

Topological constraint theory of glass

Topological constraint theory describes how microscopic physics governs the thermal, mechanical and rheological properties of glass and has proved to be a powerful tool for predicting the composition and temperature dependence of glass properties.

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A microscopic physical description of the glassy state long has eluded even the top scientists in condensed matter physics because of the complicated non-crystalline nature of glass structure. Currently, many theorists turn to molecular dynamics or other atomistic simulations to determine the structure of various glass compositions. However, although available computing power has increased exponentially during the past several decades, it will be at least another 20 to 30 years before enough computing power is available for direct molecular dynamics simulations of glass on a realistic laboratory time scale. Fortunately, topological constraint theory provides another path forward. It focuses on the important microscopic physics governing the thermal, mechanical and rheological properties of glass, while filtering out unnecessary details that ultimately do not affect its macroscopic properties. Topological constraint theory has been successful in predicting the composition dependence of glass properties and can be used as a tool to enable the quantitative design of new glass compositions.

Introduction

Although perhaps better known, in general, for his later work on X-ray diffraction in crystals, Zachariasen's only paper on the structure of glass¹ established him, at 26 years of age, as the father of theoretical glass science for the century to come. Zachariasen began his famous 1932 paper on the structure of glass with the humble remark, "It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses." What followed was a brilliantly insightful analysis of glass structure as a disordered network of polyhedral units. The polyhedra themselves define the short-range order of the atomic arrangement in glass, whereas the random connectivity of the polyhedra gives rise to long-range disorder. Based on this picture, Zachariasen postulated four rules of glass formation for an arbitrary oxide compound A_mO_n :

- An oxygen atom is linked to no more than two A atoms;
- The oxygen coordination around A is small;
- The cation polyhedra share corners, not edges or faces; and
- At least three corners are shared (for a three-dimensional network).

Zachariasen's theory essentially amounts to a list of topological conditions for formation of a macroscopic disordered network. These conditions were analyzed in detail by Cooper,^{2,3} who determined that Zachariasen's first two rules are sufficient to enable formation of a glassy network. The third and fourth rules are unneces-

Topological constraint theory of glass

sary from a topological standpoint and may be regarded as just guidelines. A later paper by Gupta and Cooper⁴ put Zachariasen's theory on a rigorous mathematical foundation by deriving a general condition for the existence of an infinitely large topologically disordered network. The Gupta–Cooper approach is not restricted to three dimensions, but rather derived for an arbitrary d -dimensional space where the concept of polyhedral structural units in three dimensions is generalized to rigid polytopes of arbitrary dimensionality.⁵

At the same time as Cooper's original work on glass network topology, Phillips⁶ published a different but equally insightful approach to the same problem, which was later extended and put on a rigorous mathematical basis by Phillips and Thorpe.⁷ Although the Phillips–Thorpe and Gupta–Cooper models are equivalent in a mathematical sense, they offer different and complementary insights into the structure of glass. By explicitly considering glass as a network of rigid polytopes, the Gupta–Cooper approach follows more directly from the original work of Zachariasen, who expressed his rules for glass formation in oxide systems through the connectivity of elementary polyhedral units.

The Phillips–Thorpe model, originally considered for non-oxide covalent systems (viz., chalcogenides), takes a more microscopic approach by considering the connectivity of individual atoms in the glass network. Phillips and Thorpe predicted that a glass network is optimal (i.e., glass-forming ability is maximized) if the number of rigid two- and three-body constraints equals the number of atomic degrees of freedom, a prediction that has been confirmed by many experimental studies, such as those of Varshneya^{8–11} and Boolchand.¹²

In this paper, I provide a brief review of topological constraint theory following the Phillips–Thorpe formulation. Several recent advances are discussed which enable the quantitative design of new glassy materials through consideration of the hierarchy of constraints in a glass-forming network.

