Effect of water on topological constraints in silica glass

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ABSTRACT

A fundamental understanding of how water interacts with glass is valuable for many practical concerns due to the myriad effects of water on glass properties. Topological constraint theory, which has been shown in prior studies to be an excellent model for various thermomechanical properties, is expanded herein to account for strain on the glass network, in this application due to unbonded interstitial species. Literature T_g data have been collected for silicate glasses containing various alkali and water contents and an expanded constraint theory model has been successfully applied to describe the effects of water on the glass transition temperature.

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Water in glass has been shown to affect numerous macroscopic properties: optical [1-4], mechanical [5,6], electrical [7-9], and thermal [3,4,10-15], among others. In particular, the glass transition temperature, T_g, and viscosity, η, have been shown to vary widely with water content [3,4,10-16]. This effect is especially pronounced in SiO_2. The microscopic speciation of water as either a bonded hydroxyl group or an unbonded H_2O molecule has also been studied — for silica glass, the reaction takes the following form [3,12,17-19]:

$$\equiv Si - O - Si \equiv +H_2O \rightleftharpoons \equiv Si - OH + HO - Si \equiv . \tag{1}$$

For silicate glasses with low water content, this reaction is hypothesized to proceed essentially to completion [3,4,10,12,15,18]. Unlike with alkali modifiers, the hydroxyl content reaches a saturation value and additional water entering the glass remains in molecular form [3,11-13,15,18]. However, the structure-property connection remains elusive, despite the putative benefit of such an understanding. To this end, a topological constraint model has been developed to account for these effects.

Topological constraint theory has successfully predicted several fundamental thermomechanical properties and has vastly simplified the industrial design process for new glass products [20-25]. It has even been expanded to include more complex systems such as calcium-silicate-hydrate [26]. Phillips and Thorpe characterized the degrees of freedom f for each network-forming atom for a glass network of dimensionality d [27]. The total number of degrees of freedom is then the difference between the spatial dimensionality d and the average number of constraints per atom n [22,27]:

$$f = d - n. \tag{2}$$

Any glass system may then be characterized by the difference between the dimensionality and the average number of constraints per atom: networks can be floppy ($n < d$), isostatic ($n = d$), or stressed-rigid ($n > d$) [22,24,28].

Constraint theory has been extended to include a temperature dependence [20-23,29,30], which enables it to predict the glass transition temperature (T_g), fragility, and viscosity of a glass based on the onset temperature of each one of the constraints (T_α, T_β, and T_γ) [20,21,24,28,31]. With an accurate structural model for a system (used to calculate f), a single experimental T_g may be used with Eq. (3) to predict T_g for any other composition in that system [20,21,28,31].

Previous works by Naumis [28] and Mauro et al. [20,21,31] have shown that the glass transition temperature of a glass is governed largely by the configurational entropy of the system, which is in turn governed largely by the degrees of freedom of the network. These

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relationships were rearranged by Mauro et al. to form the following relationship:

$$\frac{T_g(x)}{T_g(x_r)} = \frac{S_c[T_g(x_r),x_r]}{S_c[T_g(x),x]} = \frac{f[T_g(x_r),x_r]}{f[T_g(x),x]}, \tag{3}$$

where S_c is the configurational entropy defined for a given composition x, and x_r refers to some reference composition [20-24,28-32].

By rearranging the left- and rightmost portions of Eq. (3) it follows that the quantity

$$T_g(x) \cdot f[T_g(x),x] = T_g(x_r) \cdot f[T_g(x_r),x_r], \tag{4}$$

the product of the total degrees of freedom with the glass transition temperature, is conserved. To determine f, three types of constraints are considered:

- α, the linear constraints associated with N—O bonds in oxide glasses, where N is some network former;
- β, the angular constraints associated with the O—N—O bond angle and can be calculated as $2n - 3$, where n is the coordination of the glass former; and
- γ, an angular constraint associated with the N—O—N bond [20,21].

α and β constraints typically govern this quantity due to the sub-$T_g \gamma$ onset temperature [20,21]. If the predicted T_g would exceed T_β, it instead takes on a constant value, $T_g \approx T_\beta$, such that Eq. (4) remains satisfied [21]. Mauro et al. suggested that the γ constraint onset temperature can be a limiting factor [21]; this is seen in the range of compositions for which T_g remains largely unchanged, and this lower bound on T_g should correspond to T_γ.

