Self-organization and rigidity in network glasses

M.V. Chubynsky, M.F. Thorpe*

Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48823, USA

Abstract

Rigidity theory has helped in our understanding of the properties of network glasses. We analyze the connection between rigidity and various non-random features in the network structure. Lack of small rings in the network can lead to a sharper rigidity transition. We review a model of network self-organization that we have proposed, in which the existence of an intermediate phase that is rigid, but stress-free, is predicted. Finally, we discuss recent experiments, in which this intermediate phase may have been observed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The systems under consideration in this mini-review are non-metallic glasses with covalent bonding, also known as network glasses. In 1932, Zachariasen introduced the continuous random network (CRN) [1]. In this model, the structure is viewed as a network of bonds between atoms that is topologically disordered (i.e. cannot be continuously deformed into an ordered crystal), yet, as implied by the word 'continuous', has no macro- or mesoscopic voids and thus is about as dense as the crystal (Fig. 1). This has become a well-established model mostly through extensive diffraction studies [2].

In 1983, Thorpe [3] considered chalcogenide compounds of the type $Ge_xAs_ySe_{1-x-y}$, where Ge stands for any atom that is fourfold bonded, As any atom that is threefold bonded and Se any atom that is twofold bonded. An assumption is made that the most important forces between the atoms are nearest-neighbor *bond-stretching* forces and angular *bond-bending* forces (the dihedral, van der Waals and other forces are neglected). Thus small displacements from the equilibrium structure can be described by a Kirkwood [4] or Keating [5] potential, which we can write *schematically* as

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta}{2}(\Delta \theta)^2 \qquad (1)$$

where Δl and $\Delta \theta$ are the changes in the bond length and bond angle, respectively.

When twofold-coordinated Se atoms dominate, the network is *flexible*, and does not resist external strain, so

the elastic moduli are zero in this model and remain quite small when the neglected forces are included [6], as external strains can be accommodated without changing covalent bond lengths and bond angles in the network. As the chemical composition is changed and the concentration of As and Ge atoms increases, at some point the network becomes rigid and the elastic moduli reflect the strong α and β forces in Eq. (1). This means that bond lengths and/or bond angles must be changed, at a considerable cost in energy, when the network is deformed. This situation is described as *rigidity percolation* and can be understood by the following analogy. In more familiar *connectivity percolation* [7], a network of sites and bonds is considered and *clusters* are defined as sets of sites such that all sites in the set are connected by at least one path. When the concentration of bonds increases, the sizes of the clusters grow and at some point a cluster connecting opposite sides of the sample emerges (i.e. percolation occurs). This percolating cluster will be infinite in the thermodynamic limit $N \rightarrow \infty$. Similarly, we define a *rigid cluster* as a set of mutually rigid sites. Again, as the number of bonds increases, these clusters grow and eventually a percolating rigid cluster emerges, and it is at this concentration of bonds that the elastic moduli start to become significant. This point was first described by Phillips [8] as the composition for optimal glass formation.

Rigidity percolation has been studied in detail and some computational methods have emerged to deal efficiently with the phenomenon [*9,10,*11–*13]—this is described in the next section. However, one concern that remains is the way the networks themselves are modeled. CRNs, as the name suggests, are supposed to be 'random', yet exactly what is meant by 'random' has always been a little mysterious. In early hand-built models using plastic ball

