Topology and Rigidity of Silicate Melts and Glasses

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INTRODUCTION

From a fundamental viewpoint, glasses are out of equilibrium systems, so that concepts and techniques from statistical mechanics cannot be applied in a straightforward fashion given the presence of broken ergodicity, which results from an incomplete sampling of the phase space on reasonable time scales. The breakdown of the relationship between spontaneous fluctuations and dissipation leads to time dependent thermodynamic quantities that induce ageing phenomena typical of glasses, i.e., their properties can vary quite substantially with the thermal history of the melt and the waiting time before the experiment/measurement is performed. Given these intrinsic features of the glassy state, atomistic simulations have proven to be extremely useful for the understanding of structure and dynamics or relaxation (Kob and Binder 2005). However, while the available computing power has increased exponentially over the past decades, large enough computing power for direct molecular dynamics (MD) simulations of glass with large system sizes and realistic laboratory time scales is still out of reach. The method appears not necessarily helpful in the context of property optimization or new functionalities ruled by changes in composition, which would require a huge amount of time spent in exploring the compositional phase diagram.

Among promising alternatives, albeit carrying its own limitations, approaches using topology and rigidity focus on the key microscopic physics governing the thermal, mechanical and rheological properties of glass and amorphous materials, while filtering out unnecessary numerical details which ultimately do not affect the overall results. The concept of rigidity in disordered solids such as glasses, amorphous networks or sphere packing actually traces back to the early work of Maxwell (1864) on the stability of trusses and macroscopic structures such as bridges, and to the introduction of mechanical constraints by Lagrange (1788). Inspired by this pioneering work Phillips (1979) proposed at the beginning of the 80's to apply the analysis of trusses to disordered molecular networks such as glasses or amorphous solids which exhibit a lack of periodicity at long range but have some structural order at short range.

Corresponding materials were then viewed in terms of their topological and rigidity properties, involving in most cases the way atoms connect together, and, more importantly, the way they interact together. The transposition appears to be somewhat obvious: nodes are being replaced by atoms and the bar tensions are replaced by the most relevant interactions at the molecular level which are 2-body radial and 3-body angular interactions resulting in stretching and bending motions. Using the tools provided by structural rigidity which predicts the flexibility of ensembles formed by rigid bodies connected by flexible linkages or hinges, mechanical properties of glassy networks were calculated from the enumeration of constraints at zero temperature. It was, furthermore, highlighted that the notion of mechanical isostaticity (i.e., optimally constrained) is crucial for the promotion of glass-forming tendency in covalent systems. While the approach has been limited to chalcogenide glasses, recent applications of this approach have enabled the prediction of mechanical and thermal properties from a combination of topological methods using empirical models and molecular simulations.

In the present chapter, we review these recent contributions. We first introduce the basic notions of rigidity theory, that is, how an atomic network constrained by interactions can be treated from a mechanical viewpoint as a collection of bars and nodes on which an appropriate constraint enumeration allows identification of a stability point, known as the isostatic condition. Then, we review the application of such ideas to silicate glasses, prior to an extension of the models incorporating a temperature dependence. By combining molecular dynamics simulations and rigidity, one is also able to investigate multicomponent systems under various excitations (temperature, pressure, deformation,...) and this allows one to reduce the complexity of the involved phenomena to a picture that reveals the crucial role played by network topology while also providing clues for property optimization ruled by changes in composition.

ROLE OF NETWORK RIGIDITY

There is an attractive way to analyze and predict various properties in the liquid state (viscosity, diffusivity,...), glass transition-related properties (relaxation, fragility,...) as well as typical glass e.g., mechanical properties using rigidity theory. Using the underlying network structure, this framework provides, indeed, an atomic scale approach to understanding the physico-chemical behavior of network glasses.

Rigidity theory of network glasses

Basic concepts and ideas of mechanical constraints have been introduced in the pioneering contributions of Lagrange and Maxwell (Lagrange 1788; Maxwell 1864). The approach has been extended to disordered atomic networks (Phillips 1979, 1981) and it was recognized that the glass-forming tendency of covalent alloys is optimized for particular compositions in chalcogenide network glasses. Specifically, glasses with some optimal connectivity or mean coordination number \bar{r} satisfying exactly the Maxwell stability criterion of mechanically isostatic structures could be formed with a minimal cooling rate (Azoulay et al. 1975). In the Maxwell approach, this condition obtains when $n_c = n_d$, where n_c is the count of atomic constraint density arising from interactions and n_d the network dimensionality (usually 3).

In glasses and liquids, the dominant interactions are usually near-neighbor bond-stretching (BS) and next-near-neighbor bond-bending (BB) forces and the number of constraints n_c per atom can be exactly computed using a mean-field approach. One obtains:

$$n_{\rm c} = \frac{\sum_{r \ge 2} n_r \left(\frac{r}{2} + 2r - 3\right)}{\sum_{r \ge 2} n_r} \tag{1}$$

where n_r is the concentration of species being *r*-fold coordinated. The contribution of the two terms in the numerator arises from BS and BB contributions. Each bond being shared by two neighbors, the density is r/2 for bond-stretching (BS) constraints for an *r*-fold atom. For BB constraints, it has to be remarked that a two-fold (e.g., oxygen) atom involves only one angle, and each additional bond needs the definition of two more angles, leading to the estimate of (2r - 3).

By defining the network mean coordination number \overline{r} of the network $\overline{r} = \sum_{r \ge 2} rn_r$ (Eqn. 1) reduce to:

$$n_{\rm c} = \frac{\overline{r}}{2} + \left(2\overline{r} - 3\right) \tag{2}$$

The application of the Maxwell stability criterion now indicates (i.e., solving Eqn. 2) that isostatic glasses and liquids ($n_c=3$) are expected to be found at the mean coordination number of $\overline{r}=2.40$ in 3D (Phillips 1979), corresponding usually to a nonstoichiometric composition where the glass-forming tendency has been found to be optimized experimentally (Bresser et al. 1986).

The physical content and more rigorous picture of this "*heuristic*" stability criterion has been established from a vibrational analysis of bond-depleted random networks (Thorpe 1983) constrained by harmonic BS and BB interactions. By performing an eigenmode analysis of the dynamical matrix, it has been demonstrated that the number f of eigenmodes having a zero frequency vanishes when rigidity percolates in the network which is achieved for $\bar{r}=2.38$. It has, thus been acknowledged that the Maxwell isostatic condition $n_c = n_d$ defines a mechanical stiffness transition that is driven by the network connectivity \overline{r} , which acts as an external parameter like the temperature in a ferromagnetic transition, the order parameter being the density of floppy modes (similar to magnetization in the same analogue of the ferromagnetic transition). For $\overline{r} > \overline{r_c}$, redundant constraints produce internally stressed networks and correspond to a stressed-rigid phase (He and Thorpe 1985; Thorpe 1985). For $n_c < n_d$ however, floppy modes can proliferate, and these lead to a flexible phase where local deformations with a low cost in energy are possible (Kamitakahara et al. 1991), the density being given by: $f = 3 - n_c$ (Thorpe 1983). Different experimental probes of this peculiar transition have been reported in chalcogenides from Raman scattering (Boolchand et al. 1995), stress relaxation (Böhmer and Angell 1992), viscosity measurements (Tatsumisago et al. 1990), vibrational density of states (Kamitakahara et al. 1991), Brillouin scattering (Duquesne and Bellassa 1985), resistivity (Asokan et al. 1989). For a full account of early experimental probes and verification of rigidity percolation as well as the mathematical description using graph theory, one should refer to books devoted to the subject (Thorpe and Duxbury 1999; Phillips and Thorpe 2001; Micoulaut and Popescu 2009).

The situation in silicate glasses

While the application of constraint enumeration has been first performed on chalcogenide glasses, the question of its applicability to silicate glasses has emerged and discussed in the 1990's. It has been realized that for one-fold terminal atoms (as e.g., expected for alkali ions in the neighbourhood of a NBO), a special count has to be achieved as no BB constraints are involved (Boolchand and Thorpe 1994; Zhang and Boolchand 1994). This count leads, indeed, to the correct prediction of the threshold composition in sodium silicates, albeit counter-intuitive given the expected larger coordination number (five) of sodium that might induce some additional stiffening (Zwanziger et al. 1995). However, it has become obvious that for non-directional bondings as those expected for Na–O ionic interactions, some constraints might be ineffective (see below; Micoulaut 2008). This is also revealed by the analysis from molecular dynamics simulations which suggest that alkali–oxygen distances are not all equivalent, the Na–NBO distances being slightly shorter than the Na–BO distances (Cormier et al. 2003). Experimentally, Debye–Waller factors measured in X-ray absorption studies on Ba or Ca binary silicates are also slightly different, suggesting that the O neighbors of Ca are, again, not all equivalent (Taniguchi et al. 1997).

