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Non-Randomness in Network Glasses and Rigidity[1]

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Abstract—The continuous random network model is widely used as a realistic description of the structure of covalent glasses and amorphous solids. We point out that, in real glasses and amorphous materials, there are nonrandom structural elements that go beyond just simple chemical ordering. We propose that the network can self-organize at its formation or fictive temperature and examine some of the possible consequences of such self-organization. We find that the absence of small rings can cause the mechanical threshold to change from a second-order to a first-order transition. We show that, if stressed regions are inhibited in the network, then there are two phase transitions and an intermediate phase that is rigid but stress-free. This intermediate phase is bounded by a second-order transition, on the one hand, and a first-order transition, on the other. Recent experiments in chalcogenide glasses give evidence for this intermediate phase.

1. INTRODUCTION

The study of the structure of network glasses has progressed steadily since the initial work of Zachariasen [1] in 1932 that introduced the idea of the continuous random network (CRN). Zachariasen envisaged such networks maintaining local chemical order, but by incorporating small structural distortions, having a topology that is noncrystalline. This seminal idea has met some opposition over the years from proponents of various microcrystalline models, but today is widely accepted, mainly as a result of careful diffraction experiments from which the radial distribution function can be determined.

The CRN has been established as the basis for the most modern discussions of covalent glasses, and this has occurred because of the interplay between diffraction experiments and model building. The early model building involved building networks with ~500 atoms from a seed with free boundaries in a roughly spherical shape [2]. Subsequent efforts have refined this approach and made it less subjective by using a computer to make the decisions and incorporating periodic boundary conditions. The best of these approaches was introduced by Wooten *et al.* [3] and consists of restructuring a crystalline lattice with a designated large unit supercell, until the supercell becomes amorphous. The large supercell contains typically ~5000 atoms. Both the hand-built models and the Wooten–Winer–Weaire model are relaxed during the building process using a potential. The final structure is rather insensitive to the exact form of the potential, and a Kirkwood [4] or Keating [5] potential is typically used.

Despite this success in understanding the structure, some concerns remain. Perhaps, the most serious of these is that the network cannot be truly random. Even though bulk glasses form at high temperatures where entropic effects are dominant, it is clearly not correct to ignore energy considerations that can favor particular local structural arrangements over others. A simple example of this is a local chemical separation where, for example, bonding between like atoms is favored over bonding between unlike atoms. This can lead to chemical thresholds, as discussed later. A more subtle effect of interest to us here is how the structure itself can incorporate nonrandom features in order to minimize the free energy at the temperature of formation. This is even more important in amorphous solids, which are usually formed at lower temperatures, and so energy considerations are relatively more important, and one can expect more nonrandom local structural arrangements. Such subtle structural correlations, which we refer to as *self-organization*, will almost certainly not show up in diffraction experiments but may have other manifestations. In this paper, we focus on the mechanical properties and critical mechanical thresholds, as this is where it is easiest to make theoretical progress at this time.

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How can such an idea be developed theoretically? A proper procedure might be to use a very large supercell containing ~5000 atoms and use a first-principles approach, like that of Car and Parrinello [6], to form the glass at the appropriate temperature. It is not clear if this would lead to any self-organization of the kind discussed above, but it might. However, this is unlikely, in the same way that the superconducting state would be hard to find from a brute force solution of the Schrödinger equation for a solid. We therefore need to look at other ways of generating self-organized networks. One promising approach is that of Barkema and Mousseau [7] who explore the energy landscape of a glass by moving over saddle points to try and find successively lower minima. In this paper, we look at even more simplified approaches that show what kinds of effects self-organization, and the resulting non-randomness, can lead to.

The first of these approaches asks the questions as to what would happen to the properties of a CRN if the small rings were to be eliminated as much as is possible. We show that network models can be built where the smallest ring is ten-membered, and we demonstrate that this can dramatically alter some properties of the network. In particular, the mechanical transition from a rigid to a floppy network that occurs as the mean coordination is reduced below 2.4, seems to become *first-order* rather than *second-order* in character. We also study a *self-organized* model of a random network in which configurations that are stressed are avoided if possible. This leads to *two* phase transitions and an *intermediate phase* that is rigid but stress-free. Preliminary results show that the phase transition at the lower mean coordination is second-order, and at the upper mean coordination, it is probably first-order. There has been some recent evidence of a first-order transition being seen in chalcogenide glasses as the composition is varied and as seen through Raman scattering, and also some evidence for the intermediate phase using differential scanning calorimetry [8–10].

