Amorphous and Nanostructured Chalcogenides



## **Topological Phases of Chalcogenide Glasses Encoded in the Melt Dynamics**

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Select Raman scattering and modulated differential scanning calorimetry (DSC) experiments on specially homogenized binary Ge<sub>x</sub>Se<sub>100-x</sub> and Ge<sub>x</sub>S<sub>100-x</sub> chalcogenide glasses, supported by ab initio MD simulations are undertaken. In both chalcogenides, the glasses exhibit a super-strong behavior (with a melt fragility index, m(x) < 20 in the 20(1)% < x < 26(1)% composition range, defining the fragility window, and with m(x) > 20 as one goes away from the fragility window. Remarkably, molecular dynamics (MD) simulations confirm the existence of the fragility window. Furthermore, in both chalcogenide glasses, the enthalpy of relaxation at  $T_g$ ,  $\Delta H_{nr}(x)$ , becomes minuscule ( $\approx$ 0) in the 20(1)% < x < 26(1)% range, defining the reversibility window, and with  $\Delta H_{nr}(x)$ increasing by an order magnitude abruptly with x outside that window. Thus, super-strong melts formed in the fragility window give rise to isostatically rigid glasses in the reversibility window and fragile melts formed at x < 20(1)% and at x > 26(1)% give rise to flexible- and stressed-rigid glasses, respectively. Melt dynamics for the examined glass systems unequivocally encode the nature of the glass topological phases.

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## 1. Introduction

In glass science, one has always wondered what is so special about those select melts that can bypass crystallization and be supercooled to form a glass at the transition temperature  $T_g$ ? Glass scientists have also been intrigued for some time on whether the manner in which viscosity,  $\eta(T)$ , of a glassy melt increases upon cooling to  $T_g$  has a bearing on the physical nature of the resulting glass formed. The key to both these fundamental issues of glass science have emerged directly and rather quantitatively from new developments in topological constraint theory. We address these issues in this work.

Topological constraint theory  $(TCT)^{[1-5]}$  evolved in 1979 with the basic premise that the glass forming tendency of a melt is optimized at a special connectivity usually described in terms of the mean coordination number,  $\langle r \rangle$ , equal to 2.40. Here

 $\langle r \rangle = \sum n_i \cdot r_i / N$ , where  $n_i$  is the number of atoms possessing a coordination number  $r_i$  and  $N = \sum n_i$  designates the total number of atoms comprising a network. Dangling ends  $(n_i = 1)$  were subsequently included in the theory later.<sup>[6]</sup> In this approach one reduces a complex disordered atomic network into simpler structural trusses, wherein nodes (atoms) are connected to each other by mechanical constraints (chemical bonds). As per Maxwell's stability criterion,<sup>[7,8]</sup> atomic networks are classified as belonging to either the flexible phase or stressed-rigid phase if the number of constraints per atom  $(n_c)$  is lower than or higher than the number of degrees of freedom, i.e., 3 in 3-dimensional networks (see Figure 1a). One can show that  $n_c$  directly scales with the connectivity, being equal to  $(5/2) \cdot \langle r \rangle - 3$ . The optimization<sup>[1]</sup> of the glass forming tendency then occurs when  $n_c = 3$  or  $\langle r \rangle = 2.40$  as schematically illustrated in Figure 1a. There is ample experimental evidence to support this basic premise of TCT in chalcogenides (Ge-Se, Ge-S) as we shall illustrate here.

A significant step forward in TCT emerged in 1998, when experiments on binary  $Si_xSe_{100-x}$  glasses revealed that the enthalpy of relaxation at  $T_g$ , viz.,  $\Delta H_{nr}(x)$  shows a square-well like window with walls near the composition  $x_c(1) = 20 \text{ mol.}\%$  of Si and  $x_c(2) = 26 \text{ mol.}\%$  of Si, with the enthalpy remaining minuscule in the intervening composition range 20% < x < 26% but increasing by nearly an order of magnitude outside that window. Such compositional windows within which  $T_g$  becomes thermally reversing, are also known as Thermally Reversing







**Figure 1.** a) Percolation of rigidity<sup>[4]</sup> in a flexible network ( $n_c < 3$ ) as its connectivity increases and  $n_c = 3$ , leading the glass forming tendency to optimize. With a further increase in  $n_c$ , the network becomes stressed-rigid ( $n_c > 3$ ). b) The opening of an isostatically rigid intermediate phase (IP) is observed<sup>[75]</sup> between the rigidity (x = 20%) and stress (x = 26%) transitions in binary Ge<sub>x</sub>Se<sub>100-x</sub> and Si<sub>x</sub>Se<sub>100-x</sub> glasses. In (b) one has an IP formed, which is rigid but stress-free phase, and with most unusual properties.

Windows. Such windows in  $\Delta H_{\rm nr}(x)$  have now been observed in close to 50 glass systems including chalcogenides and modified oxides. These windows are signatures<sup>[9–12]</sup> of the isostatically rigid ( $n_c = 3$ ) glassy networks also known as intermediate phases (IPs), to be distinguished from the flexible phase formed at  $x < x_c(1)$  and the stressed–rigid phase formed at  $x > x_c(2)$ . Schematically, the three generic topological phases of network glasses are illustrated in Figure 1b.The existence of IPs is a striking development in the field, since networks formed in this phase possess unique thermal,<sup>[13]</sup> optical, mechanical,<sup>[6,14–18]</sup> and electrical<sup>[19,20]</sup> properties, including nearly reversible glass transition,<sup>[9,10]</sup> weak aging,<sup>[17,21]</sup> minimum creep,<sup>[16–18]</sup> maximum fracture toughness,<sup>[22]</sup> among others. These unusual functionalities in the IPs have attracted widespread interest in applications<sup>[5]</sup> of glasses are encoded in their melt dynamics.

