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Building up a weaker network: The effect of intermediate range glass structure on liquid fragility

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ABSTRACT

Classical considerations of the stability of amorphous networks have sensibly concluded that a network should weaken when mechanical constraints are removed. In covalently-bonded glass networks, this weakening is evidenced by the “fragility” and, in many cases, the fragility increases as the density of covalent bonds decreases. However, covalent glasses that possess substantial intermediate range order (IRO) exhibit an increase of fragility with increasing bond density — a paradoxical weakening in spite of the addition of reinforcing constraints. Here we resolve this paradox by suggesting that such IRO-containing networks require a renormalization. A coarse-graining of IRO structural units is proposed that permits a network to effectively weaken despite increases in the overall density of bonds. Through this coarse-graining approach, we demonstrate the emergence of a universal dependence of fragility on network connectivity that is well obeyed by more than 75 distinct network-forming glasses including chalcogenides, borates, germanates, phosphates and aluminophosphates.

1. Introduction

Rigidity theory [1–3] teaches that a network of discrete bonds undergoes a transition from “floppy” [3] to rigid dynamics near a rigidity threshold where the total degrees of freedom for a system of N atoms are just balanced by an equal number of mechanical constraints. A simple analysis that includes both bond length and angular (Lagrangian) constraints, predicts this rigidity threshold to occur when the average number of covalent bonds per atom reaches $\langle r \rangle = 2.4$ and to date, a large number of experimental investigations have highlighted the relevance of this underlying transition in rigidity to observed trends in a variety of material properties [2–8].

In chalcogenide [4,5] and alkali phosphate glasses [9,10] (see Fig. 1), for example, the increasing bond density produces a systematic decrease in the liquid's *fragility*. Glasses with $\langle r \rangle \ll 2.4$ are kinetically fragile but become far less fragile at $\langle r \rangle \geq 2.4$ as additional constraints are introduced by the increase of more interatomic bonds. This behavior can be understood through traditional (e.g., Adam–Gibbs style) theories [11,12] that link fragility with the available configurational entropy released at the glass transition. Simply put, under-constrained glasses (those with $\langle r \rangle \ll 2.4$ that have too few interatomic bonds to produce a globally rigid network) have substantial regions of “floppy” [3] or poorly constrained structure that contribute greatly to the configurational entropy of the liquid that emerges from the glassy state while the over-constrained glasses (with $\langle r \rangle \gg 2.4$ that have more than a sufficient density of interatomic bonds to produce a globally rigid network) have little or none of this same configurational entropy. It reasons that the fragility should display a minimum near $\langle r \rangle = 2.4$, and in fact, numerous researchers [4–7,13] have reported just that.

However, both the alkali borate [14,15] and alkali germanate [16,17] glasses (included in Fig. 1) exhibit an anomalous behavior. In each instance, the fragility *increases* as additional constraints are *added* to an already over-constrained network. A resolution to this anomalous behavior was recently proposed [18] for the alkali borates by arguing for a renormalization of the covalent network in which elements of both the short range and intermediate range order (IRO) are effectively replaced by equivalent network nodes through a simple coarse-graining procedure. Viewed through the filter of this renormalization, the fragility of the alkali borates was shown to display exactly the *same* dependence on network connectivity seen for the chalcogenide and phosphate glasses — a dependence that is far more consistent with our conceptual understanding of configurational entropy.

In this paper, we consider the alkali germanate glasses that too display an anomalous trend like that seen in the alkali borates. Using available information regarding the IRO present in these germanate glasses, we show that straightforward application of the same renormalization procedure used previously for the borates similarly transforms the fragility dependence on connectivity of the germanates to coincide with that of the other network-forming glasses discussed thus far. Together with the borates, phosphates and chalcogenides, this universal dependence of fragility on network connectivity offers an exciting new insight into the relationship between glass structure and the dynamics of the melt.