Topological constraint theory

According to Phillips–Thorpe theory, glass-forming ability is determined by comparing the number of atomic degrees of freedom with the number of interatomic force field constraints. For a system in three-dimensional space, each atom has three translational degrees of freedom. These degrees of freedom are removed through the presence of rigid bond constraints. If the number of constraints is less than the available degrees of freedom, then the network is considered “flexible.” Conversely, if the number of constraints is greater than the available degrees of freedom, the network becomes overconstrained or stressed rigid.

According to Phillips and Thorpe, the optimum glass compositions are those in which the number of constraints exactly equals the degrees of freedom, in which case the glass network is isostatic. In the floppy regime, the atoms may easily arrange themselves into the minimum energy configuration of the crystalline state, whereas, in the overconstrained regime, rigid structures easily percolate throughout the system, also resulting in crystallization.

Because the original Phillips–Thorpe constraint theory was formulated for covalent systems, it considers a combination of rigid two-body (bonding) and three-body (angular) constraints. Figure 1 shows that the two-body constraints correspond to the rigid bond lengths between pairs of atoms, and the three-body constraints correspond to rigid bond angles. With this assumption, the average number of atomic constraints n in a system can be expressed as

$$n = \frac{\langle r \rangle}{2} + (2\langle r \rangle - 3) \quad (1)$$

where $\langle r \rangle$ is the average coordination number of atoms in the system.

Although a two-fold coordinated atom corresponds to one angular constraint, each new bond requires the definition of two new angles, so that the total number of angular constraints is $2\langle r \rangle - 3$. The average coordination number itself is defined as

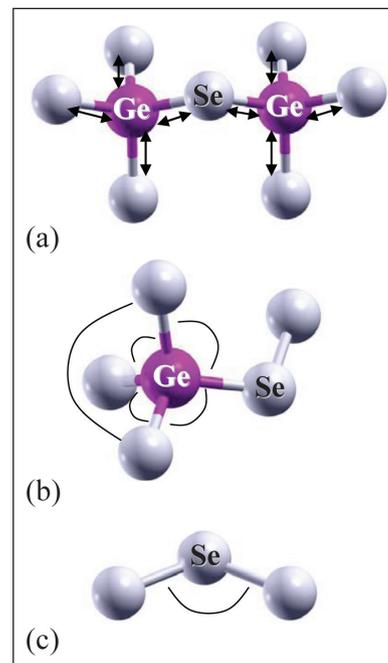


Fig. 1. Basic structural building blocks in covalent germanium-selenium glasses and their associated constraints. (a) Each pairwise bond constitutes a single two-body constraint. (b) There are five independent bond angle constraints (i.e., three-body constraints) for a rigid tetrahedron. (c) A two-coordinated atom, such as selenium, has one rigid bond angle.

$$\langle r \rangle = \sum_i x_i r_i \quad (2)$$

where x_i and r_i are the mole fraction and coordination number, respectively, of each species i in the glass. Setting Eq. (1) equal to 3 and solving for $\langle r \rangle$, Phillips and Thorpe obtained the condition for an optimum glass network in three-dimensional space, corresponding with the Maxwell stability criterion for mechanical trusses:

$$\frac{\langle r \rangle}{2} + (2\langle r \rangle - 3) = 3$$

$$\langle r \rangle = 2.4 \quad (3)$$

This critical value of $\langle r \rangle = 2.4$ is called the rigidity percolation threshold, because, at this composition, rigid structures percolate throughout the glass, leading to an isostatic network.¹³ The network is flexible with $\langle r \rangle < 2.4$, and the network is stressed rigid with $\langle r \rangle >$

2.4. It is exactly isostatic at $\langle r \rangle = 2.4$.

Phillips–Thorpe constraint theory has met with much success in predicting critical behavior of chalcogenide systems about the rigidity percolation threshold.^{8–13} It also has been extended to oxide glasses,^{14,15} glassy metals¹⁶ and proteins,^{17,18} among other systems.