## 2. Extension of Topological Constraint Theory to Finite Temperatures and Melt Dynamics Using MD Simulations

Crucial new insights in glass science are now emerging from extending TCT to finite temperatures (T > 0).<sup>[23–28]</sup> In its original formulation, TCT evolved as a description of network glasses at T = 0 K. The extension of the theory to finite T opened, for the first time, the exciting possibility to correlate melt properties with glass topological phases. The computation of  $n_c$  through molecular dynamics (MD) simulations introduced by Bauchy and  $\mathsf{Micoulaut}^{[26,29,30]}$  and then subsequently developed for a variety of materials<sup>[31-35]</sup> has permitted directly enumerating constraints and extending its application to finite temperatures (wherein constraints can be active or thermally broken),<sup>[23,25,26,36]</sup> instead of relying on the 8-N bonding rule to estimate the constraints that is known to fail at elevated temperatures and pressures. These recent developments make it now possible to reveal the common "topological genome" of supercooled liquids and glasses and place TCT on a firm foundation by including MD simulations.

Thanks to their disordered atomic structure, glasses do not have to satisfy any stoichiometric requirements.<sup>[36]</sup> In

addition, glasses can accommodate virtually all the elements of the periodic table, provided that the melt is quenched fast enough.<sup>[37]</sup> Although these features open limitless design possibilities for glasses, they also come with some serious challenges.<sup>[38,39]</sup> Indeed, the infinite number of possible glass compositions renders largely inefficient traditional Edisonian approaches that seek to systematically investigate the parametric space. As an alternative route, in the spirit of the materials genome initiative,<sup>[40]</sup> recent efforts have focused on decoding the topological genome of glasses, that is, to identify and decipher how their basic "structural building blocks" control their properties (i.e., in the same way that the human genome offers information that serves as a blueprint for an individual's growth and development).<sup>[27]</sup> To this end, topological constraint theory<sup>[4]</sup> can efficiently and elegantly capture the topology of the glasses' structural building blocks while filtering less relevant structural details that do not significantly affect their properties.

In practice, one evaluates the number of topological constraints from the calculated radial and angular excursions between pairs or triplet of atoms, based from the MD atomic configurations at fixed composition, temperature, and pressure. This enumeration is directly inspired by the classical mechanics view of mechanical constraints associating large/small radial or angular motion with the absence/presence of corresponding bond-stretching (BS) and bond-bending (BB) restoring forces. In Ge–Se glasses, it has been shown that BS constraints can simply be enumerated from the coordination number  $r_i$  of atoms, <sup>[41]</sup> and according to initial theory, and this leads, indeed, to a contributions of  $r_i/2$  for the BS constraint, each bond/interaction being shared by two neighbors.

To derive angular (BB) constraints, the angular motion around each individual atom k (k = Ge, Se) defined by a set of two neighbors is analyzed. Over the time MD trajectory, the corresponding bond angle distribution  $P_k(\theta)$  allows defining a mean (the first moment of  $P_k(\theta)$ ) and a standard deviation  $\sigma_k$  (the second moment) that displays a bimodal distribution  $f(\sigma_k)$  for the various considered conditions. Atoms subject to a rigid bending interaction contribute to the part of  $f(\sigma_k)$  with low  $\sigma_k$  ( $\sigma_k < \sigma_{k,\min}$ ) and have a corresponding angle that acts as a rigid BB constraint, inducing network stiffening.<sup>[26]</sup> The threshold value  $\sigma_{k,\min}$  is fixed by  $f(\sigma_k)$  minimum. Averages over the whole simulation box



then lead to the mean number of constraints per atom,  $n_c$ , at a given thermodynamic condition.

The main advantage of this framework is to connect melt topology influenced by the number of rigid constraints from angles and bonds to the behavior of the melt dynamics as usually performed in MD simulations. The approach permits establishing relationships between, e.g., diffusivity, relaxation time with  $n_c$ .<sup>[42]</sup> More generally, this also permits to determine the rigidity status of densified liquids in a neat way<sup>[9,11,43]</sup> given the known difficulty to establish a functional dependence of coordination numbers and constraints with pressure.

### 3. Experimental Challenges to Probing Glass Topological Phases and Melt Dynamics

Chalcogenide glasses are composed of group IV (Si, Ge, Sn) and group V (P, As, Sb) elements alloyed with the group VI (S, Se, and Te) ones. They have been widely examined since their discovery in 1960s. In the past 7 years, the recognition has emerged that mere reaction of these components at 200-300 °C above the liquidus for even 48 h is insufficient time to ensure even small size batches to be homogeneous. In several recent publications we have discussed<sup>[44]</sup> the issue because of its strong bearing on the physics of the glassy state. In the Se-rich glasses formed in the 0 < x < 34% range of the  $Ge_x Se_{100-x}$ binary, even 2 gram sized batches when alloyed at 950 °C typically require at least 7 days to homogenize. This was demonstrated by recording the FT-Raman spectra taken ex situ as melts were alloyed at 950 °C in evacuated quartz tubing of 5 mm ID and periodically water quenched for examination in Raman scattering along the length of a melt column. The process of alloying was continued till melts completely homogenized. In Figure 2 we show results<sup>[45]</sup> obtained at x = 23%. Each panel includes a plot of nine spectra taken 2 mm apart along a melt column about 25 mm high. With increasing alloving time  $(t_r)$  and in particular, when  $t_r$  increases to 216 h (panel h), one found the scattering strengths of the trimodal vibrational modes observed (near  $200 \,\mathrm{cm}^{-1}$  due to corner-sharing mode,  $217 \,\mathrm{cm}^{-1}$  due to edgesharing mode, and near 250 cm<sup>-1</sup> due to polymeric Se<sub>n</sub> chain mode) to equalize, which is taken evidence of batch homogenization.