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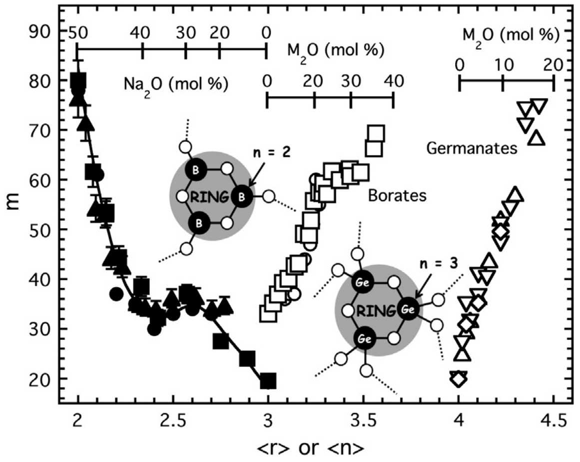

Fig. 1. The fragility of chalcogenide $Se_x(As_{0.5}Ge_{0.5})_{1-x}$ glasses [4,5] (filled circles) as a function of average coordination number, $\langle r \rangle$, follows an equivalent dependence as do a series of $(Na_2O)_x(P_2O_5)_{1-x}$ (filled squares) and $(Al(PO_3)_3)_x(NaPO_3)_{1-x}$ (filled triangles) glasses [9,10] as a function of the average bridging oxygen bond number, $\langle n \rangle$. Error bars reflect a 5% uncertainty in determining the fragility and the solid line is only a guide for the eye. By comparison, $(Li_2O)_x(B_2O_3)_{1-x}$ (open circles), $(Na_2O)_x(B_2O_3)_{1-x}$ (open squares), $(Na_2O)_x(GeO_2)_{1-x}$ (open upright triangles), $(K_2O)_x(GeO_2)_{1-x}$ (open inverted triangles) and $(Rb_2O)_x(GeO_2)_{1-x}$ (open diamonds) glasses [14–17] do not conform to the previous curve, but rather display increasing fragility with increasing network connectivity. Scales in the upper field indicate the corresponding variation with alkali oxide content. Inset contains illustrations of the boroxol ring and the 3-membered germanate ring showing the reduced connectivity discussed in the text.

2. Background

2.1. Fragility

Fragility [11] is a kinetic property of a glass forming liquid that characterizes how rapidly the melt un-thickens as it is heated above its glass transition temperature, T_g. It is frequently defined by the logarithmic slope of the viscosity near T_g as

$$m = \frac{d\log_{10}\eta}{d\left(T_g/T\right)}\Big|_{T_g}, \tag{1}$$

and the quantity m is sometimes referred to as the "steepness index" or simply the "fragility". Over the years since its introduction, numerous investigations [19–21] have sought to unravel the source behind a general pattern in the fragility that ranges from a minimum value of about $m = 20$, common to many conventional oxide glasses (e.g., SiO_2) that form networks of discrete covalent bonds, to values as high as $m = 90$ or greater seen in many simple molecular liquids and polymers that interact through comparatively weaker and more isotropic forces [11].

Aside from any purely academic interest, the consequences of fragility remain a tangible concern for commercial glass making efforts where precise control of the viscosity is required for successful manufacturing. It is not surprising then to find many studies in the literature that have explored correlations of the fragility with other properties at or below the glass transition. Notable examples include the early correlation of fragility with the thermodynamic drop in specific heat that accompanies the liquid-to-glass transition [11,12] as well as more recent correlations to the Poisson ratio [22] and the non-ergodic level (related to the Debye–Waller factor) of the glass [23,24] which have spawned an intriguing proposition that the dynamical properties of a glass forming liquid found above T_g might, in fact, be "embedded" [23] in the structural properties of its solid phase present below T_g. Even in the classic Adam–Gibbs model [25], where the increasing viscosity of the melt is associated with the vanishing of configurational entropy on approach to the so-called Kauzmann temperature [26], the fragility appears as a direct measure of the rate at which this entropy decreases as it is progressively stockpiled away into the non-ergodic phase.