Temperature-dependent constraints

The original Phillips–Thorpe theory for covalent glasses considers all two- and three-body constraints to be rigid, leading to a universal rigidity percolation threshold of $\langle r \rangle = 2.4$. The theory is designed for a fully connected network at absolute zero temperature, $T = 0$. However, the rigidity of a given constraint depends on the temperature of the system, specifically in terms of the amount of available thermal energy compared with the amount of energy required to break a constraint. The temperature dependence of constraints is illustrated in Figure 2. In the limit of low temperature, all constraints are rigid, because there is insufficient thermal energy to break any type of bond. In the high-temperature limit, all constraints are effectively broken, because bonds can break easily and reform with all the available thermal energy.

Recently, Gupta and Mauro^{19,20} have extended Phillips–Thorpe theory to account quantitatively for the effect of temperature. Their work agrees with the analysis of Naumis,²¹ who determined that the major contribution to configurational entropy in glass-forming systems is due to the presence of floppy modes. The configurational entropy decreases as temperature decreases and floppy modes vanish (i.e., they become rigid). Finally, the low-temperature glassy state has no available degrees of freedom and, hence, a vanishing of configurational entropy.^{22,23} Figure 3 shows example calculations demonstrating this effect. Molecular dynamics simulations support the theory.²⁴

The Gupta–Mauro temperature-dependent constraint theory is especially useful for predicting the composition dependence of macroscopic properties, such as glass transition temperature^{19,20} and fragility²⁵ (a measure of the non-

Arrhenius scaling of dynamics, as defined by Angell²⁶). The advantage of constraint theory is that it is a straightforward pen-and-paper calculation based on a counting of constraints. This technique already has been applied to derive analytical expressions for the composition dependence of glass transition temperature in oxide and non-oxide systems.

For example, Figure 4 shows ternary diagrams for glass transition temperature and fragility in the ternary $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3$ system.²⁷ Such calculation would be impossible using traditional atomistic modeling techniques, such as molecular dynamics, because these techniques are currently unable to capture essential structural features, such as the boron coordination change with composition. Also, molecular dynamics simulations are much too time consuming to be applied for compositional studies.

Recently, the temperature-dependent constraint approach has been extended by Smedskjaer et al.^{28,29} to provide a predictive model for the composition dependence of glass hardness. Figure 5 shows that constraint theory provides a quantitatively accurate solution to this previously unsolved problem in condensed-matter physics.

Another notable success of temperature-dependent constraint theory is its application to modeling the temperature dependence of liquid viscosity via the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) equation for liquid viscosity:³⁰

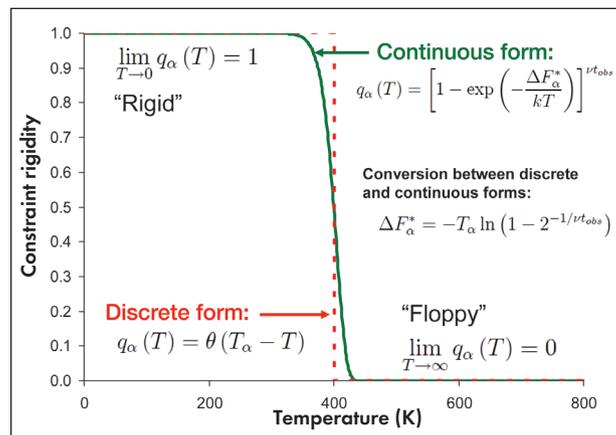


Fig. 2. Each type of bond constraint α in temperature-dependent constraint theory is assigned a constraint onset temperature, T_{α} . At high temperatures ($T > T_{\alpha}$), there is enough thermal energy to overcome the bond constraint. Therefore, it is considered floppy, i.e., $q_{\alpha}(T) \rightarrow 0$. Conversely, at low temperatures ($T < T_{\alpha}$), the constraint is rigid, i.e., $q_{\alpha}(T) \rightarrow 1$. Following Gupta and Mauro,¹⁹ the temperature dependence of constraints can be written in either continuous or discrete forms. The discrete form, a simple unit step function, is useful for deriving analytical formulas for the composition dependence of properties, such as glass transition temperature and hardness. The continuous form is useful for obtaining numerical solutions for liquid fragility.²⁰ Here, ΔF_{α}^* is the free energy to break constraint α , k is Boltzmann's constant and νt_{obs} is the product of vibrational frequency and observation time.