## 4. Molecular Origin of Delayed Melt Homogenization in Chalcogenides

By analyzing the Raman lineshapes acquired<sup>[44,45]</sup> in the 24 h  $< t_r < 219$  h alloying time-period (Figure 2), we could deduce the local stoichiometry "x" of Ge<sub>x</sub>Se<sub>100-x</sub> melts/glasses at the nine locations where the spectra of the melt column were probed and then obtain the variance in x for the batch. These results on glass stoichiometry are summarized in **Figure 3**, and provide crucial insights into how these melts actually homogenize. After 1 day of reaction, as revealed by the red data points in the plot, the Ge stoichiometry varied from approximately Ge<sub>17</sub>Se<sub>83</sub> at the top location "9" to nearly Ge<sub>27</sub>Se<sub>73</sub> at the lowest location "1" of the melt column. And after 216 h the green square data points show the melt column to be completely homogenized, and to have the





**Figure 2.** FT-Raman profiling spectra of a Ge<sub>23</sub>Se<sub>77</sub> melt column taken ex situ after water quenching, as the starting elements (Ge, Se) are alloyed in an evacuated quartz tube at 950 °C for the indicated reaction time ( $t_r$ ) in hours in a vertical configuration. Each panel has a superposition of nine spectra taken 2 mm apart along melt column about 25 mm high. The variation in the scattering strength of the observed trimodal vibrational modes is found to steadily lower and vanish as  $t_r$  increases to 216 h (panel h) when the 2 gram batch completely homogenized. See Figure 3 for analysis of spectra.<sup>[45]</sup>

weighed stoichiometry corresponding to the composition x = 23%. In the intervening alloying times  $t_p$  the Ge(Se) atomic scale diffusion respectively up (down) the melt column slows down qualitatively when the melt composition reaches the blue panel in the 21.5% < x < 23.0% range of Ge. In this range of composition, the measured fragility index (*m*) of these specially homogenized melts show a rather low value of m = 15. The super-strong character of glassy melts in this range of stoichiometry gives signature of the least diffusing species. The kinetics of homogenization at all *x* in Ge<sub>x</sub>Se<sub>100-x</sub> melts in the 0 < x < 33.33% range will be controlled by the least diffusing species near x = 23% of Ge, and will result in delayed homogenization as demonstrated by us.<sup>[44]</sup>

It is useful to inquire what is meant by homogeneity of a melt/ glass in the context of a topologically disordered network. A perusal of the inset of Figure 3 reveals that the global stoichiometry variance across the batch of the Ge<sub>23</sub>Se<sub>77</sub> melt column after alloying for  $t_r$  = 48, 120, and 216 h are found to be near 3.25, 1.0, and less than 0.25%, respectively. Clearly melt compositions in the blue region of Figure 3 play an important role in arresting homogenization. The "rigidity" and "stress"







**Figure 3.** The results of Raman spectral lineshape (Figure 2) analysis is shown. The plot displays the variation in the local glass stoichiometry "*x*" as a function of the height "*h*" in the quartz tube, with h = 9, the top most, and h = 1, the lowest position in the column. After  $t_r = 24$  h, the red data points (**●**) show the glass stoichiometry to change from about x = 17% at h = 9 to x = 27% at h = 1. At  $t_r = 216$  h, the green square data set (**■**) shows the glass stoichiometry to be x = 23% at all h, as expected, once the batch composition completely homogenized. The blue panel delineates the composition in x where in melts become super-strong, leading to a drastic lowering the atomic-scale diffusion of Ge up and Se down the melt column. See text for details.

elastic phase transitions are widely believed to be percolative in nature<sup>[46]</sup> and are intrinsically sharp. The compositional sharpness of these transitions observed in experiments serves as a crucial "measure" of melt/glass homogeneity. For the specially homogenized binary  $Ge_x Se_{100-x}$  glasses that were reported recently,<sup>[44]</sup> the two elastic phase transitions defined by the reversibility window are found to be abrupt with a width less than  $\frac{1}{2}$ % in x consistent with the homogeneity deduced from the FT-Raman profiling experiments described above. Our previous attempts to observe the reversibility window in the Ge-Se binary resulted in a nearly triangular window<sup>[47]</sup> and then a Gaussianshaped one<sup>[21]</sup> as the alloying period at 950 °C for the 2 gram batches in each case was increased from 2 to 4 days. The triangular window in the experiments of Feng et al.<sup>[47]</sup> is a direct consequence of the 3% variance in the Ge stoichiometry variation of melts alloyed for 48 h as discussed elsewhere.<sup>[44]</sup> Thus, melt stoichiometry variation across a batch composition which steadily narrows by prolonged alloying, leads to the sharpening of the reversibility window edges, underscoring in no uncertain terms that a square-well like window is a crucial test of homogeneous melt/glassy samples.

## 5. Fragility Index of $Ge_xSe_{100-x}$ Melts

When a liquid is quenched at a cooling rate that is high enough, the rapid increase in viscosity ( $\eta$ ) of a melt upon decreasing temperature (*T*) can prevent its crystallization.<sup>[48]</sup> At the glass transition temperature ( $T_g$ ), the relaxation time of the melt starts to exceed the observation time, so that the atomic network undergoes a structural arrest and freezes into a glass.<sup>[36]</sup> The

temperature dependence of the viscosity around  $T_g$  can be captured by the fragility index (*m*), which is a dimensionless parameter that describes the rate of the viscous slowdown undergone by a melt in the vicinity of the glass transition  $m = [d \log(\eta)/d(T_g/T)]_{T=T_R}$ .

The fragility index "*m*" gives the slope of the  $\eta(T)$  plot in **Figure 4** as *T* approaches  $T_{g}$ . Melts with high or low *m* values are referred to as fragile or strong, respectively.<sup>[48,49]</sup> When *m* approaches its theoretical minimum value (m < 20), melts are viewed as superstrong (e.g., SiO<sub>2</sub> or GeO<sub>2</sub>)<sup>[45,51]</sup> and their viscosity exhibit an Arrhenius-like behavior (see Figure 4).