---

*Corresponding author. Tel.: +1-517-355-9279.
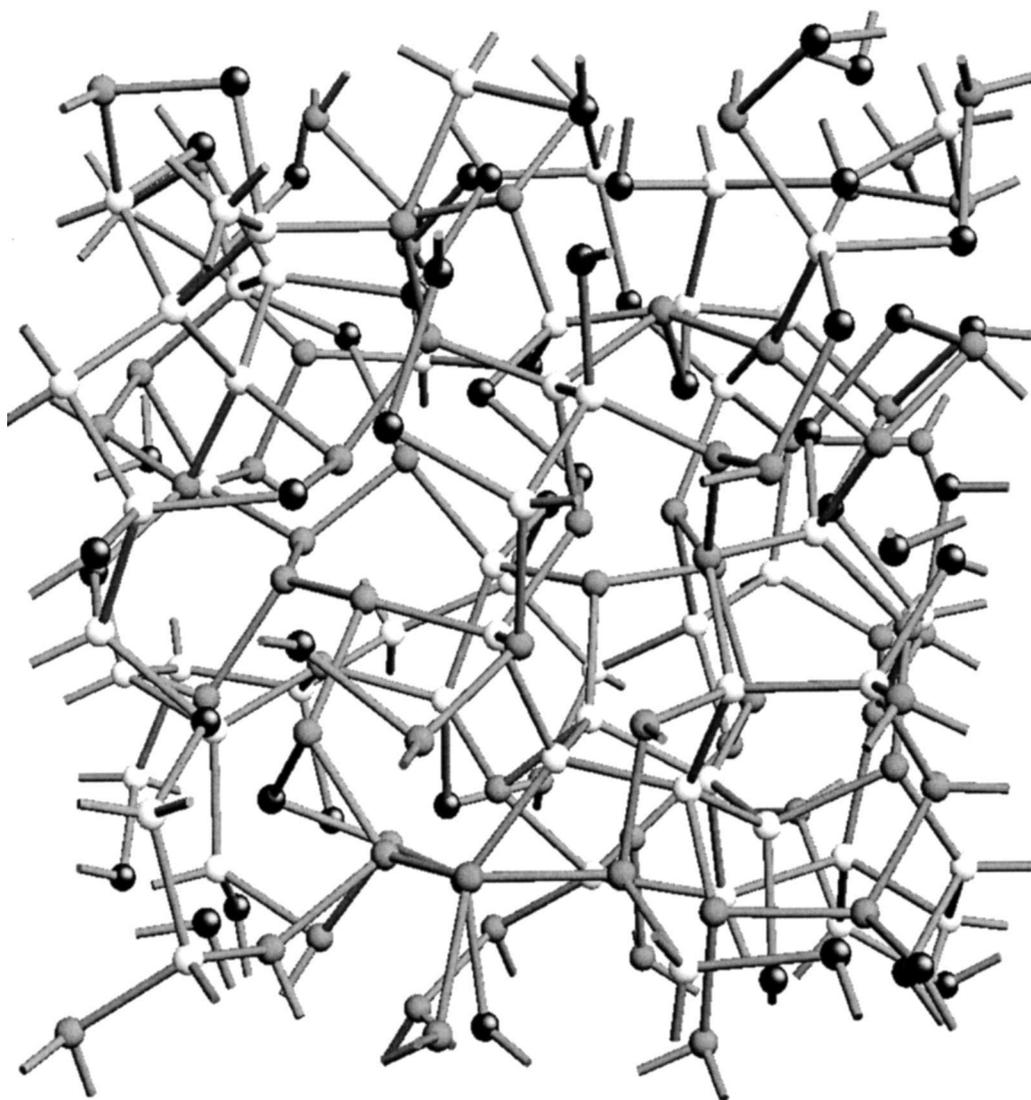*E-mail address:* thorpe@pa.msu.edu (M.F. Thorpe).

Fig. 1. A continuous random network (CRN) consisting of atoms of coordination number 2 (black balls), 3 (gray balls) and 4 (white balls).

and stick units of various kinds [14,15], building started from a seed and proceeded outwards. The model would be rotated frequently, maintaining a roughly spherical shape with the seed at the center. Each additional unit was added in as haphazard a manner as possible at the perimeter of the model while maintaining the desired local coordination. Indeed it was often thought that a glass of wine of a suitable vintage drunk before and during the model building, as well as many distractions, would actually improve the quality of the subsequent model! Later these models were relaxed, using an appropriate potential [16] while maintaining the topology established during the construction. This was the operational definition of 'random' and great efforts were made to maximize the randomness, consistent with network connectivity.

This philosophy was later extended to computer generated network models [17] where for example a large supercell of crystalline silicon was reconstructed to produce a model of amorphous silicon with periodic boundary conditions. The original technique, known as the Wooten–Winer–Weaire (WWW) algorithm [17], has since been improved [18,19] and produces networks that are considered good, as determined by comparison with diffraction results [20] and also by the reasonable results obtained in electronic structure calculations [21]. This approach can be extended to make any desired networks by 'decorating' bonds with atoms to create two-coordinated sites and/or removing bonds to create two- and threefold coordinated sites. This is somewhat unsatisfactory as it builds in the original topology of the unmodified network. How can this be improved? Various impressive ab initio approaches (such as Car-Parrinello [22]) produce models that are still too small (with only ~100 atoms) for most purposes. The small size, coupled with the periodic boundary conditions, leads to spurious internal strain. Modifications based on linear-scaling electronic structure calculations [23] or molecular dynamics with empirical potentials [24] can alleviate the size problem, but are still

too slow to achieve full relaxation of the network at appropriate temperatures. Some hopes are being placed on new methods of accelerated dynamics, such as the activation–relaxation technique by Barkema and Mousseau [25] and other methods [26–28].