2.2. Network-forming liquids

For the network-forming liquids, it is reasonable to anticipate that fragility would be directly influenced by the overall connectivity of the network of covalent bonds and early studies of certain chalcogenide glasses [4,5] (included in Fig. 1), as well as more recent studies [13], do display a systematic decrease in fragility as the average number of covalent bonds per atom increased from $\langle r \rangle = 2$ (a system of polymeric chains) to a highly over constrained network with $\langle r \rangle$ well in excess of the rigidity threshold [1–3] of $\langle r \rangle = 2.4$.

A remarkably similar decrease in fragility with increasing network connectivity was observed [9] for a series of sodium phosphate glass forming melts in which the average number of bridging oxygen bonds per PO_4 tetrahedra, $\langle n \rangle$, varied from $\langle n \rangle = 2$ at the so-called metaphosphate composition whose structure consists of long polymer chains [27] to $\langle n \rangle = 3$ in the instance of P_2O_5. Indeed, the fragility of both the chalcogenide and sodium phosphate melts is found to coincide provided that the network connectivity of the latter is characterized by $\langle n \rangle$ instead of $\langle r \rangle$. In the phosphate study [9] it was argued that this adoption of $\langle n \rangle$ in difference to $\langle r \rangle$ reflects a traditional view of oxide glass structure as being (topologically) composed of well-defined structural units (typically tetrahedra such as SiO_4, PO_4, and GeO_4) that connect one to another via bridging oxygen bonds [28]. Viscous flow occurs primarily via the breaking and reformation of these same bridging oxygen linkages [29], and in many respects, the adoption of $\langle n \rangle$ for oxide networks can be viewed as a *coarse-graining* of the original covalent network wherein the bridging oxygen bonds become the weakest links between otherwise rigid structural units.

As seen in Fig. 1, this coarse graining concept fails for the case of both alkali borate and alkali germanate glasses. In both these systems, the initial addition of alkali oxides produces an increased connectivity through the formation of additional bridging oxygen bonds: for B_2O_3, borate units with $n = 3$ are converted to units with $n = 4$ bridging bonds [30,31], and for GeO_2, germanate units with $n = 4$ are converted to either $n = 5$ [32–34] or $n = 6$ [35]. Non-bridging oxygens do begin to form at concentrations above $x_{max} \approx 0.2$ to 0.3 and the bond densification followed by rarefication produces compositional "anomalies" [17,30] wherein properties such as the mass density and glass transition exhibit maxima at compositions near x_{max}. An example of such an anomaly is shown in the inset to Fig. 2 for the T_g of several alkali germanate glasses [17]. Ignoring the initial drop in T_g between $x = 0$ and 3 mol% alkali oxide, T_g displays a maximum in the vicinity of $x_{max} \approx 20$ mol%. As for the drop in T_g between $x = 0$ and 3 mol%, this is unique to the germanate system and, while several explanations have been proffered [17], the origins for this "second anomaly" remain largely uncertain. It is clear that the drop correlates well with a rapid decrease between 0 and 10 mol% of the viscosity (measured at 1300 °C by Riebling [36]), as shown in Fig. 2.

For the case of alkali borates, some success in accounting for the anomalous increase in fragility with increasing connectivity has been obtained using a temperature-dependent constraint theory [37–42] in which constraint counting of covalent bonds is compounded by thermal activation of these same bonds to produce a multi-parameter model capable of fitting the compositional dependence of the fragility. Although the theory can qualitatively model the increasing fragility of the borates [38], it has yet to be applied [42] to describe the fragility of alkali phosphates which, as seen in Fig. 1, present an important counter example to the alkali borates.

Something of a simpler explanation for the fragility in the alkali borates was proposed on the basis of the intermediate range order that is unique to this system. In addition to the changes in local coordination of the B atom mentioned above, a rich variety of larger structural motifs appear [31]. This includes the large number of rigid, 3-membered