

# Towards Ultrastrong Glasses

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The development of new glassy materials is key for addressing major global challenges in energy, medicine, and advanced communications systems. For example, thin, flexible, and large-area glass substrates will play an enabling role in the development of flexible displays, roll-to-roll processing of solar cells, next-generation touch-screen devices, and encapsulation of organic semiconductors. The main drawback of glass and its limitation for these applications is its brittle fracture behavior, especially in the presence of surface flaws, which can significantly reduce the practical strength of a glass product. Hence, the design of new ultrastrong glassy materials and strengthening techniques is of crucial importance. The main issues regarding glass strength are discussed, with an emphasis on the underlying microscopic mechanisms that are responsible for mechanical properties. The relationship among elastic properties and fracture behavior is also addressed, focusing on both oxide and metallic glasses. From a theoretical perspective, atomistic modeling of mechanical properties of glassy materials is considered. The topological origin of these properties is also discussed, including its relation to structural and chemical heterogeneities. Finally, comments are given on several toughening strategies for increasing the damage resistance of glass products.

## 1. Introduction

Glassy materials have a unique history of continuous use spanning more than thirty thousand years. Their enabling role in numerous society-changing applications has often been taken for granted, and the brittleness of glass has been perceived as its gravest handicap. Over the centuries, accepting this handicap and benefiting from optical properties and universal processability, glasses have found their role in applications with low levels of tensile stress. In recent years, however, new and very high demand has arisen for novel approaches towards stronger or, more precisely, more damage resistant glasses.<sup>[1]</sup> Strength, toughness, and elastic properties of glass are now a major bottleneck for further development of short-haul high-capacity telecommunication and fiber-to-the-home technologies; flexible substrates and roll-to-roll processing of displays, solar modules, and planar lighting devices; large-scale and high-altitude architec-

tural glazing; lightweight packaging; ultrastiff composites; and numerous other applications. Increasing the strength and toughness of glass would not only enable exciting new applications, but also lead to a significant reduction of material investment for existing applications. In this respect, both oxide and metallic glasses have come to a crossroads: a significant leap in practical toughness will be possible only if a new level of conceptual understanding can be attained and applied.

While the understanding that the experimental strength of glass is primarily determined by macro- and microstructural defects (Figure 1) became well accepted in the early 20th century,<sup>[2,3]</sup> more recently it has been recognized that glass constitutes the intrinsically strongest man-made material that can be produced on a large scale (e.g., a tensile strength of up to 26 GPa was demonstrated for vitreous silica<sup>[4]</sup>). However, these high intrinsic strengths are compromised by the material's low resistance to surface damage. At the same time, wholly new classes of glassy materials have entered the scene, and the interplay between brittleness, plasticity, and elasticity of disordered solids must now be put into a much broader context. For example, it now appears as if, on a laboratory scale, the physical limits of strength and toughness are in close reach, at least for certain metallic glass compositions.<sup>[5,6]</sup> Identification of determinant parameters and their engineering towards ultrahigh toughness is the major challenge in the field.<sup>[1,7]</sup>

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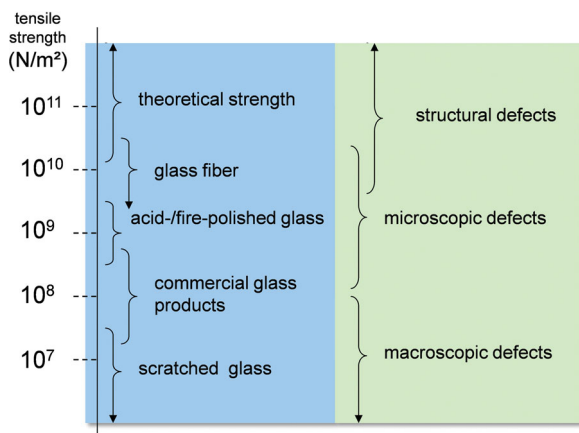
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**Figure 1.** Schematic of the dependence of tensile strength of silicate glasses on the presence of surface defects.

Here, we provide a concise review of this rapidly emerging field, indicating potential paths towards the development of ultrastrong glasses. For this purpose, we will jointly consider metallic and oxide materials.