The purpose of the work reviewed here is more modest: to see what effects deviations from randomness can have on the properties of networks. We describe this nonrandomness as *self-organization*, as the glasses organize themselves in such a way as to minimize their free energy at the temperature of glass formation, which is sometimes called the fictive temperature [29].

2. Constraint counting and the 'pebble-game' algorithm

We start by examining a large random covalent network that contains no dangling bonds, of the type $Ge_xAs_ySe_{1-x-y}$, consisting of atoms of coordination 4, 3 and 2, as described earlier. The total number of atoms is N, and there are n_r atoms with coordination r

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

and we can define the mean coordination

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} = 2 + 2x + y \tag{3}$$

We note that $\langle r \rangle$ (where $2 \leq \langle r \rangle \leq 4$) gives a partial but very important description of the network. It has been found to be the dominant determining parameter in describing many experimental results that relate to structure, vibrations, hardness, the glass–transition temperature, etc. [30–33]. This is sometimes referred to as the *isocoordinate rule* [33,34].

As mentioned before, we describe the small displacements of the atoms by a potential of the form of Eq. (1). The bond-bending force (β) in this equation 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 for many purposes. This division into *strong* and *weak* forces is essential to our approach.

The solution of the eigenmodes of the potential of Eq. (1) is a problem in classical mechanics [3,6,35], where the dynamical matrix has a dimensionality of $3N$, corresponding to the $3N$ degrees of freedom in the system. If any eigenmodes having zero frequency are present in the system, then the smaller terms in the potential will give these modes a small finite frequency, thus warranting the name 'floppy modes'. The total number of zero-frequency modes can be estimated by *Maxwell constraint counting*

[35], as was first done by Thorpe [3] following the work of Phillips [8] on optimal glass formation.

The constraint counting proceeds as follows. There is a single constraint associated with each bond. We assign $r/2$ constraints to each r-coordinated atom. In addition there are constraints associated with the angular forces in Eq. (1). 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 [3]. The total number of constraints is therefore

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

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

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

This expression can be conveniently rewritten in the compact form

$$f = 2 - \frac{5}{6}\langle r \rangle \tag{6}$$

where $\langle r \rangle$ is defined in Eq. (3). Note that this result depends only upon the combination $\langle r \rangle = 2 + 2x + y$ and not on x and y separately, making $\langle r \rangle$ 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 higher coordination than two are added to the network as crosslinks, f drops and goes to zero at $\langle r \rangle_c = 2.4$. The network then becomes rigid, as it goes through a phase transition from *floppy* to *rigid*.

These ideas have been made rigorous using an exact algorithm, the pebble game [*9,10,*11,*12]. This algorithm is applied to a particular network, which is then decomposed into unstressed (*isostatic*) rigid regions, and stressed (*overconstrained*) rigid regions, with flexible joints between the rigid regions. It is found that the result (6) is a good guide, and for example the randomly diluted diamond lattice has a transition at a mean coordination of 2.375 [*36].

The case when atoms of coordination 1 are present can also be treated [37]. In this case, Maxwell counting applied straightforwardly gives

$$\langle r \rangle_c = 2.4 - 0.4 n_1 \tag{7}$$

where n_1 is the concentration of the singly coordinated sites. This result is not completely reliable, though, since long dangling chains may be present that do not contribute to the network's rigidity. The proper procedure would be to strip the network of these chains until no singly-coordinated sites remain and applying Maxwell counting to the residual 'skeleton' network. However, when n_1 is low and the singly-coordinated atoms only bind to atoms of coordination 3 and higher, Eq. (7) is good enough.

The order parameter characterizing the rigidity transition

can be chosen, again by analogy with connectivity percola-tion, as the fraction of the network belonging to the percolating cluster, or, alternatively, as the fraction belong-ing to the percolating stressed region (percolating set of stressed bonds). Both these quantities are zero in the floppy phase and non-zero in the rigid phase. In this case, there is no discontinuity in these quantities at the transition, and the transition is second order. Also, it was suggested [*38] that the negative of the number of floppy modes can serve as the free energy for the problem, and the order of the transition can be determined from the behavior of this quantity. This correspondence with the free energy has not been proved in general except for the simplest cases [*38].

