Editorial: topology of disordered networks and their applications

Editorial on the Research Topic

Topology of Disordered Networks and Their Applications

Understanding the physicochemical properties of glasses has attracted widespread interest over the entire twentieth century. Glasses form disordered network structures and cannot be treated as regular lattices on an atomic scale. It has led not only to contributions in basic science such as the improved description of the glass transition phenomenon but also to contributions in materials science, and these have stimulated worldwide applications as smart window glass, flat panel displays, touch screens, protective sheets for cell phones, realization of high-K Dielectrics in standard 3-Terminal devices (Lucovsky et al., 2003), and phase change memories for information storage. The latter two applications alone represent a $1. 6 billion market worldwide in 2020.

A profound step forward in understanding network glasses and amorphous materials at an atomic level began nearly 40 years back as the foundations of topolocial constraint theory (TCT) emerged, and interest in manifestations of the theory has continued to grow. The beginnings of the theory started with an innocent query—what optimizes the glass-forming tendency of a melt—and led to the finding (Phillips, 1979) that such melts possess an " ideal" connectivity. In this approach, a glass network is broadly viewed as a network of chemical bonds linking atoms, with the bonds between nearest neighbor (nn) atoms, and bond-angles between second nn atoms serving as *mechanical constraints* . The network as a whole is then viewed to be either in a *flexible phase* (FP) or an *isostatically rigid intermediate phase* (IP) or a *stressed-rigid phase* (SRP) if the number of constraints per atom, n_c , is,

respectively, lower than, equal to, or higher than the number of degrees of freedom per atom, i. e., $n_d = 3$ for 3D networks. These three topological phases (TPs) have now been observed in scores of network glasses (Yildirim et al., 2016 ; Chbeir et al.). The term " ideal" connectivity was traced to the basic condition $n_c = n_d$, which for the case of group IV (Si, Ge)-based chalcogenides corresponds to Corner-Sharing $GeSe_4$ tetrahedra percolating in the network at a mean coordination number of $<r> = 2. 40$. The structure of such systems continues to be investigated using diffraction techniques including use of isotopically enriched glasses in neutron diffraction (Rowlands et al.). For the case of group V (P, As)-based chalcogenides, the same condition, $n_c = n_d$ led to $<r> = 2. 28$ for the quasi-tetrahedral $[Se = P (Se_{1/2})_3]$ local structures (Boolchand et al., 2009) and to 2. 40 for pyramidal $(PSe_{1/2})_3$ local structures percolating through the network. Such geometrical motifs seem to have specific spectroscopic signatures (Micoulaut and Boolchand). The condition, $n_c = n_d$, was originally envisaged by Maxwell (1864) in understanding the mechanical stability of macroscopic structures such as bridges and trusses. Such a rigidity treatment can also be undertaken using a polytope approach (Sen and Mason).

Some of the objectives of the research within our Topic have included issues such as how pervasive is the notion of topological phases across the wide array of glass-forming systems? What challenges does one face in probing them, both experimentally and theoretically? What applications can these phases/materials be put to use for? And finally, what new science links the

picture above T_g to the one below T_g? On all these scores, new information has emerged from the contributions we received for the Collection.

The inclusion of T-dependent bonding constraints for bond-bending and bond-stretching forces opened an entirely new domain in TCT in 2011 (Gupta and Mauro, 2009 ; Bauchy and Micoulaut, 2011). It made feasible to model structure and dynamics of glassy melts using molecular dynamics (MD) simulations (Bauchy, 2012). By establishing the variance in bond lengths and bond angles as a function of temperature, one could establish constraints that are either fully or partially intact. For Na^+ in sodium silicate glasses, the approach showed that even though the count of O near-neighbors of a Na^+ cation typically varies between 5 and 6, the variance in Na-O bond lengths demonstrated that the bond-stretching constraint is intact for only one of those five or six oxygen neighbors, underscoring (Bauchy and Micoulaut, 2011) that the " mechanically effective" coordination number of Na^+ is 1 consistent with its chemical valence. Here, additional numerical tools are provided and tested for the case of dense liquids, and these suggest dynamical gaps for the transverse part of viscoelastic transport, which have permitted evaluating a constraint density (Toledo-Marín and Naumis).