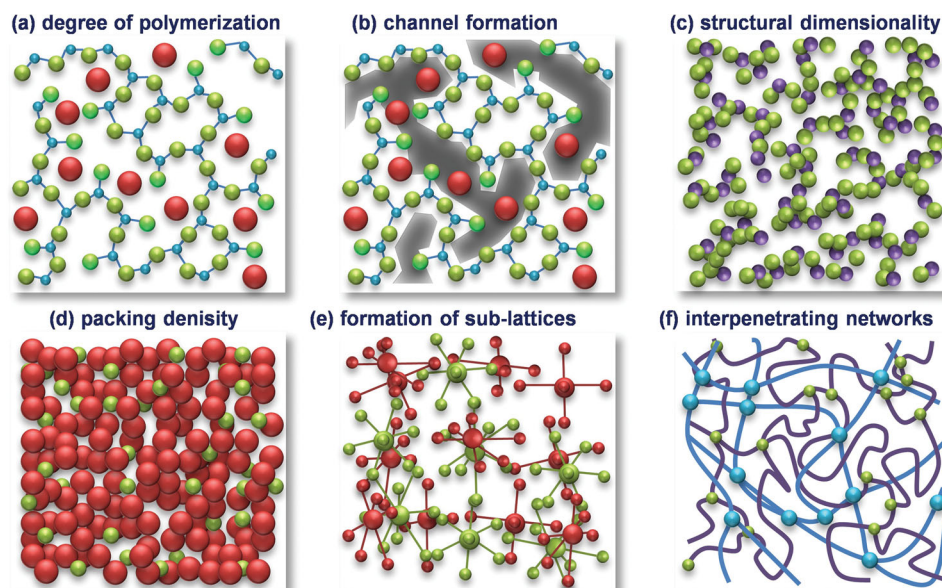
## 2. Long-Range Homogeneity and Topological Heterogeneity of Inorganic Glasses

One of the unique properties of glass is its ultimate long-range homogeneity. Glasses do not possess a microstructure in the traditional sense, where phase/grain boundaries or structural defects (twins, stacking faults, etc.) largely determine the mechanical (and other) properties. With this absence of microstructure, the topology of the disordered glass network then controls the material's response to mechanical stress. The

network topology, dynamics, and surface properties, in turn, are determined largely by the chemical composition. In Figure 2, volume topological concepts for leveraging ("engineering") these mechanical properties are illustrated schematically. A consequence of homogeneity is the well-known conchoidal fracture of glasses. Considering the high degree of homogeneity at length scales  $>10\text{--}20\text{ nm}$ , mid-range (topological) heterogeneity<sup>[8,9]</sup> becomes an important parameter. In real glasses, topological heterogeneity is understood as a result of density and/or compositional fluctuations. The respective length scale is of the order of only a few nanometers (see ref. [10,11]). It depends not only on chemical composition but also strongly on the conditions that were employed during glass preparation.<sup>[12,13]</sup> Actual relations between structural heterogeneity and resulting mechanical behavior remain mostly<sup>[9]</sup> unresolved. However, some indications may be obtained when considering the fractal dimension of fracture surfaces as compared to various other materials. If the roughness of a fracture surface of any given material is measured as a function of observation length scale  $r$ , a proportionality to  $r^\zeta$  is found, where  $\zeta$ , the roughness exponent, appears to converge to a universal value of  $\approx 0.8$  for wood, concrete, ceramics, glass, metals, etc. The difference among these materials lies in the scale of the damage correlation length, which may vary from several centimeters to several nanometers. For glasses, the ultimate value of the damage correlation length remains unknown, but it may be related to the length scale of topological heterogeneity. Interestingly, evidence for a secondary fractal regime has been found at a very low length scale only for glassy materials.<sup>[14]</sup>

## 3. Elastic Properties

Elastic properties, specifically Young's modulus  $E$ , have attained paramount interest for a variety of glass applications such as

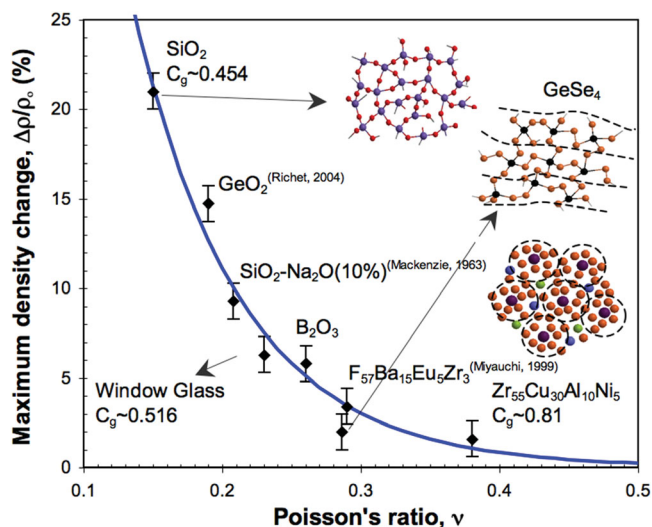


**Figure 2.** Schematic types of topological principles for designing the mid-range structure and structural heterogeneity and, hence, bulk mechanical properties of glasses.

accelerated devices, including hard discs and surgery equipment, lightweight construction, and composite materials. Young's modulus is intimately linked to the average interatomic bond energy and to the volume density of bonds. When designing glasses, there are thus various ways to reach a specific stiffness via either bond strength or by filling the intermolecular space (free volume) through addition of different sized elements. The highest values for  $E$  are not found for the most refractory glasses such as  $\text{SiO}_2$  because these high glass transition temperature,  $T_g$ , glasses are usually characterized by a low atomic packing density. On the other hand, the high packing density of metallic glasses counterbalances their low bond energy, thereby challenging the common idea that  $E$  scales with  $T_g$ . In fact, one can easily find glasses with very different  $T_g$  values that exhibit the same value of  $E$ .<sup>[15]</sup> For instance,  $\text{Mg}_{65}\text{Cu}_{20}\text{Y}_{15}$ ,  $\text{Pd}_{80}\text{Si}_{20}$ , standard soda-lime-silica window glass, typical borosilicate glasses for fiber reinforcement, and vitreous  $\text{SiO}_2$  all have  $E \approx 70$  GPa, although  $T_g$ s for these glasses are 420, 607, 835, 1119, and 1463 K, respectively.

