N_b(T, x)}{N_i(T, x)} = \frac{g_b(T, x) \exp\left(-\frac{E_g(x)+H(x)}{kT}\right)}{g_i(T, x) \exp\left(-\frac{E_g(x)}{kT}\right)} \quad (15)$$

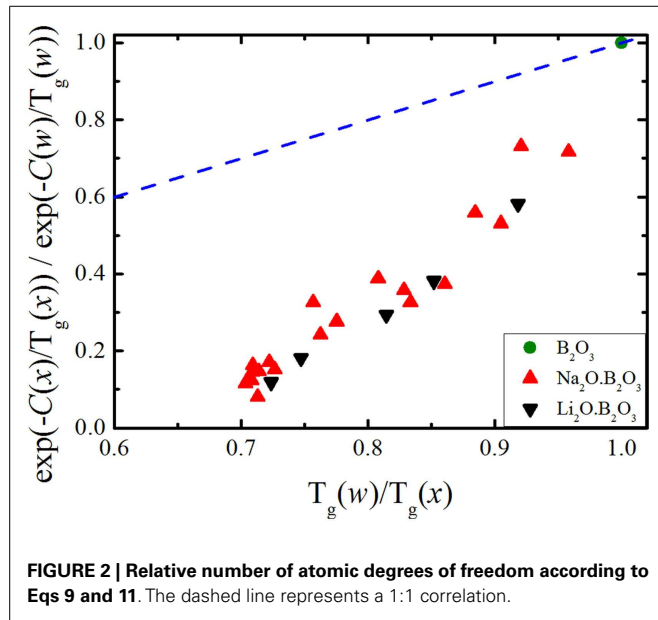
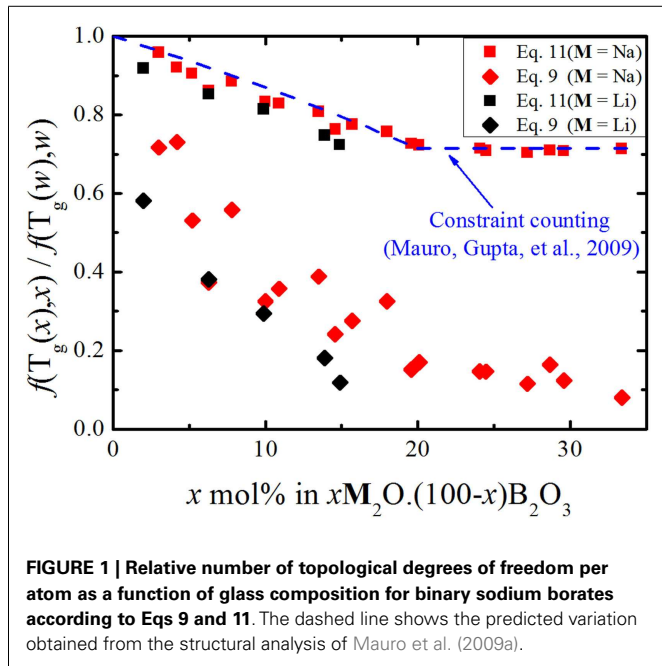
Table 1 | Parameters of Eqs 7 and 8 as a function of chemical composition for binary $x\text{Na}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$ and $x\text{Li}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$.

