Fracture Toughness Anomalies: Viewpoint of Topological Constraint Theory

Mathieu Bauchy^{a,*}, Bu Wang^a, Mengyi Wang^a, Yingtian Yu^a, Mohammad Javad Abdolhosseini Qomi^b, Morten M. Smedskjaer^c, Christophe Bichara^d, Franz-Josef Ulm^{e,f}, Roland Pellenq^{e,f,g}

^a*Physics of Amorphous and Inorganic Solids Laboratory (PARISlab), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095, United States*

^b*Department of Civil and Environmental Engineering, Henry Samueli School of Engineering, University of California, Irvine, CA 92697, United States*

^c*Department of Chemistry and Bioscience, Aalborg University, 9220 Aalborg, Denmark*

^d*Centre Interdisciplinaire des Nanosciences de Marseille, CNRS and Aix-Marseille University, Campus de Luminy, Marseille, 13288 Cedex 09, France*

^e*Concrete Sustainability Hub, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States*

^f*MIT-CNRS joint laboratory at Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States*

^g*Centre Interdisciplinaire des Nanosciences de Marseille, CNRS and Aix-Marseille University, Campus de Luminy, Marseille, 13288 Cedex 09, France*

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 and calcium–silicate–hydrates 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 sodium silicate and calcium–silicate–hydrates, 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,

*Corresponding author

Email address: bauchy@ucla.edu (Mathieu Bauchy)

which has long been a "holy grail" within the non-metallic materials chemistry community.

Keywords: fracture toughness, toughening, crack blunting, brittle-to-ductile transition

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 [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. However, the fracture mechanism of these materials is quite complex as, e.g., even archetypical brittle material like silicate glasses can exhibit some ductility at nanoscale [3, 4, 5, 6]. In addition, as opposed to elastic moduli and hardness, which typically increase with connectivity and bond energy [7, 8, 9], toughness shows non-monotonic behaviors [10, 7], which highlights the fact that fracture energy is not simply the energy required to break bonds and to create two new surfaces [10]. Tuning the fracture mechanism, e.g., through composition design, provides potential opportunities to improve the fracture resistance, but requires an unified model that can capture the mechanism transition between ductile and brittle behaviors and predict its compositional dependence for a broad range of materials.

To this end, topological constraint, or rigidity theory [11, 12, 13, 14] appears to be an efficient tool. The theory reduces the complex atomic structure of materials into a simple mechanical truss, in which the atoms are connected to each other through topological constraints, that is, the chemical interac-

tions that constrain the values of bond lengths and bond angles. Following this framework and inspired by Maxwell’s study on the stability of mechanical trusses [15], 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 [16], *stressed-rigid*, being locked by its high connectivity and featuring eigen-stress [17, 18], 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 [19], 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 [20, 21], weak aging phenomena [22], and anomalous dynamical and structural signatures [23, 24, 25, 26]. Rigidity theory has been shown to be a powerful tool for predicting the mechanical properties of glass [8, 27, 9] and has been used to design the Corning[®] Gorilla[®] Glass 3 [28, 29, 30], a scratch- and damage-resistant glass used on more than one billion smartphones and tablets screens.

Here, we investigate two families of materials that suffer from low fracture toughness, densified sodium silicate glasses (NS) and calcium-silicate-hydrates (CSH). 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 [31]). 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 [32]. Based on molecular dynamics (MD) simulations, we report anomalous fracture toughness behaviors for both materials. Interestingly, in both cases, a maximal resistance to fracture is observed for isostatic networks, analog to the reported data of germanium-selenium (GS) chalcogenide glass. We find that, although these materials substantially differentiate in the nature of their structure and chemistry, rigidity theory ubiquitously predicts the mechanistic transition in the

fracture behavior as a function of their atomic topology. We therefore expect it to provide a versatile tool for efficient composition design of tougher materials.

2. Methods

The topology and resistance to fracture of permanently densified NS glasses and CSH of different compositions are investigated through MD simulations. The atomic configurations of these systems are prepared and validated relying on the following procedure.

