

Topological Constraints and the Makishima Mackenzie Model

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Abstract

Computations of the elastic properties of networks with bond stretch and bond angle bend forces are carried out in order to study their behavior as a function of average coordination number. It is found that the elastic constants essentially vanish as the average coordination number drops to 2.4. It is argued this phenomenon is responsible for the failure of the Makishima Mackenzie model to predict accurately the elastic properties of borate glass, originating with B₂O₃ itself which also has an average coordination number of 2.4. Finally, a new model is proposed, similar to the Makishima Mackenzie model but including explicitly the dependence on network connectivity.

Keywords:

Young's modulus, Makishima Mackenzie model, Elastic constants, constraint theory

1. Introduction

The Makishima-Mackenzie (MM) model [1, 2] provides an estimate for the Young's modulus of glass based on its composition and properties of the components. In particular, the model posits

$$E = 2V_t \sum_i G_i x_i, \quad (1)$$

where E is the Young's modulus, V_t is the atomic packing fraction (the fraction of space filled with ions of all types), G_i the dissociation energy per unit volume of component i , and x_i the mole fractions. The components of the glass are understood to be the oxide constituents, for example SiO₂, Na₂O, and CaO in a soda-lime-silicate glass.

This model is widely used to make simple estimates of glass stiffness and to correlate data with composition. Indeed, it is found experimentally that silicate glasses are rather well described by this model, with accuracy to about 20%. This level of agreement is remarkable given the simplicity of the model. Borates on the other hand, and especially B₂O₃ itself, are very poorly described, with the model in error by a factor of about 5. In particular, B₂O₃ is markedly less stiff than predicted by the MM model. In the original work of Makishima and Mackenzie, as well as later works on borates that quote these papers, it is argued that this lack of agreement for borates is due to boroxol ring-ring interactions, or differences between three and four-fold coordinate boron, and to "correct" the discrepancy, the dissociation energy G for B₂O₃ is scaled by a factor of 5. Given this scaling, the predictions of the model are then in reasonable agreement with experiment.

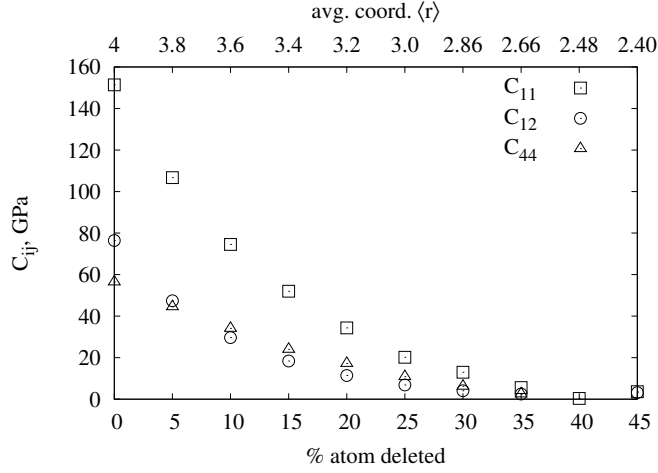
We argue in this paper that such a scaling is unjustified and in fact, the lack of agreement between the model and experiment in borates is due to the lack of consideration of network topology in the MM model. Our arguments are justified by consideration of computation of the elastic constants of network models with various random bond deletions, and we show that such models soften when the average coordination number is reduced to 2.4, the same coordination number that characterizes B₂O₃. Finally we will suggest the form for an extended model of the Young's modulus, with a factor including average coordination number.

2. Models and Methods

To study the elastic properties of disordered systems, a series of models were created based on random deletions from the silicon crystal structure, similar to what has been done by Thorpe and co-workers [3]. In one series of models, disorder was generated by removing bonds at random, subject to the rule that no atomic nearest-neighbor coordination number was allowed to fall below two. A variant to this approach involved targeted deletion, such that the deletion was biased towards atoms with a particular coordination number, in order to generate models with different bond distributions. A different series of models was created by randomly deleting atoms and their associated bonds, so that atomic density could be probed in addition to random bonding. Although the starting point of these models was the structure of crystalline silicon, the models themselves are not meant to represent amorphous silicon, rather our goal is simply to investigate the elastic properties of a disordered network of bonds. We chose silicon as a starting point simply because it provided a useful check of our simulations in the limit of little disorder.