#### 5.1. Melt Fragility Index from Modulated DSC

In a series of publications, Carpentier et al.<sup>[52,53]</sup> have shown how modulated-DSC (MDSC) can be used to extract the fragility index of glass forming melts. Such calorimetric fragility measurements have been found to match those usually determined from dielectric relaxation. Close analogies have been drawn between dielectric relaxation and specific heat spectroscopy. For many glass formers the susceptibility relaxation time examined as a function of decreasing T smoothly extrapolates to the specific heat relaxation time accessed from MDSC, thus providing some confidence in the deduced fragility index. In specific heat spectroscopy one examines the glass transition event in a cooling mode starting from slightly above  $T_{\rm g}$  at a low scan rate of  $0.5\ ^\circ C \min^{-1}$  and analyzes the glass transition exotherm in terms of the complex  $C_p$ , with the real part,  $C_p^{re}$ , representing the inphase component of the heat flow showing a step-like feature and the imaginary part,  $C_p^{\text{im}}$ , representing the out-of-phase component of the heat flow showing a Gaussian-like peak. Furthermore, MDSC scans are undertaken as a function of modulation frequency ( $\omega_{\rm m}$ ), and one finds the peak of  $C_{\rm p}^{\rm im}$  to systematically shift to higher T as the modulation frequency is increased. At the peak location of  $C_p^{\text{im}}$ , the enthalpic relaxation time ( $\tau$ ) of a glass network tracks the impressed *T*-modulation, i.e.,  $\omega_{\rm m} \cdot \tau = 1$ . By establishing the temperature (T) where the peak in  $C_{\rm p}^{\rm im}$  occurs, one deduces how  $\tau$  varies as a function of Tas the modulation frequency  $\omega_{\rm m}$  is altered. By plotting log  $\tau$ against 1/T, one deduces the activation energy ( $E_A$ ) for enthalpy



Figure 4. Schematic  $T_{g}$ -scaled plot of viscosity, illustrating Angell's strong/fragile classification.<sup>[50]</sup>





relaxation, and the fragility index is obtained by knowing  $T_g$  using the relation  $E_A = m \cdot T_g \cdot \ln(10)$ .

The fragility index (m(x)) results on the specially homogenized  $Ge_xSe_{100-x}$  glass compositions in the 10% < x < 33.3%range were examined using MDSC. In Figure 5 we reproduce<sup>[45]</sup> the fragility index variation, m(x), of these melts. There are two noteworthy features of these m(x) trends (Figure 5): i) in the 20% < x < 26% composition range, the shaded light blue range, the reversibility window, the fragility index acquires values less than 20. We define this blue range of compositions (Figure 5) where m < 20, the fragility window. ii) Furthermore, at a select composition near 22% of Ge, one finds the fragility index shows a rather low value of about 15, i.e., melts become super-strong. The composition range near 22% of Ge is shown in Figure 3 as the blue panel. Melts in this blue composition range possess the highest viscosity at elevated temperatures than any other composition in the  $Ge_x Se_{100-x}$  binary. Thus, one can begin to understand why melts in the 21.5% < x < 23% range of Ge possess the lowest Ge and Se atomic diffusivity or mobility at elevated temperatures. It was not until the ab initio MD simulations of the compositional dependence of melt viscosity came to the fore that one could understand the deep consequences of the present observation, as we discuss in Section 5.2.

There is evidence to suggest that the magnitude of the melt fragility index deduced from the complex  $C_p$  analysis is tied to homogeneity of melts. Specifically, heterogeneous melts promote while homogeneous ones lower the fragility index.<sup>[54]</sup> In specially homogenized As<sub>x</sub>Se<sub>100-x</sub> glassy melts trends in m(x) in the composition range 15 < x < 40% are found to be systematically lower by about 15 units<sup>[54]</sup> than those reported in another study<sup>[55]</sup> of unknown homogeneity, both measurements using the complex  $C_p$  method using MDSC.<sup>[54,55]</sup>

We have also examined the fragility index of the homogenized Ge–Se melts using the Moynihan approach.<sup>[51,56]</sup> In this



**Figure 5.** Fragility index of the specially homogenized Ge<sub>x</sub>Se<sub>100-x</sub> melts reported by Gunasekera et al.<sup>[45]</sup> (•) compared to previous reports of viscosity derived fragility index by Stolen et al.<sup>[76]</sup> (•) and by Senapati and Varshneya<sup>[77]</sup> (•). The global minimum in "*m*" observed presently is consistent with the work of Stolen et al., although the absolute value are different. The strong character of SiO<sub>2</sub> glass with *m* = 20 is delineated with the broken line. Melt compositions in the 20% < *x* < 26% range show *m* < 20, giving evidence of a fragility window.

approach one examines the scan rate (q = dT/dt) dependence of  $T_{\rm g}$  in a DSC experiment. And using the  $T_{\rm g}$  onset value from the DSC scans, one finds, in general, that the expected linear correlation of log q versus  $1/T_{\rm g}$  occurs over a narrow scan rate region, and is not clearly defined in these homogeneous melts. From the available data, the fragility index is found to be about 10 units greater for the IP range compositions, and almost 20–40 units greater outside the IP than those deduced from the complex  $C_{\rm p}$  analysis. This is an issue of continued investigations.

#### 5.2. Melt Viscosity from MD Simulations in Chalcogenides

It is useful to inquire how the obtained experimental results on fragility index compare with calculated properties in the liquid state. In **Figure 6**, we represent a compilation of numerical results obtained from the accumulated atomic trajectories<sup>[42]</sup> using first principles molecular dynamics simulations (for methodology, see Ref. <sup>[41]</sup>). It is important to emphasize that the obtained structural models have been validated from neutron scattering experiments. Specifically, these lead to reproducing to an unprecedented level of accuracy the pair correlation functions and structure factors from neutron diffraction experiments performed at various compositions and temperatures.