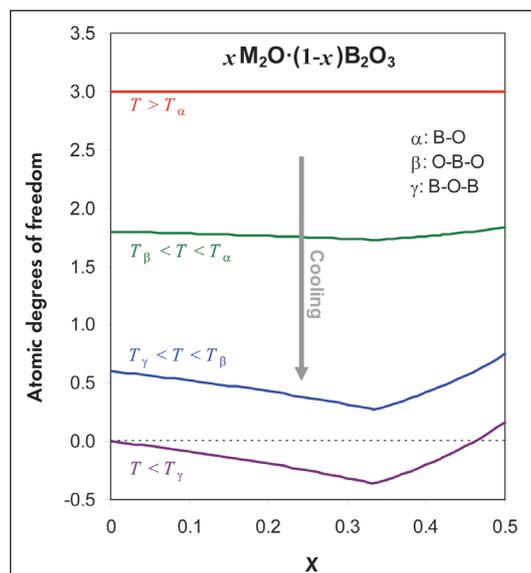


Fig. 3. Plot of average atomic degrees of freedom as a function of alkali concentration in a binary alkali borate system. At high temperatures ($T > T_{\alpha}$), all constraints are floppy. Therefore, the number of atomic degrees of freedom is three for all compositions. As the system is cooled, the first constraint to become rigid is the linear B–O bond constraint ($T_{\beta} < T < T_{\alpha}$). Continued cooling leads to a freezing of the O–B–O bond angles ($T_{\gamma} < T < T_{\beta}$) followed by the B–O–B bond angles ($T < T_{\gamma}$) in the solid glassy state. Reproduced from Mauro et al.²⁰

Topological constraint theory of glass

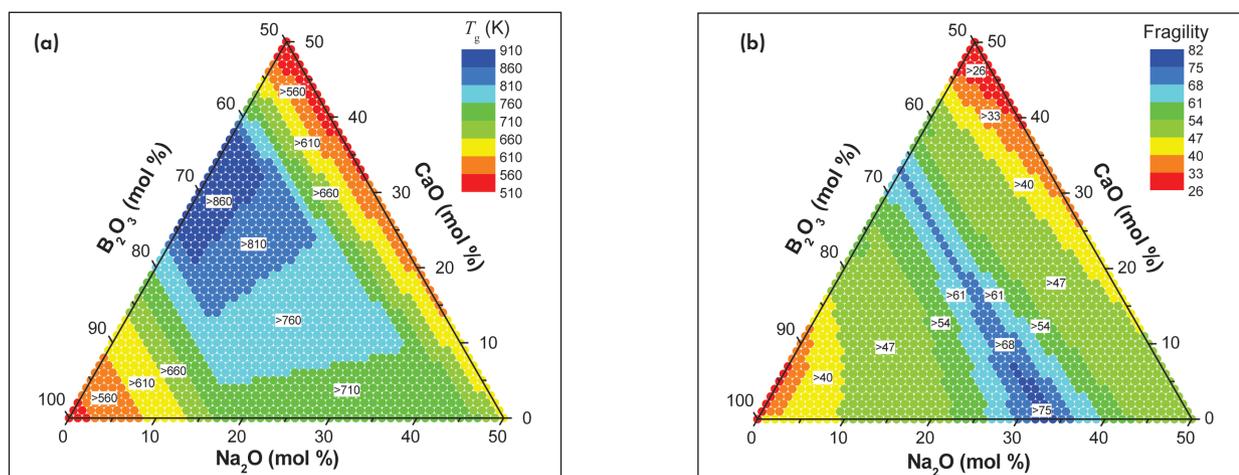


Fig. 4. Calculation of the composition dependence of (a) glass transition temperature $T_g(x,y)$ and (b) fragility $m(x,y)$ for the $x\text{Na}_2\text{O}\cdot y\text{CaO}\cdot(1-x-y)\text{B}_2\text{O}_3$ system. $T_g(x,y)$ is calculated analytically based on the discrete form of temperature-dependent constraint theory, whereas $m(x,y)$ is calculated numerically based on the continuous form of the theory. Constraint theory is an effective method for the quantitative design of new glass compositions. Reproduced from Smedskjaer et al.²⁷

$$\log_{10}\eta(T,x) = \log_{10}\eta_\infty + \frac{K(x)}{T} \exp\left(\frac{C(x)}{T}\right) \quad (4)$$