The elastic modulus of inorganic glasses covers a wide range of values, i.e., from 5 GPa for glassy water to 180 for oxynitride glasses and 309 GPa for tungsten-based metallic glasses. Poisson's ratio ( $\nu$ ) scales from as low as 0.1 for oxycarbide glasses to a high value of 0.4 for bulk metallic glasses.<sup>[16–22]</sup> Besides the essential role of elastic properties for materials selection in mechanical design, the study of macroscopic elastic properties offers an interesting way to obtain structural insights on short and intermediate length scales. In particular,  $\nu$ , the atomic packing density, and the glass network dimensionality appear to be strongly interconnected.<sup>[15,17,19,23]</sup> First,  $\nu$  correlates positively with the atomic packing density and negatively with the glass network dimensionality. Second, structural disorder was reported to favor high  $E$  while the atomic packing density seems to dominate over bond strength. Structural disorder implies lateral diversity in coordination, topology (e.g., the presence of certain structural units such as rings, chains, or layers), and/or chemical composition. For the latter, highly coordinated atoms or cations added (or alloyed) to the main glass-forming species and, in inorganic glasses, anions of higher valence than oxygen (e.g., nitrogen and carbon) contribute to glass stiffening. However, poor knowledge of the actual ionic or atomic radii, coordination numbers, and density (or free volume), as well as the wide range of glass compositions, make it very difficult to find universal expressions for elastic moduli. Reliable quantitative calculations based on ab initio simulations is, at the moment, only possible on the edges of glass forming regions with compositions close to those of crystalline reference substances.

Also strength and fracture toughness may be directly related to the elastic properties. For instance, the strength of a solid with a semicircular surface flaw of radius  $R$  is  $\sigma_r = \sqrt{2\gamma E / \pi R(1 - \nu^2)}$ , where  $\gamma$  is the fracture surface energy and is related to the fracture toughness ( $K_{IC}$ ) through  $\gamma = K_{IC}^2 / 2E$ . Glass is hence expected to become stronger when  $\nu$  approaches its extremes ( $-1$  and  $1/2$ ). Additionally,  $\nu$  provides a remarkable (and easy-to-assess) measure to discriminate between mechanisms that lead to permanent deformation below  $T_g$ , i.e., densification and isochoric shear flow.<sup>[24]</sup> Although  $\nu$  is defined for small-strain elastic perturbations, it correlates with the packing density of the glass; open structures exhibit low  $\nu$  values and can be



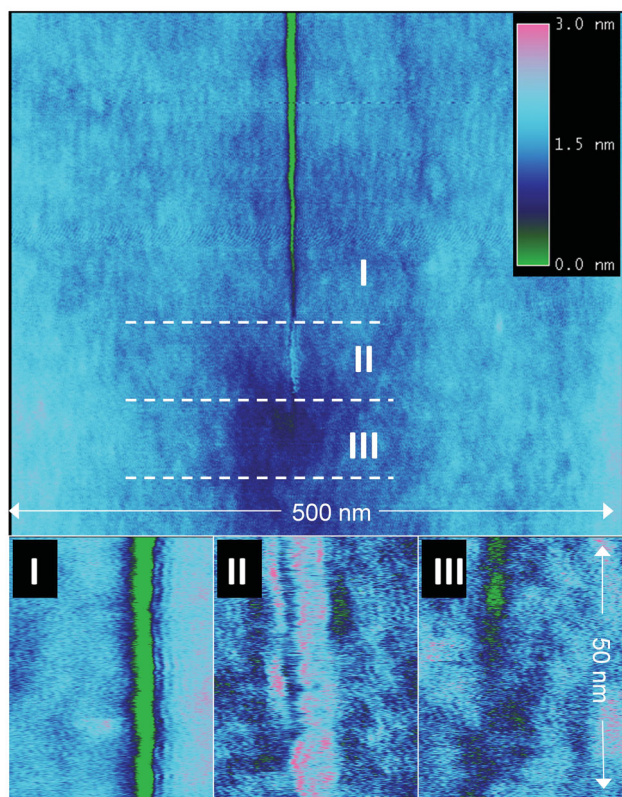
**Figure 3.** Maximum observed changes of the relative specific mass (apparent saturation plateau) after high-pressure treatments of up to 25 GPa at room temperature as a function of the Poisson's ratio of the pristine materials. Reproduced with permission.<sup>[25]</sup> Copyright 2008, The American Physical Society.