The permanently densified $(\text{Na}_2\text{O})_{30}(\text{SiO}_2)_{70}$ samples are constructed via quenching liquid melts consisting of 3000 atoms at constant selected pressures. The simulations use a classical potential set developed by Teter [33] that has been extensively studied and shown to provide realistic results for the structural, dynamical, and mechanical properties of NS glasses and supercooled liquids [33, 34, 31, 35, 36]. Following the procedure described in Ref. [37], the quenching procedure is performed by equilibrating the melts at 3000 K for 1 ns to lose the memory of the initial configurations, and linearly cooling the melts from 3000 to 300 K at a cooling rate of 1 K/ps and under constant pressure to form permanently densified glasses. When the glass is quenched under a series of pressure from 0 to 22 GPa, the rigidity of the structure increases as the densification induces an increase in the coordination number of the network-former atoms, that is, one observes the formation of five- and six-fold coordinated Si and three-fold "tricluster" O atoms [38]. Prior to fracture simulations, the obtained NS glasses are relaxed to zero pressure, but these highly coordinated species are retained and the glasses remain permanently densified.

On the other hand, the CSH samples $(\text{CaO})_x(\text{SiO}_2)(\text{H}_2\text{O})_y$ are generated by introducing defects in an 11 Å tobermorite [39] configuration, following a combinatorial procedure [40, 41]. 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 [42, 43]. 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 [44]. 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 SiO₂ groups, to reach the range of compositions observed experimentally for CSH [41]. The defects in the silicate chains provide possible sites for the adsorption of extra water molecules, which is 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 [41]. The ReaxFF potential [45], a reactive potential, is finally used to account for the reaction of the interlayer water with the defective calcium–silicate sheets, thereby creating hydroxyl groups [46]. The details of the simulations of the CSH samples, as well as their hardness computation, can be found in Supplementary Note 1 and 3 and Ref. [41].

After realistic atomistic samples are obtained, topological constraint analyses and simulations of fracture are performed, the details of which are reported in the results section.

3. Results

To investigate the atomic topology and resistance to fracture, we rely on realistic MD simulations of permanently densified NS glasses and CSH of different compositions (see the Methods section). These systems are interesting as, in addition to their industrial relevance, their atomic networks feature varying degree of connectivity with respect to the pressure during quenching and composition, respectively.

As discussed in the Introduction, the mechanical constraints experienced by the atoms inside a molecular network include radial BS and angular BB constraints. Counting the number of constraints has been well established in fully connected glasses featuring covalent bonds like Ge_xSe_{1-x} (GS). In such glasses, each atom experiences $r/2$ BS constraints (note that each BS constraint is shared by two atoms) and $2r - 3$ BB constraints, where r is the coordination number [14]. On average, the number of atomic constraints per atom is then given by $n_c = \langle r \rangle / 2 + (2\langle r \rangle - 3)$, where $\langle r \rangle$ is the average coordination number. In GS,

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 ($n_c=3$). [9]

Ge and Se atoms feature a coordination number of 4 and 2, respectively, so that the rigidity of the network (n_c) can be evaluated from the mere knowledge of the composition. However, in more complex materials, the enumeration of the constraints requires care, 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 [47, 48]. To tackle this issue, we refine a method originally developed in Ref. [49], and widely applied to chalcogenide and oxide glasses since then [26, 24, 23, 25]. 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 σ of the bond lengths and angular distributions, respectively. The basic idea is that intact constraints induce low σ , whereas broken ones result in large σ . The constraints enumeration method used in NS and CSH can be found in Refs. [37] and [50], 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 when densified by quenching the glass forming melt under high pressure, due to the permanent increase of the coordination number of Si and O atoms (see Fig. 1a) [37]. In the same fash-

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.

ion 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 Ca/Si ≈ 1.5 [9].

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.* [51], which relies on the energetic approach of fracture mechanics [52, 53, 54]. 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 (1%) of the tensile strain ϵ . During each step, the system is relaxed for 50 ps, followed by another 50 ps for statistical averaging of the properties. Note that we examined the effect of the strain rate and found that, provided it is sufficiently low ($< 0.5 \text{ ns}^{-1}$), no significant influence on the obtained stress-strain curves is observed. More details can be found in the Supplementary Fig. 2 and Supplementary Note 2. 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 is introduced by Irwin [55] 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 [55]. 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. [36] and [56], 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 [51], both systems show some nano-ductility [36], 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.

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 [10] (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 [58]. This manifests itself by some variability in the mechanical properties (elasticity and hardness [58]) for a given composition and free energy, depending on the atomic structure. The existence of such a polymorphism for toughness is tested by simulating the fracture of three CSH samples with $\text{Ca/Si} = 1.71$ and

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 [10]). 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 [57]), and GS (experimental [10]).

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 .

competitive free energies. However, considering the extent of the error bars, no significant variation of fracture toughness is identified.