Melts of stoichiometric glass compositions where an underlying crystalline phase or phases occur apparently homogenize quicker than their non-stoichiometric counterparts do. Non-stoichiometric melts/glasses in the 2. 0 $<< r > <$2. 7 range of connectivity undergo " delayed" homogenization, a feature discovered in 2011 (Bhosle et al., 2012a , b), which appears to be

tied to the super-strong character of IP melts formed (Chakravarty et al. ; Chbeir et al. ; Mohanty et al.), with the fragility index m in the range of 20> × > 15, in the fragile-strong classification. The latter can also alternatively be analyzed from a chalcogenide deficiency viewpoint (Lucas et al.). The feature emerged only once homogenized melts became available, thereby altering the landscape of fragility index results. The rigidity—and stress— elastic phase transitions are percolative in nature and first order in 3D (Jacobs and Thorpe, 1995), and experiments show that once the variance (<Δx>) in Ge content " x," across a batch composition of a binary GexSe100-x glass for example, is <0. 1%, the rigidity and stress transitions are found to be rather abrupt since the network connectivity $< r > = 2 (1 + x)$ is tied to the variance <Δx>. Smearing of these two phase transitions was noted in melts/glasses in which the variance <Δx>> 2%. In modified oxides such as the sodium phosphates, the observation of the three TPs posed more challenges—melts/glasses had to be dry as well as homogeneous (Mohanty et al.). The existence of IPs with remarkable properties such as nearly reversible glass transitions, weak aging, forming compacted networks with reduced molar volumes, forming networks than can adapt, minimum creep, maximum fracture toughness (Bauchy et al., 2011) has come to the fore in more than scores of glass systems (Bauchy and Micoulaut, 2015) and has opened new awareness of the notion of self-organization.

There are three contributions on statistical mechanics origin of the IP and the application to network glasses. In one contribution, the role of topological fluctuations is considered in determining the compositional width of the IP (Kirchner and Mauro). In the second (Toledo-Marín and Yan), a prediction for

the existence of a liquid–liquid phase transition in IP phase melts is made. If confirmed, the authors suggest that IPs will represent a new thermodynamic phase of disordered condensed matter. In the third one, a statistical mechanics modeling leads to the prediction of composition–structure relations in alkali borosilicate glasses (Bødker et al.).

Striking suggestions for existence of an IP in calcium-silicate hydrates was presented from numerical simulations by Zhou et al. , who have identified the appropriate experimental observables to establishing the rigidity—and stress—elastic phase transitions.

Although TCT has been widely used to describe network glasses composed of atoms, the case of icosahedral borocarbide forming highly coordinated networks of " superatoms" whose connectivity can be controlled by hydrogenation is considered by Nordell et al. . The group has synthesized thin films of hydrogenated icosahedral borocarbide over a wide range of hydrogen contents and examined these in Young's modulus experiments. They observe evidence of rigidity onset near $<r> = 2.40$, and the Young's modulus is found to increase as a power-law in $<r>$ with a value of 1.50 in the stressed-rigid regime in harmony with simulations.

The fragility index variations with mean coordination number $<r>$, in the GexAsxSe100-2x chalcogenide and the modified oxide (Na2O)x(P2O5)100-x (SPGs), led sidebottom to recognize TPs using a coarse graining model (CGM) approach. In the CGM approach, one excludes the P-O $_t$ dangling ends in SPGs and estimates network connectivity, $<r>$, by the count of P-O $_{bridging}$ contacts defining the backbone. In this approach, the onset of rigidity is

expected near $<r> = 2.40$, or 37. 5% of Na_2O, a prediction that is confirmed by the observation of the rigidity transition at that composition by Mohanty et al. from modulated-differential scanning calorimetry (MDSC) experiments. The observation is consistent with dangling ends playing no role at the rigidity transition. However, such is not the case for compositions away from the rigidity transition (Boolchand et al., 1996). The presence of dangling ends in stressed-rigid (flexible) networks softens (stiffens) the networks. Indeed, Mohanty et al. also observe the stress transition to occur near $x = 46.0 (2)$% of Na_2O, underscoring that compositions at $x > 37.5$% are in the rigid phase, while in the CGM, one views such compositions to be in the flexible phase since $<r> < 2.40$. Thus, the TPs in the SPGs deduced using the CGM approach are found to be inverted with respect to those obtained using the complete network when dangling ends are explicitly included.

Peak force quantitative nanoindentation modulus (NIM) on ternary bulk $Ag_x(Ge_ySe_{1-y})$ alloy glasses over a wide range of Ag alloying " x," and base glass " y" chemistry measurements have permitted mapping of NIM and correlating it with the Ag content of the glasses, thus providing new insights into the topologically segregated nature of the ternary glass system.