The MYEGA equation provides a significantly improved description of the temperature dependence of viscosity compared with the standard Vogel–Fulcher–Tammann (VFT) equation, while maintaining the same number of fitting parameters. Here, η_∞ is the extrapolated viscosity in the infinite temperature limit, and $K(x)$ and $C(x)$ are composition-dependent parameters indicative of the activation barrier for viscous flow and the temperature dependence of the constraints, respectively. Complete details of the MYEGA equation are provided in Ref. 30.

Linking molecular dynamics and constraint theory

The implicit assumption of constraint theory is that we know enough about the structure of a given glass to identify the important structural units and associated constraints. Often the best source of this information comes from structural characterization, such as nuclear magnetic resonance experiments. For example, recent NMR experiments³¹ of the germanium-selenium system at various temperatures reveal the important structural units of this system as well as the composition and temperature dependence of the constraints.

In the absence of direct experimental measurements, it is often useful to turn to molecular dynamics simulations. Although the simulations themselves may not provide the direct results regarding macroscopic properties, such as hardness, they can provide important structural information and the energies associated with various types of constraints. Two methods proposed to link molecular dynamics with constraint theory – one by Mauro and Varshneya^{32,33} and another by Micoulat^{34,35} – provide that accurate interatomic potentials are known if one deals with classical molecular dynamics.

In their molecular dynamics simulations of the germanium-selenium system, Mauro and Varshneya³² provided the first direct evidence for a rigidity percolation threshold from atomistic simulations. Their approach is based on calculating the normal modes of vibration associated with a given configuration of atoms. The high-frequency modes correspond to deeper energy wells and rigid constraints, whereas the low-frequency modes are indicative of shallow wells cor-

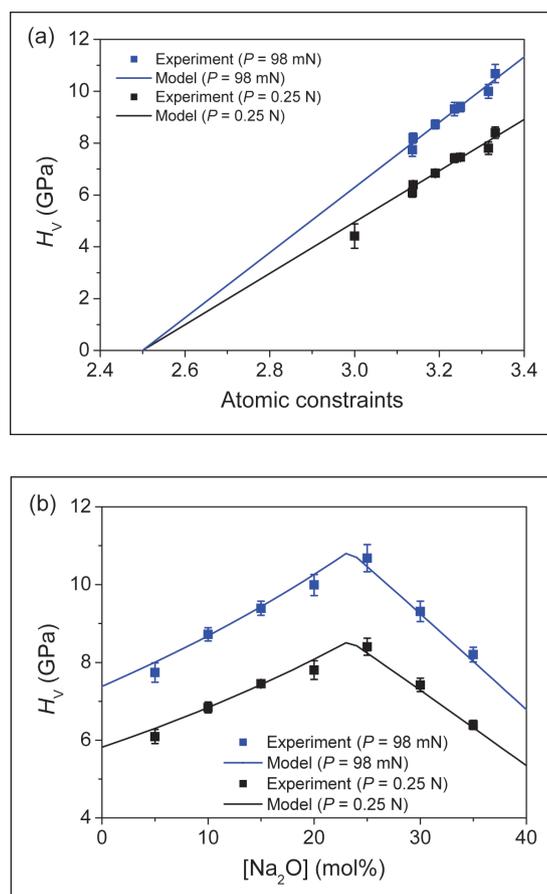


Fig. 5. Predicted versus measured Vickers hardness (H_v) for $x\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot(89-x)\text{B}_2\text{O}_3\cdot 1\text{Fe}_2\text{O}_3$ (mole percent) glasses at loads (P) of 98 millinewtons and 0.25 newtons. Hardness is plotted as a function of (a) the average number of atomic constraints in the glass at room temperature and (b) the concentration of Na_2O (x). The solid lines represent model predictions using temperature-dependent constraint theory. Reproduced from Smedskjaer et al.²⁸