In the next section, we review ideas of rigidity percolation that lead to a mechanical threshold around a mean coordination of 2.4. In Sections 3 and 4, we examine the effect of the absence of rings and discuss the random bond model that contains no rings at all. In Section 5, we show how self-organization can lead to an intermediate phase that is rigid but stress-free. Finally, we discuss how these ideas may lead to a better understanding of the nature of the glassy state, and compare with experimental results.

2. RIGIDITY PERCOLATION

We start by examining a large random covalent network that contains no dangling bonds, such as $Ge_xAs_ySe_{(1-x-y)}$, where Ge stands for any fourfold-coordinated atom, As for any threefold-coordinated atom, and Se for any twofold-coordinated atom. The total number of atoms is N, there are n_r atoms with coordination r ($r = 2, 3,$ or 4)

$$N = \sum_{r=2}^{4} n_r, \tag{1}$$

and we can define the mean coordination

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} = 2 + 2x + y. \tag{2}$$

We note that $\langle r \rangle$ (where $2 < \langle r \rangle < 4$) gives a partial but very important description of the network.

In covalent networks, like $Ge_xAs_ySe_{(1-x-y)}$, the bond lengths and angles are well defined. Small displacements from the equilibrium structure can be described by a Kirkwood [4] or Keating [5] potential, which we can write *schematically* as

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta}{2}(\Delta \theta)^2. \tag{3}$$

The mean bond length is l, Δl is the change in the bond length, and $\Delta \theta$ is the change in the bond angle. The bond-bending force β is essential to the constraint counting approach for stability, in addition to the bond stretching term α. The other terms in the potential are assumed to be much smaller and can be neglected at this stage. If floppy modes are present in the system, then these smaller terms in the potential will give the floppy modes a small finite frequency [11]. This division into *strong* and *weak* forces is essential to the constraint counting approach.

We will regard the solution of the eigenmodes of the potential of Eq. (3) as a problem in classical mechanics [11–13], where the dynamical matrix has a dimensionality of $3N$, corresponding to the $3N$ degrees of freedom in the system. The total number of zero frequency modes can be estimated by Maxwell counting [12], as was first done by Thorpe [11] following the work of Phillips [14, 15] on optimal glass formation.

The constraint counting proceeds as follows. There is a single constraint associated with each bond. We assign $r/2$ constraints associated with each r-coordinated atom. In addition, there are constraints associated with the angular forces in Eq. (3). For a twofold-coordinated atom, there is a single angular constraint; for an r-fold coordinated atom, there are a total of $(2r - 3)$ angular constraints. Therefore, the total number of constraints is

$$\sum_{r=2}^{4} n_r[r/2 + (2r - 3)]. \tag{4}$$

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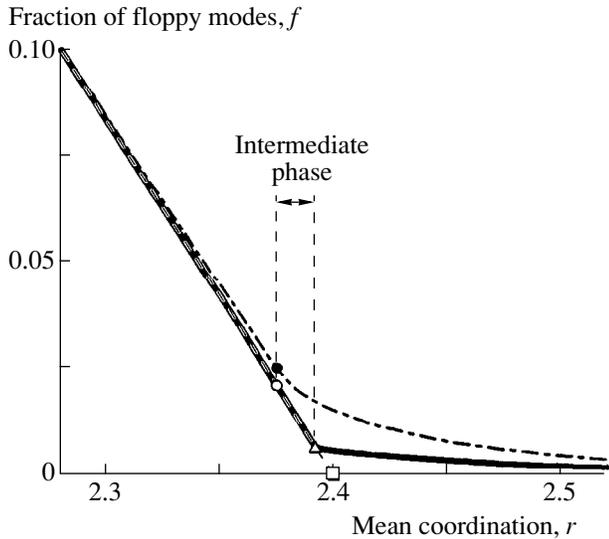Fraction of floppy modes, *f*