In the initial and mean-field approach, the coordination numbers r of Si, O, and the alkali cation are respectively set to four, two, and one, and depending on the size of the cation a certain number of BB (angular) constraints can be broken, i.e. their angular excursion (as determined from bond angle distributions) can be modified and eventually increased because of size mismatch.

The simplest case is the lithium silicate system $(1-x)SiO_2-xLi_2O$ for which all constraints are considered intact due to the small size of the Li cation (Fig. 1), the ionic radius of Li being of the same order as the one of oxygen so that there is no size mismatch.



Figure 1. The elemental building blocks of silicate networks: (a) $SiO_{4/2}$ tetrahedron (Q⁴ species) connected to the rest of the network by four BOs, and (b) an $NaSiO_{5/2}$ tetrahedron (Q³ species) having a sodium atom in the vicinity of an oxygen that is a so-called NBO. The angular excursion around the NBO can be small (in Li silicates) or large (in Na silicates), the latter situation leading to a broken bond-bending constraint for the NBO (see Table 1).

Table 1 provides a survey of the enumeration of constraints of the various alkali and alkaline-earth silicate systems (Micoulaut 2008). Using Table 1 and Equation (1), it is easy to check that for the Li case, the number of floppy modes $f = 3 - n_c$ is equal to:

$$f_{\rm Li} = 3 - \frac{1}{3} [11 - 8x] \tag{3}$$

which vanishes at the the composition $x = x_c = 0.250$. In a mean-field picture of rigidity, Li silicate glasses in the silica rich domain can therefore be considered as stressed rigid ($n_c > 3$), whereas the increased depolymerization leads to a flexible phase ($n_c < 3$) at higher concentrations.

With increasing metal–O bond distance (from 1.97 Å for Li to 2.36 Å for Na), the cation field strength should be weaker (Mysen and Richet 2019). According to Pauling, the bond strength (i.e., the mechanical constraint) is a systematic function of the bond distance so that an increase of the metal–oxygen bond would induce a reduction of the constraint. This suggests thatan increase in cation size will induce additional local degrees of freedom or broken constraints arising from weaker interactions, necessarily a NBO bond-bending, given the reduced BB energy (Kamitakahara et al. 1991). For the Na case, a broken NBO BB constraint shifts the rigidity transition to $x=x_c=0.20$, the global tendency being that flexibility onsets at lower compositions as an increased number of constraints becomes ineffective. In magnesium and calcium silicates, with the alkaline earth cation having r=2, the stability criterion is found for $x_c=0.50$ which corresponds to the Wollastonite or Enstatite composition around which stable glasses can be formed (Micoulaut et al. 2005; Bourgel et al. 2009).

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	Si		BO		NBO		М		n _c	x _c	
	Si ^{BS}	Si ^{BB}	BOBS	BO ^{BB}	NBO ^{BS}	NBO ^{BB}	\mathbf{M}^{BS}	$\mathbf{M}^{\mathbf{B}\mathbf{B}}$			
Li	2(1-x)	5(1-x)	2 - 3x	2 - 3x	2x	2x	x	-	11 - 8x	0.250	
Na	2(1-x)	5(1-x)	2-3x	2 - 3x	2x	_	x	-	11 - 10x	0.200	
Κ	2(1-x)	5(1-x)	2 - 3x	2-5x	2x	_	x	-	11 - 12x	0.167	
Rb	2(1-x)	5(1-x)	2 - 3x	2 - 7x	2x	_	x	-	11 - 14x	0.143	
Cs	2(1-x)	5(1-x)	2 - 3x	2 - 9x	2x	_	x	-	11 - 16x	0.125	
Mg, Ca	2(1-x)	5(1-x)	2 - 3x	2 - 3x	2x	2x	x	x	11 - 7x	0.500	
Sr	2(1-x)	5(1-x)	2 - 3x	2 - 3x	2x	2x	x	-	11 - 8x	0.400	
Ba	2(1-x)	5(1-x)	2 - 3x	2 - 3x	2x	_	x	_	11 - 10x	0.285	

Table 1. BS and BB constraint counting in alkali silicate $(1-x)SiO_2-xM_2O$, and alkaline earth silicate glasses $(1-x)SiO_2-xMO$, total number of constraints *n*, and the location of the isostatic composition *x*.

Experimental verification. Compositional trends can be quite useful in detecting the signature of rigidity percolation while providing also a simple picture for the understanding of threshold behaviors in physical and chemical properties of silicates. It has been suggested that materials which are optimally constrained (i.e., $n_c = 3$) should form glasses more easily (Phillips 1979) as observed experimentally for the Ge–Se system (Azoulay et al. 1975) or, more recently from the difference temperature $\Delta T = T_x - T_g$ between the glass (T_g) and the crystallization (T_x) (Piarristeguy et al. 2015). The critical cooling rate to avoid crystallization or the vitrification enthalpy as a function of composition appears to be a reasonable indicator for optimal glass formation. Such a critical cooling rate has been measured as a function of composition for Na and K silicates (Fang et al. 1983), and a minimum is obtained at a composition that is located in the interval where optimal glass formation is expected from Maxwell counting (respectively x = 20 and 16.7%). It parallels recent findings on the NS4 glass (x=20%) which has been found to display minimal ageing phenomena (Ruta et al. 2014), in agreement with the fact that enthalpic relaxation has been optimized in the absence of stress. In this respect, the enthalpy of vitrification measured from calorimetry (Tatsumisago et al. 1990) should also display characteristic changes when the system changes from a flexible to a stressed rigid phase. A study of vitrification in MgO–SiO₂ melts between the enstatite (50%) and forsterite (66% MgO) compositions has shown that the heat of vitrification increases (Tangeman et al. 2001), an increase that is accompanied by a large change in connectivity (Wilding et al. 2004), the optimal glass composition in Mg silicates being estimated to be at $x = x_c = 50\%$ (Table 1). This composition can be produced by conventional methods, whereas extensions of the glass-forming region toward glasses with high melting temperatures (e.g., forsterite) needs high-temperature containerless synthesis (Kohara et al. 2004).

An indirect indication of glass-forming tendency is also found from the inspection of viscosity with composition at a fixed temperature, as the glass-forming tendency is known to improve for systems that are able to increase their melt viscosity down to lower temperatures (Richet et al. 2006). For such materials able to explore freezing-point depressions (i.e., eutectics), glass forms, indeed, more easily as the liquid is able to reach lower temperatures and higher viscosities which act as a barrier for possible recrystallization. When the viscosity of different (Li, Na, K) silicates are investigated along their liquidus branches, compositions having a minimum in the critical cooling rate correlate very well with the viscosity maximum from the freezing depressions (Richet et al. 2006; Micoulaut 2008).

Raman scattering provides an interesting probe of local and intermediate-range structural changes across the rigidity transition, and in selected cases some modes have been sensitive to the nature of the elastic phases with optical elasticities (i.e., the Raman mode frequency for stretching

vibrations) displaying typical features of rigidity, i.e., a power-law variation typical of the elasticity of stressed rigid amorphous networks (Feng et al. 1997). In contrast with chalcogenide network glasses, silicate glasses display a much larger variety of possible Raman modes, most of them being clearly assigned (Zotov 2001). In the context of flexible to rigid transitions, a Raman study of the Calcium and Barium silicate systems has shown that certain modes (e.g., the stressed Q⁴ rigid SiO_{4/2} corresponding to a stretching mode) exhibit a marked change in behavior in the line frequency and linewidth at concentrations which are close to the thresholds predicted from the mean-field estimate of Table 1 (Micoulaut et al. 2005; Bourgel et al. 2009).