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Figure 1: Elastic constants C_{ij} for models based on silicon, using a simplified Stillinger-Weber potential, as a function of random deletion of the atoms (indices i and j refer to the stress in direction i generated by strain in direction j). The computed average coordination number for each deletion level is indicated across the top of the graph.



The bonds themselves were modeled with a simplified form of the Stillinger-Weber potential [4]. This potential includes a two-body term with exponential short-range repulsion and a more gradual attractive part, resulting in a local minimum. There is also a three-body term centered around the tetrahedral bond angle. This potential is known to reproduce accurately the elastic properties of silicon. We simplified the potential by making quadratic fits to the bond-stretch and bond-angle-bend terms around the equilibrium geometry of crystalline silicon (the local minima of the Stillinger-Weber potential), in order to have just two parameters in the model. This fitting resulted in a bond-stretch force constant of 2.5 around a minimum of 2.35, and a bond-angle-bend force constant of 0.58 around the tetrahedral bond angle (all numbers in atomic units).

The elastic properties of a given model were computed using the LAMMPS package, a general purpose molecular dynamics code [5]. A given model and the potential described above were supplied to the code, and then, using periodic boundary conditions, the structure was relaxed until all forces were below 10^{-10} eV/Å. This relaxation displaced the atoms from their original diamond-lattice positions. Finally, elastic constants C_{ij} were computed using a finite difference method, in which the stress in direction i as a function of strain in direction j was calculated for both positive and negative strains in both positive and negative directions. In this way the entire elastic tensor was reconstructed for each model.

3. Results

The elastic constants computed for the models created by random atom deletion are plotted in Figure 1. This figure shows that all three elastic constants of the pseudo-cubic system vanish as the average coordination number drops to 2.4, in agreement with the earlier results of He and Thorpe [3].

Figure 2 shows the Young's modulus plotted as a function of average coordination number, for models generated by bond

Figure 2: Elastic constants for models based on silicon, using a simplified Stillinger-Weber potential, as a function of atom deletion followed by random bond deletions. Model number densities (atoms \AA^{-3}) are indicated in the legend.

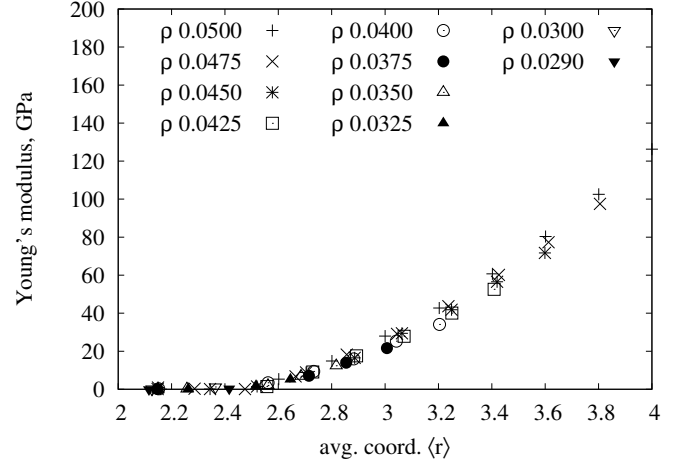
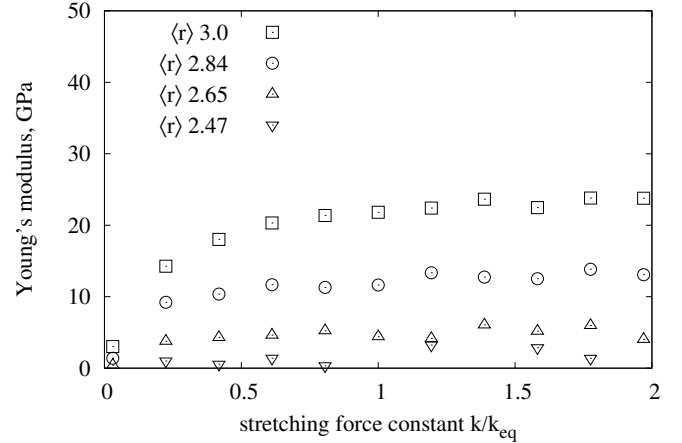