Fig. 1. The number of floppy modes plotted against the mean coordination for Maxwell counting (dashed line) with the associated mean field transition shown by the open square at $\langle r \rangle = 2.4$, and for a randomly diluted diamond lattice (dot-dash line), where the second-order transition is indicated by the solid circle at $\langle r \rangle = 2.375$. The self-organized model described in Section 5 follows the Maxwell curve, is shown by a solid line, and gives a second-order transition at $\langle r \rangle = 2.375$ (shown by an open circle) from a floppy to an unstressed rigid state and a first-order transition at $\langle r \rangle = 2.392$ (shown by an open triangle) to a stressed rigid state. The range of $\langle r \rangle$ over which the intermediate phase exists is indicated.
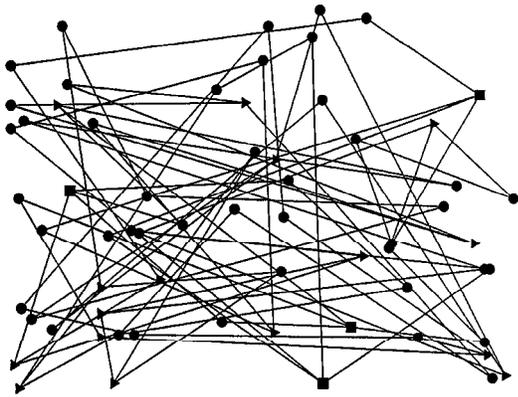

Fig. 2. The random bond model (RBM) where the squares are fourfold-coordinated sites, the triangles are threefold-coordinated sites, and the circles are twofold-coordinated sites.

The *fraction f* of zero–frequency modes is given by

$$f = \left[3N - \sum_{r=2}^{4} n_r [r/2 + (2r - 3)] \right] / 3N. \quad (5)$$

This expression can be conveniently rewritten in the compact form

$$f = 2 - \frac{5}{6} \langle r \rangle, \quad (6)$$

where $\langle r \rangle$ is defined in Eq. (2). This result is shown in Fig. 1, where the transition at a mean coordination of 2.4 is indicated by an open square. Note that this result depends upon the combination $\langle r \rangle = 2x + y$, which is the only relevant variable. When $\langle r \rangle = 2$ (e.g., Se chains), then $f = 1/3$; that is one third of all the modes are floppy. As atoms with a coordination higher than two are added to the network as cross-links, f drops and goes to zero at $\langle r \rangle_c = 2.4$. The network becomes rigid, as it goes through a phase transition from *floppy* to *rigid*.

These ideas of Maxwell have been made rigorous by using an exact algorithm, the pebble game [16–18]. This algorithm is applied to a particular network which is then decomposed into the unstressed (isostatic) rigid regions, the stressed (overconstrained) rigid regions, with flexible joints between them. It is found that the Maxwell result is a good guide, and, for the randomly diluted diamond lattice, there is a transition at a mean coordination of 2.375, as shown in Fig. 1.

3. RANDOM BOND NETWORK

We have constructed networks for glasses like $Ge_xAs_ySe_{(1-x-y)}$ by randomly positioning points in the plane as shown in Fig. 2. The main feature of these rather artificial random bond models (RBM) is that there are no loops or rings of bonds in the thermodynamic limit [18–20], and so they become equivalent to a Bethe lattice solution which has been recently discussed [19, 20]. Thus, they serve as a useful soluble guideline for what may be expected when there is a deficit of small rings. The bond lengths are quite unrealistic, but as rigidity is primarily a topological quantity, this does not make a significant difference in itself when compared to real networks that can be embedded in a three-dimensional space. Of course, it is the three-dimensional rigidity that is examined, as each vertex or atom has three degrees of freedom. The way rigidity is nucleated is rather interesting and a little different in the two cases. The rigidity transition is first order on these RBM networks, and in the Bethe lattice, rigidity nucleates from a rigid external busbar [18–20]. In the RBM shown in Fig. 2, there is no busbar, and so rigidity must nucleate using the (few) large rings that are present on any finite RBM. The transition from rigid to floppy occurs at $\langle r \rangle_c = 2.3893$ in both the RBM and the Bethe lattice which are mathematically equivalent in the thermodynamic limit. The transition occurs in an *explosive-like* manner, when an infinite rigid cluster emerges all at once with the addition of a few constraints. In Fig. 3, we show the result for this first-order transition in the RBM [18–20].

4. RINGS

It is highly desirable to construct a more realistic network but with properties similar to the RBM. Real networks inevitably have rings, yet not all of them are equally significant: isolated rings of size larger than 6 are floppy and can be a part of a rigid cluster only if they border other rings, and the larger the ring, the more bordering rings are needed. Therefore, the smaller rings seem to be important for creating local rigid regions and can act as nucleating centers.