Composition $x\text{M}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$ (mol%)	$K(x)$ (Eq. 7)	$C(x)$ (Eq. 7)	m (Eq. 8)	T_g (Eq. 8)	Reference
0	2653	557	31.3	522.9	Sasek et al. (1984), Shartis et al. (1953a,b), Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Volarovich and Tolstoi (1934), Rabinovich (1942), Yamate and Kadogawa (1984)
M = Na					
3	2022	763	36.0	545.5	Shartis et al. (1953a,b), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962); Nemilov (1966)
4.2	2146	783	35.7	567.9	Sasek et al. (1984), Yamate and Kadogawa (1984)
5.2	1586	981	40.5	577.8	Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Nemilov (1966), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
6.3	1174	1245	45.7	607.5	Shartis et al. (1953a,b), Volarovich and Tolstoi (1934), Li et al. (1960), Li et al. (1962), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
7.8	1706	975	39.7	591.2	Sasek et al. (1984), Nemilov (1966)
10	1056	1372	47.8	627.3	Shartis et al. (1953a,b), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962)
10.9	1166	1321	46.4	631.0	Matusita et al. (1980); Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984)
13.5	1299	1301	45.2	647.1	Nemilov (1966)
14.6	857	1704	52.3	685.7	Sasek et al. (1984) Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Yamate and Kadogawa (1984), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973), Stolyar et al. (1984), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977)
15.7	963	1586	50.3	674.7	Shartis et al. (1953a), Shartis et al. (1953b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Nemilov (1966), Visser and Stevels (1972a), Visser and Stevels (1972b), Stevels (1973)
18	1163	1512	47.8	691.1	Sasek et al. (1984), Nemilov (1966), Jenckel (1935)
19.6	565	2123	59.3	719.6	Shartis et al. (1953a,b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Nemilov (1966)
20.1	638	2052	57.5	723.9	Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Volarovich and Tolstoi (1934), Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977), Jenckel (1935)
24.1	556	2186	59.8	732.4	Sasek et al. (1984), Volarovich and Tolstoi (1934), Nemilov (1966), Leedecke and Bergeron (1976), Leedecke and Bergeron (1977)
24.5	556	2205	59.8	737.6	Shartis et al. (1953a,b), Matusita et al. (1980), Volarovich and Tolstoi (1934), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962), Nemilov (1966), Visser and Stevels (1972a,b), Stevels (1973), Stolyar et al. (1984), Jenckel (1935)
27.2	443	2398	63.4	743.3	Sasek et al. (1984), Nemilov (1966), Stolyar et al. (1984)
28.7	623	2121	58.2	737.2	Shartis et al. (1953a,b), Stolyar et al. (1984), Jenckel (1935)
29.6	475	2326	62.3	738.5	Matusita et al. (1980), Suzuki et al. (1979), Suzuki et al. (1981a,b), Imaoka and Suzuki (1982), Nemilov (1966), Visser and Stevels (1972a,b), Stevels (1973), Jenckel (1935)

(Continued)

Table 1 | Continued

Composition $xM_2O \cdot (100-x)B_2O_3$ (mol%)	$K(x)$ (Eq. 7)	$C(x)$ (Eq. 7)	m (Eq. 8)	T_g (Eq. 8)	Reference
33.4	305	2627	68.8	733.1	Sasek et al. (1984), Shartis et al. (1953a,b), Volarovich and Tolstoi (1934), Rabinovich (1942), Yamate and Kadogawa (1984), Li et al. (1960), Li et al. (1962), Nemilov (1966), Stolyar et al. (1984), Jenckel (1935), Danek and Licko (1981)
M = Li					
2	1711	916	39.1	569.4	Shartis et al. (1953a,b), Yamate and Kadogawa (1984)
6.3	1211	1245	45.4	613.8	Shartis et al. (1953a,b), Matusita et al. (1980), Visser and Stevels (1972a,b), Stevels (1973)
9.9	975	1470	49.4	642.0	Shartis et al. (1953a,b), Yamate and Kadogawa (1984)
13.9	656	1941	56.6	699.9	Shartis et al. (1953a,b), Yamate and Kadogawa (1984), Visser and Stevels (1972a,b), Stevels (1973)
14.9	441	2312	63.0	722.4	Matusita et al. (1980), Visser and Stevels (1972a,b), Stevels (1973)



where $N_b(T, x)$ is the number of broken bond constraints, $N_i(T, x)$ is the number of intact bond constraints, $g_b(T, x)$ is the degeneracy of the broken state, and $g_i(T, x)$ is the degeneracy of the intact state. Eq. 15 simplifies to:

$$\frac{N_b(T, x)}{N_i(T, x)} = \frac{g_b(T, x)}{g_i(T, x)} \exp\left(-\frac{H(x)}{kT}\right) \quad (16)$$

The number of floppy modes is equal to the number of broken constraints, $N_b(T, x) = f(T, x)$, and according to Gupta and Mauro (2009) the number of floppy modes is also given by $f(T, x) = d - n(T, x)$, where d is the dimensionality of the network and $n(T, x)$ is the number of intact bond constraints.

