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## Topological Origin of the Network Dilation Anomaly in Ion-Exchanged Glasses

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Ion exchange is commonly used to strengthen oxide glasses. However, the resulting stuffed glasses usually do not reach the molar volume of as-melted glasses of similar composition—a phenomenon known as the network dilation anomaly. This behavior seriously limits the potential for the chemical strengthening of glasses and its origin remains one of the mysteries of glass science. Here, based on molecular dynamics simulations of sodium silicate glasses coupled with topological constraint theory, we show that the topology of the atomic network controls the extent of ion-exchange-induced dilation. We demonstrate that isostatic glasses do not show any network dilation anomaly. This is found to arise from the combined absence of floppy modes of deformation and internal eigenstress in isostatic atomic networks.

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### I. INTRODUCTION

Ion exchange [1–3] is a technique that is commonly used to strengthen oxide glasses. In this process, the alkali ions present in a glass (e.g., Na<sup>+</sup>) are replaced by larger ones (e.g., K<sup>+</sup>), which is usually achieved by placing the glass in a molten salt bath at a temperature below the glass transition [4]. This induces the formation of a compressive stress layer at the surface of the glass, which limits the propensity for crack initiation and growth. In unconfined conditions, atomic networks tend to expand upon ion exchange due to difference in size between stuffed and host ions, which is captured by the linear network dilation coefficient (LNDC)  $B$ :

$$B = \frac{1}{3} \frac{1}{V} \frac{\partial V}{\partial C}, \quad (1)$$

where  $C$  is the concentration of substituted atoms and  $V$  the molar volume of the glass [5]. However, ion-exchanged glasses have been shown to feature a “network dilation anomaly”, namely,  $B$  is 2–4 times lower than its theoretical value in typical commercial glasses), as calculated by the molar volumes of the compositionally equivalent as-melted glasses [6]. In practice, this seriously limits the extent of strengthening that can be achieved through ion exchange.

Although the network dilation anomaly had originally been suggested to arise from some plasticity [1], ion stuffing is found to be entirely elastic [7]. The failure of

the network to reach the full elastic expansion is suggested to arise from the inability of the stuffed atoms to reach the local environment achieved in as-melted glasses [8]. As such, ion-exchanged glasses access a forbidden configurational state, i.e., a state that cannot be achieved by any cooling path from the melt [9]. However, the mechanism that controls the ability of an atomic network to adjust its structure upon ion exchange remains poorly understood.

Here, we rationalize the ability of an ion-exchanged atomic network to reach the molar volume of its as-melted counterpart by relying on the framework of topological constraint theory (TCT [10–13]). TCT reduces the complex atomic networks of glasses into simple mechanical trusses, wherein nodes (the atoms) are connected to each other through constraints (the chemical interactions). As such, TCT captures the important atomic topology while filtering out less relevant chemical details, which ultimately do not affect macroscopic properties. In this framework, atomic networks can be classified as (i) flexible, having internal degrees of freedom that allow for local deformations [14], (ii) stressed rigid, being locked by their high connectivity and featuring internal eigenstress [15,16], or (iii) isostatic, the optimal intermediate state, being rigid but free of eigenstress. As per Maxwell’s criterion of stability [17], the isostatic state is achieved when the number of constraints per atom  $n_c$ , comprising radial bond stretching and angular bond bending, equals three, the number of degrees of freedom per atom. Isostatic systems have been found to exist inside a window [18,19], located between the flexible and the stressed-rigid domains, and show anomalous properties, e.g., a space-filling tendency [20], weak

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aging phenomena [21], maximum fracture toughness [22], and anomalous dynamical and structural signatures [23,24].

## II. SIMULATION METHODOLOGY

To elucidate the influence of the atomic topology on the ability of an atomic network to adjust its structure upon ion exchange, we rely on molecular dynamics (MD) simulations of permanently densified  $(\text{Na}_2\text{O})_{30}(\text{SiO}_2)_{70}$  glasses (denoted NS thereafter), a base material for various multicomponent industrial silicate glasses. All simulations are performed using the empirical potential parametrized by Teter [25], which has been extensively studied and shown to provide realistic results for the structural, dynamical, and mechanical properties of NS glasses and supercooled liquids [22,25–28]. All glasses are made of 3000 atoms and are formed by (i) equilibrating the melts at 3000 K for 1 ns to lose the memory of the initial configurations, (ii) linearly cooling the melts from 3000 to 300 K at a cooling rate of 1 K/ps under constant selected pressures  $P$  (from 0 to 22 GPa), and (iii) relaxing the formed glasses to zero pressure at 300 K for 1 ns. All simulations are performed in the  $NPT$  ensemble. For selected pressures, varying sample sizes (300, 996, 3000, 9000, and 18 000 atoms) and cooling rates (0,01, 0,1, 1, 10, and 100 K/ps [29]) are considered to assess the robustness of the presented results.

Since they are quenched under pressure, the formed glasses remain largely frozen in their densified states, even after relaxation to zero pressure [22]. In particular, the application of pressure during cooling results in the formation of overcoordinated network-forming species, namely, fivefold and sixfold Si and threefold tricluster O atoms (see Ref. [30]). As shown in Fig. 1, the increase of the network connectivity upon pressure induces a rigidity transition: flexible at low  $P$  and stressed rigid at high  $P$  (see the details of the constraints enumeration in Ref. [31]). This effectively delimits an isostatic pressure window of

8–14 GPa (or  $n_c = 3\text{--}3.4$ ), inside which NS has been shown to feature a reversible glass transition, maximum fracture toughness, and maximum diffusion constants [23,31,32]. Within this pressure window, the structure of NS supercooled liquids is found to self-organize by breaking some of the weaker constraints to avoid the onset of internal stress [23,31]. Through this adaptive behavior, the systems can achieve an isostatic state over an extended window rather than at a single threshold [23,31]. Note that sodium silicate glasses also exhibit a rigidity transition with respect to the concentration of  $\text{Na}_2\text{O}$  [33]. However, the permanently densified glasses considered herein allow us to assess the sole effect of the network topology on ion exchange, without any compositional effect.

## III. RESULTS

Next, taking the permanently densified sodium silicate systems as host glasses, we simulate the effect of ion exchange by directly replacing a given fraction of Na by K, thereby neglecting the kinetics of the process [8,34,35]. After ion exchange, the glass is relaxed to zero pressure in the  $NPT$  ensemble and the LNDC is calculated from Eq. (1) (the relaxed ion-exchanged glasses are noted IX hereafter). All ion-exchange simulations are performed at 300 K in order to avoid stress relaxation [36]. For comparison, permanently densified  $(\text{K}_2\text{O})_{30}(\text{SiO}_2)_{70}$  glasses (noted KS hereafter) are prepared by following the methodology as for the NS glasses. As shown in Fig. 2, the molar volume of the IX glass (cooled under zero pressure) increases linearly with the fraction of substituted atoms, as suggested by Eq. (1) and in agreement with experiments (see Ref. [34] for a complete validation of the simulation method used herein). As expected, a network dilation anomaly is observed, that is, after all Na have been replaced by K atoms, the IX glass does not reach the molar volume of the as-melted KS glass.

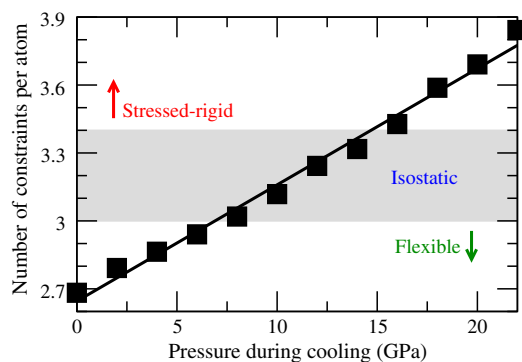


FIG. 1. Number of constraints per atom  $n_c$  for permanently densified sodium silicate glasses, with respect to the pressure applied during the cooling path. The solid line is a linear fit. The gray area indicates the domain of maximum expansion due to ion exchange, as shown in Fig. 3.

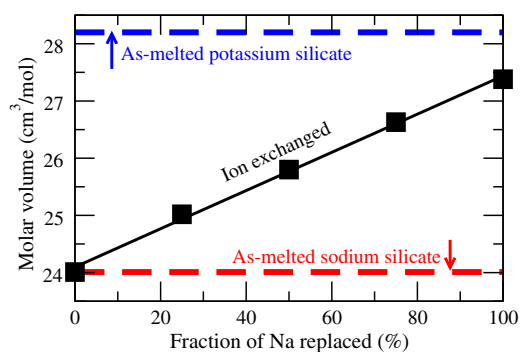


FIG. 2. Molar volume of a sodium silicate glass, cooled under zero pressure, after replacement of a given fraction of Na by K atoms. The solid line is a linear fit. The red (blue) dashed line indicates the molar volume of as-melted sodium (potassium) silicate.

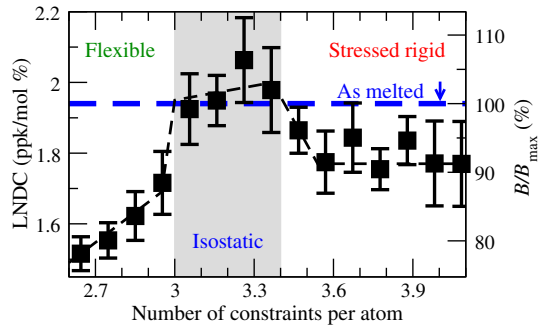


FIG. 3. Linear network dilation coefficient (LNDC,  $B$ ) after substitution of all Na by K atoms, with respect to the number of constraints per atom. The black dashed line serves as a guide for the eye. The blue dashed line indicates the maximum theoretical LNDC  $B_{\max}$ , as obtained from the molar volumes of as-melted sodium and potassium silicate glasses. The gray area indicates the domain of maximum expansion due to ion exchange.

We now focus on the effect of the atomic topology on the LNDC. Note that the stuffing of even a single K atom impacts the system over an extended region (around 8 Å from the stuffed atom), so that we consider herein the overall rigidity of the network rather than the local one around stuffed atoms. Figure 3 shows the calculated LNDC, computed after the replacement of all Na by K atoms. We observe that the LNDC shows a broad maximum within the isostatic window ( $n_c = 3\text{--}3.4$ ). On the other hand, we note that the maximum theoretical LNDC  $B_{\max}$ , as calculated from the molar volumes of as-melted NS and KS glasses, remains fairly constant with the cooling pressure ( $B_{\max} = 1.93$  ppk/mol %). Interestingly, we note that, in the isostatic window, the LNDC reaches its theoretical maximum value  $B_{\max}$ .

We now ensure the robustness of the trend observed herein. To ensure the absence of any finite size effect in our system, we compute the LNDC for varying system sizes. As shown in Fig. 4, we do not observe any finite size effect, except in the smallest system (300 atoms), wherein we observe a drop in the value of  $B$ . We therefore feel

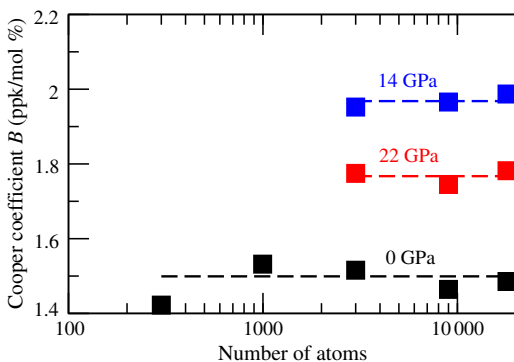


FIG. 4. Cooper coefficient  $B$  as a function of the number of atoms for selected pressures. The lines serve as guides for the eye.

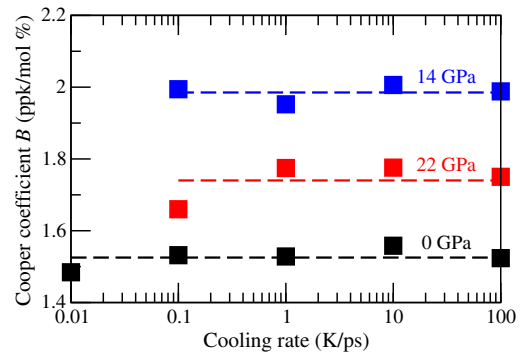


FIG. 5. Cooper coefficient  $B$  as a function of the cooling rate for selected pressures. The lines serve as guides for the eye.

confident that a size of 3000 atoms is large enough for the present study. Further, to ensure that the thermal history of the glasses does not significantly impact our results, we assess the effect of the cooling rate on the LNDC. As shown in Fig. 5, a 4-orders-of-magnitude variation in the cooling rate does not significantly affect the value of  $B$ . In all cases, the difference in  $B$  between the flexible (low pressure), stressed rigid (high pressure), and isostatic (intermediate pressure) remains well defined and larger than the error bars. Hence, the fact that  $B$  exhibits a maximum within the isostatic window does not arise from any spurious effects linked to finite size effects or fast cooling.

Next, we consider the question of the origin of the maximum of dilation for isostatic glasses. Upon ion exchange, the replacement of smaller by larger atoms imposes an internal strain to the rest of the silicate network, which has been shown to share a common origin with thermal expansion [34]. Because of the low temperature, limited modes of relaxation are available to the system to release this strain. Two main mechanisms can prevent the atomic network from expanding. (i) If the packing density is low enough and floppy modes of relaxation can be activated, it is more favorable for the network to locally reorganize and increase the packing density around the stuffed atom than to macroscopically expand. (ii) On the other hand, if the atomic network cannot locally adjust its structure without breaking high-energy bonds, the insertion of larger atoms will induce the formation of internal eigenstress, that is, some bonds are under compression and others under tension while the system is macroscopically at zero pressure. Hence, both internal (i) flexibility and (ii) stress can limit expansion upon ion exchange.

To establish this mechanism, we first assess the ability of the network to locally relax upon ion exchange (mechanism 1). To this end, we compute the average coordination number (CN) of Na and K atoms in the NS, IX, and KS glasses. In the zero-pressure as-melted glasses, Na and K show an average CN of around 6 and 8, respectively. As such, if relaxation can occur within the network upon ion exchange, the CN of the replaced atoms should increase—in order for K atoms to reach their natural coordination shell.



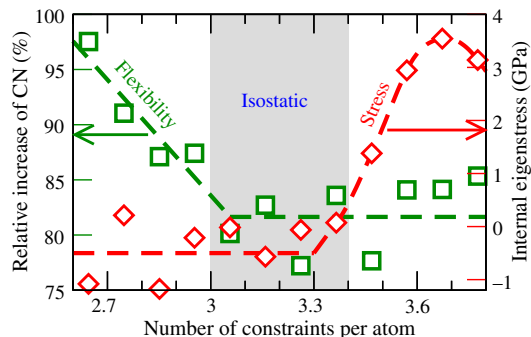


FIG. 6. (left axis) Increase in the average coordination number (CN) of the replaced atoms upon ion exchange, normalized by the difference of CN between the as-melted sodium and potassium silicate glasses. (right axis) Average tensile stress experienced by Si atoms in the ion-exchanged glasses, using as-melted potassium silicate glasses as a reference. The dashed lines serve as guides for the eye. The gray area indicates the domain of maximum expansion due to ion exchange, as shown in Fig. 3.

Figure 6 shows the average increase of the CN of the replaced atoms upon ion exchange, normalized by the difference of CN between the as-melted NS and KS glasses. We observe that, for flexible glasses ( $n_c < 3$ ), the CN significantly increases upon exchange, eventually approaching the value observed in KS glasses. In contrast, the increase of CN saturates at around 80% for rigid glasses ( $n_c > 3$ ). This shows that flexible glasses feature an increased ability to locally reorganize their structure, which appears to be fairly proportional to the number of floppy modes per atom  $f = 3 - n_c$ . In turn, as  $f$  drops to zero, rigid glasses lose their ability to fully relax.

Finally, we investigate the appearance of internal eigenstress within the network upon ion exchange (mechanism 2). To this end, using the virial definition of stress [37], we compute in all glasses the stress tensor applied on each Si atom, which captures the stress within the silicate network. Note that, to account for the structural effect only, the kinetic contribution of the virial stress is removed by relaxing the configurations to zero temperature by energy minimization prior to the stress calculation. The trace of the stress tensor of each atom is then averaged to obtain the local pressure applied to Si atoms. We observe that although the pressure of the whole system is maintained at zero, some bonds are under tension while some others are under compression. Namely, in all glasses, Si atoms are systematically found to be under tension, whereas O atoms are under compression, that is, they mutually compensate each other. Figure 6 shows the difference between the average local pressure experienced by Si atoms in the IX and KS glasses. We observe that, for stressed-rigid glasses ( $n_c > 3.4$ ), Si–O bonds experience more tensile stress in the IX glasses than in KS, that is, the stuffing of larger K atoms imposes an internal tension inside the silicate backbone of the IX glass, while, in turn, the K atoms undergo a compressive stress. In contrast, no significant

stress develops upon ion exchange for flexible and isostatic glasses.

#### IV. DISCUSSION

Altogether, these results suggest the following atomic picture. (i) Because of their low-energy modes of deformation [38], flexible glasses ( $n_c < 3$ ) can adjust their structure and locally increase their packing fraction upon ion exchange, which limits any macroscopic expansion. (ii) In contrast, due to their high connectivity, stressed-rigid glasses ( $n_c > 3.4$ ) are mostly locked, which prevents their local structure from significantly changing upon ion exchange. As such, the silicate backbone of the glass cannot deform to accommodate the larger K atoms and thus becomes under tension, thereby putting K atoms under compression. Hence, ion exchange results in the formation of internal eigenstress [15] rather than macroscopic expansion. (iii) Eventually, isostatic glasses ( $3 < n_c < 3.4$ ) are both free of local floppy modes and internal stress. The percolation of rigidity through the system prevents significant local reorganizations to relax the strain imposed by the stuffed atoms. However, the absence of stress percolation through the system enables the network to globally expand to release the internal strain. As such, isostatic glasses feature the highest magnitude of swelling upon ion exchange, so that no network dilation anomaly is observed.

These results highlight the fact that isostatic networks feature an optimal ability for stress or displacive perturbations to propagate through the system, whereas such propagation is hindered by stress or internal modes of deformation. Besides ion exchange, this unique ability of isostatic networks is likely to impact the propagation of phonons through the network and its resistance to irradiation or external loads. This ability is also expected to enhance the propensity for collective motion of atoms and dynamical heterogeneities [39]. This behavior is also observed in isostatic stiff granular contact networks [40,41]. In such systems, the stretching of any bond (equivalent to the replacement of a small cation by a larger one herein) is noted to affect a large region of the system, which indicates that all bonds are critical. In contrast, the presence of mutually dependent constraints in the stressed-rigid regime results in fewer nodes of the network being displaced upon the perturbation of a constraint. A susceptibility (capturing the sensitivity of the network to such perturbations) is shown to diverge while approaching the isostatic threshold from the stressed domain [40,41]. Interestingly, the sodium silicate system considered herein also features a divergence of susceptibility (representing here the volume over which structural relaxation processes are correlated [39]) at the isostatic threshold, which suggests that this is a universal property of isostatic networks.

The fact that the flexible-to-rigid transition ( $n_c = 3$ ) occurs at a different threshold than the unstressed-to-stressed transition ( $n_c = 3.4$ ) suggests a strong analogy

between the pressure window identified herein and the composition-driven Boolchand intermediate phase [18], wherein glasses are expected to self-organize to become rigid while avoiding the appearance of internal stress [42]. These results are also in line with the space-filing tendency observed within the Boolchand intermediate phase [20], which here manifests itself by the inability of the glasses to locally densify upon stuffing.

From a practical viewpoint, these results suggest that tuning the atomic topology of glasses is a promising route to develop more damage-resistant glasses. In practice, ion exchange is the method of choice to strengthen silicate glasses. Thanks to ion-exchange treatments, stronger glasses have enabled various life-changing applications, including the development of touch-screen devices (e.g., using Corning® Gorilla® Glass [43–45]). However, the level of strengthening induced by ion exchange remains low as compared to its theoretical upper limit, which suggests that its potential is not fully explored. The development of even stronger glasses would be highly desirable, glass's brittleness is still a major bottleneck for further developments in short-haul high-capacity telecommunication, fiber-to-the-home technologies, flexible substrates and roll-to-roll processing of displays, solar modules, planar lighting devices, large-scale and high-altitude architectural glazing, etc. [46,47].

In practice, the level of stress induced by ion exchange remains limited by (i) the network dilation anomaly and (ii) the existence of stress relaxation after treatment. Here, our results suggest that the network dilation anomaly can virtually disappear in the case of isostatic atomic networks. Such an isostatic state can be achieved through the application of pressure during quenching [48,49] or, in a more conventional fashion, by tuning the composition of the glass [50,51]. Note that the application of pressure may, in turn, slow down the kinetics of ion exchange as a side effect [52]. In addition, recent results have also suggested that the stress relaxation of disordered molecular systems is also controlled by the topology of the atomic network [53]. Interestingly, isostatic systems are noted to exhibit a minimum in the propensity for relaxation. This has been attributed to the fact that (i) the presence of floppy modes in flexible systems facilitates relaxation (i.e., the kinetic resistance to relaxation is low), whereas (ii) the internal stress present in stress-rigid systems acts as local instabilities that stimulate relaxation (i.e., the thermodynamic driving force for relaxation is high). (iii) In turn, isostatic systems exhibit very limited relaxation due to the combined absence of floppy modes and internal stress. Altogether, these results suggest that optimizing the atomic rigidity of glasses and the balance between internal floppy modes and eigenstress is key to greatly enhancing the extent of strengthening induced by ion exchange.

## V. CONCLUSIONS

Based on molecular permanently densified dynamics simulations of sodium silicate glasses, we show that the

topology of the atomic network controls the extent of the dilation due to ion exchange. We show that, thanks to the absence of internal floppy modes of deformation and eigenstress, isostatic glasses do not exhibit any network dilation anomaly. Such behavior is found to occur within a range of pressure, wherein glasses are able to self-organize to remain rigid (i.e., low internal flexibility) while avoiding the appearance of mutually dependant constraints that would result in internal stress. In that sense, the pressure window identified herein appears to be analogous to a Boolchand intermediate phase.

## ACKNOWLEDGMENTS

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