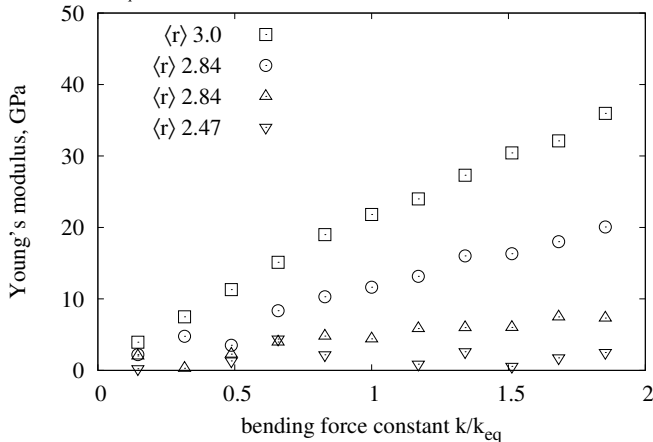
Figure 3: Dependence of the Young's modulus on variations in the linear force constant, with the bond angle force constant held fixed at its equilibrium value k_{eq} , for several average coordination numbers.



deletion, followed by atom deletion. By this method, models with varying densities for the same average coordination number were generated. It can be seen that while the Young's modulus varies strongly with average coordination number its dependence on density is actually quite weak.

Figures 3 and 4 show the dependence of the Young's modulus on variation of bond stretch and bond angle force constants respectively. In Figure 3 the bond angle force constant was kept fixed at its equilibrium value while the bond stretch force was varied over a wide range, from a fraction of its equilibrium value to twice the equilibrium value. For each average coordination, the Young's modulus is seen to be largely independent of the bond stretch force value. In Figure 4 the same procedure was followed except that the bond stretch force was held constant while the bond angle force was varied. In this way the Young's modulus was observed to be much more sensitive to the bond angle force than the bond stretch force.

Figure 4: Similar to Figure 3 but with the linear force constant held fixed at its equilibrium k_{eq} and the bond angle force constant varied.



4. Discussion

The Makishima Mackenzie model estimates the Young's modulus from two factors: bond strength and atomic packing. The model quite reasonably assumes that bulk stiffness should be related to the strength of bonds and their density, and tries to capture this behavior by estimating bond strength from the dissociation energy and bond density from the combination of using the specific bond energy and the atomic packing fraction. Indeed the atomic packing fraction is the key point where glass structure enters the model, however, details of intermediate range order are averaged over in this description.

While the Young's modulus of silicates and aluminosilicates are described reasonably well by this model, with typical errors of under 20% [1], borates and B_2O_3 in particular are poorly described. The heat of formation of B_2O_3 similar between the glass and crystal, at -1245 kJ/mol and -1263 kJ/mol respectively. The densities differ significantly, with the glass density at about 1.86 g/cc. The atomic radii in the glass can be estimated from various scales, including the Pauling and Shannon tables, leading to an atomic packing fraction of at least 0.37. Thus the Makishima Mackenzie model predicts a Young's modulus of at least 62 GPa. However, this quantity is typically quoted experimentally as about 17 GPa, and a detailed study of thermal history effects, taking into account humidity, found values of the elastic constants even lower, leading to Young's modulus estimates of 8–11 GPa [6]. In contrast, applying the Makishima Mackenzie model to fused quartz leads to an estimate 67.6 GPa for the Young's modulus, in good agreement with the standard literature value of 71.7 GPa. It seems clear that using the Makishima Mackenzie model as originally formulated leads to a significant overestimate of the Young's modulus in B_2O_3 glass.

Enhancing the Makishima Mackenzie model could proceed through an improved description of bond strength, or of structure, but should also respect or at least explain the fact that the current model works satisfactorily for silicates and aluminosilicates. As a bulk description of bond strength the dissociation energy seems reasonable, and the specific dissociation

energy as energy per unit volume is already dimensionally correct to describe Young's modulus. On the other hand, as noted the description of bonding simply through atomic packing fraction clearly averages over any possible intermediate range order, which as the simulations show has a very strong correlation with elasticity. Incorporation of connectivity into the Makishima Mackenzie model is therefore where we now turn our attention.

The effect of intermediate range order as described by connectivity (topology) has been considered from several approaches. Gupta and Cooper [7, 8] considered the problem of rigid polyhedra linked through vertices, edges, and faces, and determined the residual degrees of freedom after linking such objects in d dimensions. For corner-linked tetrahedra in three dimensions, as in fused quartz, they found zero residual degrees of freedom, while for corner-linked triangles, as in B_2O_3 , one degree of freedom remains after condensation. This view thus suggests that fused quartz should be "stiff" as compared to B_2O_3 because it has no further modes to absorb energy.

In contrast to the rigid polyhedra models, the Phillips-Thorpe construction focuses on atoms linked by bonds, including typically bond stretch and bond angle bend forces [9, 10]. Analysis of such networks leads to the conclusion that as the average coordination number drops to 2.4, "floppy" regions percolate through the material so that system should become macroscopically soft. Both the Gupta-Cooper and Phillips-Thorpe models suggest that the B_2O_3 network, whether viewed as corner-linked triangles or atoms with average coordination number 2.4, should be macroscopically soft, as indeed it is compared to silicates (note that fused quartz has an average coordination number of 2.67).

In order to interpolate between the limits of a stiff and soft network, it is easier to adopt the Phillips-Thorpe perspective because of its dependence on the essentially continuous parameter $\langle r \rangle$. Indeed, the data of Figure 2 provides the dependence of stiffness on $\langle r \rangle$ for the model system described above, and these data can be satisfactorily fit to the exponential form

$$E \propto (\langle r \rangle - 2.4)^{1.7}, \quad (2)$$

as shown in Figure 5. The exponent 1.7 is in satisfactory agreement with the value 1.5 ± 0.2 obtained by He and Thorpe [3]. It is essential to recognize, though, that beyond this agreement the exponential fit also shows only a very weak at most dependence on number density, in contrast to the linear dependence posited by the Makishima Mackenzie model.

Based on the above observations that the Young's modulus depends on bond stiffness and connectivity, but hardly on density, we might posit a simple model as follows:

$$E = a(\langle r \rangle - 2.4)^{1.7} \sum_i G_i x_i + b, \quad (3)$$

where G_i is the dissociation energy per volume as before, $\langle r \rangle$ is the average connectivity, a is a dimensionless scaling constant, and b is the "background" elasticity, that is, the Young's modulus due to longer-range forces that will be present even as the connectivity drops to 2.4 or below. In contrast to the original Makishima-Mackenzie formulation, this approach has

Figure 5: Data of Figure 2 replotted as an exponential function of the average coordination number, shifted to $\langle r \rangle = 2.4$.

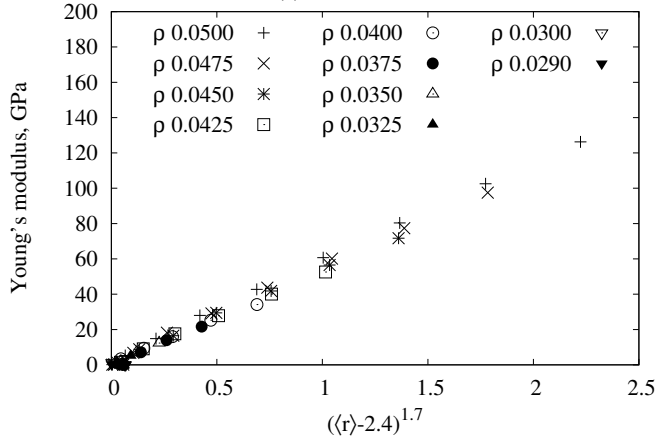
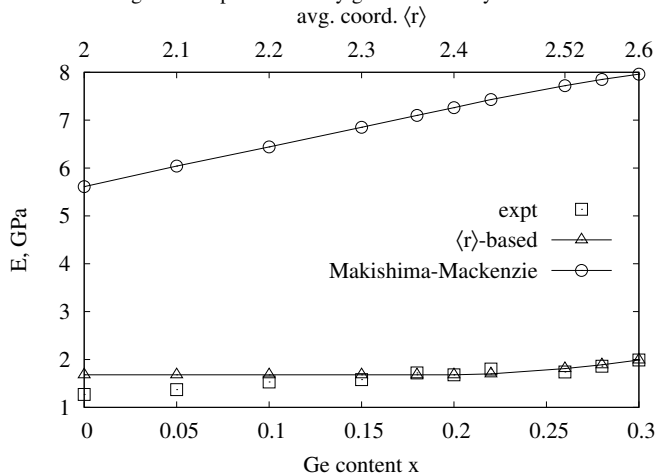