In our case $d=3$, resulting in $n(T, x) = N_i(T, x) = 3 - f(T, x)$. As $C(x) = H(x)/k$, Eq. 16 can be rewritten as:

$$\frac{g_b(T_g(x), x)}{g_i(T_g(x), x)} = \frac{f(T_g(x), x)}{3 - f(T_g(x), x)} \exp\left(\frac{C(x)}{T_g(x)}\right) \quad (17)$$

By taking values of $C(x)$ and using Eq. 11 to calculate $f(T_g(x), x)$, as it gives the best agreement with structural data, we can estimate the relative degeneracy of states as a function of chemical composition (Figure 3B).

As the glasses get richer in alkali (i.e., more polymerized), the floppy modes get more degenerate in relation to the intact bond constraints. This might provide an explanation for the transition in the type of floppy mode, which controls the glass transition temperature in these alkali borate glasses (Mauro et al., 2009a).

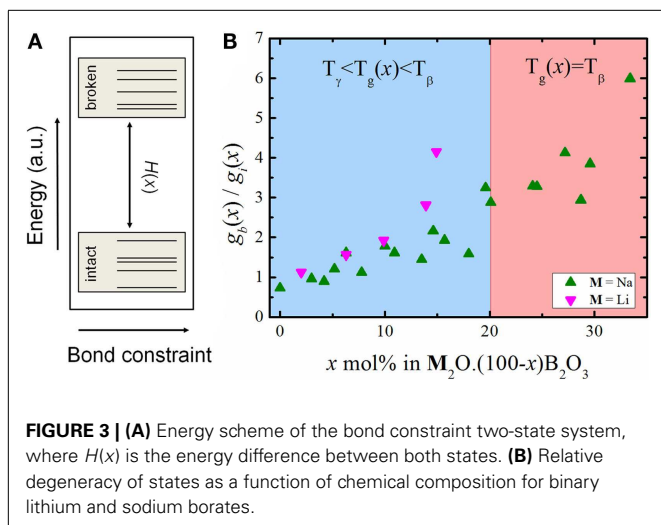


FIGURE 3 | (A) Energy scheme of the bond constraint two-state system, where $H(x)$ is the energy difference between both states. **(B)** Relative degeneracy of states as a function of chemical composition for binary lithium and sodium borates.

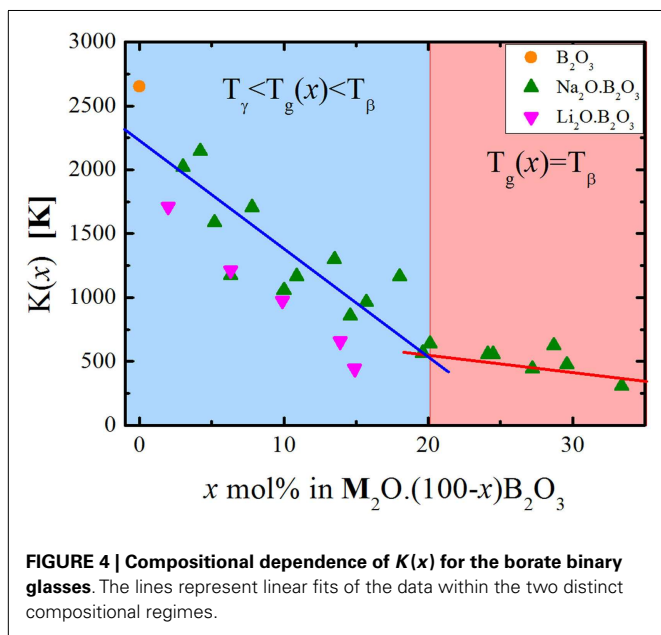


FIGURE 4 | Compositional dependence of $K(x)$ for the borate binary glasses. The lines represent linear fits of the data within the two distinct compositional regimes.