densified, whereas materials with  $\nu = 1/2$  are incompressible and solely deform by means of shear processes.<sup>[24,25]</sup> Hence,  $\nu$  also reflects the free volume of a given glass and its densification behavior at high local pressure (Figure 3). Consequently, understanding the microscopic origin of  $\nu$  is of significant interest for understanding and optimizing resistance to indentation deformation and contact damage.<sup>[24–26]</sup>

#### 4. Mechanochemical Aspects of Subcritical Crack Propagation

Crack initiation and propagation are typically studied using standardized fracture experiments. However, some existing methods must be questioned because they reflect a purely elastoplastic analysis of the relevant stress-strain fields but do not consider, e.g., permanent volume changes under sharp contact loading.<sup>[25]</sup> Fracture energy, either measured by Charpy impact testing or calculated from the fracture toughness, depends crucially on the chemical composition of the glass. In metallic glasses, a universal correlation appears to exist between the fracture energy and the ratio between shear and bulk moduli,  $\mu/B$ .<sup>[27]</sup> When  $\mu/B$  is low ( $<0.43$ ), a metallic glass is intrinsically ductile even though it exhibits no macroscopic plastic deformation. Plasticity is then confined to very localized shear bands where the strain can reach up to 100%. On the contrary, for high  $\mu/B$ , the material is intrinsically brittle and characteristic cleavage features are observed on the fracture surface. In this context, the classical understanding of glass fracture, including the existence of ideal brittleness based on a series of chemical bond rupture events<sup>[28]</sup> and the absence of plastic deformation, have been put into question and even refuted for metallic,<sup>[29,30]</sup> as well as, to some extent, oxide glasses.<sup>[31]</sup> In many aspects, this has been based primarily on the availability and applicability,





**Figure 4.** In situ view at the tip of a propagating crack ( $\approx 10^{-11} \text{ m s}^{-1}$ ) in silica glass as obtained by atomic force microscopy at relative humidity  $\approx 60\%$ ,  $22^\circ \text{C}$ .<sup>[33]</sup> The crack tip can be divided into three regions I: the continuous crack opening, II: a condensation zone, and III: a discontinuous zone.

respectively, of advanced in situ experimental (e.g., atomic force microscopy<sup>[31–33]</sup> and advanced electron microscopy<sup>[30,34]</sup>) and modeling techniques (see Section 7). Strong similarity was suggested for the fracture behavior of metallic and oxide glasses on the basis of the existence of nanoscopic ductility. In this scenario, fracture was proposed to occur in a sequence of nucleated structural cavitation processes, cavity growth, and final coalescence. A major difference in the behavior between metallic and covalent glasses was expected in the length scale of ductility.<sup>[31]</sup> This view, however, has subsequently been put into question<sup>[34,32]</sup> and the general picture of crack propagation (crack nucleation, thermal activation, dissipative effects, etc.) in glassy materials remains, at best, fuzzy.<sup>[35]</sup>

Subcritical defect formation and growth must be treated from both mechanical and chemical standpoints.<sup>[36,37]</sup> A propagating crack tip must then be understood as a highly confined (2–0 nm) chemical environment where various processes of capillary condensation and closing forces, chemical reactions, stress-induced diffusion, etc., take place in parallel (Figure 4).<sup>[33,38,39]</sup> Toughness thus results from the interplay between the surface and its environment (adsorption, chemisorption, solubility, tribology, and capillary effects), the material's volumetric (continuum) topology, and the presence of structural defects. Surface topology results from the intrinsic defect concentration at

the surface, geometric roughness, and atomic reactivity. Such properties largely depend on glass composition,<sup>[40]</sup> where the mobility of specific constituents may be strongly decoupled from the dynamics of the network. The latter may additionally result in the formation of fabrication- and composition-dependent chemical and physical depth gradients at the surface. Knowledge of all these factors is, up to now, scarce for both oxide and metallic glasses. On the other hand, such knowledge might provide another starting point for the development of defect-tolerant glasses.

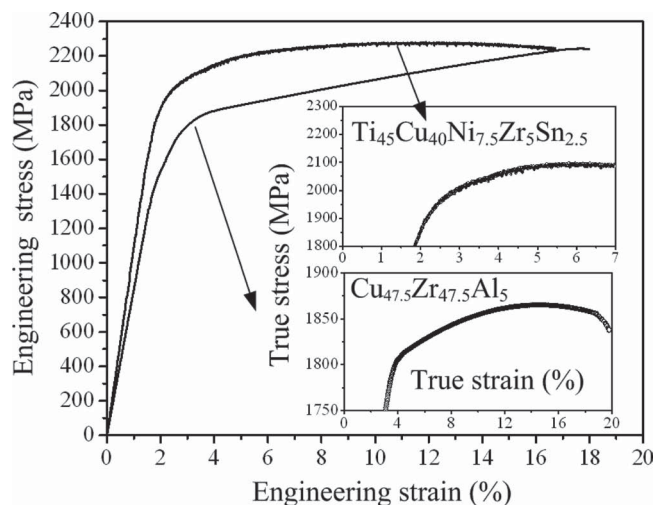
## 5. Metallic Glasses

Metallic glasses commonly exhibit elastic deformation of about 2% prior to yielding at strains that scale with temperature.<sup>[41]</sup> This is because they do not possess slip systems and lattice dislocations as seen in crystalline materials, and as a result, they can approach yield strengths that are well in excess of conventional structural materials. Cobalt-based glasses CoFeTaB<sup>[42]</sup> and CoFeTaBMo<sup>[43]</sup> achieve room-temperature compressive fracture strengths ( $\sigma_f$ ) of 5.2 and 5.5 GPa, respectively, which approach their theoretical strength. Many Fe-based bulk metallic glasses (BMGs) have  $\sigma_f \approx 4 \text{ GPa}$ <sup>[44]</sup>; Ni-based glasses have  $\sigma_f \approx 3 \text{ GPa}$ , and both Zr- and Cu-based glasses have  $\sigma_f \approx 2 \text{ GPa}$ . As noted previously, high hardness and fracture strengths have been correlated with Young's modulus<sup>[45]</sup> and other characteristic properties (e.g.,  $T_g$ ) of BMGs<sup>[46]</sup>. The correlation with  $T_g$  holds for the family of hardest BMGs. As  $T_g$  increases from near 700 K to over 900 K,  $\sigma_f$  increases from less than 2 GPa to over 5 GPa. The large range of elastic strain allows for large reversible mechanical energy storage. This property is made use of in various niche applications, including sports equipment, pressure gauges, and springs. However, when strained beyond the elastic range, most metallic glasses fail with little macroscopic plastic deformation.<sup>[47]</sup>

In the absence of crystallographic slip systems and dislocation-based options for flow, deformation in metallic glasses occurs in narrow shear bands initially only about 10 nm thick. A sharp drop in viscosity occurs in the deformation zones and facilitates additional flow in the existing shear bands, usually referred to as “shear-softening”, leading to further localization of plastic flow and shearing-off failure with no significant macroscopic plasticity. However, while most BMGs fail in this manner, some undergo surprisingly large amounts of plastic deformation in compression, bending, or under high levels of confining pressure. This phenomenon has been reported for Pt-, Cu-, Pd-, Ti-, Zr-based glassy alloys.<sup>[48–55]</sup>

Interestingly, when BMGs manifest room temperature plasticity, the flow behavior is “jerky” and stress–strain curves are serrated,<sup>[56]</sup> reminiscent of the solute-dislocation interactions responsible for the Portevin–Le Chatelier effect in crystalline materials, even in the absence of gliding dislocations. Each serration may correspond to the emission of a shear band that then ceases to operate (at least temporarily) despite the predicted shear softening.

Different explanations have been given for factors contributing to the intrinsic ductility of some bulk metallic glasses: i) large values of  $v_f$ ,<sup>[46,49,57,58]</sup> ii) nanocrystallization during



**Figure 5.** Room-temperature stress–strain curves for Cu- and Ti-based BMGs showing large plastic deformability. Inset: true stress–true strain curves showing a work hardening-like behavior. Adapted with permission.<sup>[53]</sup> Copyright 2007, Materials Research Society.

deformation,<sup>[47,59]</sup> iii) liquid phase separation,<sup>[51,59]</sup> iv) the presence of distinct short- or medium-range order,<sup>[49,60]</sup> and v) the development of “glassy martensite” in supercooled martensitic alloys.<sup>[61]</sup>

Hajlaoui et al.<sup>[48,59]</sup> reported nanocrystal growth in shear bands during compressive deformation of a ZrAlNiPd and CuZr BMGs. This feature was suggested to result from increasing excess free volume<sup>[62]</sup> and a high rise in local temperature that accompany the intense localized shear at large shear offsets. Temperature increases at or near shear bands have been measured using a variety of techniques.<sup>[63–64]</sup> These phenomena can lead to growth of nanocrystals, which then block propagation of shear bands and cracks.<sup>[48,59]</sup> An increase of the stress level is then necessary to propagate shear and could explain the work-hardening-like behavior in the stress–strain curves for Cu- or Ti- based structurally inhomogeneous BMGs (Figure 5).<sup>[50,53]</sup>

Altogether, understanding the role of atomic structure and structural and compositional fluctuations in the deformation behavior are key to designing tailored metallic glasses with desired ductility to improve mechanical performance.

## 6. Structural Constraints and Prediction of Mechanical Properties

Topological constraint theory, first introduced by Phillips<sup>[65]</sup> in 1979, provides a powerful tool for predicting the composition dependence of glass properties.<sup>[66]</sup> Originally focusing on the prediction of glass-forming regions, Phillips postulated that optimum glass-forming ability would occur when the number of bond constraints is equal to the number of atomic degrees of freedom.<sup>[65]</sup> Here, the number of constraints is determined by counting the total number of rigid two-body (radial) and three-body (angular) bonds. The atoms begin with three translational degrees of freedom, and the imposition of each independent constraint serves to remove one of these degrees of freedom.

If the number of constraints is less than the available degrees of freedom, then the network is underconstrained or flexible. Conversely, if the number of constraints is greater than the available degrees of freedom, the network becomes overconstrained or stressed rigid. Optimized glass-formers occur when the network is isostatic, i.e., when the number of constraints perfectly balances the number of degrees of freedom.<sup>[67]</sup>

The connection between network topology and the mechanical properties of glass is based on the notion of floppy modes, i.e., zero-frequency modes along which atomic rearrangements are allowed at very little cost in energy. These floppy modes vanish at the so-called rigidity percolation threshold, i.e., the composition at which the network first becomes isostatic. These concepts, introduced by Thorpe,<sup>[68–70]</sup> indicate that glasses should exhibit critical behavior of mechanical properties about the rigidity percolation threshold. This theory has been successful in explaining observed trends in mechanical properties for a wide variety of glass compositions.<sup>[66,71–73]</sup> For example, a recent study of the  $\text{As}_x\text{Se}_{1-x}$  system by Yang et al.<sup>[73]</sup> shows distinct extremum behavior of several mechanical properties about the topologically optimized composition ( $\text{As}_2\text{Se}_3$ ), including a minimum in Poisson's ratio and maxima in the density, Young's modulus, and the shear and bulk moduli.

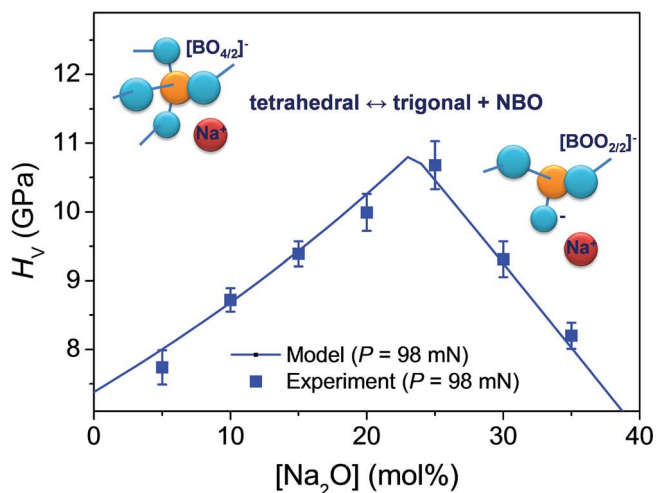
In addition to these bulk properties, the mechanical deformation behavior of glass under indentation can also be connected directly to the underlying network topology. Both experimental<sup>[74]</sup> and simulation<sup>[75]</sup> studies show that glasses display a maximum in elastic recovery around the rigidity percolation threshold. Also, cracking from Vickers indentation was found to be minimized around the topologically optimized compositions. These compositions also correspond to a maximum in indentation toughness and minimum in brittleness.<sup>[74]</sup>

Gupta and Mauro<sup>[76]</sup> have extended topological constraint theory to include the effects of temperature. As the temperature is lowered, floppy modes progressively vanish leading to an increasingly rigid glass network. Temperature-dependent constraint theory has proven especially useful for making quantitative predictions of glass properties, as demonstrated for both oxide and nonoxide systems.<sup>[66]</sup> For example, a predictive model for the composition dependence of glass hardness was introduced recently (Figure 6).<sup>[77]</sup>

## 7. Computational Simulation

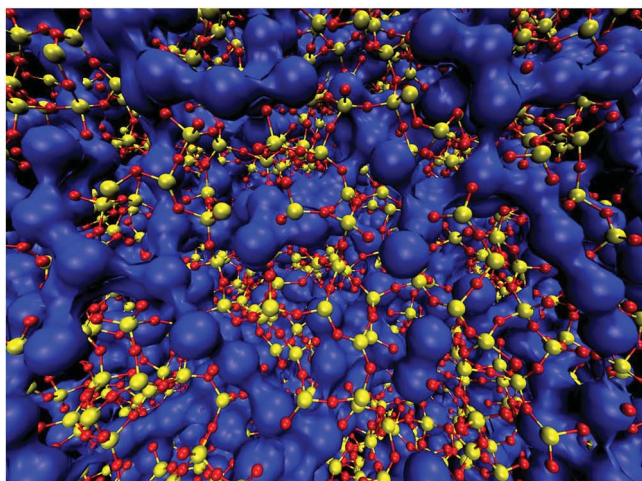
Computational simulations provide useful insights into the mechanical properties of glass-forming liquids on microscopic and mesoscopic scales. From particle-based simulation techniques, such as molecular dynamics (MD), detailed atomistic knowledge can be obtained on structure, transport, and relaxation processes for both simple and realistic models of metallic or oxide glasses. As an example, Figure 7 shows a snapshot from a MD simulation of sodium trisilicate that illustrates diffusion channels for the fast movement of  $\text{Na}^+$  through the quasi-frozen Si-O network.<sup>[78]</sup> It remains an open question how the presence of such channels (or other topological elements) and, in the specific case, the related dynamics of  $\text{Na}^+$  species affect and are affected by the material's response to an external mechanical load.





**Figure 6.** Predicted versus measured Vickers hardness ( $H_v$ ) for  $x\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot (89-x)\text{B}_2\text{O}_3 \cdot 1\text{Fe}_2\text{O}_3$  (mol%) glasses at a load ( $P$ ) of 98 mN. Hardness is plotted as a function of the concentration of  $\text{Na}_2\text{O}$  ( $x$ ). The solid line represents model predictions using temperature-dependent constraint theory. Adapted with permission.<sup>[77]</sup> Copyright 2010, American Physical Society.

The majority of recent MD simulation studies of glass-forming systems in external fields, including hard sphere models, models based on Lennard–Jones potentials, embedded atom models, and pair-potential models, address elastic and plastic properties under shear,<sup>[79–83]</sup> the occurrence of shear bands,<sup>[84,85]</sup> and the microscopic understanding of brittle and ductile fracture.<sup>[86–91]</sup> For example, multimillion-atom MD simulations have been performed to investigate nanoscale crack propagation.<sup>[88,90]</sup> However, most questions remain unanswered. Of particular importance may be the link between molecular-scale relaxation processes and macroscopic properties.



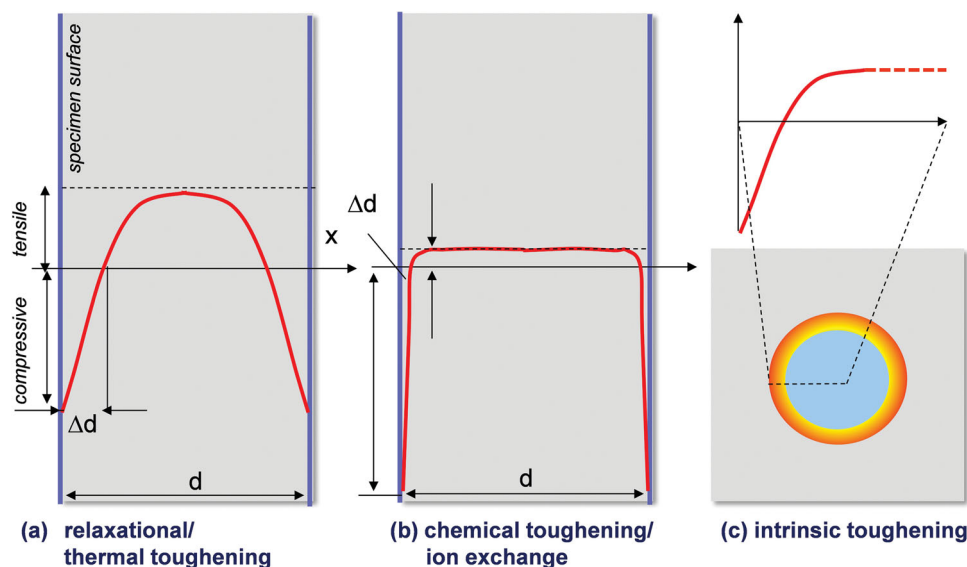
**Figure 7.** Molecular dynamics snapshot of the structure of sodium trisilicate at 2100 K at the density of  $2.2 \text{ g cm}^{-3}$ . The blue spheres that are connected to each other represent the Na atoms. The Si–O network is drawn by yellow (Si) and red (O) spheres that are connected to each other by covalent bonds shown as sticks between Si and O spheres. Reproduced with permission.<sup>[78]</sup> Copyright 2004, American Physical Society.

For some simple flow problems, classical hydrodynamics appear to apply down to the atomistic scale (see ref. [92]). This leads to the hope that large-scale MD simulations can fill the gap between atomistic and continuum considerations and, hence, clarify the range of validity of constitutive equations. Multiscale approaches can be established where MD simulations on atomistic and mesoscopic scales are directly coupled to finite element calculations in the continuum (see ref. [93–95]).

## 8. Toughening Strategies

Brittleness and, by definition, toughness depend crucially on the presence of defects. Research on less brittle glasses has focused on the incidence of flaws and on the possibility of reinforcement by appropriate surface treatments or intrinsic strain. It seems that most studies followed Griffith's original path where fracture mechanics account both for the critical flaw characteristics (an extrinsic parameter for the majority of technical glasses) and for the intrinsic resistance towards crack initiation. However, the critical load for flaw generation (contact load) as well as the flaw extension threshold (initiation of crack propagation) are essential parameters for a complete description of mechanical resistance. As noted previously, the divergence between theoretical strength (expected from the interatomic bond energy of the constituents) and experimental strength is usually ascribed to surface damage. Strategies for improving mechanical performance (particularly toughness) then focus on either overcoming this divergence or increasing the intrinsic resistance to defect propagation. They strongly differ between conventional oxide glasses and metallic glasses. Established concepts in oxide glasses typically aim at the generation of compressive layers close to the surface or at protecting the surface against contact damage. In large-scale applications, these techniques typically lead to bending strength values of up to  $\approx 0.5\text{--}1 \text{ GPa}$  in commercial alkali aluminosilicate glasses. On the contrary, metallic glasses are mostly toughened by compounding or the generation of microstructural heterogeneity. Generally, one may consider three basic strategies for improving the toughness and/or fracture energy of glasses, excluding dedicated reinforcement by compounding, surface finishing or polishing, strength screening, protective coatings, and self-healing strategies. These basic strategies are:

- 1) Thermal or relaxational toughening, where rapid quenching of a glass from above its glass transition temperature results in a permanent compressive stress field at the surface (Figure 8a). This stress field originates from a gradient in thermal history, and hence a gradient in internal strain. The thermal tempering process is widely employed for commercial flat glasses, especially solar glasses. Applied to metallic glasses, different (local) cooling conditions over the cross-section of bulk specimens can also create a variation in degree of relaxation and generate internal stress. However, unlike oxide glasses, this process has not yet been examined in detail with respect to the resulting variations in the mechanical properties of the surface.
- 2) Chemical (ion-exchange) toughening,<sup>[96]</sup> including the selective exchange of ions or atoms at the surface with geometrically larger species at temperatures below the glass transition, e.g., using salt baths, pastes, or implantation techniques. With



**Figure 8.** General principles for glass toughening by generation of residual stress at the material's surface (a,b) or bulk (c).

this approach, a compressive zone with a depth of up to several tens of micrometers is created at the surface of the glass (Figure 8b). Compression is a result of unrelaxed internal strain. While the underlying diffusion processes are often well characterized, the topological considerations that lead to stress formation and relaxation are not known in sufficient detail to allow the development of dedicated engineering tools. Chemical toughening by cation exchange is well-established for oxide glasses, but it remains an open field for metallic glasses, where surface modification by in-diffusion, even of trace elements, and hence modification of local packing density appears to be an interesting approach for the modification of surface mechanical properties. Also anion exchange may deserve more attention than it is given today because it provides a measure for creation of stressed surface layers and also significantly affects network topology and mechanochemical behavior (see ref. [97]).

- 3) Intrinsic toughening,<sup>[98]</sup> where internal stress is created on the basis of chemical or density fluctuations. Dedicated engineering of topological heterogeneity is presently considered as the most successful strategy for increasing the toughness and ductility of metallic glasses (see ref. [99–101]). With the exception of the development of tough and stiff glass ceramics,<sup>[102]</sup> this approach has long been neglected for oxide glasses. It was observed that composite microstructures containing crystalline (or non/crystalline) phases show better performance under mechanical stress than monolithic glasses.<sup>[103]</sup> Of special interest is the interdependence among preparation conditions, microstructural design by variation of composition, and the resulting mechanical properties. BMG composites can be prepared by different procedures, i.e., through mechanical alloying and consolidation,<sup>[104]</sup> solidification,<sup>[105,106]</sup> or partial devitrification of glassy precursors by either severe plastic deformation or high pressure torsion<sup>[107]</sup> or thermal treatment.<sup>[108,109]</sup> With respect to oxide glasses, only the latter approach is considered to be of particular interest.<sup>[102]</sup>

Deeper conceptual understanding of toughening strategies is required, including the further application and advancement of the general techniques outlined above and the development of entirely new strategies for improving mechanical properties. Open questions concern the role of molecular structure and network topology in resistance to contact damage and, consequently, dedicated engineering of these properties by varying bulk and surface chemical composition. As interesting examples, one may consider oxide glasses with mixed network formers or clustering in metallic glasses and its control by using micro-alloying techniques.

## 9. Conclusions and Outlook

Building a fundamental understanding of the universal physics governing glass strength, toughness, and fracture behavior is essential for developing the next generation of ultrastrong glassy materials. All glasses, regardless of chemistry, follow similar constitutive principles pertaining to their non-crystalline structure, packing density, and relaxation dynamics. They also share common features of structural and topological heterogeneity over short distances, while maintaining homogeneity over intermediate and longer distances. Together, these principles are believed to provide the microscopic origin of the mechanical properties of glass and its behavior under an applied stress. For example, Poisson's ratio is largely dependent on packing density while the character of chemical bonds, surprisingly, does not play a major role. Elastic properties and hardness may be approached on the basis of topological considerations. Plastic deformation and crack propagation may both be considered in terms of similar topological dynamics, with the latter being understood as the result of plasticity over a range of nano- and microscopic length scales. Despite these similarities, progress in different classes of glassy material, e.g., oxide and metallic glasses, has been made along very different directions. To

obtain maximum benefit for glassy materials in general, these distinct branches of knowledge and understanding should be transferred among these diverse classes of materials.

In addition to the structural and topological considerations of the glass itself, advanced toughening techniques can provide a significant enhancement of material damage resistance. Techniques such as thermal tempering, lamination, and ion-exchange strengthening are already effective means for improving damage resistance. However, the presence of overly high internal tension can lead to catastrophic failure if the glass becomes frangible. A combination of these methods, or alternative techniques based on intrinsic toughening, may offer significant advantage while avoiding frangibility, especially if coupled with appropriately optimized glass compositions. Building on the fundamental understanding of glass physics and the processing involved with various toughening techniques, our hope is that these optimized glass compositions can be designed to achieve the desired properties in the end product. Such tailor-designed glasses will open new markets and opportunities for glass products to address many of the urgent problems facing society today.

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