Figure 6: Data from ref. [11] of the Young's modulus of $\text{Ge}_x\text{Se}_{1-x}$ glass as a function of composition and average coordination number. Experimental data points are squares, while the triangles represent the coordination-number based model of Eq. 3 and the circles the original Makishima-Mackenzie model. The lines connecting the data points are only guides for the eye.



two fit parameters, which can be seen as a deficiency; on the other hand, it does address the significant errors made by the Makishima-Mackenzie model in the case of weakly connected glasses, as we know discuss.

The $\text{Ge}_x\text{Se}_{1-x}$ system provides a range of glass compositions over which the average coordination number can be varied from 4 (pure Ge) to 2 (Se). The electronegativity difference between these atoms is small so if connectivity models work anywhere they should work in this system. Yun *et al.* published data on the elastic properties of these glasses [11] and we plot some of them in Fig. 6. The data show that the Young's moduli fall between 1–2 GPa, and show a mild increase with added Ge (and hence increased coordination number), and a concave curvature. The Makishima-Mackenzie model applied to this system, using elemental Ge and Se as constituents, leads to a uniform overestimate of the Young's modulus (6–8 GPa) and a convex curvature. The connectivity-inspired model of Eq. 3 leads to a similar curvature, and can of course be scaled to fit the experi-

mental data very well.

Applying Eq. 3 to an oxide glass like lithium silicate leads to poorer agreement with experiment than the Makishima-Mackenzie model, primarily because, as usual with topological models, it is hard to know how to count the constraints broken or imposed by the alkali ions. If the lithium ions are counted as four-coordinate and fully constrained, then Eq. 3 leads to a broader range of predicted Young's moduli than observed experimentally (50–90 GPa as compared to 74–79 GPa). This range could be reduced by counting the constraints differently but then the predictive value of the model is lost.

We remark that the Makishima-Mackenzie model is most successful in glasses like quartz and silicates where the atomic packing fraction is around 50%. In B_2O_3 it is only 37% while in the Ge-Se system considered above it is about 20–22%. On the other hand, the connectivity-based model of Eq. 3 performs best for the Ge-Se system and less so for silicates. While both packing fraction and connectivity encode some information about structure, we surmise that in densely packed systems, packing fraction is sufficient and captures the many-body contributions to elasticity adequately. In low-density glasses, packing fraction appears to be a poor marker for structure and instead explicitly counting the direct-bond interactions, through connectivity, is more suitable. It is not clear at this point how to interpolate in a well-founded way between these two descriptions.

5. Conclusions

By considering networks of elastic force constants we showed by simulation that all elastic constants reduce to zero as the average connectivity drops to 2.4, and most importantly that this result is essentially insensitive to the model packing fractions. These observations lead to several conclusions. First, the poor agreement of the Makishima-Mackenzie model with experiment for B_2O_3 glass is likely due to the inaccuracy of packing fraction as a descriptor of structure in a glass with average coordination of only 2.4. Secondly, the dependence of Young's modulus in Ge-Se glasses is reasonably well reproduced by a model that depends only on connectivity, especially in accounting for compositions with low connectivity. Third, the success of the Makishima-Mackenzie model in silicates is likely because in dense classes, packing fraction does describe structure adequately and accounts for the many-body interactions when many atoms are relatively close.

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