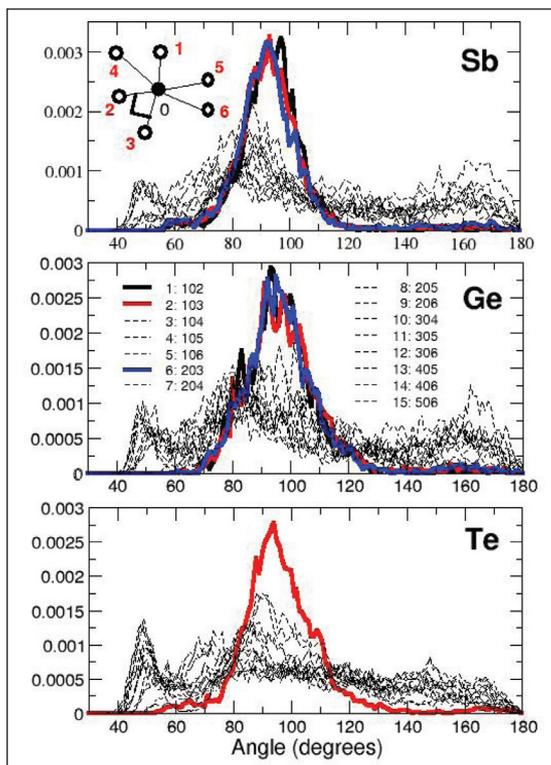


Fig. 6. In heavier chalcogenides, such as germanium-antimony-telluride glasses, where the 8-N (octet) rule does not apply in a straightforward fashion, constraint counting can be achieved using molecular dynamics. From an accumulated trajectory of GeSb_2Te_4 , one selects a central atom 0, and, for a given number of neighbors (here equal to six), all possible partial bond angle distributions between sets of neighbors (e.g., marked as 203) are computed for germanium-, antimony- and telluride-centered atoms (102, 103, 104, etc., see panel for germanium). Results show that germanium and antimony have three intact constraints (sharp colored distributions) although their coordination number is four (one would expect seven constraints according to the standard counting procedure). Although the coordination of tellurium is found to be larger than two, consistent with experimental data, this leads only to one intact angular constraint, as for sulfur and selenium. Special thanks to M. Micoulaut for providing this figure.

responding to floppy constraints.

In the Mauro–Varshneya approach, each mode is classified as either rigid or floppy depending whether it falls above or below a certain threshold for rigidity. This threshold depends on the temperature of the system, with a higher threshold required for higher temperatures. Therefore, this approach captures the composition and temperature dependence of the constraints. Also, the eigenvectors associated with each normal mode reveal the exact atomic

motions involved with a particular constraint, because each element of the eigenvector is associated with the x , y or z motion of a particular atom. Because the eigenvectors are orthonormal, all of the constraints considered are mutually independent, i.e., there is no risk of overcounting dependent constraints.

Micoulaut^{24,34,35} has proposed an alternative approach designed specifically for angular constraints. Here, bond-stretching constraints are routinely computed from the number of neighbors, whereas a more subtle analysis is needed to quantify angular constraints based on calculating the standard deviation of partial bond angle distributions for a glassy system. In his simulations, Micoulaut found that the standard deviations show a bimodal distribution indicating either floppy or rigid behavior.

This technique clearly identifies which bond angles are floppy (having a high standard deviation) versus rigid (having a low standard deviation), such as depicted in Figure 6. A key advantage of the Micoulaut technique is its computational efficiency for large systems. These features can be followed with composition and temperature. A particularly interesting finding of this work is that, to elucidate the nature of constraints, one must consider the nearest neighbors around network formers and modifiers, such as alkali ions in oxide glasses. When applying this technique, one must be careful to count only independent constraints, because not all bond angles are mutually independent.