The compositional changes might render the intact B–O–B angular constraints less degenerate and we interpret this as a reduction in the angular flexibility, meaning that as the degeneracy decreases these constraints become more rigid. At some compositional range, these transitions become so unlikely that it becomes more probable to break other constraints, in this case, the O–B–O angular constraint. The transition between floppy modes is very discernible independently of how the number of topological degrees of freedom is calculated (Figure 1). This also correlates with the variation of $K(x)$ with the chemical composition, as can be seen in Figure 4.

According to Mauro et al. (2009b), $K(x)$ is written as:

$$K(x) = \frac{B(x)}{3Nk \ln \Omega} \quad (18)$$

Therefore, any change in $K(x)$ means that either $B(x)$ and/or Ω are changing. If the assumption that $B(x) \approx B(w)$ used in the

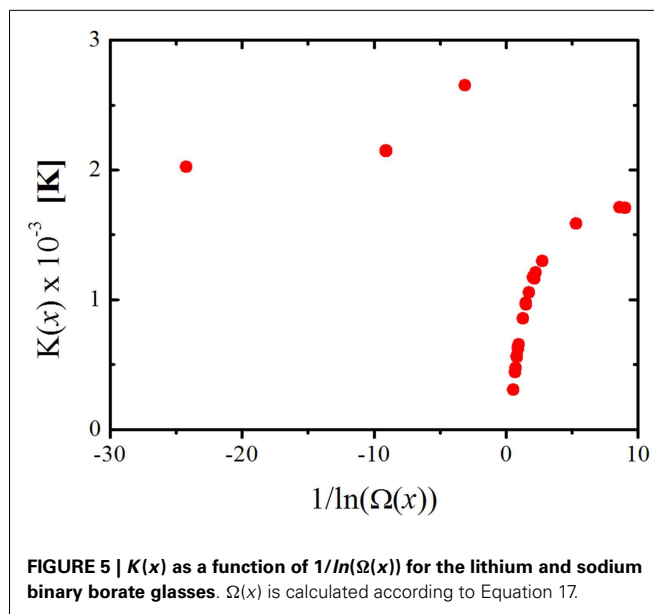


FIGURE 5 | $K(x)$ as a function of $1/\ln(\Omega(x))$ for the lithium and sodium binary borate glasses. $\Omega(x)$ is calculated according to Equation 17.

derivation of Eq. 11 is correct, then plotting the values of $K(x)$ as a function of $1/\ln(\Omega(x))$ should result in a straight line passing through the origin, but as we can see from Figure 5 this is far from what we get. Therefore, not only the degeneracy is causing $K(x)$ to change with composition but also the energy barrier of structural rearrangement, $B(x)$. From Eqs 1 and 7 we get that, at $T = T_g$:

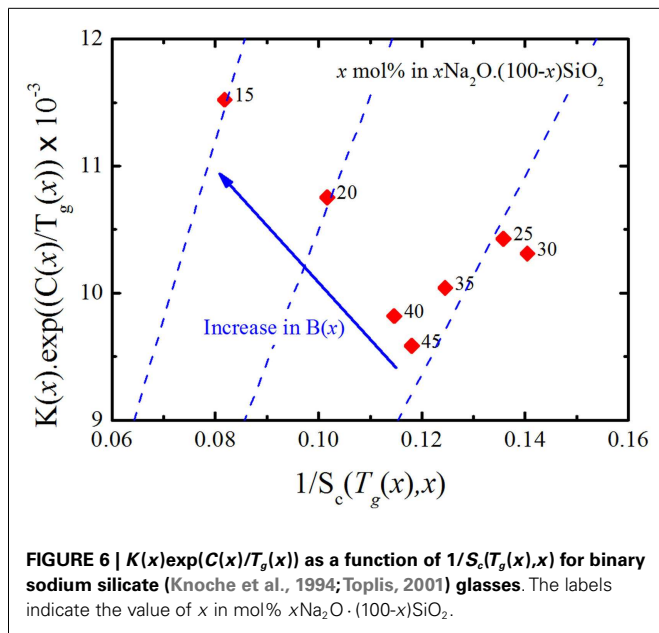
$$\frac{B(x)}{S_c(T_g(x), x)} = K(x) \cdot \exp\left(\frac{C(x)}{T_g(x)}\right) \quad (19)$$

Thus, plotting $K(x)\exp(C(x)/T_g(x))$ as a function of $1/S_c(T_g(x), x)$ should yield a straight line passing through the origin with a constant, positive slope of $B(x)$ for all glasses of the same “family.” Analyzing the available thermodynamic and viscosity data for $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ glasses (Knoche et al., 1994; Toplis, 2001) resulted in the graph in Figure 6, where one can see that even though $B(x)$ appears to be constant for $x \geq 0.25$, it increases as the glass compositions get richer in silica. The observed change in the behavior of $B(x)$ at $x \approx 0.2$ is consistent with the glass network transitioning from stressed-rigid to floppy. Such transition has already been reported in experimental (Vaills et al., 2005) and MD simulations (Bauchy and Micoulaut, 2011).

Adam and Gibbs (1965) demonstrated that $B(x)$ is given by:

$$B(x) = \frac{n_p \Delta\mu(x) S_c^*(x)}{k} \quad (20)$$

where n_p is the number of particles in the system, $\Delta\mu(x)$ is the average energy barrier each rearranging region has to overcome during cooperative motion, and $S_c^*(x)$ is the configurational entropy of the smallest rearranging region. As argued before, the number of particles in the system is considered to be constant, meaning that the observed variations in $K(x)$ are due to changes in $\Delta\mu(x)$ and $S_c^*(x)$. These two parameters are sensitive to changes in the medium- and long-range orders, as they are associated with cooperative rearranging regions (CRRs); thus, we suggest that the



observed variation of $K(x)$ as a function of composition stems from the changes in the CRRs, which can only change if the floppy modes enable these regions to become more or less flexible. This line of reasoning suggests that the properties of the CRRs are deeply connected to the number and types of floppy modes in the glass network, as they should dictate the possible rearrangements a certain region can reach.

As $B(x) \neq B(w)$, one should observe a decoupling on the values of topological degrees of freedom per atom estimated from viscosity and bond constraint counting. We propose that the main reason for this decoupling is that while the viscosity reflects the behavior of the whole system, combining the responses of short-, medium-, and long-range interactions, the bond constraints are, by their own definition, restricted to short-range interactions. It is known that medium-range interactions affect the measured viscosity of polymers, with the molecular weight of side groups (Rogers and Mandelkern, 1957; Gargallo et al., 1987, 1988) and the shape of chains (Gonzalez et al., 1988; Hur et al., 2011; Khalyavina et al., 2012) having significant influence even though the covalent chemical bonds that make the backbone of the chains stay constant; and recent evidence points that the same effects may be present in inorganic oxide glasses (Rodrigues and Wondraczek, 2013). The coulombic interactions between the modifiers and the non-bridging oxygens extend beyond its first coordination shell, and it has been shown that they are a major part of the constraints present in phosphate glasses (Hermansen et al., 2014; Rodrigues and Wondraczek, 2014; Rodrigues et al., 2014), so they might also have an effect here. The apparent influence of the medium range also ties with the possible differentiability of the floppy modes. When counting, the constraints are either intact or broken and two floppy modes are considered the same even if their surroundings are very different. For example, in the binary alkali borate glasses, when considering the breakage of the angular constraints of the bridging oxygens, each trigonally coordinated boron has three floppy modes regardless of the fact that it may be bonded to three other trigonal borons or three tetragonal borons. But these two

different configurations may very well have different configurational entropies associated, influencing the CRRs and, ultimately, the viscosity of the system. This may indicate that the parameter $K(x)$ can be used to probe changes in the medium-range order of super-cooled liquids as a function of chemical composition.

CONCLUSION

In this paper, the viscosity of binary alkali borates and silicates was used to estimate the number of topological degrees of freedom as a function of glass composition. The number of floppy modes estimated from viscosity decouples from the values, which are obtained by bond constraint counting. We suggest that the origin of this decoupling is due to the difference in scale: while viscosity covers the whole system, bond constraint counting only handles short-range interactions; hence the observed inequality of $B(x)$. We provide evidence that the degeneracy of floppy modes changes with chemical composition and that the parameter $K(x)$ of the MYEGA viscosity equation could be used to assess changes in the medium-range order.

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