4. Discussion

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 γ_s by $G_c = 2\gamma_s + G_{\text{diss}}$, where G_{diss} captures all forms of dissipated energy and would be equal to zero for a perfectly brittle material. Here, γ_s is 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. [56]). Fig. 4 shows G_c , $2\gamma_s$, and G_{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 [3, 4] and simulations [5, 6, 59] suggesting that, although glasses are brittle at the macroscale, they show some ductility at the nanoscale. Second, we realize that, both for NS and CSH, γ_s monotonically increases with n_c . This is not surprising as γ_s is the energy needed to break the chemical bonds and

Figure 5: (Color online) Brittleness index parameter as a function of n_c . The gray area highlights the intermediate window where the fracture toughness is maximal. The inset shows the eccentricity of the elliptic crack as a function of strain for three NS systems: flexible, isostatic, and stressed-rigid.

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 [10, 7], 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) [60]. 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.

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. Crack blunting as a toughening mechanism exists in many natural composite materials, such as wood and bone,[61] and bioinspired structural materials [62]. Here, for the isostatic glass structures, we also observe such a blunting mechanism at the atomic scale, 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 fit 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 ϵ 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 [37]. 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.

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 [41]. Nano-indentation tests offer access to (1) the indentation modulus, indicative of the

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 [41] 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 $a = 9.10 \text{ Å}$ and $b = 11.6$.

stiffness of the material, given by [41]:

$$M = 4G \frac{3K + G}{3K + 4G} \quad (1)$$

where K and G are the bulk and shear moduli, respectively, and (2) the indentation hardness H , which characterizes the resistance to plastic deformations [9].

First, it has been found that both M and H monotonically decrease with the Ca/Si molar ratio, that is, increase with n_c [41] and, as such, do not appear to be correlated with the fracture toughness. This is expected, as, since each topological constraint can be seen as a spring acting between the atoms in the network, an increase of the number of such springs should indeed result in the increase of the macroscopic stiffness of the material. 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 [63]. 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 [6] occur. The FPZ can be evaluated by using

the Dugdale–Barenblatt formula [64, 65, 66]:

$$\text{FPZ} = \frac{\pi}{8} \left(\frac{K_{Ic}}{H} \right)^2 \quad (2)$$

Note that the pre-factor of the Dugdale–Barenblatt formula is 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) [67], 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 *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. Conclusions

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 [68], 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.

Acknowledgement

MB acknowledges partial financial support for this research provisioned by the University of California, Los Angeles (UCLA). This work has initially been carried out within the framework of the ICoME2 Labex (ANR-11-LABX-0053) and the A*MIDEX projects (ANR-11-IDEX-0001-02) cofunded by the French program "Investissements d'Avenir" which is managed by the ANR, the French National Research Agency. It was also supported by Schlumberger under the MIT-Schlumberger X-Cem research collaboration and by the CSHub@MIT.

References

- [1] J. C. Mauro, C. S. Philip, D. J. Vaughn, M. S. Pambianchi, Glass Science in the United States: Current Status and Future Directions, *International Journal of Applied Glass Science* 5 (2014) 2–15.
- [2] J. C. Mauro, Grand challenges in glass science, *Fontiers in Materials* 1 (2014) 20.
- [3] F. Celarie, S. Prades, D. Bonamy, L. Ferrero, E. Bouchaud, C. Guillot, C. Marlière, Glass Breaks like Metal, but at the Nanometer Scale, *Physical Review Letters* 90 (2003) 075504.
- [4] A. Livne, E. Bouchbinder, J. Fineberg, Breakdown of Linear Elastic Fracture Mechanics near the Tip of a Rapid Crack, *Physical Review Letters* 101 (2008) 264301.

- [5] Y.-C. Chen, Z. Lu, K.-i. Nomura, W. Wang, R. K. Kalia, A. Nakano, P. Vashishta, Interaction of Voids and Nanoductility in Silica Glass, *Physical Review Letters* 99 (2007) 155506.
- [6] B. Wang, Y. Yu, M. Wang, J. C. Mauro, M. Bauchy, Nanoductility in silicate glasses is driven by topological heterogeneity, *Phys. Rev. B* 93 (2016) 064202.
- [7] A. K. Varshneya, D. J. Mauro, Microhardness, indentation toughness, elasticity, plasticity, and brittleness of Ge–Sb–Se chalcogenide glasses, *Journal of Non-Crystalline Solids* 353 (2007) 1291–1297.
- [8] M. M. Smedskjaer, J. C. Mauro, Y. Yue, Prediction of Glass Hardness Using Temperature-Dependent Constraint Theory, *Physical Review Letters* 105 (2010) 115503.
- [9] M. Bauchy, M. J. A. Qomi, C. Bichara, F.-J. Ulm, R. J.-M. Pellenq, Rigidity Transition in Materials: Hardness is Driven by Weak Atomic Constraints, *Physical Review Letters* 114 (2015) 125502.
- [10] J.-P. Guin, T. Rouxel, J.-C. Sangleboeuf, I. Melscoët, J. Lucas, Hardness, Toughness, and Scratchability of Germanium–Selenium Chalcogenide Glasses, *Journal of the American Ceramic Society* 85 (2002) 1545–1552.
- [11] J. C. Phillips, Topology of covalent non-crystalline solids .1. Short-range order in chalcogenide alloys, *Journal of Non-Crystalline Solids* 34 (1979) 153–181.
- [12] J. C. Phillips, Topology of covalent non-crystalline solids II: Medium-range order in chalcogenide alloys and As-Si-Ge, *Journal of Non-Crystalline Solids* 43 (1981) 37–77.
- [13] M. F. Thorpe, Continuous deformations in random networks, *Journal of Non-Crystalline Solids* 57 (1983) 355–370.

- [14] J. C. Mauro, Topological constraint theory of glass, American Ceramic Society Bulletin 90 (2011) 31–37.
- [15] J. C. Maxwell, L. On the calculation of the equilibrium and stiffness of frames, Philosophical Magazine Series 4 27 (1864) 294–299.
- [16] G. G. Naumis, Energy landscape and rigidity, Physical Review E 71 (2005) 026114.
- [17] F. Wang, S. Mamedov, P. Boolchand, B. Goodman, M. Chandrasekhar, Pressure Raman effects and internal stress in network glasses, Physical Review B 71 (2005).
- [18] M. V. Chubynsky, M.-A. Brière, N. Mousseau, Self-organization with equilibration: A model for the intermediate phase in rigidity percolation, Physical Review E 74 (2006) 016116.
- [19] X. Feng, W. J. Bresser, P. Boolchand, Direct Evidence for Stiffness Threshold in Chalcogenide Glasses, Physical Review Letters 78 (1997) 4422–4425.
- [20] K. Rompicharla, D. I. Novita, P. Chen, P. Boolchand, M. Micoulaut, W. Huff, Abrupt boundaries of intermediate phases and space filling in oxide glasses., Journal of physics. Condensed matter : an Institute of Physics journal 20 (2008).
- [21] M. Micoulaut, M. Bauchy, Anomalies of the first sharp diffraction peak in network glasses: Evidence for correlations with dynamic and rigidity properties, physica status solidi (b) 250 (2013) 976–982.
- [22] S. Chakravarty, D. G. Georgiev, P. Boolchand, M. Micoulaut, Ageing, fragility and the reversibility window in bulk alloy glasses, Journal of Physics: Condensed Matter 17 (2005) L1.
- [23] M. Bauchy, M. Micoulaut, Transport Anomalies and Adaptive Pressure-Dependent Topological Constraints in Tetrahedral Liquids: Evidence for

- a Reversibility Window Analogue, *Physical Review Letters* 110 (2013) 095501.
- [24] M. Bauchy, M. Micoulaut, M. Boero, C. Massobrio, Compositional Thresholds and Anomalies in Connection with Stiffness Transitions in Network Glasses, *Physical Review Letters* 110 (2013) 165501.
 - [25] M. Bauchy, M. Micoulaut, Percolative heterogeneous topological constraints and fragility in glass-forming liquids, *EPL (Europhysics Letters)* 104 (2013) 56002.
 - [26] M. Bauchy, Topological constraints and rigidity of network glasses from molecular dynamics simulations, *American Ceramic Society Bulletin* 91 (2012) 34–38A.
 - [27] M. M. Smedskjaer, Topological model for boroaluminosilicate glass hardness, *Frontiers in Materials* 1 (2014) 23.
 - [28] P. Ball, Material witness: Concrete mixing for gorillas, *Nature Materials* 14 (2015) 472–472.
 - [29] J. C. Mauro, A. J. Ellison, L. D. Pye, Glass: The Nanotechnology Connection, *International Journal of Applied Glass Science* 4 (2013) 64–75.
 - [30] J. C. Mauro, M. M. Smedskjaer, Unified physics of stretched exponential relaxation and Weibull fracture statistics, *Physica A: Statistical Mechanics and its Applications* 391 (2012) 6121–6127.
 - [31] M. Bauchy, B. Guillot, M. Micoulaut, N. Sator, Viscosity and viscosity anomalies of model silicates and magmas: A numerical investigation, *Chemical Geology* 346 (2013) 47–56.
 - [32] A. J. Allen, J. J. Thomas, H. M. Jennings, Composition and density of nanoscale calcium–silicate–hydrate in cement, *Nature Materials* 6 (2007) 311–316.

- [33] J. Du, A. Cormack, The medium range structure of sodium silicate glasses: a molecular dynamics simulation, *Journal of Non-Crystalline Solids* 349 (2004) 66–79.
- [34] M. Bauchy, M. Micoulaut, From pockets to channels: Density-controlled diffusion in sodium silicates, *Physical Review B* 83 (2011) 184118.
- [35] A. Pedone, G. Malavasi, A. N. Cormack, U. Segre, M. C. Menziani, Insight into elastic properties of binary alkali silicate glasses; prediction and interpretation through atomistic simulation techniques, *Chemistry of Materials* 19 (2007) 3144–3154.
- [36] B. Wang, Y. Yu, Y. J. Lee, M. Bauchy, Intrinsic Nano-Ductility of Glasses: The Critical Role of Composition, *Frontiers in Materials* 2 (2015) 11.
- [37] M. Bauchy, M. Micoulaut, Densified network glasses and liquids with thermodynamically reversible and structurally adaptive behaviour, *Nature Communications* 6 (2015).
- [38] M. Bauchy, Structural, vibrational, and thermal properties of densified silicates: Insights from molecular dynamics, *The Journal of Chemical Physics* 137 (2012) 044510.
- [39] S. Hamid, The Crystal-Structure of the 11-A Natural Tobermorite, *Zeitschrift Fur Kristallographie* 154 (1981) 189–198.
- [40] R. J.-M. Pellenq, A. Kushima, R. Shahsavari, K. J. V. Vliet, M. J. Buehler, S. Yip, F.-J. Ulm, A realistic molecular model of cement hydrates, *Proceedings of the National Academy of Sciences* 106 (2009) 16102–16107.
- [41] M. J. Abdolhosseini Qomi, K. J. Krakowiak, M. Bauchy, K. L. Stewart, R. Shahsavari, D. Jagannathan, D. B. Brommer, A. Baronnet, M. J. Buehler, S. Yip, F.-J. Ulm, K. J. Van Vliet, R. J.-M. Pellenq, Combinatorial molecular optimization of cement hydrates, *Nature Communications* 5 (2014).

- [42] M. J. Abdolhosseini Qomi, M. Bauchy, R. J.-M. Pellenq, F.-J. Ulm, Applying Tools from Glass Science to Study Calcium-Silicate-Hydrates, in: Mechanics and Physics of Creep, Shrinkage, and Durability of Concrete: A Tribute to Zdenek P. Bazant: Proceedings of the Ninth International Conference on Creep, Shrinkage, and Durability Mechanics (CONCREEP-9), September 22-25, 2013 Cambridge, Massachusetts, ASCE Publications, 2013, pp. 78–85. doi:10.1061/9780784413111.008.
- [43] M. Bauchy, M. J. Abdolhosseini Qomi, F.-J. Ulm, R. J.-M. Pellenq, Order and disorder in calcium–silicate–hydrate, The Journal of Chemical Physics 140 (2014) 214503.
- [44] M. J. Abdolhosseini Qomi, M. Bauchy, F.-J. Ulm, R. J.-M. Pellenq, Anomalous composition-dependent dynamics of nanoconfined water in the inter-layer of disordered calcium-silicates, The Journal of Chemical Physics 140 (2014) 054515.
- [45] H. Manzano, S. Moeini, F. Marinelli, A. C. T. van Duin, F.-J. Ulm, R. J.-M. Pellenq, Confined Water Dissociation in Microporous Defective Silicates: Mechanism, Dipole Distribution, and Impact on Substrate Properties, Journal of the American Chemical Society 134 (2012) 2208–2215.
- [46] M. Bauchy, M. J. Abdolhosseini Qomi, R. J. M. Pellenq, F. J. Ulm, Is cement a glassy material?, Computational Modelling of Concrete Structures (2014) 169.
- [47] M. M. Smedskjaer, J. C. Mauro, S. Sen, Y. Yue, Quantitative Design of Glassy Materials Using Temperature-Dependent Constraint Theory, Chemistry of Materials 22 (2010) 5358–5365.
- [48] M. Bauchy, M. Micoulaut, Atomic scale foundation of temperature-dependent bonding constraints in network glasses and liquids, Journal of Non-Crystalline Solids 357 (2011) 2530–2537.

- [49] M. Micoulaut, J.-Y. Raty, C. Otjacques, C. Bichara, Understanding amorphous phase-change materials from the viewpoint of Maxwell rigidity, *Physical Review B* 81 (2010) 174206.
- [50] M. Bauchy, M. J. Abdolhosseini Qomi, C. Bichara, F.-J. Ulm, R. J.-M. Pellenq, Nanoscale Structure of Cement: Viewpoint of Rigidity Theory, *The Journal of Physical Chemistry C* 118 (2014) 12485–12493.
- [51] L. Brochard, G. Hantal, H. Laubie, F. Ulm, R. Pellenq, Fracture Mechanisms in Organic-Rich Shales: Role of Kerogen, in: *Poromechanics V*, volume 5, American Society of Civil Engineers, Vienna, Austria, 2013, pp. 2471–2480. doi:10.1061/9780784412992.288.
- [52] A. A. Griffith, The phenomena of rupture and flow in solids, *Philosophical transactions of the royal society of london. Series A, containing papers of a mathematical or physical character* 221 (1921) 163–198.
- [53] J.-B. Leblond, *Mecanique de la rupture fragile et ductile*, lavoisier ed., Lavoisier, Paris, 2003.
- [54] T. L. Anderson, *Fracture mechanics: fundamentals and applications*, CRC PressI Llc, 2005.
- [55] G. R. Irwin, *Fracture in “Handbuch der Physik,”* vol. V, New York, NY: Springer, 1958.
- [56] M. Bauchy, H. Laubie, M. J. Abdolhosseini Qomi, C. G. Hoover, F. J. Ulm, R. J. M. Pellenq, Fracture toughness of calcium–silicate–hydrate from molecular dynamics simulations, *Journal of Non-Crystalline Solids* 419 (2015) 58–64.
- [57] N. P. Bansal, R. H. Doremus, *Handbook of Glass Properties*, Elsevier, 2013.
- [58] M. J. A. Qomi, M. Bauchy, F.-J. Ulm, R. Pellenq, Polymorphism and Its Implications on Structure-Property Correlation in Calcium-Silicate-Hydrates, in: K. Sobolev, S. P. Shah (Eds.), *Nanotechnology in Con-*

- p>struction, Springer International Publishing, 2015, pp. 99–108. URL:
- http://link.springer.com/chapter/10.1007/978-3-319-17088-6_12
- .
- [59] Y. Yu, B. Wang, Y. J. Lee, M. Bauchy, Fracture Toughness of Silicate Glasses: Insights from Molecular Dynamics Simulations, in: Symposium UU – Structure-Property Relations in Amorphous Solids, volume 1757 of *MRS Online Proceedings Library*, 2015. URL: http://journals.cambridge.org/article_S1946427415000500. doi:10.1557/opl.2015.50.
 - [60] Y. Shi, J. Luo, F. Yuan, L. Huang, Intrinsic ductility of glassy solids, *Journal of Applied Physics* 115 (2014) 043528.
 - [61] P. Fratzl, R. Weinkamer, Nature’s hierarchical materials, *Progress in Materials Science* 52 (2007) 1263 – 1334.
 - [62] U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, Bioinspired structural materials, *Nature Materials* 14 (2015) 23–36.
 - [63] C. G. Hoover, F.-J. Ulm, Experimental chemo-mechanics of early-age fracture properties of cement paste, *Cement and Concrete Research* 75 (2015) 42–52.
 - [64] D. Dugdale, Yielding of steel sheets containing slits, *Journal of the Mechanics and Physics of Solids* 8 (1960) 100–104.
 - [65] G. Barenblatt, The mathematical theory of equilibrium cracks in brittle fracture, *Advances in applied mechanics* 7 (1962) 104.
 - [66] J. M. Lemm, *Advances in applied mechanics*, Academic Press, 1962.
 - [67] S. M. Wiederhorn, T. Fett, J.-P. Guin, M. Ciccotti, Griffith Cracks at the Nanoscale, *International Journal of Applied Glass Science* 4 (2013) 76–86.
 - [68] P. Chen, P. Boolchand, D. G. Georgiev, Long term aging of selenide glasses: evidence of sub-Tg endotherms and pre-Tg exotherms, *Journal of Physics-Condensed Matter* 22 (2010).

Figure1

Figure 2

Figure3

Figure4

Figure5

Figure6

***Graphical Abstract**