Self-organization and the intermediate phase

The original Phillips–Thorpe theory predicts a single optimized glass composition, where the microscopic struc-

ture is isostatic (i.e., having the same number of bond constraints as atomic degrees of freedom). However, more recent experiments by Boolchand^{36–40} reveal a second transition providing a finite width to these isostatic compositions and offering not only a single optimized glass composition, but a whole range of such compositions, as depicted in Figure 7. The exploration of this so-called intermediate phase has been a large focus of recent experimental and modeling work in understanding constraint theory.

The original experimental work of Boolchand is based on the technique of modulated differential scanning calorimetry, in which a small sample of glass is subjected to a linear heating or cooling path modulated with a sinusoidal variation of amplitude. The resulting signal of the MDSC can be divided in two contributions: reversing heat flow that tracks the sinusoidal modulation and nonreversing heat flow that is indicative of aging behavior in the glass transition range and captures most of the kinetics occurring in this temperature interval.

The Boolchand experiments have shown that many oxide and non-oxide glassy systems exhibit a minimum in nonreversing heat flow over a range of compositions within the intermediate phase. However, the signature of the intermediate phase is not restricted to calorimetric data, because optical measurements have shown that two vibrational thresholds have been found at the boundary of the intermediate phase.⁴¹ Subsequent experiments also have shown signatures of the intermediate phase in ionic conductivity data.⁴⁰ For selected systems, the centroid of the intermediate phase coincides with a minimum in molar volume, underscoring space-filling tendency.⁴² The intermediate phase for several different glassy systems is shown in Figure 8.

The intermediate phase is attributed to a self-organization of the glassy network, where the network attempts to achieve an isostatic condition even if that means introduction of defects in either the short-range or intermediate-range structures. To account for these effects, the Phillips–Thorpe model

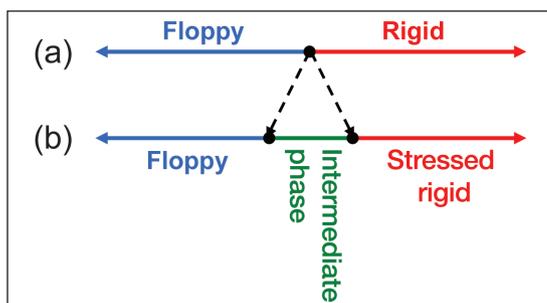


Fig. 7. (a) Traditional Phillips–Thorpe constraint theory with a single rigidity percolation threshold separating floppy and rigid compositions. (b) According to Boolchand’s results, the rigidity percolation threshold is really two thresholds yielding an intermediate phase of finite width between the floppy and stressed rigid phases. The intermediate phase corresponds to a range of compositions that can self-assemble in optimally constrained (i.e., isostatic) configurations. Beyond a certain limit, additional constraints cannot be accommodated by changes in clustering or intermediate-range order, and then the system enters a stressed rigid phase.

has been extended by Micoulaut and Phillips^{43–47} to consider various configurations of clusters within a glass. In the Micoulaut–Phillips approach, clusters are constructed of increasing size, the probability of each cluster depending on the energy associated with the elementary units.

The more favorable configurations are those leading to an isostatic condition, which gives an overall lower free energy of the system. This self-organization of various cluster configurations enables the intermediate-range ordering necessary to produce the intermediate phase. The optimized configurations of the glass within the intermediate phase also mean there is less driving force for relaxation and, hence, a minimum in nonreversing heat flow. The stress-free nature also has been shown from Raman pressure experiments.⁴⁸

The discovery of the intermediate phase has not been without controversy. In particular, Simon^{49,50} has shown that the integration of the nonreversing heat flow from MDSC does not correspond exactly to the enthalpy of aging through the glass transition. Subsequent work by Carpentier et al.⁵¹ has provided a thorough analysis of relaxation using MDSC.

Also, currently, there is no clear evidence from NMR³¹ or neutron diffrac-

tion⁵² data to discern the structural signatures of the intermediate phase. For example, recent NMR measurements of Lucas⁵³ have led to a proposed model of germanium-selenium glass structure composed of selenium-rich (flexible) and GeSe₂-rich (stressed rigid) nanophases in which no intermediate phase would be possible. Nevertheless, Micoulaut and Malki⁵⁴ have shown direct evidence for a characteristic dynamical length scale associated with the intermediate phase in fast-ion-conducting glasses.

In the current author’s opinion, the existence of such controversy serves as great evidence for the amount of exciting research that is yet to be done in this area. No matter what the final outcome, we are sure to learn much along the way to further our understanding of the glassy state in terms of structure and properties.

Conclusions and further reading

Topological constraint theory is arguably the most powerful tool available today to predict the relationship between the composition and structure of a glass and its measurable properties. Because constraint theory focuses on the key physics that governs the

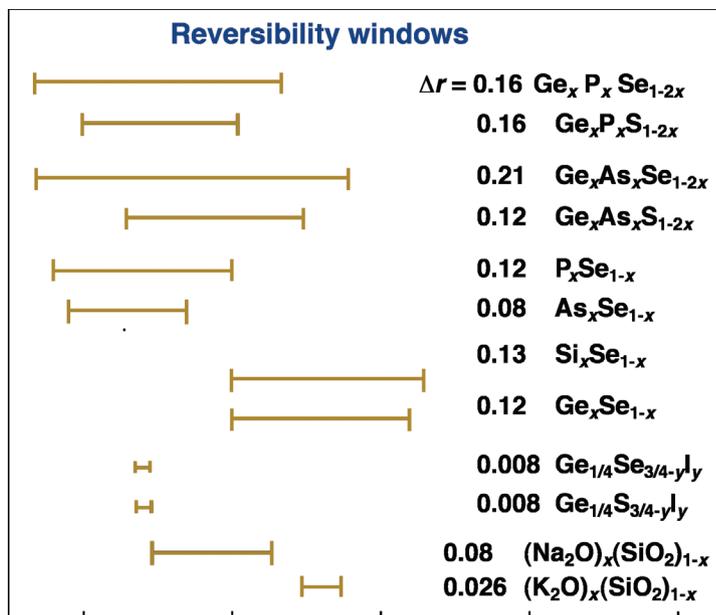


Fig. 8. Observed reversibility windows from modulated DSC experiments for various glass systems. The reversibility window corresponds to the intermediate-phase compositions, here shown as a function of average coordinate number. Window centroids in group IV selenides are at $\langle r \rangle > 2.40$, whereas group V selenides are at $\langle r \rangle < 2.40$. Ternary alloys encompass both regions of $\langle r \rangle$ space. Special thanks to P. Boolchand for providing this figure.

glassy state, viz., the network of bond constraints, it effectively bypasses the limitations associated with traditional atomistic modeling techniques, such as molecular dynamics. However, there remains much work to be done regarding the theoretical and applied aspects of constraint theory, such as the extension to new compositions and properties of interest. One cannot help but be excited by the future prospects of this approach, which is poised to make the computational design of new glassy materials a reality.

Readers interested in learning more about constraint theory are encouraged to check out the new book, *Rigidity and Boolchand Intermediate Phases in Nanomaterials*, edited by Micoulaut and Popescu.⁵⁵ It provides an excellent overview of recent advances in constraint theory, including generous doses of experimental and modeling work. This book is a celebration of the constraint theory approach to glass science, following the original work of Phillips and Thorpe, and of the exciting theoretical and experimental work that has been published in the ensuing decades. The

book is written in a very readable and accessible fashion, making it an ideal introduction to the field for newcomers. It also makes an excellent reference for those who are already well versed in the field. Perhaps the most exciting feature of this book is that the diverse range of chapters offers essentially a blueprint for future discoveries yet to be made. In many ways, this book is Micoulaut and Popescu's invitation for all of us to come and join the fun!

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