3. Ring-deficient networks

We have constructed networks for glasses like $Ge_xAs_ySe_{1-x-y}$ by randomly positioning points as shown

in Fig. 2. The main feature of these rather extreme Random Bond Models (RBM) is that there are _no_ finite loops or rings of bonds in the thermodynamic limit $N \to \infty$ and a RBM becomes equivalent to a Bethe lattice solution which has been recently discussed [*36,*38,*39,40]. 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. The rigidity transition in a RBM occurs in an _explosive-like_ manner, when an infinite rigid cluster emerges all at once with the addition of a few constraints (with no finite loops, there is no way to have a finite rigid cluster in this case). So the rigidity transition is first order on RBM networks. This is seen in both order parameters as defined above (the fractions in the percolating rigid cluster and percolating stressed region both have a jump at the transition) and also in the number of floppy modes, whose derivative is discontinuous at the transition. The transition
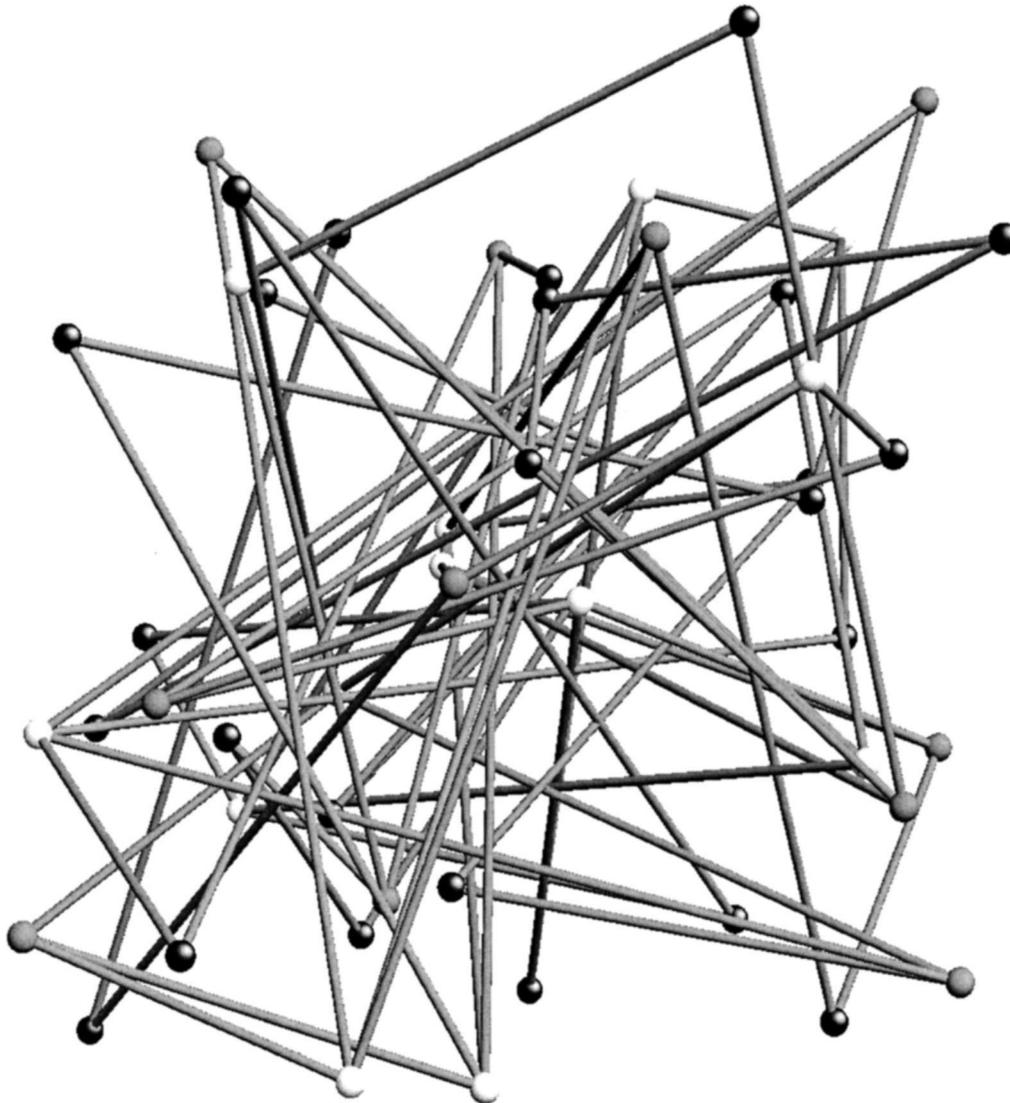

Fig. 2. A random bond model (RBM) consisting of atoms of coordination number 2 (black balls), 3 (gray balls) and 4 (white balls).

occurs at $\langle r \rangle_c = 2.3893$, which is very close to where it is in CRNs like that shown in Fig. 1.