Figure 6a shows the behavior of the Ge diffusivity  $D_{Ge}$  as a function of Ge content in the liquid (1050 K).  $D_{Ge}$  is accessed from the calculated mean-square displacement  $\langle r_i^2(t) \rangle$  in the long-time limit using the Einstein relation  $D = \langle r_i^2(t) \rangle / 6t$ . One obtains a global decrease of the diffusivity with increasing Ge content, consistent with the stiffening of the network structure that progressively hinders atomic motion. However, in the IP range of compositions  $D_{Ge}$  displays an even more striking decrease, about a factor 2-3 more than what would be expected if a smooth decrease of  $D_{Ge}$  were to be considered. As a result, assuming a Stokes-Einstein relationship for the liquid (valid at the considered high temperature of 1050 K), one expects the viscosity to display an enhanced minimum in the same interval of composition. The anomalous decrease of  $D_{Ge}$  is compatible with the large increase in the calculated relaxation time (right axis in Figure 6a) obtained from an intermediate scattering function  $^{\left[ 42\right] }$  that displays a maximum in the IP region near x = 22% of Ge. This also shows that the viscosity  $(\eta = G_{\infty} \cdot \tau)$ must also display a maximum near 22% of Ge of about three times larger than outside the IP window.

The striking anomaly near 22% of Ge can be linked with the evolution of topological constraints determined from the MD simulations. Such numerical constraint counting algorithms are applied and represented as a function of Ge content in Figure 6b. Here it is seen that at 300 K,  $n_c$  follows exactly the mean-field estimate  $n_c = 2 + 5x$  (broken line), leading to an isostatic condition ( $n_c = 3$ ) at  $\approx 20\%$  Ge that agrees with the experimentally measured threshold value. More importantly, when such constraints are investigated in the liquid (Figure 6b, red curve), a reduction of  $n_c(T)$  is acknowledged, due to the softening of the rigid interactions from thermal activation, as also proposed from empirical models using temperature-dependent topological constraints.<sup>[57,58]</sup> However, for IP compositions, changes are small and for the 22% composition, the calculated  $n_c(x,T)$ 







**Figure 6.** a) Calculated diffusion constant  $D_{Ge}$  as a function of Ge content in Ge–Se melts (1050 K). The right axis represents the calculated relaxation time  $\tau_{\alpha}$  at the same temperature. b) Calculated total constraint density ( $n_c$ ) at ambient temperature (300 K) and in the liquid state (1050 K). The broken line corresponds to the mean-field Maxwell estimate,  $n_c = 2 + 5x$ . c) Ge bond-bending density  $n_c^{BB}$  (black symbols) as a function of Ge content in Ge–Se melts (1050 K). The right axis represents the variance  $\sigma_{nc}$  of the constraints and provides a measure of constraint heterogeneity in the liquid.

displays a minimum change with temperature in the 20–22% Ge range. Note that the obtained change in  $n_c$  in the liquid compared to the glass is a minimum near 22% of Ge. This is a robust result from MD simulations.<sup>[42]</sup> The details of the analysis (Figure 6c) indicates that this minimum change is essentially driven by a reduced softening of Ge bond-bending interactions and for 22% Ge, these are, indeed found to be nearly equal to their expected low-temperature value ( $n_c^{BB} = 5$ ). Recently, it has been shown<sup>[9,59]</sup> that such angular constraints were responsible for dynamic anomalies in the liquid phase. The present results appear, therefore, to be in line with such a generic behavior.

As a consequence, one acknowledges the crucial role played by rigidity in the anomalous relaxation dynamics of Figure 6a that helps to clarify the unexpected delayed homogenization manifested for IP compositions driven by the fragility index minimum (Figure 5). In fact, within temperature-dependent rigidity theory,<sup>[23]</sup> the fragility index m has been found to be directly related to the number of topological degrees of freedom  $f = 3 - n_c$ via the equation  $m = m_0[1 + (d \ln(f)/d \ln(T))_{T=Tg}]$ , which depends only on the scaling of f(x,T) with temperature. The validity and predictive power of this equation has been checked on a certain number of glasses such as Ge-Se, alkali-borates or -phosphates. The minimal variation of our obtained  $n_c(T)$  thus leads to a minimum in fragility. In addition, the same analysis can be performed over the entire simulation box to yield the spatial variation of constraints that can be quantified by the variance  $\sigma_{nc}$  as a function of Ge content (Figure 6c, right axis). It appears that the IP compositions also display a homogeneous distribution of topological constraints, and this feature is obviously linked to the weak variation of  $n_c$  with temperature.

Finally, for the composition at 22% of Ge, constraints are nearly homogeneously distributed and this reduces the role of possible fluctuations. Homogeneity of stress (i.e., interactions or constraints) will not only induce a cascade of dynamic anomalies as detected from the diffusivity minima (Figure 6a) and viscosity/relaxation time maxima (Figure 6a, right axis) but also represents a more stable state at the nanoscale. And it is most rewarding to note that the global minimum in fragility index measurements<sup>[45]</sup> (Figure 5) near x = 22% of Ge, is directly confirmed by the present MD simulations which show a global minimum in the diffusivity of these binary Ge–Se liquids at the same composition.