A strong piece of evidence for flexible to rigid thresholds can be detected from Brillouin scattering (Vaills et al. 2001, 2005; Chaimbault 2004), the measured elastic energy change upon annealing $\Delta \Phi(x)$ between as-quenched (virgin) and annealed samples being almost zero in the stressed rigid phase (e.g., x < 20% in sodium silicates, Fig. 2) and increases linearly for a modifier content that is larger than the threshold x_c predicted by Maxwell constraint counting (Table 1). The threshold behavior is an indication that changes in the elastic energy occur only in the flexible phase where local deformation modes induce a measurable value for the associated relaxation energy. The shift of the threshold with cation size (from Na to K, see Fig.2) is also compatible with the possibility that some constraints become ineffective (Table 1). Using Brillouin experiments, it has been found that the spectra between as-quenched (virgin) and annealed samples can be very different and depends substantially on the composition, while also permitting to measure and elastic energy ΔF under annealing which has the property $\Delta F = 0$ for $x < x_c$ and $\Delta F > 0$ for $x > x_c$. It has been found that such an elastic energy is a measure of the floppy mode density of the network, i.e., $\Delta F \propto Ef$ with E the floppy mode energy. A fit using Equation (3) (or Table 1) in the identified flexible phase has led to a floppy mode energy of E=0.11 meV and 0.12 meV for potassium and sodium, respectively (Micoulaut 2008). Using, the same technique, longitudinal $C_{11}(x)$ and shear $C_{44}(x)$ elastic constants exhibit a power-law variation for the Na silicate, with an exponent p of 1.68–1.69 (Vaills et al. 2005), in fair agreement with the theoretical prediction of Thorpe (1983).



Figure 2. (a) Anomalies (i.e., thresholds or extrema) in physical properties in Ge–Se glasses rescaled as a function of the number of topological constraints (Bhosle et al. 2011): Non reversing heat flow ΔH_{nr} (left axis, black symbols) and molar volume (right axis, red symbols). (b) Non-reversing enthalpy ΔH_{nr} in sodium silicates $(1-x)SiO_2-xNa_2O$ (black filled symbols) and Elastic energy released during annealing (right axis) as a function of modifier content in Na (blue filled circles) and K (blue open circles) silicates and. Adapted from (Vaills et al. 2005; Micoulaut 2008).

Lastly, the signature of the loss of rigidity with increasing modifier content is detected in the behavior of the dc ionic conductivity σ , as two obvious conduction regimes are identified over two compositional intervals. A first regime sets in at low modifier concentration where the conductivity is negligibly small because of strong barriers against local deformation due to the stressed rigid nature of the network. Once the system has become flexible, a second regime displays a conductivity trend that is exponential or with a power-law behavior. From a series of investigations on different modified oxides (Novita et al. 2007; Bourgel et al. 2009; Micoulaut et al. 2009), it has become clear that the onset of ionic conductivity in the flexible phase is related to the breakdown of the stressed-rigid network for $x > x_c$.

The special case of silica. The case of vitreous silica desserves some attention. The Si–O–Si bond angle distribution has been extensively studied by various experimental techniques (Mozzi and Warren 1969; Galeener 1985; Pettifer et al. 1988; Poulsen et al. 1995) and molecular simulations (for details, see Yuan and Cormack 2003), the more recent measurements leading to a mean bond angle of about 148–152° with a full-width at half maximum of 17–38°. Because of this broad angular distribution, O can display wide excursions around its average position, with a restoring force that is weak (Smith et al. 1995). On this basis, it has been proposed that bond-bending constraints of O should be broken in vitreous silica (Zhang and Boolchand 1994), and a mean-field constraint count leads indeed to $n_c = 3$, the optimally constrained nature of the network being suggested to be responsible for the relative ease of glass formation of silica.

The addition of alkali modifiers induces a narrowing of the Si–O–Si bond angle distribution and a subsequent lengthening of the Si–O bond distance (Boisen et al. 1990), as demonstrated from a X-ray absorption study (Henderson 1995), and from an NMR study on silica and K silicates (Farnan et al. 1992). The increased presence of Na atoms leads to an increase of the Si–O distance but to a decrease of the Si–Si distance, implying a reduction of the Si–O–Si bond angle distribution that is characterized from a reduced full-width at half maximum for the $K_2Si_4O_9$ glass, the average bond angle remaining essentially the same. The narrowing of the bond angle distribution indicates that the broken O bond-bending constraints of silica are restored in alkali silicates and corresponding BB constraints must be taken into account (Table 1). This view is supported by the potential energy curve determined by an ab inito molecular orbital approach (Newton and Gibbs 1980), which shows that lower angles (i.e., lower than 120°) lead to an increased interaction energy.

Rigidity Hamiltonians and floppy modes

The rigidity approach builds essentially on fully connected networks, that is, at T=0 when neither bonds nor constraints are broken by thermal activation. In fact, an inspection of Equation (1) shows that temperature is absent and this represents a serious drawback. The use of this initial theory is certainly valid as long as one is considering strong covalent bonds or when the viscosity η is very large once the system is trapped in the glassy state, but obviously some elements are missing in order to appropriately treat a high temperature liquid. However, for covalent liquids Nuclear Magnetic Resonance indicate that the low temperature constraint count can be readily extended to the liquid (Bermejo et al. 2008).

Naumis has established a rigidity related Hamiltonian that serves for subsequent modelling in multicomponent silicates (Naumis 2005, 2006), and it builds on the fact that cyclic variables in phase space are identified with floppy modes $f=3-n_c$ because when one of these variables is changed, the system will display a change in energy that is close to zero due to the small energetic contribution of such deformation modes (about 5 meV, Kamitakahara et al. 1991). Since it is assumed that floppy modes have a zero frequency, they will not contribute to the total energy of the system so that the sum over coordinates only runs up to 3N(1-f) and the Hamiltonian reads:

$$H = \sum_{j=1}^{3N} \frac{P_j^2}{2m} + \sum_{j=1}^{3N(1-j)} \frac{1}{2} m \omega_j^2 Q_j^2$$
(4)

where Q_j (position) and P_j (momentum) are the *j*-th normal mode coordinates in phase space, and w_j is the corresponding eigenfrequency of each normal mode. The corresponding partition function derived from Equation (4) leads to the expression of the free energy and the specific heat which are found to depend on the fraction of floppy modes, that is, on the rigidity status of the network (Naumis 2006). The number of accessible states $\Omega(f)$ can also be calculated in the microcanonical ensemble, and using the Boltzmann relation $S_c(f) = k_B \ln \Omega(f)$, one finds that the configurational entropy S_c provided by an energy landscape altered by the presence of floppy modes is simply given by: $S_c = f N k_B \ln V$, i.e., the floppy mode density is contributing to the configurational entropy and the dynamics of the glass-forming system. There is not a unique relationship for $S_c(f)$ as an alternative class of interaction potentials (i.e., different from the harmonic one shown in Equation (4) has led to a slightly different behavior with S_c scaling as f^3 (Foffi and Sciortino 2006). However, it is essentially the result from Naumis that has been used in the modelling of transport and relaxation properties of silicates, as discussed next.

An elemental viscosity fit. Using those ideas on constraints, in combination with the Adam-Gibbs model for viscosity $\ln \eta = \ln \eta_{\infty} + A / TS_c$, Mauro and co-workers (Mauro et al. 2009a) have shown that the expression of the configurational entropy S_c as a function of the density of topological degrees of freedom f induces a new form for the viscosity dependence, the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) form given by:

$$\ln \eta = \ln \eta_{\infty} + \frac{K}{T} \exp\left[\frac{C}{T}\right]$$
(5)

which avoids a divergence at low temperature found in the Vogel–Fulcher–Tamman equation, and has been tested for a variety of systems. Here η_{∞} is the viscosity at infinite (high) temperature and *C* and *K* are constants which can be related to the fragility and the glass transition temperature.

Temperature dependent constraints

Building on the Naumis relationship between floppy modes or topological degrees of freedom and the configurational entropy *Sc* (Naumis 2005), Gupta and Mauro have extended the initial T=0 rigidity theory and the constraint enumeration to account explicitly for thermal effects (Mauro and Gupta 2009), in an analytical model that uses a two-state thermodynamic step function q(T). This function quantifies the number of rigid BS and BB constraints as a function of temperature, and has the property of a step function with two obvious limits as all relevant constraints can be either intact at low temperature (q(T)=1, as in the initial theory) or fully broken at high temperature ($q(\infty)=0$) because temperature is much larger than the constraint energy barriers. At a finite temperature, however, only a fraction of these constraints can become rigid once their associated energy is less than k_BT. This modifies Equation (1) which becomes:

$$n_{c} = \frac{\sum_{r \ge 2} n_{r} \left[\frac{r}{2} q_{r}^{BS}(T) + (2r - 3) q_{r}^{BB}(T) \right]}{\sum_{r \ge 2} n_{r}}$$
(6)

where $q_r^{BS}(T)$ and $q_r^{BS}(T)$ represent the step functions associated with BS and BB interactions, respectively. Different forms can be proposed for such functions, based either on an energy landscape approach (Mauro et al. 2009c) with an onset temperature T_0 or involving a simple exponential activation energy (Angell et al. 1999). A general behavior of q(T) can be computed for any thermodynamic condition from MD simulations (Bauchy and Micoulaut 2013a, see below).

A certain number of thermal and relaxation properties of silicate glasses have been determined from a direct application of Equation (6) in conjunction with structure models.

In order to calculate the glass transition temperature, it is, again, assumed that the Adams– Gibbs model for viscosity $\ln \eta = \ln \eta_{\infty} + A/TS_c$ holds in the temperature range under consideration, and that the corresponding barrier height A is a slowly varying function with composition. Using the estimation of the configurational entropy from the floppy mode density (Naumis 2005), the general statement of $\eta(T_e)=10^{12}$ Pa.s is written for two compositions x and x_R , following:

$$\frac{T_{g}(x)}{T_{g}(x_{R})} = \frac{S_{c}(T_{g}(x_{R}), x_{R})}{S_{c}(T_{g}(x), x)} = \frac{f(T_{g}(x_{R}), x_{R})}{f(T_{g}(x), x)} = \frac{3 - n_{c}(T_{g}(x_{R}), x_{R})}{3 - n_{c}(T_{g}(x), x)}$$
(7)

and $T_g(x)$ can now be determined as a function of composition from the glass transition temperature of a reference composition $x_{\rm R}$.

Using the expression for $S_c(T_g(x), x)$ in Equation (7) and the definition of fragility:

$$M = \left[\frac{\partial \ln \eta}{\partial T / T_g}\right]_{T = T_g}$$
(8)

one can express the fragility index M as a function of composition:

$$M = M_0 \left[1 + \frac{\partial \ln S_c(T, x)}{\partial \ln T} \right]$$
(9)

These predictions have been verified for simple chalcogenides (Mauro and Gupta 2009), borates (Mauro et al. 2009b), borosilicates (Smedskjaer et al. 2011) phosphates (Hermansen et al. 2014), or borophosphate glasses (Hermansen et al. 2015). Equation (9) leads to a good reproduction of fragility data with composition (Fig. 3), but requires a certain number of onset temperatures T_0 that act as parameters for the theory. Such fragility predictions permits one to infer which interactions (species dependent bending or stretching interactions) contribute most to the evolution of fragility with composition. For instance, in borosilicates, *M* is found to be mostly influenced by the bond angle interactions constraining Silicon and Boron bending motion, whereas the BS interactions contribute only at a large silicon to boron ratio.



Figure 3. Modeling the composition dependence of the liquid fragility index (*m*) for borosilicate glasses (Smedskjaer et al. 2011). (a) Prediction of the fragility index (solid line) as a function of composition, compared to experimental data measured from DSC experiments. Reprinted with permission from Smedskjaer MM, Bauchy M, Mauro JC, Rzoska SJ, Bockowski M (2015) Unique effects of thermal and pressure histories on glass hardness: Structural and topological origin. J Chem Phys 143:164505. Copyright (2011) American Chemical Society.

Using the same formalism, the heat capacity change ΔC_p at the glass transition can be readily estimated and compared to measurements accessed from DSC. Using the temperature dependence q(T) for the constraints, it is assumed that the dominant contribution to the heat capacity at the glass transition comes from configurational contributions $C_{p,conf}$ that can be related to S_c , so that one has: $\Delta C_p = C_{pl} - C_{pg} \approx C_{p,conf}$ with C_{pl} and C_{pg} the heat capacity of the liquid and the glass, respectively. The heat capacity change can be written as a function of the configurational enthalpy and S_c :

$$\Delta C_{\rm p} = \left(\frac{\partial H_{\rm conf}}{\partial T}\right)_{\rm p} = \left(\frac{\partial H_{\rm conf}}{\partial \ln S_{\rm c}}\right)_{\rm p} \left(\frac{\partial \ln S_{\rm c}}{\partial T}\right)_{\rm p}$$
(10)

and using the Adam–Gibbs expression and Equation (9), one can, furthermore, write the jump of the heat capacity at the glass transition with composition:

$$\Delta C_{\rm p}(x_i, T_{\rm g}(x_i)) = \frac{1}{T_{\rm g}(x_i)} \left(\frac{\partial H_{\rm conf}}{\partial \ln S_{\rm c}}\right)_{p, T_{\rm g}} \left(\frac{M(x_i)}{M} - 1\right)$$
(11)

Equation (11) can be recast in a more compact form given that $S_c(T_g)$ is inversely proportional to T_g , and by assuming that $\partial H_{conf} / \partial S_c$ is, by definition, equal to a configurational temperature at constant pressure (Araujo and Mauro 2010) which is close to the glass transition temperature. This, ultimately, leads to a decomposition-dependent prediction of the heat capacity jump at T_g :

$$\Delta C_{p}(x_{i}, T_{g}(x_{i})) \approx \frac{\left[A(x_{i})\right]_{R}}{T_{g}(x_{i})} \left(\frac{M(x_{i})}{M} - 1\right)$$
(12)

As in the previous examples, the heat capacity jump is evaluated with respect to some reference composition because the parameter $[A(x_i)]_R$, appearing in equation (12) connects the configurational entropy $S_c(T_g)$ with T_g for a reference composition x_R . Applications have been performed on the borosilicate glasses and successfully compared to experimental measurements (Smedskjaer et al. 2011). Again, such predictions have the merit to accurately reproduce experimental data, and to provide some insight into the validity of structural models that can be checked independently from a variety of other experimental (e.g., spectroscopic) probes.

MOLECULAR DYNAMICS AND RIGIDITY

A more general way to enumerate topological constraints for any thermodynamic condition, including under pressure, builds on MD simulations which also permits establishing relationships with thermodynamic and dynamic properties from the ensemble averaged statistics of such atomic scale simulations. In all approaches, classical or first principles (FPMD), Newton's equation of motion is solved for a system of *N* atoms or ions, representing a glass or a liquid material. Recent applications give a very accurate description of the structural and dynamic properties of most archetypal network-forming systems: SiO₂ (Zeidler et al. 2014), GeO₂ (Micoulaut et al. 2006; Salmon et al. 2012), B₂O₃ (Ferlat et al. 2008; Zeidler et al. 2014) in the glassy or liquid state, and in ambient or densified conditions. Similar agreement holds for the modified oxides such as alkali silicates (Cormack et al. 2002; Horbach and Kob 1999; Bauchy et al. 2013), sodalime silicates (Cormack and Du 2001; Laurent et al. 2014), borosilicates (Cormier et al. 2000; Pedesseau et al. 2015) or aluminosilicates (Winkler et al. 2003).

Topological constraints are extracted from atomic scale trajectories by recording the radial and angular motion of atoms. This connects directly to the enumeration of BS and BB constraining interactions but instead of treating the forces mathematically and querying motion – the standard procedure in MD simulations – one identifies the absence of a restoring force (i.e., a constraint) with an increased atomic radial or angular motion. This strategy is somewhat different from the '*culture of force*' discussed by Wilcek (2004) given that one does not necessarily need to formulate the physical origin of the forces to extract the constraints. As a result, large radial and angular excursions of doublets (bonds) or triplets (of atoms (angles)) will be identified with broken radial or angular constraints. In practice, once the atomic scale trajectories have been accumulated at different thermodynamic conditions from MD, a structural analysis is applied in relationship with the constraint counting (Fig. 4).



Figure 4. (a) Ca-centered partial pair correlation function for three compositions in soda-lime silicate glasses SiO₂–CaO–Na₂O at two different temperatures (300 K, black; 2,000 K, red). Blue curves correspond to calculated neighbor distributions functions (Laurent et al. 2014). (b) Corresponding Ca–O radial standard deviations σ_r/d as a function of neighbor number for three compositions (colored curves). Here *d* is the peak position of the relevant neighbor distributions. The shaded areas correspond either to the second shell of neighbors, which is not relevant for constraint counting, or to the approximate limit ($7 \pm 1\%$) between intact (low σ_r) or broken (large σ_r) bond-stretching constraints. Reprinted with permission from Laurent L, Mantisi B, Micoulaut M (2014) Structure and topology of soda-lime silicate glasses: implications for window glass. J Phys Chem B 118:12750–12762. Copyright (2014) American Chemical Society.

Bond-bending and bond-stretching

NDFs can be defined by fixing the neighbor number n (first, second, etc) during the bond lifetime, the sum of all NDFs yielding the usual *i*-centred pair correlation function $g_i(r)$. An integration up to the first minimum gives the coordination numbers r_i , and hence the corresponding number of bond-stretching constraints $r_i/2$ that can be estimated independently from the radial excursions of such bonds defining NDFs.

To determine BB constraints one uses partial bond angle distributions (PBADs) $P(\theta_{ij})$ defined as follows (Micoulaut et al. 2010; Bauchy et al. 2011): for each type of a central atom 0, the *N* first neighbors *i* are selected, leading to N(N-1)/2 possible angles *i*0*j* (*i* = 1...*N*-1, *j* = 2...*N*), i.e., 102, 103, 203, etc. The standard deviation $\sigma_{\iota\varphi}$ of each distribution $P(\theta_{ij})$ gives a quantitative estimate of the angular excursion around a bond angle and provides a measure of the bond-bending strength (Fig. 5). Large excursions correspond to a bond-bending weakness giving rise to an ineffective constraint, whereas small values for $\sigma_{\iota\varphi}$ correspond to an intact bond-bending constraint which maintains a rigid angle at a fixed value.



Figure 5. Schematic method of constraint counting from MD generated configurations. Large (small) radial (**top**) or angular (**bottom**) excursions around a mean value are characterized by large (small) standard deviations on radial or angular distributions, representing broken (intact) constraints. Reprinted with permission from Laurent L, Mantisi B, Micoulaut M (2014) Structure and topology of soda-lime silicate glasses: implications for window glass. J Phys Chem B 118:12750–12762. Copyright (2014) American Chemical Society.

Figure 6 shows the PBADs for the silicon atom in a soda-lime silicate glass (Laurent at al. 2014). Broad angular distributions are found in most of the situations, but a certain number of sharper distributions (colored) can also be found, and these are identified with intact angular constraints because these arise from a small motion around an average bond angle. In the displayed example, only six angles have nearly identical and sharp distributions, and these are the six angles defining the tetrahedra. The calculated second moments are shown in the inset and one realizes that six standard deviations are nearly identical, associated with bending motions around the tetrahedral angle of 109°.

Applications have been performed on a variety of systems including chalcogenides and modified oxides, or densified oxide glasses and liquids (see applications below). In the forthcoming, we will apply such methods on silicate network glasses and liquids which are probably the most well documented systems in the context of flexible to rigid transitions.

The enumeration of constraints on realistic models of silicates glasses (Laurent et al. 2014) and liquids (Bauchy and Micoulaut 2011, 2013a) shows that six Si standard deviations have a low value (10°) , i.e., four times smaller than all the other angles (Fig. 6). One thus recovers the result found for the stoichiometric oxides (SiO₂, GeO₂), Bauchy et al. 2011).

Behavior in the liquid phase

With such MD simulations, the number of topological constraints can be investigated as a function of temperature and composition in a certain number of glass-forming systems. For all, intact constraints dominate at 300 K (leading to a low standard deviation) but will soften as temperature increases. A limit between a "broken" (or ineffective) and an "intact" constraint can be defined from reasonable limits suggested by for example, the inspection of calculated values in the glassy state (Fig. 6, inset). We note, indeed, that intact constraints arise from strong bonds or angles having a low standard deviation of about 0.02 Å or 5–10 degrees (Bauchy and Micoulaut 2011). On this basis, the constraint density can be evaluated as a function of temperature and pressure and corresponding probabilities indicate that they behave rather similarly to the onset functions q(T) proposed by Mauro and Gupta (Bauchy and Micoulaut 2011, 2013a).



Figure 6. Angles around a silicon atom in a soda-lime silicate glass, defined by the N=6 first neighbors leading to 15 possible partial bond angle distributions (Laurent et al. 2014). Colored curves correspond to PBADs having a low standard deviation s_{θ} (inset, blue bars). Reprinted with permission from Laurent L, Mantisi B, Micoulaut M (2014) Structure and topology of soda-lime silicate glasses: implications for window glass. J Phys Chem B 118:12750–12762. Copyright (2014) American Chemical Society.

ISOSTATIC RELAXATION

The use of MD simulation together with constraint enumeration reveals that isostatic glasses fulfilling merely $n_c=3$ relax in a very different fashion from other glass-forming liquids. The behavior of transport properties appears to be different too, as recently demonstrated for densified silicates (Bauchy et al. 2013; Bauchy and Micoulaut 2015). These conclusions build on the computation of liquid viscosity using the Green–Kubo (GK) formalism which is based on the calculation of the stress tensor auto-correlation function, given by:

$$\eta = \frac{1}{k_{\rm B}TV} \int_{0}^{\infty} P_{\alpha\beta}(t) P_{\alpha\beta}(0) dt$$
(13)

using off-diagonal ($\alpha \neq \beta$) components $P_{\alpha\beta}(t)$ of the molecular stress tensor defined by:

$$P_{\alpha\beta}(t) = \sum_{i=1}^{N} m_i v_i^{\alpha} v_i^{\beta} + \sum_{i=1}^{N} \sum_{j>i}^{N} F_{ij}^{\alpha} r_{ij}^{\beta}$$
(14)

where the brackets in Equation (13) refer to an average over the whole system. In Equation (14), m_i is the mass of atom *i*, and F_{ij} is the component α of the force between the atoms *i* and *j*, and r_{ij}^{α} and v being the β component of the distance between two atoms i and j, and the velocity of atom *i*, respectively. Such calculated viscosities are investigated at fixed pressure/density as a function of inverse temperature in an Arrhenius plot, a linear behavior is obtained (Fig. 7) which is found to be compatible with experimental measurements at zero pressure (Bockris et al. 1955; Knoche et al. 1994; Neuville 2006). The corresponding calculated activation energy $E_{\rm A}$ for viscous flow is found to display a similar trend as the one determined from the calculated diffusivity, and, interestingly, both display a minimum with the calculated number of constraints. This suggests that isostatic networks $(n_c=3)$ will lead to singular relaxation behavior with weaker energy barriers, as also detected for a select number of chalcogenide liquids (Yang et al. 2012; Gunasekera et al. 2013; Ravindren et al. 2014) where the condition of isostaticity ($n_c=3$) coincides with a network mean coordination number of \bar{r} =2.4. As one also has $M = E_A \ln 10/k_B T_g$, the combination of a minimum in activation energy and a smooth or constant behavior of $T_{\rm g}$ usually also leads to a minimum in fragility for isostatic liquids. Such observations have been made for certain chalcogenide and modified oxides melts for which minima in E_A and M coincide and, under certain assumptions regarding structure, the link with the isostatic nature of the network could be established (Chakraborty and Boolchand 2014; Mohanty et al. 2019).



Figure 7. Calculated viscosity using Equation (13) in a densified sodium silicate for different system pressures, compared to experimental data (Bockris et al. 1955; Knoche et al. 1994; Neuville 2006), inset: Calculated activation energies E_A for diffusion (red) and viscosity (black) as a function of the number of constraints n_c , derived from an Arrhenius plot of oxygen diffusivity and Green–Kubo calculated viscosity (Bauchy and Micoulaut 2015).

Such anomalies have been found to also occur in other dynamic properties such as the structural relaxation time determined from the long time behavior of the intermediate scattering function which measures the decay of density–density correlations in Fourier space (Bauchy and Micoulaut 2015; Yildirim et al. 2016). They are also supported from the results of a simplified Kirkwood–Keating model containing only harmonic interactions between atoms. In this model, the glass transitions of isostatic glass-forming liquids involve an activation energy for relaxation time which is minimum (Micoulaut 2010).

Reversibility windows

Another intriguing observation related to isostatic glasses is a minimum in enthalpic relaxation that is, by far, much smaller than in flexible or stressed rigid glasses. Experimentally, such anomalies lead to reversibility windows measured from calorimetry, i.e., there is a tendency for the system to undergo a glass transition with a minimum of thermal changes. This obviously relates to the particular relaxation behavior described above.

Signature from MD simulations. When MD numerical cycles are performed across the glass transition from a high temperature liquid, one finds a hysteresis between the cooling and heating curve. This behavior simply signals the nature of the glassy state that induces slow dynamics at $T < T_g$ with a subsequent volume or enthalpy relaxation as the glass is annealed back to the liquid phase, consistent with experimental observation (Fig. 8). However, it has been found that for selected thermodynamic conditions (pressure, density) and fixed numerical cooling/heating rate the hysteresis curves become minuscule (Bauchy and Micoulaut 2015; Mantisi et al. 2015), and the cooling/heating curves nearly overlap. When the area of the enthalpy/energy (or volume) hysteresis is investigated as a function of pressure or density, a deep minimum is found which reveals a so-called *reversibility window* (RW, Fig. 8 inset).



Figure 8. Numerical cooling-heating cycle of a densified sodium silicate for different densities representing a rescaled energy $E^*(T)/E^*(500 \text{ K})$ with temperature. The inset represents the hysteresis area A^{ρ} for different cooling rates as a function of system density, and defines a reversibility window (Mantisi et al. 2015). Curves are shifted by 0.002 for clarity. Reprinted figure with permission from B. Mantisi, M. Bauchy, and M. Micoulaut, Phys. Rev. B 92:134201 (2015). Copyright (2015)by the American Physical Society.

These thermal anomalies are actually linked with the isostatic nature of the glass-forming liquid, as detected from the MD-based constraint count which shows that the total number of constraints shows a plateau-like behavior around the isostatic value $n_c=3$ in the temperature range where the glass transition occurs (Fig. 9). The detail shows that angular adaptation drives the mechanical evolution of the liquid under pressure because BS constraints increase due to conversion of the low pressure tetrahedral order (r=4) into octahedral order (r=6) which dominates at elevated pressure (Bauchy and Micoulaut 2015; Mantisi et al. 2015; Yildirim et al. 2016), and which is typical of the short-range order of stishovite. However, for systems beyond a certain threshold pressure/density, further compression leads to a decrease of the number of BB (angular) constraints which indicates that some of the angular interactions have softened (Bauchy and Micoulaut 2015). Results indicate an obvious correlation between the RW thresholds and those obtained from the constraint count, while identifying the isostatic nature of the RW (Fig. 10).



Figure 9. Constraint density n_c as a function of pressure in supercooled (2000 K) and glassy sodium disilicate (NS2). The plateau behavior in the liquid corresponds to pressures (gray zone) for which cooling/heating cycles are minimum (adapted from Bauchy and Micoulaut 2015). The inset shows the BO BB constraint density inside the simulation box, and highlights the heterogeneous character of such constraints (Bauchy and Micoulaut 2013b). Adapted figure with permission from B. Mantisi, M. Bauchy, and M. Micoulaut, Phys. Rev. B 92:134201 (2015). Copyright (2015)by the American Physical Society.



Figure 10. Area of enthalpy and volume hysteresis of densified sodium disilicates in numerical cooling/heating cycles performed in NPT Ensemble as a function of constraint density (Bauchy and Micoulaut 2015). Reprinted figure with permission from B. Mantisi, M. Bauchy, and M. Micoulaut, Phys. Rev. B 92:134201 (2015). Copyright (2015)by the American Physical Society.

In addition, it has been found that the distribution of constraints is not randomly distributed (Fig. 9, inset), and corresponding liquids display a heterogeneous distribution with zones of thermally activated broken constraints that dominate the liquid dynamics (Bauchy and Micoulaut 2013b; Yildirim et al. 2016). In addition, the spatial extent of these flexible regions shows a percolative behavior which is not only connected to flexible–rigid transitions but also to dynamic heterogeneities (Bauchy and Micoulaut 2017). For the particular case of sodium silicate liquids, the temperature at which constraints become homogeneously distributed across the liquid structure is found to depend both on pressure and temperature.

Experimental signature from calorimetry. To support the MD results, a vast body of experimental data has been accumulated during the past fifteen years. One of the most direct signatures of reversibility windows which has a nearly one-to-one correspondence with the result from MD is provided from mDSC measurements (modulated differential scanning calorimetry) which exhibit a deep minimum (Fig. 2) or even a vanishing of a so-called non-reversing enthalpy (ΔH_{nr}) which represents a rough measure of the enthalpy of relaxation during the glass transition. The use of such calorimetric methods to detect the nearly reversible character of the glass transition has not been without controversy, in part, because of the intrinsic measurement of ΔH_{nr} depends on the imposed frequency, albeit frequency corrections are brought to the tempereature scans and these build on a robust methodology (Verdonck et al. 1999).

A large number of network glasses (chalcogenides, oxides) display RWs, and these are summarized in Figure 11. These represent systems which cover various bonding types, ranging from ionic (silicates), iono-covalent, covalent (Ge–Se), or semi-metallic (Ge–Te–In–Ag). For simple covalent network glasses such as $\text{Ge}_x\text{Se}_{1-x}$, the experimental boundaries of the RW are found close to the mean-field estimate of the isostatic criterion (Eqn. 1) satisfying $n_c=3$ because coordination numbers of Ge/Si and S/Se can be safely determined from the 8- \mathcal{N} (octet) rule to yield an estimate of the constraints $n_c=2+5x$ using Equation (1). For such systems, aspects of topology fully control the evolution of rigidity with composition, as there is a weak chemical effect in the case of isovalent Ge/Si or S/Se substitution, and the lower boundary of the RW ($x_c=20\%$) coincides with the Phillips–Thorpe mean-field rigidity transition $n_c=3$. However, for most of the systems among which silicates, uncertainties persist regarding the constraint count derived from the local structures (e.g., Q^n species) and geometries as coordination numbers or constraints must be derived from specific structural models.

The presence of relaxation phenomena (Fig. 7) that induce RWs for select compositions leads to various other anomalous behaviors in physical, chemical and mechanical properties (see applications) which manifest by maxima or minima with thermodynamic conditions (temperature, composition, pressure). These signatures provide other alternative and complementary evidence of the RW signature from calorimetric measurements. For instance, it has been suggested that glasses will display an increased tendency towards space-filling because of the isostatic nature of the networks (i.e., absence of stress), which manifests by a minimum

in the molar volume (Fig. 2a), a salient feature that has been reported for different silicates, germanates and oxides with composition (Rompicharla et al. 2008; Bourgel et al. 2009) or under pressure (Trachenko et al. 2004). Ionic conductors display an onset of ionic conduction only in compositions belonging to the flexible phase (Novita et al. 2007), i.e., when the network can be more easily deformed at a local level because of the presence of floppy modes which promote mobility. This leads to an exponential increase in the conductivity once $n_c < 3$, as detected from the evolution of ionic conduction in alkali and alkaline earth silicates (Micoulaut 2008).



Figure 11. Location of experimental reversibility windows (RW) driven by composition for different chalcogenide and modified oxide glass systems (Mantisi et al. 2015). In the same families of modified oxides (e.g., silicates see Fig. 2 or germanates), there is an effect due to the cation size. Using the octet rule, only a select number of systems can be represented as a function of n_c using the mean-field estimate of Equation (1). Reprinted figure with permission from B. Mantisi, M. Bauchy, and M. Micoulaut, Phys. Rev. B 92:134201 (2015). Copyright (2015)by the American Physical Society.

Nature of reversibility windows from models. While the results of Figures 9 and 10 obviously point to the isostatic nature of the RW, a certain number of other/complementary scenarios have been proposed to describe the observed behaviors, building on the role of fluctuations in the emergence of a double threshold/transition that defines an intermediate phase (IP) between the flexible and the stressed rigid phase (Thorpe et al. 2000; Micoulaut and Phillips 2003; Barré et al. 2005; Brière et al. 2007). Other models inspired by the mean-field treatment of jammed solids neglect the role of coordination fluctuations and propose that the IP is the result of a local distinct configurations that organize due to long-range elastic interactions (Yan and Wyart 2014; Yan 2018).

An alternative path builds on the initial mean-field rigidity treatment and a certain number of models (Thorpe et al. 2000; Brière et al. 2007) propose that at finite temperature, the glass forming under increasing stress induced by the growing cross-linking density, is able to adapt during the cooling in order to reduce the energy, a feature termed as "self-organization" (Thorpe et al. 2000). In detail, it can be shown that such adaptation manifests by an increased angular excursion for the BO atoms in densified liquid silicates which have networks with a growing bond density induced by pressure (Bauchy and Micoulaut 2013a). On simple bar networks or cluster approaches, the IP is defined by a double percolative transition at \bar{r}_l (rigidity) and \bar{r}_2 (stress), which can be fully characterized from algorithms taking into account the non-local characteristics of rigidity, and this allows one to locate over-constrained zones in an amorphous network, and to define the size of isostatic rigid and stressed-rigid zones or clusters as a function of the control parameter \bar{r} (Thorpe et al. 2000; Micoulaut and Phillips 2003). In absence of self-organization or network adaptation, both transitions at \bar{r}_1 and \bar{r}_2 coalesce into the single mean-field transition. Since such approaches or alternatives (Barré et al. 2005) do not explicitly consider temperature effects (and the underlying associated energy barriers), Mousseau and co-workers have considered the possibility of having finite energy barriers to allow for some equilibration (Chubynsky et al. 2006; Brière et al. 2007). The main outcome from these models is that an increased sensitivity for single bond addition or removal exists close to the IP, and this suggests that the system is maintained in a critical state on the rigid-floppy boundary throughout the IP, as also suggested in the liquid phase in densified silicates (Bauchy and Micoulaut 2017).

Using the phenomenology of the elasticity of soft spheres and jamming transitions in combination with a mean-field scenario of rigidity, different authors (Yan and Wyart 2014, Yan 2018) have also shown that temperature considerably affects the way an amorphous network becomes rigid under a coordination number increase, and the existence of an isostatic RW not only depends on *T*, but also on the relative strength of weak forces present in the system. The related vibrational analysis furthermore suggests that vibrational modes for IP compositions are similar to the anomalous modes observed in the packing of particles near jamming, thus providing an interesting connection with jamming transitions that might also be embedded in the anomalous variation of the molar volume (Fig. 2a). The mean-field scenario for the IP is also used for the problem of rigidity percolation model on a Bethe lattice (Moukarzel 2013) and under certain conditions of bond addition/removal, two discontinuous transitions are found, and the associated IP displays an enhanced isostaticity at the flexible boundary. The main result is that throughout the IP, the network displays a low density of redundant bonds and contains, therefore, low self-stress.

OTHER APPLICATIONS

Diffusivity anomalies

A certain number of densified tetrahedral liquids display diffusivity anomalies, following the well-known example of densified water (Errington and Debenedetti 2001), i.e., *D* exhibits minima and maxima with pressure/density at fixed temperature in the liquid state. This is also the case for silica (Shell et al. 2002), germania (Pacaud and Micoulaut 2015) and sodium disilicate NS2 (Bauchy et al. 2013). The diffusivity anomalies for the NS2 liquid actually also relate to the elastic nature of the liquid, flexible or stressed, and the correlation becomes obvious when the sodium D_{Na} and oxygen D_0 diffusivities are represented, instead of density, as a function of the constraint density (Fig. 12). One now recognizes that such diffusivity anomalies of liquid NS2 connects to the RW, and these are driven by the evolution of constraint density which is the dominant feature controlling the evolution of the transport coefficient in liquids under pressure. In stressed-rigid liquids, both Na and O diffusivities behave the same with an exponential decay of the form $\exp[-An_c]$ and a coefficient *A* being similar for both species. Close to the isostatic condition however, transport coefficients evolve rapidly and for liquids in the flexible phase (where the *P*=0 belongs to the flexible phase), sodium diffusivity are now markedly larger.



Figure 12. Calculated oxygen and sodium diffusivity in a liquid (2000 K) sodium silicate 2SiO_2 -Na₂O as a function of the calculated number of constraints n_c . Transport properties are obviously affected by the elastic nature of the liquid. Adapted from Bauchy et al. (2013) and Bauchy and Micoulaut (2015).

It has been furthermore identified that the diffusivity minima D_{\min} (e.g., at 2.1g/cm³ or $n_c=2.87$ for 2000 K) and maxima D_{\max} (at 3.2 g/cm³ or $n_c=3.05$) can be related to the boundaries of the RW (Mantisi et al. 2015). In light of these correlations, the locus of D_{\min} is related to the boundary for the onset of a rigid but stress-free network-forming liquid, whereas the location of D_{\max} is related to the upper boundary of the IP.

Prediction of glass hardness

The hardness of glasses captures their resistance to permanent deformations (Oliver and Pharr 1992; Smedskjaer et al. 2015). Interestingly, although hardness is intrinsically a far-from-equilibrium property, it has been suggested to be governed by an equilibrium structural feature, namely, the number of constraints per atom n_c . Smedskjaer et al. (2010) proposed that glass hardness can be expressed as:

$$H = \left(\frac{\partial H}{\partial n_{\rm c}}\right) \left[n_{\rm c} - n_{\rm crit}\right] \tag{15}$$

This model relies on the following reasoning. First, a critical minimum number of constraints (n_{crit}) is required for the glass to be macroscopically cohesive. The value n_{crit} =2.5 (i.e., the minimum number of constraints that are needed to achieve rigidity in two dimensions) was found to be appropriate to describe the hardness of several oxide glasses (Smedskjaer et al. 2010), although this value does not apply to chalcogenide glasses (Bauchy et al. 2015c). Starting from this minimum number of constraints, each additional constraint then contributes to increasing hardness, wherein the contribution of each unit constraint per atom is given by the parameter $\partial H/\partial n_c$. Note that this term has thus far remained a fitting parameter (i.e., with no clear physical foundation) that depends on the indenter geometry, the indentation load, and the specific glass family (although this parameter is composition-independent within a given glass family). This equation has been found to offer realistic predictions of glass hardness for various oxide systems (Smedskjaer et al. 2010; Smedskjaer 2014).

As a recent development, it was suggested that BS and BB constraints may not contribute in the same fashion to increase hardness. In details, hardness has been found to primarily be governed by the number of angular BB constraints, while remaining fairly unaffected by the number of radial BS constraints (see Fig. 13) (Bauchy et al. 2015c). This behavior was suggested to arise from the fact that, during indentation, glass networks deform by following lowest-energy paths—which suggests that deformation occurs via the breakage of weak angular BB constraints rather than stronger radial BS constraints. Note that it has also recently been proposed that hardness is governed by the volumic density (rather than atomic density) of constraints (Zheng et al. 2017).



Figure 13. Hardness of various oxide and chalcogenide phases as a function of their number of angular BB constraints per atom (Swiler et al. 1990; Sreeram et al. 1991; Varshneya and Mauro 2007; Smedskjaer et al. 2010; Abdolhosseini Qomi et al. 2013 2014, 2017; Bauchy et al. 2014a,b,c, 2015c; Qomi et al. 2015a,b; Bauchy 2017).

Prediction of glass stiffness

Stiffness characterizes the resistance of glasses to reversible, elastic deformations (Rouxel 2006). In contrast with hardness, stiffness is a near-equilibrium property and, hence, it is less surprising that the macroscopic stiffness of glasses should depend on the density of constraints. Indeed, within the framework of topological constraint theory, glasses can be viewed as networks, wherein atoms are connected to each other via some "small springs" (i.e., the interatomic mechanical constraints). Hence, it is indeed not surprising that the macroscopic stiffness of glasses should be governed by the number of interatomic constraints—in the same fashion as one can calculate the resultant stiffness of a system of several springs in series and/or parallel. In fact, the relationship between stiffness and topological constraints finds its roots in the origins of topological constraint theory (Thorpe 1983). In model lattices, it was shown, that stiffness vanishes in flexible systems ($n_c < 3$) and then scales with n_c once the system is stressed-rigid ($n_c > 3$). A similar relationship was also observed in amorphous semiconductors (Paquette et al. 2017; Bhattarai et al. 2018; King et al. 2018; Su et al. 2018) and chalcogenide glasses (Plucinski and Zwanziger 2015).

More recently, some topological models of glass stiffness applicable to silicate glasses have been proposed (Wilkinson et al. 2019; Yang et al. 2019b). The model proposed by Yang et al. builds on the original model of glass hardness introduced by Smedskjaer et al. (see above) (Yang et al. 2019b). Since the stiffness (e.g., the Young's modulus *E*) has the dimension of an energy per unit of volume, it was postulated that *E* can be expressed in terms of the volumetric density of the energy created by each constraint. Further, it was postulated that BS and BB constraints do not contribute with equal weight to increasing the Young's modulus. This arises from the fact that BS and BB constraints exhibit different free energies and that different types of constraints may be activated under different loading conditions (Gupta and Mauro 2009; Bauchy and Micoulaut 2011; Bauchy et al. 2015c). Based on these considerations, the following model was proposed:

$$E = \varepsilon_{\rm BS} n_{\rm BS} + \varepsilon_{\rm BB} n_{\rm BB} \tag{16}$$

where n_{BS} and n_{BB} are the volumetric density of BS and BB constraints, respectively, and ε_{BS} and ε_{BB} are some fitting parameters that correspond to the typical energies of BS and BB constraints, respectively. This model assumes that the Young's modulus of glasses vanishes when the density of BS and BB constraints becomes zero. As shown in Figure 14, the topological model offers excellent agreement with experimental and molecular dynamics data (Yang et al. 2019a,b) with significant improvement as compared to the traditional Makishima–Mackenzie model (Makishima and Mackenzie 1973).



Figure 14. (a) Comparison between the Young's modulus values predicted by the topological model (Eqn. 16) and computed by molecular dynamics simulations. A coefficient of determination $R^2 = 0.979$ and a root mean squared error (RMSE) of 4.26 GPa are obtained. (b) Comparison between the Young's modulus values computed by molecular dynamics simulations, predicted by the topological model, and predicted by the Makishima–Mackenzie (MM) model for a series of $(CaO)_x(Al_2O_3)_{40-x}(SiO_2)_{60}$ glasses (Makishima and Mackenzie 1973). The data are compared with available experimental data (Eagan and Swearekgen 1978; Yamane and Okuyama 1982; Ecolivet and Verdier 1984; Rocherulle et al. 1989; Yasui and Utsuno 1993; Inaba et al. 2000; 2001; Sugimura et al. 2002; Hwa et al. 2003; Gross et al. 2009; Bansal and Doremus 2013; Weigel et al. 2016).

Origin of fracture toughness anomalies

The fracture toughness of glasses captures their resistance to crack propagation and fracture (Bauchy et al. 2015a; Wang et al. 2015; Yu et al. 2015; Januchta et al. 2017a,b; Rouxel and Yoshida 2017; Frederiksen et al. 2018). Interestingly, various glasses have been observed to exhibit maximum fracture toughness at the isostatic threshold (see Fig. 15) (Bauchy et al. 2016; Bauchy 2017). This behavior was explained as follows. On the one hand, flexible glasses ($n_c < 3$) exhibit low cohesion (low surface energy) due to their low connectivity. This tends to limit their resistance to cracking. On the other hand, stressed-rigid glasses ($n_c > 3$) break in a brittle fashion since their fully locked network cannot exhibit any ductile atomic reorganization upon loading. In between these two regimes, isostatic glasses ($n_c=3$) feature an optimal balance between cohesion and ability to plastically deform (Bauchy et al. 2016).



Figure 15. Fracture toughness (normalized by the fracture toughness at $n_c = 3$) of densified sodium silicate glasses (NS), calcium–silicate–hydrates (C–S–H), and Ge–Se glasses as a function of their number of constraints per atom (Guin et al. 2002; Yu et al. 2015; Bauchy et al. 2015a, 2016).

Prediction of dissolution kinetics

Recently, a topological model was introduced to predict the dissolution rate K of oxide glasses in dilute conditions (i.e., forward rate, far from saturation). It was proposed that the dissolution rate can be expressed in terms of the number of constraints per atom as (Pignatelli et al. 2016b):

$$K = K_0 \exp\left(-\frac{n_c E_0}{RT}\right) \tag{17}$$

where K_0 is a rate constant that depends on the solution phase pH/chemistry (i.e., the barrier-less dissolution rate of a completely depolymerized material for which $n_c=0$), $E_0=20$ -to-25 kJ/mol is the energy barrier that needs to be overcome to break a unit atomic constraint, R is the perfect gas constant, and T is the temperature. Based on this equation, the effective activation energy of dissolution can be expressed as:

$$E_{\rm A}^{\rm eff} = n_{\rm c} E_0 \tag{18}$$

The physical root of this model can be understood as follows. Starting from a hypothetic fully depolymerized phase (n_c =0), each additional unit constraint per atom tends to increase the dissolution activation energy and, hence, reduce the kinetics of dissolution (Pignatelli et al. 2016b).

This was explained by the fact that the number of constraints per atom $n_{\rm c}$ captures the local stiffness of the atomic network—so that the stiffer the network, the higher the energy cost associated with local atomic reorganizations. Indeed, independently of its underlying mechanism (e.g., hydrolysis or ion exchange), dissolution involves some atomic reorganizations within the network. For instance, hydrolysis requires the formation of intermediate overcoordinated species (5-fold coordinated Si or three-fold coordinated O), while ion exchange requires some local opening of the network to enable the jump of mobile cations from one pocket to another (Bunker 1994). In both cases, the activation energy associated with these atomic reorganizations depends on the ability of the network to locally adjust its structure, which decreases as its local stiffness increases (Guo et al. 2016). This picture echoes results from density functional theory, which have shown that the activation energy associated with the hydrolysis of inter-tetrahedra bridging oxygen atoms increases with network connectivity and, hence, rigidity (Pelmenschikov et al. 2000). As shown in Fig. 16, this model has been extensively validated over a broad range of oxides and is able to predict the dissolution rate of silicate glasses over four orders of magnitude (Oey et al. 2015, 2017a,b,c; Pignatelli et al. 2016a,c; Hsiao et al. 2017; Mascaraque et al. 2017, 2019).



Figure 16. Dissolution rate of various silicate phases as a function of the number of constraints per atom (Oey et al. 2017a,b; Mascaraque et al. 2017, 2019; Pignatelli et al. 2016b).

Other applications and conclusion

Several other glass behaviors and properties have been shown to be largely governed by the topology of their atomic networks (Micoulaut and Yue 2017). Notably, isostatic glasses have been found to feature various unusual and often desirable behaviors, namely, (i) maximum strengthening following ion exchange (Wang and Bauchy 2015; Svenson et al. 2016; Wang et al. 2017a,b), (ii) maximum elastic volume recovery upon loading–unloading cycles (Mauro and Varshneya 2007; Bauchy et al. 2017), (iii) minimum relaxation and aging (Chen et al. 2010; Bauchy and Micoulaut 2015; Mantisi et al. 2015; Bauchy et al. 2017), (iv) minimum propensity for creep (Masoero et al. 2015; Bauchy et al. 2015b, 2017; Pignatelli et al. 2016a), and (v) maximum resistance to irradiation (Krishnan et al. 2017; Wang et al. 2017a). Sub-critical crack growth in oxide glasses exposed to sustained load in humid conditions has also been shown to be controlled by the atomic topology (Smedskjaer and Bauchy 2015). More recently, it has been suggested that topology of the glass surface (rather than that of the bulk) is governing the degree of hydrophilicity/hydrophobicity of silica surfaces (Yu et al. 2018).

Besides oxide glasses, the thermal, mechanical, electrical, and optical properties of amorphous SiC:H thin films were shown to be correlated to the topology of their atomic network (King et al. 2013). Rigidity concepts have also enabled the nanoengineering of new cementitious phases (Bauchy 2017; Liu et al. 2019). The susceptibility of granular systems was found to be maximal at the isostatic threshold (Moukarzel 1998, 2002). Fast-ion conduction was observed to offer a clear signature of the intermediate phase (Novita et al. 2007, 2009; Micoulaut et al. 2009). The performances of phase-change materials were noted to be controlled by their atomic topology (Micoulaut et al. 2010). Finally, it was found that protein folding is controlled by the topology of their molecular architecture (Rader et al. 2002; Phillips 2004, 2009). The large variety of properties and material families for which topological engineering concepts have been successfully applied establish network topology as a generic, fundamental, and promising approach to decode the genome of complex materials.

In this context, further applications to silicate glasses and melts should provide new attractive ways to understand and predict physical and chemical properties as a function of composition and temperature.

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