The RBM, in particular, serves as a useful soluble model for what may be expected when there is a deficit of small rings. It would be desirable to construct more realistic networks 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 smaller rings are important for creating local rigid regions that can act as nucleating centers.

We have studied the effects of removing rings on a diamond lattice, which has rings of even sizes 6, 8, 10, and up, and then using the pebble-game algorithm to analyze the resulting network [**41]. Starting from the diamond lattice, we first remove those bonds that maximally decrease the number of small rings. After the desirable number of rings of each size is reached, bond dilution is continued in a random manner. The transition does indeed sharpen up as the number of rings of sizes 6 and 8 is decreased and looks first order when such rings are completely absent. However, a *tricritical point*, where the transition changes from first to second order has proved elusive to pinpoint. In any case, if for some reason, the structure of a glass is ring-deficient, the rigidity transition is expected to be sharper and hence more robust. Note that large numbers of edge-sharing tetrahedra in glasses like Ge_xS_{1-x} are irrelevant for rigidity as the resulting fourfold rings can be shrunk to a point. However as an indirect result there are likely to be fewer rings of size 6 and above in the network, and hence the transition is pushed in the direction of being discontinuous.

4. Self-organizing networks

Within the pebble-game approach there is a rather unique opportunity to construct stress-free networks without a huge computational overhead. The basic idea is to 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 adjust by the surrounding environment. If adding a bond would result in that bond being redundant and hence create a stressed (overconstrained) region, then that move is abandoned. In this way the network *self-organizes* to avoid stress. When no independent (non-redundant) bond can be inserted, stress becomes inevitable and further insertion is continued at random. More technical details of this procedure are presented in Refs. [**41–**43].

The results obtained for this model are as follows. First, almost the whole network becomes isostatically rigid before stress becomes inevitable, so rigidity percolates

before any stress appears. When stress first appears, it immediately percolates and at this point the *stress percolation* transition occurs. Thus we observe two separate transitions, the rigidity-percolation transition at a lower mean coordination and the stress-percolation transition at a higher mean coordination, and in between these two thresholds the *intermediate phase* forms, which is rigid, but unstressed. This is illustrated in Fig. 3, in which the fractions of sites in the percolating rigid cluster and the percolating stressed region are shown as a function of the mean coordination. It was already mentioned that these quantities serve as order parameters. From this plot, the rigidity transition is second order, is located at $\langle r \rangle = 2.375 \pm 0.0015$ and has the cluster-size critical exponent $\beta \approx 0.185$. The stress transition is much sharper, being consistent with the exponent $\beta' \approx 0.11$, but could very well be first order; its position is at $\langle r \rangle = 2.392 \pm 0.001$.

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 $\langle r \rangle$ as given in Eq. (6)). The rigidity transition is not seen in the number of floppy modes, while the stress transition is accompanied by the change in the slope of $f(\langle r \rangle)$, as would be expected for the first-order transition (Fig. 4).

The *intermediate phase* has interesting mechanical properties. Despite being rigid, the network in the intermediate phase has zero elastic moduli in the thermodynamic limit [**42,**43], so it can be said to be just *marginally rigid* (of course, it is implied that the weak forces are neglected). So again, only the upper stress transition is seen in the elastic moduli. Of course in reality in experiments, the intermediate phase will have small
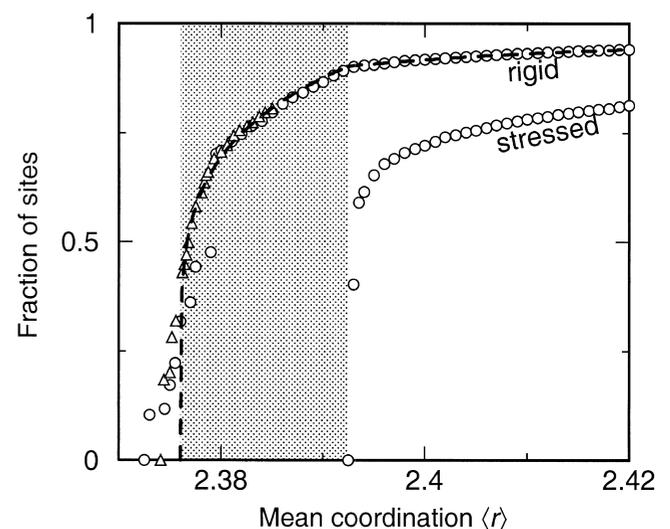