Upon application of this model to pure SiO$_2$, the sum of the average number of α and β constraints ($\approx n$) per atom becomes three for an ideal silica glass (defect-free). Here, a skeletal enumeration of constraints is used as per [20] and [21], considering the floppy modes of non-bridging oxygen atoms to contribute to the cooperative motions of atoms via the decrease in connectivity of the silicate tetrahedra (cf. [33-35]). blackOxygen composes $\frac{2}{3}$ of the network and has one α constraint for each of its bonded silicon atoms, whereas silicon composes $\frac{1}{3}$ of the glass network and has two β constraints for each of its four bonded oxygens. Summing these contributions to the network rigidity results in f tending toward zero. Assuming a nontrivial solution to Eq. (3) ($T_g \neq 0$) and finite values for f and T_g of a maximally-modified reference glass suggests an infinite T_g for pure silica glass. The silica glass transition, however, has been experimentally measured to occur around 1200 °C. Defects in nominally "pure" silica glass such as trace impurities, vacancies, or other point defects must then cause the effective degrees of freedom to take on a non-zero value. Furthermore, because this value is small, any slight addition of modifier to the network results in a large relative change in f, and therefore a corresponding large relative change in T_g. A practical value for f in nominally "pure" silica is approximated herein.

Glasses with significant alkali content were used to obtain T_γ, as the onset should be reached quickly due to the large number of degrees of freedom relative to pure silica glass. For glasses with large water content, T_g is observed to dip dramatically below T_γ. It is proposed that this is due to an alteration of the strength of the γ constraint due to molecular water present in the glass.

The effects of different water species are considered separately in this treatment. Water reacting with the silica network removes a bridging oxygen from the network and introduces two non-bridging oxygens (see Eq. (1) for the constituent reaction equilibrium). This reaction removes two α constraints, four β constraints, and one γ

constraint. The reduction of the number of constraints, however, only affects the value of $n[T_g(x),x]$; T_g should still be bound by T_γ. Thus since T_g continues to diminish, the value of T_γ must be reduced with increasing water content.

Using the equipartition theorem, one may define

$$U_\gamma = \frac{3}{2} k_B T_\gamma, \tag{5}$$

where k_B is the Boltzmann constant and U_γ is the potential energy associated with a single γ constraint (the energy required for the constraint to undergo a rigid-to-floppy transition). Despite not breaking constraints, interstitial H$_2$O will introduce strain (U_ϵ), weakening the constraints. This can be seen graphically in Fig. 1, where it is also apparent that the γ constraint is the only constraint affected by this strain. U_γ may then be modified as follows:

$$U'_\gamma = U_\gamma - U_\epsilon, \tag{6}$$

which may be substituted into Eq. (5) and solved for the corrected γ constraint onset temperature T'_γ:

$$T'_\gamma = \frac{2}{3k_B} [U_\gamma - U_\epsilon]. \tag{7}$$

Since it was assumed earlier that the effects of the two water species are separate, the presence of molecular H$_2$O depresses T_γ as shown, but does not have any direct effect on T_g.

Eq. (4) may be rewritten as follows:

$$\frac{T_g(x_r) \cdot f[T_g(x_r),x_r]}{T_g(x)} = f[T_g(x),x]. \tag{8}$$

Assuming the number of intrinsic defects (those present in pure silica) in the modified silicate glass network scales linearly with SiO$_2$ content:

$$\frac{T_g(x_r) \cdot \left[f[T_g(x_r),x_r] + (1 - x_a)f_{SiO_2}\right]}{T_g(x_{SiO_2})} = f_{SiO_2}, \tag{9}$$

where x_a is the combined alkali and bonded hydroxyl content of the glass in mole percent. This equation was fit to hydrated silicate T_g data from literature — data from low-water-content glasses were used to ensure that all water was dissolved into the network as hydroxyl and to avoid the T_γ asymptote [11,13,14,36-38]. Data for
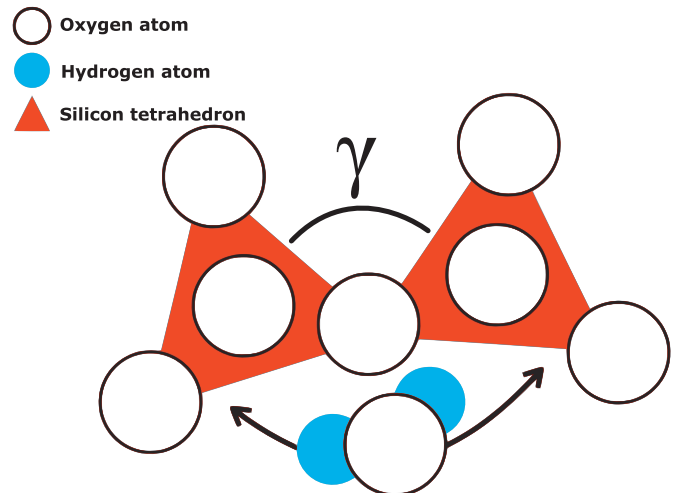

○ Oxygen atom

● Hydrogen atom

▲ Silicon tetrahedron

Fig. 1. Schematic diagram of an Si—O—Si bond angle strained by interstitial water.