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Conflict of Interest

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References

Bauchy, M. (2012). Topological constraints and rigidity of network glasses from molecular dynamics simulations. *Am. Ceramic Soc. Bull.* 91, 34A−38A. Available online at: https://arxiv. org/abs/1506. 06483

Google Scholar

Bauchy, M., and Micoulaut, M. (2011). Atomic scale foundation of temperature-dependent bonding constraints in network glasses and liquids. *J. Non Cryst. Solids* 357, 2530–2537. doi: 10. 1016/j. jnoncrysol. 2011. 03. 017

CrossRef Full Text | Google Scholar

Bauchy, M., and Micoulaut, M. (2015). Densified network glasses and liquids with thermodynamically reversible and structurally adaptive behaviour. *Nat. Commun.* 6: 6398. doi: 10. 1038/ncomms7398

PubMed Abstract | CrossRef Full Text | Google Scholar

Bauchy, M., Micoulaut, M., Celino, M., Le Roux, S., Boero, M., and Massobrio, C. (2011). Angular rigidity in tetrahedral network glasses with changing composition. *Phys. Rev. B* 84: 054201. doi: 10. 1103/PhysRevB. 84. 054201

PubMed Abstract | CrossRef Full Text | Google Scholar

Bhosle, S., Gunasekera, K., Boolchand, P., and Micoulaut, M. (2012a). Melt homogenization and self? organization in chalcogenides-part I. *Int. J. Appl. Glass Sci.* 3, 189–204. doi: 10. 1111/j. 2041-1294. 2012. 00093. x

CrossRef Full Text | Google Scholar

Bhosle, S., Gunasekera, K., Boolchand, P., and Micoulaut, M. (2012b). Melt homogenization and self? organization in chalcogenides-part II. *Int. J. Appl. Glass Sci.* 3, 205–220. doi: 10. 1111/j. 2041-1294. 2012. 00092. x

CrossRef Full Text | Google Scholar

Boolchand, P., Chen, P., and Vempati, U. (2009). Intermediate phases, structural variance and network demixing in chalcogenides: the unusual case of group V sulfides. *J. Non Cryst. Solids* 355, 1773–1785. doi: 10. 1016/j. jnoncrysol. 2008. 11. 046

CrossRef Full Text | Google Scholar

Boolchand, P., Zhang, M., and Goodman, B. (1996). Influence of one-fold-coordinated atoms on mechanical properties of covalent networks. *Phys. Rev. B Condensed Matter* 53, 11488–11494. doi: 10. 1103/PhysRevB. 53. 11488

PubMed Abstract | CrossRef Full Text | Google Scholar

Gupta, P. K., and Mauro, J. C. (2009). Composition dependence of glass transition temperature and fragility. I. A topological model incorporating temperature-dependent constraints. *J. Chem. Phys.* 130: 094503. doi: 10. 1063/1. 3077168

CrossRef Full Text | Google Scholar

Jacobs, D. J., and Thorpe, M. F. (1995). Generic rigidity percolation: the pebble game. *Phys. Rev. Lett.* 75, 4051–4054. doi: 10. 1103/PhysRevLett. 75. 4051

PubMed Abstract | CrossRef Full Text | Google Scholar

Lucovsky, G., Phillips, J. C., and Boolchand, P. (2003). A new approach to gate dielectric integrity based on differences between i) strained and ii) strain-free interfacial regions: applications to devices with alternative high-k dielectrics. *Int. Conf. Solid State Devices Mater* , 422–423. doi: 10. 7567/SSDM. 2003. P2-6

CrossRef Full Text | Google Scholar

Maxwell, J. C. (1864). L. On the calculation of the equilibrium and stiffness of frames. *Philos. Magaz. Ser.* 27, 294–299. doi: 10. 1080/14786446408643668

CrossRef Full Text | Google Scholar

Phillips, J. C. (1979). Topology of covalent non-crystalline solids. 1. Short-range order in chalcogenide alloys. *J. Non Cryst. Solids* 34, 153–181. doi: 10. 1016/0022-3093(79)90033-4

CrossRef Full Text | Google Scholar

Yildirim, C., Raty, J.-Y., and Micoulaut, M. (2016). Revealing the role of molecular rigidity on the fragility evolution of glass-forming liquids. *Nat. Commun.* 7: 11086. doi: 10. 1038/ncomms11086

PubMed Abstract | CrossRef Full Text | Google Scholar