Fig. 3. Fractions of sites in the rigid and stressed percolating clusters in the self-organized model. The intermediate phase is shaded. Circles are averages over four networks with 64 000 sites, triangles are averages over five networks with 125 000 sites. The dashed lines are power-law fit below the stress transition and for the guidance of the eye above.
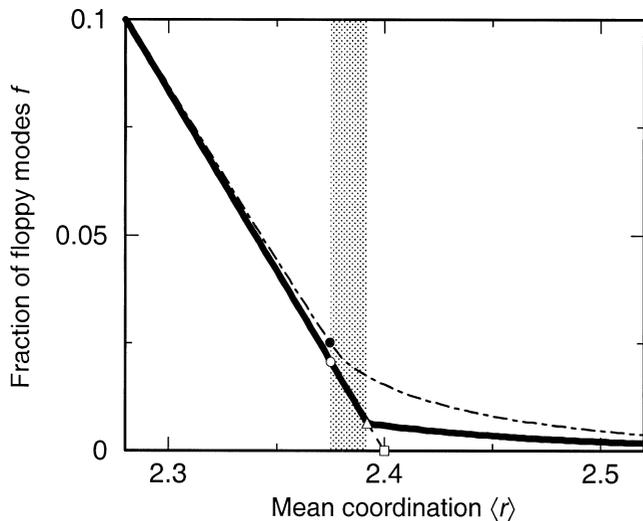
Fig. 4. The fractions of floppy modes per degree of freedom for the diluted diamond lattice for both self-organized (solid line) and random (dot–dashed line) cases. Various thresholds are shown with symbols: rigidity (open circle) and stress (triangle) in the self-organized case and the combined rigidity and stress threshold (filled circle) in the random case. The Maxwell counting prediction (Eq. (6)) is shown with the dashed line and the corresponding threshold is indicated with a square. The intermediate phase in the self-organized case is shaded. The Maxwell counting line (dashed) is seen only above the stress transition point in self-organized networks, as below this point it coincides with the line for the self-organized case.

non-zero elastic moduli because of the weaker neglected terms in the potential, as discussed earlier.

5. Experimental results

It is possible that the intermediate phase mentioned in this paper has been observed experimentally. Boolchand et al. have carefully studied a number of systems by Raman scattering and modulated differential scanning calorimetry (MDSC), monitoring various quantities as the chemical composition was varied. Their experiments are reviewed in detail in [**44]. In particular, in Si_xSe_{1-x} glasses, they observed two kinks in the composition dependence of the Raman mode corresponding to the symmetric stretch of $Si(Se_{1/2})_4$ tetrahedra, at $\langle r \rangle = 2.40$ and $\langle r \rangle = 2.54$ [*45] (Fig. 5a). Also, in their MDSC measurements in the same system, they observed a broad minimum of the non-reversing heat flow measured across the glass transition, and the minimum is bounded by the same values of $\langle r \rangle$ [*45] (Fig. 5b, filled circles). Boolchand et al. interpret this as an indication of the intermediate phase, so that the rigidity transition occurs at 2.40 and the stress transition at 2.54. Note that this range is wider than the theoretical intermediate phase discussed earlier, but it is probable that the theoretical model is just too simple to get all the details
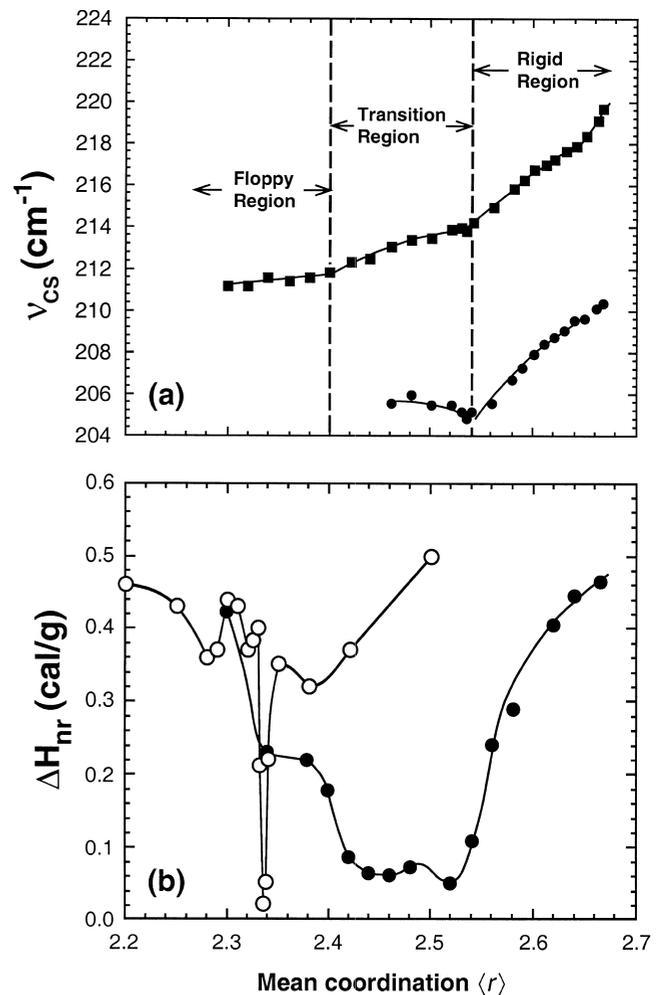

Fig. 5. (a) Frequencies of two Raman modes corresponding to the motion of corner-sharing tetrahedra in Si_xSe_{1-x} shown as a function of mean coordination. (b) Non-reversing heat variation in Si_xSe_{1-x} (filled circles) and $Ge_{0.25}S_{0.75-x}I_x$ (open circles) glasses. Both panels are adapted from Ref. [**44].

correct. Wide minima in the non-reversing heat flow were also observed in other systems (Ge–As–Se [46], Ge–Se [*47,48], As–Se [49]), but apparently no sharp thresholds. On the other hand, in the $Ge_{0.25}S_{0.75-y}I_y$ system [*50], the minimum is very narrow (Fig. 5b, open circles) and it is concluded that the intermediate phase is absent in this system; the threshold is shifted down from 2.4 in exact accordance with Eq. (7). Returning to Raman scattering, in some cases the results seem to depend qualitatively on the input laser *power*: in the Ge–Se system, two transitions are seen at low power [48] and one at high power [*47] (the latter case is shown in Fig. 6), which Boolchand et al. explain by *photomelting*. Also worth mentioning are the results by Wang et al. [*51] who measured the ratio of the intensities at the maximum and minimum in the low-frequency spectra (the Boson peak) and saw a single threshold at 2.4 in both Ge–Se (Fig. 7) and Ge–S systems
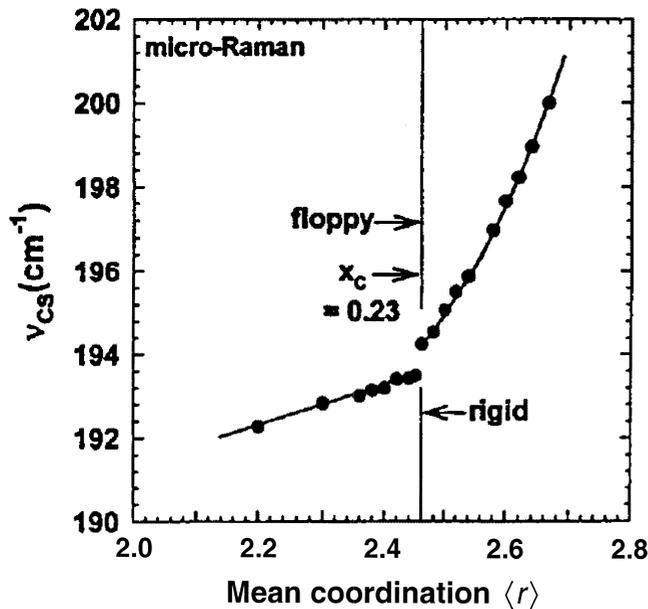
Fig. 6. Corner-sharing mode frequency variation in Ge_xSe_{1-x} glasses from high-intensity Raman measurements. The intermediate phase has collapsed to a single point. Adapted from Ref. [**44].

(the input power was comparable to that of the high-power experiments of Boolchand et al.).

6. Conclusions

Just as this paper was being prepared, a preprint by M. Micoulaut [**52] proposes a different, although related, mechanism of self-organization and formation of the intermediate phase. Indeed, this is an exciting time to be
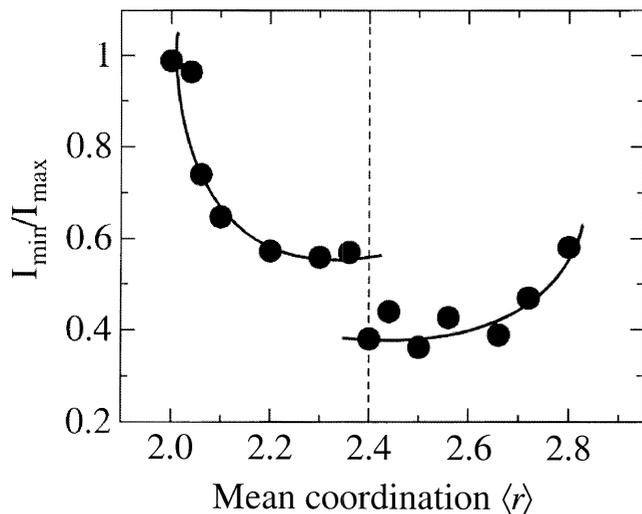

Fig. 7. The ratio of Raman intensities at the minimum and the maximum around the Boson peak in Ge_xSe_{1-x} glasses. Adapted from Ref. [**51].

studying glasses, with plenty of ideas around and the status and ubiquity of the intermediate phase in glasses under debate. It is important in the future to try and establish the stress-free nature of the intermediate phase, possibly by experiments that directly show that all covalent bonds and angles in the glass have their natural (unstrained) lengths.

Acknowledgements

References

Papers of particular interest, published within the annual period of review, have been highlighted as:
* of special interest;
** of outstanding interest.

[1] Zachariasen WH. The atomic arrangement in glass. J Am Chem Soc 1932;54:3841–51.
[2] Wright AC. X-ray and neutron diffraction: experimental techniques and data analysis. In: Thorpe MF, Mitkova MI, editors, Amorphous insulators and semiconductors, Dordrecht: Kluwer, 1997, pp. 83–131.
[3] Thorpe MF. Continuous deformations in random networks. J Non-Cryst Solids 1983;57:355–70.
[4] Kirkwood JG. Skeletal modes of vibration of long-chain molecules. J Chem Phys 1939;7:506–9.
[5] Keating PN. Theory of the third-order elastic constants of diamond-like crystals. Phys Rev 1966;145:674–8.
[6] Cai Y, Thorpe MF. Floppy modes in network glasses. Phys Rev B 1989;40:10535–42.
[7] Stauffer D, Aharony A. Introduction to percolation theory, 2nd ed. London: Taylor and Francis, 1992.
[8] Phillips JC. Topology of covalent non-crystalline solids. 1. Short-range order in chalcogenide alloys. J Non-Cryst Solids 1979;34:153–81.
[*9] Jacobs DJ, Thorpe MF. Generic rigidity percolation: the pebble game. Phys Rev Lett 1995;75:4051–4.
[10] Jacobs DJ, Hendrickson B. An algorithm for two-dimensional rigidity percolation: the pebble game. J Comput Phys 1997;137:346–65.
[*11] Jacobs DJ, Thorpe MF. Generic rigidity percolation in two dimensions. Phys Rev E 1996;53:3682–93.
[*12] Jacobs DJ. Generic rigidity in three-dimensional bond-bending networks. J Phys A Math Gen 1998;31:6653–68.
[*13] Moukarzel C, Duxbury PM. Stressed backbone and elasticity of random central-force systems. Phys Rev Lett 1995;75:4055.
[14] Bell RJ, Dean P. Properties of vitreous silica: analysis of random network models. Nature 1966;212:1354–6.
[15] Polk DE. Structural model for amorphous silicon and germanium. J Non-Cryst Solids 1971;5:365–76.
[16] Steinhardt P, Alben D, Weaire D. Relaxed continuous random network models. I. Structural characteristics. J Non-Cryst Solids 1974;15:199–214.

[17] Wooten F, Winer K, Weaire D. Computer generation of structural models of amorphous Si and Ge. Phys Rev Lett 1985;54:1392–5.

[18] Mousseau N, Barkema GT, Nakhmanson SM. Recent developments in the study of continuous random networks. Phil Mag B 2002;82:171–83.

[19] Vink RLC, