Fracture Toughness Anomalies: Viewpoint of Topological Constraint Theory

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Abstract

The relationship between composition, structure, and resistance to fracture remains poorly understood. Here, based on molecular dynamics simulations, we report that
sodium silicate glasses (NS) and calcium–silicate–hydrates (CSH) feature an anomalous maximum in fracture toughness. In the framework of topological constraint theory, this anomaly is correlated to a flexible-to-rigid transition, driven by pressure or composition for NS and CSH, respectively. This topological transition, observed for an isostatic network, is also shown to correspond to a ductile-to-brittle transition. At this state, the network is rigid but free of eigen-stress and features stress relaxation through crack blunting, resulting in optimal resistance to fracture. Our topological approach could therefore enable the computational design of tough inorganic solids, which has long been a "holy grail" within the non-metallic materials chemistry community.

1 Introduction

Resistance to fracture, or fracture toughness, is of primary importance in materials science, with direct application to infrastructures and manufacturing. Indeed, tougher materials permit an increased resistance under extreme conditions, or the use of less materials while achieving comparable performances. To design tougher materials, one needs to understand the relationship between composition, structure, and toughness. This question has been identified as a "Grand Challenge" for non-metallic materials\cite{1,2} since these solids (ceramics, cements, glasses etc.) are generally not able to undergo much plastic deformations, which inhibits the local dissipation of high stresses that cause the material to fracture. Indeed, as opposed to elastic moduli and hardness which typically increase with connectivity and bond energy,\cite{3–5} toughness shows non-monotonic behaviors,\cite{3,6} which highlights the fact that fracture energy is not simply the energy required to break bonds and to create two new surfaces.\cite{6}

To this end, topological constraint, or rigidity theory\cite{7–10} appears to be an efficient tool. Indeed, inspired by Maxwell’s study on the stability of mechanical trusses,\cite{11} rigidity theory has been extensively used to understand the compositional dependence of the properties of network glasses. As such, an atomic network is classified as flexible, having internal degrees
of freedom that allow for local deformations,\textsuperscript{12} stressed–rigid, being locked by its high connectivity and featuring eigen-stress,\textsuperscript{13,14} or isostatic, the optimal intermediate state, rigid but free of eigen-stress. The isostatic state is achieved when the number of constraints per atom $n_c$, comprising radial bond-stretching (BS) and angular bond-bending (BB), equals three, the number of degrees of freedom per atom. Compositions offering an isostatic behavior have been found to exist inside a window,\textsuperscript{15} located between the flexible ($n_c < 3$) and the stressed–rigid ($n_c > 3$) domains, and show some anomalous properties such as space-filling tendency,\textsuperscript{16,17} weak aging phenomena,\textsuperscript{18} and anomalous dynamical and structural signatures.\textsuperscript{19–22} Rigidity theory has been shown to be a powerful tool for predicting the mechanical properties of glass\textsuperscript{4,5,23} and has been used to design the Corning\textsuperscript{®} Gorilla\textsuperscript{®} Glass 3,\textsuperscript{24–26} a scratch- and damage-resistant glass used on more than one billion smartphones and tablets screens.

Here, based on molecular dynamics (MD) simulations, we report anomalous fracture toughness behaviors in densified sodium silicate glasses (NS) and calcium–silicate–hydrates (CSH), two classes of materials which suffer from low fracture toughness. NS is a base material of various multi-components silicate glasses found in industry (e.g., window glasses) as well as in geoscience (e.g., magmas\textsuperscript{27}). On the other hand, CSH is the binding phase of concrete, a ubiquitous material in our built environment, and is responsible for its mechanical properties.\textsuperscript{28} Interestingly, in both cases, a maximal resistance to fracture is observed for isostatic networks.

\section{Computational details}

Investigating the topology and fracture resistance of solids through MD simulations requires realistic potentials. The potential used for the NS glasses has been extensively studied and has been shown to provide realistic results for structure, dynamics, and mechanics.\textsuperscript{27,29–32} The simulated $(\text{Na}_2\text{O})_{30}(\text{SiO}_2)_{70}$ glasses are made of 3000 atoms and are permanently densified
via quenchings at constant selected pressures. At ambient pressure, pure silica consists of a network of four-fold coordinated silicon tetrahedra interconnected by two-fold bridging oxygen atoms (BO). In NS, sodium atoms tend to depolymerize the network by breaking Si–BO–Si bonds, thereby creating non-bridging oxygen atoms (NBO). In contrast, the pressure experienced during the cooling tends to increase the coordination number of Si and O atoms, thus increasing the rigidity of the network. Prior to fracture simulations, the obtained NS glasses are relaxed to zero pressure, but they remain permanently densified, retaining highly coordinated network-former atoms, that is, five- and six-fold coordinated Si and three-fold "tricluster" O atoms. The details of the simulations of the NS glasses can be found in Ref.33

On the other hand, the CSH samples (CaO)$_x$(SiO$_2$)(H$_2$O)$_y$ are generated by introducing defects in an 11 Å tobermorite configuration, following a combinatorial procedure. 11 Å tobermorite consists of pseudo-octahedral calcium oxide sheets, which are surrounded on both sides by silicate tetrahedral chains, made of BO atoms and $Q^2$ silicon atoms. These negatively charged calcium–silicate sheets are separated from each other by an interlayer spacing, which contains water molecules and charge-balancing extra calcium cations. In the present models, starting from 11 Å tobermorite, the Ca/Si molar ratio is increased from 1.0 to 1.9 through randomly removing SiO$_2$ groups, to reach the range of compositions observed experimentally for CSH. The defects in the silicate chains provide possible sites for the adsorption of extra water molecules, which was performed through Grand Canonical Monte Carlo simulations. The computed amount of adsorbed water is in excellent agreement with experimental data, which reflects the relevance of the present approach in describing CSH. The ReaxFF potential, a reactive potential, was finally used to account for the reaction of the interlayer water with the defective calcium–silicate sheets, thereby creating hydroxyl groups. The details of the simulations of the CSH samples can be found in Ref.37
3 Results

3.1 Rigidity transition

![Graph showing rigidity transition](image)

Figure 1: (Color online) Number of constraints per atom in (a) NS and (b) CSH as a function of pressure and Ca/Si molar ratio, respectively. The gray area is an approximate boundary between the flexible and the stressed–rigid regimes ($n_c=3$).

The enumeration of the mechanical constraints experienced by the atoms inside a molecular network requires care. Although the counting is obvious in fully connected glasses with covalent bonds like Ge$_x$Se$_{1-x}$ (GS), in which $n_c = 5x + 2$, it is not as straightforward in more complex materials, as their coordination numbers are not necessarily known. Moreover, it has been shown that the constraints can be intact or broken depending on the temperature. To tackle this issue, we refined a method originally developed in Ref., and widely applied to chalcogenide and oxide glasses since then. The enumeration is based on the analysis of atomic trajectories obtained through molecular dynamics simulations, from which the numbers of BS and BB constraints are computed by computing the standard deviations $\sigma$ of the bond lengths and angular distributions, respectively. The basic idea is that intact constraints induce low $\sigma$, whereas broken ones result in large $\sigma$. The constraints enumeration method used in NS and CSH can be found in Refs. and, respectively, and clearly distinguishes intact from broken constraints. As shown in Fig. 1, both NS and CSH show a rigidity transition. Indeed, NS becomes stressed–rigid at high pressure, due to the increase
of the coordination number of Si and O atoms (see Fig. 1a). In the same fashion as GS, CSH shows a composition-driven rigidity transition, being flexible \( (n_c < 3) \) at high Ca/Si ratio, stressed-rigid \( (n_c > 3) \) at low Ca/Si ratio, and isostatic \( (n_c = 3) \) at \( \text{Ca/Si} \approx 1.5 \).

### 3.2 Anomalous fracture toughness

![Figure 2: (Color online) Tensile stress as a function of the tensile strain in (a) NS and (b) CSH for three systems: flexible, isostatic, and stressed–rigid. Snapshots of the molecular configurations at different strains are displayed.](image)

We now focus on the fracture behavior of NS and CSH in mode I, that is, under a tensile stress orthogonal to the plane in which the crack propagates. To this end, we have followed the method introduced by Brochard et al., which relies on the energetic approach of fracture mechanics. We first manually insert a sharp initial crack, expected to appear naturally, i.e., during cooling or handling for NS, or setting for CSH. After a relaxation to zero pressure, the system is elongated step-wise in the weakest direction \( z \) by small increments of the tensile strain \( \epsilon \). At each step, after an initial equilibration, the stress along the \( z \) axis \( \sigma_z \) is averaged. Once the system is broken, the stress goes back to zero, so that the fracture energy \( G_c \) can be estimated by integrating the stress over the strain. Alternatively to the energetic approach, the notion of fracture toughness \( K_{Ic} \) is usually used in engineering applications. This quantity was introduced by Irwin as the maximum stress intensity at the crack tip that a solid can undergo, and below which propagation cannot occur. The relationship between \( K_{Ic} \) and \( G_c \) is given by the Irwin formula. The details of the methodology as well
as the validation of the values of $G_c$ and $K_{Ic}$ computed for NS and CSH can be found in Refs.\textsuperscript{32} and,\textsuperscript{53} respectively.

Fig. 2 shows the obtained stress–strain curves, both for NS and CSH, in the case of three flexible, isostatic and stressed–rigid systems. At low strain, the mechanical response is linear elastic. The stress thus increases linearly with the strain, up to a maximum value, the slope being related to the Young’s modulus of the system. During this stage, the crack does not propagate and the external work provided to the system is stored in the form of mechanical elastic energy. At larger strain, the crack starts to propagate. As opposed to fully brittle materials like quartz,\textsuperscript{48} both systems show some nano-ductility,\textsuperscript{32} in the sense that the crack does not propagate instantly after a given critical strain. Thanks to its internal flexibility, the network rather deforms to prevent the fracture from occurring, as it can be observed in the snapshots inside Fig. 2.

![Figure 3: (Color online) Fracture toughness $K_{Ic}$ as a function of the number of constraints per atom $n_c$ for NS, CSH (computed), and GS (experiments\textsuperscript{6}). The gray area highlights an intermediate window where $K_{Ic}$ is maximal. The inset shows the Young’s modulus as a function of $n_c$ for NS, CSH (computed, compared with an experimental value at ambient pressure for NS, empty square\textsuperscript{54}), and GS (experimental\textsuperscript{6}).](image-url)

Based on an integration of the stress–strain curves shown in Fig. 2, Fig. 3 shows $K_{Ic}$
with respect to the number of constraints per atom $n_c$, for NS and CSH. Interestingly, for both of the systems, we observe a maximum of the resistance to fracture inside a window, approximately located between $n_c=3$ and 3.2, close to the isostatic threshold $n_c=3$. This behavior is similar to the trend observed experimentally in GS$^6$ (see Fig. 3), which suggests that a maximal fracture toughness might be a general feature of isostatic networks. Note that this maximum cannot be explained by an anomaly of the elastic modulus (see the inset of Fig. 3). Rather, as it can be seen on the stress–strain curves (see Fig. 2), this maximum arises from an increased ability to reach high strain before the crack propagation.

Due to its complex structure, CSH has been shown to feature polymorphism.$^{55}$ This manifests itself by some variability in the mechanical properties (elasticity and hardness$^{55}$) for a given composition and free energy, depending on the atomic structure. The existence of such a polymorphism for toughness was tested by simulating the fracture of three CSH samples with Ca/Si = 1.71 and competitive free energies. However, considering the extent of the error bars, no significant variation of fracture toughness was identified.

4 Discussion

4.1 Ductile-to-brittle transition

We now investigate the origin of the observed toughening by evaluating the different contributions to the fracture energy. $G_c$ is linked to the surface energy $\gamma_s$ by $G_c = 2\gamma_s + G_{\text{diss}}$, where $G_{\text{diss}}$ captures all forms of dissipated energy and would be equal to zero for a perfectly brittle material. Here, $\gamma_s$ was roughly estimated from MD simulation by cutting the system into two parts among the plane of the fracture, letting it relax, and computing the change of its potential energy (see more details in Ref.$^{53}$). Fig. 4 shows $G_c$, $2\gamma_s$, and $G_{\text{diss}}$ as a function of $n_c$, for NS and CSH.. First, we note that the fracture of NS at ambient pressure shows some ductility. This is in agreement with recent experiments$^{56,57}$ and simulations$^{58-60}$ suggesting that, although glasses are brittle at the macroscale, they show some ductility at the
Figure 4: (Color online) Fracture energy (in black), surface energy (doubled, in red), and dissipated energy (in blue) for (a) NS and (b) CSH as a function of the number of constraints per atom $n_c$.

Nanoscale. Second, we realize that, both for NS and CSH, $\gamma_s$ monotonically increases with $n_c$. This is not surprising as $\gamma_s$ is the energy needed to break the chemical bonds and should, thereby, increase with the number of constraints per unit of surface. Hence, the maximal toughness of isostatic systems arises from some kind of energy dissipation rather than from the surface energy. A brittleness index $B$ can be evaluated as $B = 2\gamma_s/G_c$, which would be equal to 1 for a perfectly brittle material. Interestingly, Fig. 5 shows that, both for NS and CSH, the flexible-to-rigid transition appears fairly well correlated to a ductile-to-brittle transition, the isostatic threshold showing a local minimum of brittleness. This feature is similar to what is observed experimentally in GS,\textsuperscript{3,6} which, again, suggests that it could be a generic signature of rigidity transitions. In other words, the brittle-to-ductile transition arises from the competition between cleavage (energy penalty from new exposed surface) and shear deformation (energy penalty from compression and extension of bonds). For $n_c > 3$, the networks are locked by their high number of constraints, inducing brittleness, whereas the flexible networks with $n_c < 3$ have better ability to deform, but shows a lower surface energy as fewer constraints need to break to create new surfaces. Isostatic configurations with $n_c = 3$ appear to exhibit the best compromise between the two energy penalties.
4.2 Stress relaxation by blunting

The dissipation of energy during fracture can take different forms, such as non-reversible plasticity, zig-zag crack paths, or crack blunting. In the latter case, due to some stress relaxation, the curvature of the crack tip decreases, which reduces the concentration of stress, thereby limiting the probability of crack propagation. Here, for the isostatic systems, we observe such a blunting mechanism, in which large deformations of the shape of the crack occur before any propagation (see the snapshots in Fig. 2). With this departure from the initial sharpness of the crack, the stress concentration at the crack tip decreases, i.e., higher tensile stress is required to propagate the crack. This results in a plateau in the stress–strain curves (see Fig. 2). To quantify the extent of the blunting, we fitted the crack surface, at different strains, with an elliptic cylinder and calculated its eccentricity (0 for a circle, 1 for a parabola, see the inset of Fig. 5). First, we note that, due to atomic relaxations, the crack initially blunts at \( \epsilon = 0 \), as an infinitely sharp crack is not stable at the atomic-scale. As \( \epsilon \) increases, the crack slightly blunts as the system elastically deforms. For flexible and stressed–rigid systems, the crack becomes sharper again as soon as it starts to propagate. On the contrary, for the isostatic system, the crack continues to blunt, up to \( \epsilon = 0.25 \).
This feature is expected to arise from an optimal stress relaxation in the network, which is supported by the fact that the isostatic NS systems show a minimum relaxation time.\textsuperscript{34} The collective shearing motion involved during the crack blunting requires both flexibility, to permit the deformation, and some rigidity, to enable a rearrangement over large scales. Hence, this mechanism is only possible for isostatic networks, which are rigid, but free of eigen-stress.

### 4.3 Link with stiffness and hardness

![Diagram showing indentation modulus-to-hardness ratio and fracture process zone (FPZ) with respect to the number of constraints per atom.](image)

Figure 6: (Color online) a) Indentation modulus-to-hardness ratio $M/H$ (left axis) and fracture process zone FPZ (right axis) of the CSH samples\textsuperscript{37} with respect to the number of constraints per atom $n_c$. b) Correlation between FPZ and $M/H$. The dashed line is a linear regression following $FPZ = a(M/H - b)$, where $a = 9.10$ Å and $b = 11.6$.

Finally, we investigate whether the anomalous maximum in toughness can be inferred from the stiffness and/or hardness of the material. For this, we rely on the simulated CSH samples, as their computed mechanical properties have been extensively validated through nano-indentation measurements.\textsuperscript{37} Nano-indentation tests offer access to (1) the indentation modulus, indicative of the stiffness of the material, given by\textsuperscript{37}:

$$M = 4G \frac{3K + G}{3K + 4G}$$

where $K$ and $G$ are the bulk and shear moduli, respectively, and (2) the indentation hardness...
which characterizes the resistance to plastic deformations.\textsuperscript{5}

First, it has been found that both $M$ and $H$ monotonically decrease with the Ca/Si molar ratio, that is, increase with $n_c$\textsuperscript{37} and, as such, do not appear to be correlated with the fracture toughness. On the other hand, the indentation modulus-to-hardness ratio $M/H$ has recently been suggested to constitute a metric scaling with the extent of ductility.\textsuperscript{61} As shown in Fig. 6a, $M/H$ indeed exhibits a maximum at $n_c = 3$, that is, for the isostatic composition, for which a minimum of brittleness is obtained (see Fig. 5). The extent of ductility during the fracture can be estimated from the fracture process zone (FPZ), which corresponds to the typical size of the region in front of the crack tip, in which plastic events\textsuperscript{59} occur. The FPZ can be evaluated by using the Dugdale–Barenblatt formula:\textsuperscript{62–64}

\begin{equation}
FPZ = \frac{\pi}{8} \left( \frac{K_{Ic}}{H} \right)^2
\end{equation}

Note that the pre-factor of the Dugdale–Barenblatt formula was derived for an infinite plate and, hence, is likely to differ in the case of the geometry of the present system. As such, we expect the absolute values of the computed FPZs to be qualitative at best.

Fig. 6b shows the computed FPZs with respect to $n_c$. The order of magnitude of the calculated values is in good agreement with that recently measured in glassy silica (16 Å),\textsuperscript{65} but appears over-estimated from a direct visualization of the displaced atoms during the fracture, which suggests that the pre-factor of the Dugdale–Barenblatt formula might not apply to the present geometry. Nevertheless, we expect the computed FPZs to accurately characterize the extent of ductility on a relative basis. As shown in Fig. 6a and b, the FPZ shows a strong positive correlation with $M/H$. Therefore, our results support the fact that $M/H$ can be viewed as an indicator of ductility. Note that such a correlation is non-intuitive, as the mechanism of the formation of cracks during fracture is \textit{a priori} different that of the formation of elastic and plastic deformations during indentation tests. Nevertheless, these results suggest that nano-indentation could be potentially used as a non-destructive test to assess the toughness of materials.
5 Conclusion

It is striking to see that, although belonging to different families of materials, NS, CSH, and GS show a similar relation between their atomic topology and resistance to fracture. Therefore, this result suggests that isostatic systems, characterized by rigid but stress-free networks, are likely to universally show optimal resistance to fracture. We also expect this anomalous toughness to be linked to the weak aging phenomena that isostatic systems are reported to undergo,\textsuperscript{66} which should both arise from optimal relaxation.

By capturing the important topology of materials, while filtering out less relevant details that ultimately do not affect macroscopic properties, topological constraint theory is a powerful predictive tool. Indeed, by tuning the topology of atomic networks, which can be controlled by the chemical composition or the thermodynamics conditions $(P, T)$, it becomes possible to tailor, among others, the mechanical properties of materials. As such, topological engineering of materials is proving to be a valuable approach to explore previously unstudied compositional and thermodynamical spaces.

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