We study the effects of removing rings on a diamond lattice, which has even rings of sizes 6, 8, 10, and up, using the pebble game algorithm [16–18]. Starting from the complete lattice, we first remove those bonds that maximally decrease the number of rings of each size of our choice. After the desirable number of rings of each size is reached, the bond dilution is continued in a random manner.

In determining the order of the transition, here, we use the number of floppy modes F in the network as a free-energy-like quantity [19, 20], while $\langle r \rangle$ is the *temperature-like* quantity, with respect to which the derivatives of F are to be taken.

Figure 4 shows the first derivatives of f with respect to the mean coordination $\langle r \rangle$ for diluted diamond lattices with different numbers of small rings left. It is seen that the curves sharpen up near the transition as six- and eightfold rings are removed. In Fig. 3, we show the result from Fig. 4 corresponding to the case when there are *no* six- and eightfold rings, together with the result for RBM and for the randomly diluted diamond lattice [18]. The former apparently has a jump comparable in size to that found in RBM. Therefore, the absence of small rings, where rigidity can be nucleated, drives the transition toward being first-order [18].

5. SELF-ORGANIZING NETWORKS

Within the present approach, we have a rather unique opportunity to construct stress-free networks without a huge computational overhead. The basic idea is that we start with a low coordinated floppy network and add bonds. This leads to rigid regions being formed, and as long as they are unstressed (isostatic), they are retained. By unstressed we mean that each bond length (angle) can have its natural length (angle) without being forced to change by the surrounding environment. Otherwise, a bond is stressed. If adding a bond would result in that bond being redundant and, hence, create a stressed (overconstrained) region, then that move is abandoned.

If each bond corresponded to a single constraint (as in the case of central-force networks), it would be possible to continue up to the point when the whole network is isostatic. Indeed, in this case, each additional bond can either remove a floppy mode from the network or put stress into it, but not both, so we can incorporate those bonds in the first category only until no
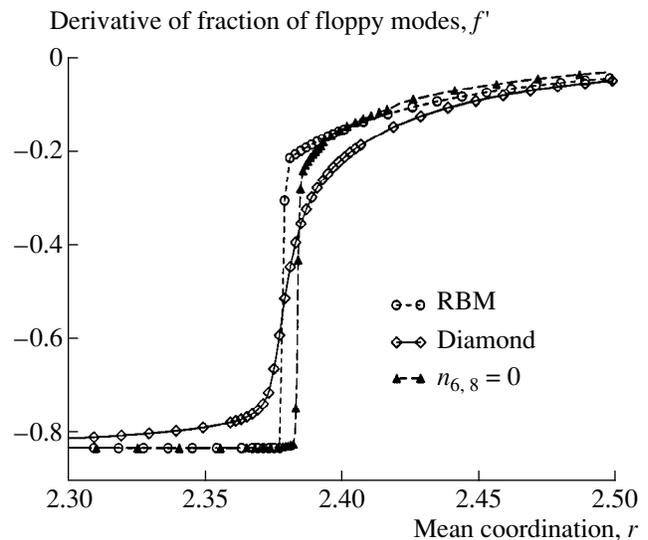
Derivative of fraction of floppy modes, f'

Fig. 3. The derivative of the fraction of floppy modes f' for the RBM, normal diamond lattice, and diamond lattice with six- and eightfold rings removed ($n_{6.8} = 0$), and then all subsequently randomly diluted.
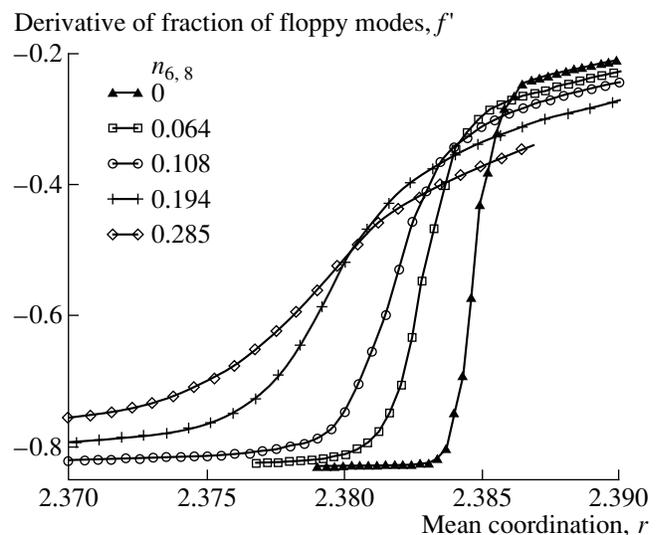
Derivative of fraction of floppy modes, f'

Fig. 4. The derivative of the fraction of floppy modes f' with respect to the mean coordination $\langle r \rangle$ for randomly diluted diamond lattices with different numbers of small rings. The total average number of six- and eightfold rings going through a site at the transition in each case is shown. The curves with diamonds and triangles are blowups of the respective curves in Fig. 3. The lines joined the symbols are drawn for the guidance of the eye only.

more floppy modes remain. This is not quite the case in glass networks, where bonds also have angular (bond-bending) constraints associated with them, so it may happen that while one part of the set of constraints associated with a given bond removes floppy modes, the other part introduces strain. In our simulations, about 0.6% of floppy modes are left when the strain becomes
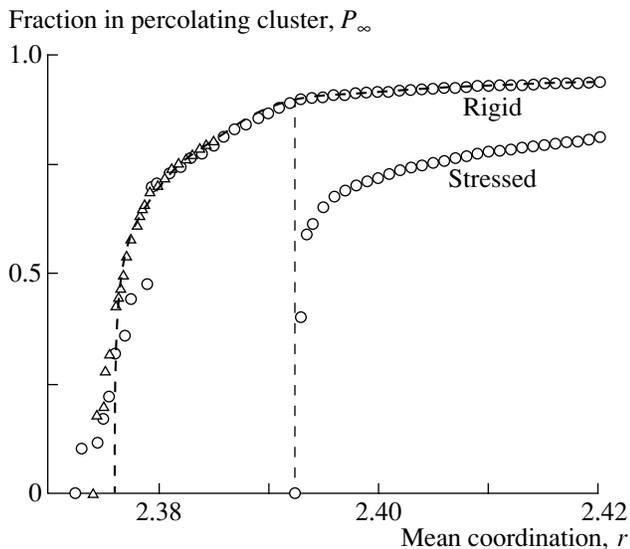
Fraction in percolating cluster, P_∞

Fig. 5. The fraction of sites P_∞ in the rigid and stressed percolating clusters. Circles are for the average over four networks with 64 000 sites, and triangles are the same for five networks with 125 000 sites. The thicker dashed lines correspond to a power law before the stress transition and are drawn for the guidance of the eye after it. Note the break in the slope of the dashed line at the first-order transition at 2.392. The intermediate phase, which is rigid but unstressed, exists for $2.375 < \langle r \rangle < 2.392$.

inevitable. At this point, which we will call the *stress transition*, a single additional bond causes a large stressed region which has a size $O(N)$ to appear, so the associated stress percolation transition is expected to be first-order.

A slight technical problem with this approach is that since we wish to model glasses having no atoms with coordination less than two, we must conduct the initial dilution in such a way that no such sites appear. It turns out to be impossible to completely remove all the redundant (stress causing) bonds. The final ratio of the number of redundant constraints to the total number of degrees of freedom is very small (typically about 0.05%) and does not grow when bonds are inserted (up to the stress transition), so it is largely irrelevant.

Before stress percolation occurs, the whole network is almost isostatic. This means that rigidity percolates through the network without any accompanying stress. This is indeed the case, as is shown in Fig. 5, in which the dependence of the fraction of sites in the percolating rigid cluster on the coordination is shown. The isostatic transition is second-order and occurs at $\langle r \rangle = 2.375 \pm 0.0015$. The critical exponent β for the size of the percolating cluster is roughly estimated from the fit as $\beta = 0.185$. This value is equal (within the error bars) to that obtained for the case of unrestricted bond insertion; i.e., when redundant bonds are also placed where $\beta = 0.175 \pm 0.02$. This is probably not accidental. Indeed, a *central-force* network obtained by restricted bond insertion is obtainable from that with unrestricted

bond insertion by removing from the latter all the bonds that where rejected while the former was built. Such a transformation does not change the cluster sizes and is smooth in $\langle r \rangle$, so the cluster size exponents are expected to be the same. Probably, a similar argument is applied when angular forces are present, though it is not as obvious.

Since restricted insertion requires the analysis of the rigidity of the network at each insertion attempt, this is a very computationally intense procedure (especially when approaching the stress transition); so in order to get several realizations, it is reasonable to do it only once to reach the stress transition and then use that network several times for further insertion. In particular, it is reasonable to insert a test bond in different random places in the network at the stress transition and then find the distribution of percolating clusters. Before each new insertion, the previous test bond is removed. It turns out that, for the network sizes used (up to 125 000 atoms), the results are strongly realization-dependent, but no noticeable size dependence was found. In some realizations, there is a single peak at about 0.5 the network size; in others, besides this peak, there are two more, with the sum of their positions giving again 0.5 of the network size (then supposedly, the jump may take place in two steps). This we consider as a strong indication of the first-order transition, with the percolating stressed cluster involving about 1/2 of the network sites after a few additional bonds are inserted at the stress transition.

Since there are no redundant constraints in the network below the stress transition, the number of floppy modes follows Maxwell counting *exactly* (which means it is perfectly linear in $\langle r \rangle$). This means that the isostatic transition is not seen in the number of floppy modes, while the stress transition is accompanied with the change of the slope, as is expected for the first-order transition (see Fig. 1).

6. DISCUSSION

We have introduced the idea of a self-organized network as a model for covalent glasses. The self-organization occurs, because, at the fictive temperature [21], which is where the glass is formed, the energy term in the free energy cannot be ignored when compared to the entropy term. This is particularly so for amorphous solids which are usually deposited at low temperatures. At the present time, it is not possible to examine all network structures and find those with the lowest free energy, and, as this is an exponentially hard computer problem, it probably will never be possible to do this for sufficiently large systems. Therefore, we have constructed simple models and looked at the effect of non-randomness, which is caused by self-organization, on the mechanical properties. In one case, this non-randomness was imposed, when the formation of small rings was inhibited. This led to a first-order transition. In another case, we avoided stressed regions and dis-

covered the existence of an intermediate phase, which is rigid but unstressed.

It is possible, but far from proven, that this later situation with an intermediate phase has been observed experimentally by Boolchand *et al.* [8–10]. They studied the $Ge_xX_{(1-x)}$ glasses (X = S or Se) by Raman scattering and found a jump in the composition dependence of the frequency of the mode which corresponds to a symmetric stretch of $Ge(X_{1/2})_4$ tetrahedra. For both S and Se, this jump occurs around the composition $x = 0.225$, which corresponds to a mean coordination $\langle r \rangle = 2.45$, and *may* correspond to the transition to the stressed state. It is also interesting to notice that there is some peculiarity observed near $\langle r \rangle = 2.40$ in both cases, where the transition appears to begin, which may correspond to the isostatic second-order transition. So, the same sequence of two transitions was probably observed, which may correspond to the first observation of the *intermediate phase* discussed in this paper. Their experimental positions (from $\langle r \rangle = 2.40$ to 2.45) do not coincide with our results (from $\langle r \rangle = 2.375$ to 2.392), which is probably due to the simplicity of our model. Note that the lower transition is second-order, and the upper transition is first-order in both the experiment and the theory. However, the theory predicts that the intermediate phase is about three times narrower and is shifted down from that seen experimentally. This may be significant and cast some doubt on making the equivalence between the experiment and the theory, or more likely, our theoretical model is just too simple to get all the details correct. Very recent works [8–10] using differential scanning calorimetry also find evidence for an intermediate phase in $Si_xSe_{(1-x)}$ glasses.

We note that there is a quite separate chemical threshold at $x = 1/3$ in $Ge_xX_{(1-x)}$ glasses at which the X–X bonds must first appear, as normally chemical alternation like Ge–X is favored. This chemical threshold is unlikely to lead to any first-order effects and is located at the mean coordination $\langle r \rangle = 2.67$ which is far from the region of interest here.

The notion of self-organized criticality [22] has been applied to many phenomena; the most familiar being avalanches in sandpiles, which appear to occur on all length scales. There are superficial connections with the work here that leads to the existence of the intermediate phase. However, much more work needs to be done—the lower isostatic transition is almost certainly of a conventional kind, and the precise nature of the upper transition to a stressed state is unclear at this time.

In this paper, we have established that the rigidity transition can be first-order if networks are not random. In the case when stressed regions were inhibited, there was also a second transition at a lower mean coordination, and a resulting intermediate phase. At this time, it is not clear how robust this intermediate phase is, although the correspondence with experimental results is encouraging and suggests it may be quite robust. It is interesting to speculate that, as a function of some yet unknown coordinate, the second-order transition may go through a *tricritical* point and become first-order and then subsequently split at a *triple* point to give the intermediate phase.

The work described in this paper was first reported at the ICAMS 18 conference in 1999 and will be published in the *J. Non-Crystalline Solids* as a special issue.

ACKNOWLEDGMENTS

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