# 6. Enthalpy of Relaxation in Chalcogenide Glasses

In glass science one has traditionally established  $T_g$  and  $\Delta H$ , the enthalpy of relaxation at  $T_g$  using DSC over the past 5 decades. With the introduction of the AC analogue of DSC, viz. MDSC, several advantages in probing the glass transition endotherm over traditional DSC have come to the fore. We have already noted how melt fragility index could be deduced using MDSC in Section 5.1. Here we show that when the glass transition endotherm is analyzed in terms of the reversing and nonreversing heat flow one obtains the  $T_{\rm g}$  and  $\Delta H_{\rm nr}$  rather uniquely. In MDSC one programs a sinusoidal T-modulation on the linear T-ramp, and deconvolutes the endothermic heat flow at  $T_{\rm g}$  into a component that tracks the sinusoidal T-modulation and the remainder signal that does not. The former heat flow signal is called the reversing heat flow, and it displays a rounded step while the remainder signal as the nonreversing heat flow displays a Gaussian-like profile as illustrated in Figure 7, which shows an actual scan of the stoichiometric GeSe2 glass. In MDSC, one obtains the modulated heat flow signal, and analyzes it using the full power of phase-sensitive lock-in detection to deduce the reversing and non-reversing heat flow signals. An important consequence is that the signals are independent of the scan rate used. In fact, this feature of MDSC has the important







**Figure 7.** MDSC scan of stoichiometric GeSe<sub>2</sub> glass taken at 3 °C min<sup>-1</sup> scan rate, 1 °C modulation amplitude, and 100 s modulation time period from Ref. [44]. The total, reversing, and non-reversing heat flow signals observed in the heating cycle, and the non-reversing heat flow signal in the cooling cycle are labeled. The modulation frequency corrected non-reversing heat flow,  $\Delta H_{nr}$  is found to be 0.50(3) cal g<sup>-1</sup>.

consequence that one uses rather low scan rates (1/3– $3^{\circ}C \min^{-1}$ ) with no loss in signal, thus permitting one to completely eliminate the kinetic effects that dominate the high scan rates ( $10^{\circ}C \min^{-1}$  or greater) used in DSC. In MDSC, the  $T_{\rm g}$  and  $\Delta C_{\rm p}$  are deduced respectively from the inflexion point and the step height of the reversing heat flow step. While the

enthalpy of relaxation at  $T_{g}$ , viz.,  $\Delta H_{nr}$  is obtained by integrating the area of the Gaussian-like non-reversing heat flow signal as illustrated in Figure 7. Such measurements are usually taken starting from about 50 °C below  $T_g$  and heating to go past  $T_g$ , then followed by a cooling cycle at a fixed modulation frequency, typically,  $\omega_{\rm m} = 2\pi/t_{\rm m} = 6.28 \times 10^{-2}$  radians/s corresponding to a modulation time period  $t_m = 100$  s. An MDSC scan of g-GeSe<sub>2</sub>, shown in Figure 7, displays the total, reversing, and non-reversing heat flow signals in the heating cycle, and only the non-reversing heat flow signal in the cooling cycle. The  $T_g$  deduced is 429.6(5) °C, and the modulation frequency independent non-reversing enthalpy of relaxation,  $\Delta H_{nr}$  at 0.50 (3) cal g<sup>-1</sup>. The observed variation in  $T_g(x)$  (Figure 8a) and the enthalpy of relaxation,  $\Delta H_{nr}(x)$  (Figure 8b) for the specially homogenized  $Ge_xSe_{100-x}$  glass compositions<sup>[44]</sup> appears in Figure 8. In the reversibility window, the configurational entropy of the glass remains high, i.e., liquid like, a feature that apparently finds theoretical support in the work of Yan.<sup>[60]</sup> The  $T_{\alpha}(x)$  increases monotonically with the network connectivity up to x = 33.33% as widely recognized.<sup>[61]</sup> However, the slope  $dT_g/$ dx shows a maximum near  $x = x_c(3) = 31.5\%$ , which is signature that at  $x > x_c(3)$ , some of the Ge now decouples from the network backbone as a Ge-rich (ethane-like Ge<sub>2</sub>Se<sub>6</sub> units) nanophase. The vanishing of the slope near x = 33.3%, the stoichiometric glass, is then in harmony with the  $T_{g}$ acquiring a maximum (not shown in Figure 8). At  $x > x_c(3)$ , the loss in backbone structure due to the decoupling of Ge-rich nanophase leads to a maximum in  $\Delta H_{nr}(x)$  as can be seen in Figure 8b. Furthermore, in Raman scattering, at  $x > x_c(3)$ , one observes the first evidence of homopolar Ge-Ge and Se-Se



**Figure 8.** Trends in (a)  $T_g(x)$  ( $\bigtriangledown$ ) and (b) non-reversing enthalpy  $\Delta H_{nr}(x)$  ( $\bigtriangledown$ ) for the 13 specially homogenized  $Ge_x Se_{100-x}$  glasses taken from Ref. [44] showing the rigidity ( $x_c(1)$ ), stress ( $x_c(2)$ ), and the nanoscale phase transition  $x_c(3)$ . These are compared to previous work of Feng et al.<sup>[47]</sup> ( $\circ$ ,  $\diamond$ ). The slope in  $dT_g/dx$  in panel (a), right scale, from the  $T_g(x)$  results of Bhosle et al.<sup>[44]</sup> show a maximum at the NSPS transition  $x_c(3) = 31.5\%$ . The loss in backbone structure at  $x > x_c(3)$  due to ethane-like  $Ge_2Se_6$  local structures segregating, as expected, leads to a maximum in  $\Delta H_{nr}(x)$  at the onset of the NSPS transition. In (b), the labels F, A<sub>1</sub>, and A<sub>2</sub> represent  $\Delta H_{nr}(x)$  values in fresh glasses ( $\bigtriangledown$ ), glasses aged at room temperature ( $\circ$ ), and aged at 240 °C ( $\square$ , c) Trends in  $T_g(x)$  on Ge–Se glasses from Zeidler et al.<sup>[62]</sup> ( $\blacksquare$ ) compared to those of Bhosle et al.<sup>[44]</sup> ( $\heartsuit$ ). d) Enthalpy of relaxation  $\Delta H_{nr}(x)$  reported by Zeidler et al.<sup>[62]</sup> ( $\blacksquare$ ) compared to those of Bhosle et al.<sup>[44]</sup> ( $\circ$ ).





bonds in the glasses to form and steadily grow in scattering strength as discussed earlier by Bhosle et al.  $^{\left[ 44\right] }$ 

But the most spectacular feature is the observation of a thermally reversing window in the homogeneous  $Ge_xSe_{100-x}$ glasses that onsets near  $x_c(1) = 19.5\%$ , the rigidity transition, and ends near  $x = x_c(2) = 26.0\%$ , the stress transition (Figure 8b). Note the abrupt nature of the rigidity transition in fresh glasses obtained after rejuvenating glass samples by a thermal cycling through  $T_{g}$ . Such was not the case in samples of Feng et al.,<sup>[47]</sup> most likely because of incomplete homogenization as we recognized earlier.<sup>[44]</sup> Upon aging the glasses at room temperature (A<sub>1</sub> data set, red circles in Figure 8b), the  $\Delta H_{nr}(x)$  term increases measurably in the flexible phase but less so in the stressed-rigid phase. This is due to the significantly higher  $T_{q}$ values of the stressed-rigid glasses (Figure 8a), thus reducing the kinetics of aging that are determined by the  $T_{\rm o}/T_{\rm g}$  fraction, where  $T_{\rm o}$  is the temperature at which aging was performed. Upon aging the glasses at  $T_{\rm o} = 240 \,^{\circ}\text{C}$  (A<sub>2</sub> data set, pink squares in Figure 8b), note that  $\Delta H_{nr}(x)$  term increases substantially near stress transition driving the transition near x = 26.0% to become abrupt. Glass samples in the composition range 30.0% < x < 32.0% when annealed at 240 °C partially crystallize with the metastable low-T Ge<sub>4</sub>Se<sub>9</sub> crystalline phase nucleated.<sup>[44]</sup> This is expected given that the phase has a stoichiometry of x = 4/11 or 30.96%.

There is a subtle observation that emerges from perusing the data of Figure 8. If one compares and contrasts the  $T_{\rm g}(x)$  and  $\Delta H_{\rm nr}(x)$  trends of Feng et al.<sup>[47]</sup> with those of Bhosle et al.,<sup>[44]</sup> one finds that although the  $T_{\rm g}(x)$  trends are virtually identical between the two sets of data, such is not the case for the trends in  $\Delta H_{\rm nr}(x)$ . While Bhosle et al. observe a square-well like thermally reversing window, Feng's result point to a triangular window whose centroid is shifted to lower *x*. We are thus led to believe that  $\Delta H_{\rm nr}$  trends are far more diagnostic of glass homogeneity than  $T_{\rm g}(x)$  trends. Here it would be useful to recall that although the batch sizes of melts (2 grams) and the alloying temperature (950 °C) used by Feng et al.<sup>[47]</sup> and Bhosle et al.<sup>[44]</sup> were the same, the alloying time was 2 days for the samples of Feng et al., while it varied in the range from 7 to 9 days for the samples of Bhosle et al. These alloying times were determined from FT-Raman profiling experiments, as illustrated earlier (Figure 2).<sup>[44,45]</sup>

Zeidler et al.<sup>[62]</sup> have recently reported on calorimetric and neutron scattering results on  $\text{Ge}_x\text{Se}_{100-x}$  glasses. The  $T_g(x)$  and  $\Delta H_{\rm nr}(x)$  trends of their samples acquired by MDSC (Figure 8c and d) are compared to those of Bhosle et al.<sup>[44]</sup> and Feng et al.<sup>[47]</sup> An examination of the results of Zeidler et al. shows that these results bear close similarities to those of Feng et al.<sup>[47]</sup> The  $T_g(x)$  trends reported Feng et al., Bhosle et al., and Zeidler et al. are remarkably similar, reflecting that the global connectivity of the glasses is quite similar. However, trends in  $\Delta H_{\rm nr}(x)$ , which are triangular-like for glasses of Feng et al. and for those of Zeidler et al., stand in sharp contrast to the square well-like variation for glasses of Bhosle et al. The triangular nature of  $\Delta H_{nr}(x)$  is suggestive that the variance of Ge stoichiometry across the batch are close to 3% as noted earlier.<sup>[44]</sup> The extended range molecular structure of these glasses, clearly does not emerge till the variance in Ge stoichiometry across the batch is less than "x" < 1/2% as the IP evolves with sharp stress and rigidity transitions (Figure 8). For the 3.6 gram batch size used by Zeidler et al.,<sup>[62]</sup> that are nearly 1.8 times greater in weight than the ones used by Feng et al. (2 gram) and Bhosle et al. (2 gram), alloying for 47 h at 975 °C in the same sized (5 mm ID) quarts tube would appear to be clearly insufficient time for melts to homogenize. The alloying time to achieve complete homogenization, we would estimate would be closer to 12 days, given that it took Bhosle et al. typically 7–9 days to homogenize 2 gram sized batch as determined from Raman profiling experiments (Figure 2). These findings of Zeidler et al.<sup>[62]</sup> confirm, in our view, that melt viscosity of compositions in the IP are rather high and serve as a barrier to atomic scale diffusion. It is also for this reason, in our view, that the reported molar volumes of their glasses are lower than those of Bhosle et al.<sup>[44]</sup>

The discrete nature of the reversibility window due to the percolative nature of the rigidity and stress transition within the topological constraint theory apparently evolves into a more continuous one<sup>[63]</sup> in the Jamming approach<sup>[64]</sup> to glasses.

## 7. Correlating Melt Dynamics with Glass Topological Phases in Chalcogenides

With the results of melt dynamics from the fragility index (Figure 5) and glass topological phases from the enthalpy of relaxation (Figure 8), we are now in a position to directly compare the view above  $T_g$  with the one below it. In **Figure 9**, we summarize results for both the Ge–Se and Ge–S binary systems. The results on Ge–S glasses are taken from the recent work of Chakraborty and Boolchand<sup>[65]</sup> where again a special effort was made to homogenize melts using FT-Raman profiling method. Our experience with Ge–S melts showed that these required an alloying time of about 21 days to completely homogenize, almost thrice as long as the time needed to homogenize Ge–Se melts.

One is tempted to compare results on the  $Ge_xSe_{100-x}$  binary with its sulfide counterpart, since topologically both these binary chalcogenides are equivalent; both Se and S take on a twofold while Ge a fourfold coordination in harmony to the 8-N bonding rule, at least in the chalcogen-rich regime (x < 33.3 mol.% of Ge) where glass formation proliferates. The results of Figure 9, indeed, also reveal that the view across  $T_{\rm g}$  has striking parallels. In both systems, the IP occurs in nearly the same Ge concentration range of 20% < x < 26%. The fragility window (m < 20) in both cases, again spans nearly the same Ge concentration range as the reversibility widow. In the Ge-Se binary there is a global minimum of the fragility index near 22-23% range, the meaning of which has emerged from recent MD simulations as we comment earlier.<sup>[42]</sup> In the Ge-S binary the global minimum in the fragility index occurs near 25% of Ge. The sulfide melts differ from the selenide melts in one respect; when these are quenched to room temperature, selenium-based polymeric chains largely persist in the glass, but in the case of sulfide glasses a substantial fraction of sulfur polymeric chains transform into S<sub>8</sub> rings particularly at x < 20% of Ge. These rings decouple from the Ge-S backbone upon room temperature aging (from a waiting time of 2-6 weeks) as revealed in Raman scattering,<sup>[65]</sup> which is independently confirmed by the enthalpy of relaxation  $\Delta H_{nr}(x)$  plot of Figure 9f. The reduction in  $\Delta H_{nr}(x)$ at x = 18% shown by the green arrow (Figure 9f) is due to some







**Figure 9.** The left panels give results on Ge–Se binary: (a) the expected melt viscosity at 950 °C based on measured fragility index using the MYEGA relation, (b) measured fragility index (m), and (c) measured enthalpy of relaxation. The right panels give results on Ge–S binary: (d) the expected melt viscosity at 950 °C based on measured fragility index using the MYEGA relation, (e) measured fragility index (m), and (f) measured enthalpy of relaxation.

 $S_n$  polymeric chains in the backbone transforming into  $S_8$  rings, and driving the backbone Ge-richer, and thus less flexible. And from the available Raman scattering results (not shown) one cannot completely rule out that a very small fraction of S8 rings might persist on the low x side (left side) of the IP. And we speculate that it is this feature of structure that is probably responsible for the super-strong melt composition in the Ge-S binary to shift to x = 25% of Ge (Figure 9e). A perusal of the published literature<sup>[65]</sup> on the  $T_g$  of the Ge<sub>25</sub>S<sub>75</sub> glass composition shows a large spread of nearly 200 °C for the  $T_g$  of this glass as reported by various groups. We take these results to suggest that there are severe challenges to homogenize this glass composition because of the intrinsically super-strong behavior of this melt composition as suggested by the low fragility index (m = 15) (Figure 9e) and the anticipated high melt viscosity based on the MYEGA model<sup>[66]</sup> as shown in Figure 9d.

The central finding of the present work is the most remarkable correlation between m(x) and  $\Delta H_{\rm nr}(x)$  noted here for both Ge–Se and Ge–S binary systems (Figure 9). The result underscores that super-strong melts (m < 20) upon structural arrest at  $T_{\rm g}$  will give rise to IP glasses, while fragile melts (m > 20) will lead to either flexible or stressed-rigid glasses.

Furthermore, one can also uniquely distinguish fragile melts that will form flexible glasses from those that will form stressed-rigid ones. Fragile melts that show an increase in the fragility index with an increase in  $T_g$  upon changing their composition, will give rise to stressed-rigid glasses. On the other hand, if fragile melts show an increase in fragility index with a decrease in  $T_g$  upon changing their composition, such melts would give rise to flexible glasses. We expect these correlations between *m* (*x*) and  $\Delta H_{\rm nr}(x)$  to extend to other chalcogenides in general.

Topological constraint theory has opened a new avenue to accelerate the discovery of new materials with tailored properties in which the usual and unusual<sup>[67]</sup> tools of experimental condensed matter physics and ab initio MD simulations are now playing a crucial role. In a recent issue of MRS Bulletin,<sup>[5]</sup> varied glass functionalities were examined using the approach. Some of the functionalities included enhanced thermal stability,<sup>[13]</sup> Vickers hardness,<sup>[68]</sup> chemical doping of photonic glasses to promote radiative transition and emission bandwidth,<sup>[69]</sup> optimization of amorphous semiconductors and low-/high-k dielectrics for modern micro-/nanoelectronics devices,<sup>[70]</sup> phase-change materials,<sup>[71]</sup> granular materials,<sup>[72]</sup> and nanoengineering of concrete.<sup>[18]</sup> In multicomponent bulk Telluride

glasses<sup>[73,74]</sup> recent evidence of the role of flexibility, isostatic rigidity, and stressed-rigidity on hardness and network packing has also come to the fore.

## 8. Conclusions

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We have designed and carried forward a series of select Raman scattering, modulated differential scanning calorimetric experiments, and MD simulations to elucidate a fundamental issue does the viscous slowdown behavior of a melt determine the nature of the glass formed? Our results show that in specially homogenized  $Ge_x(Se \text{ or } S)_{100-x}$  melts/glasses, the fragility index (*m*) and the glass enthalpy of relaxation ( $\Delta H_{nr}$ ) at  $T_g$  each display striking minima with composition, described in terms of the fragility window and reversibility window, respectively. The two windows are found to extend in the same 20(1)% < x < 26(1)%composition range for both glass systems. Remarkably, MD simulations confirm the existence of the fragility window. These findings show that super-strong melts (m < 20) formed in the fragility window give rise to isostatically rigid glassy networks formed in the reversibility window. Melt compositions both below (x < 20%) and above (x > 26%), are fragile and give rise to flexible and stressed-rigid glasses, respectively. These results lead to the central finding - the topological phases of chalcogenide glasses are, indeed, encoded in their melt dynamics.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## Keywords

chalcogenide glasses, melt fragility, molecular dynamics, topological constraint theory

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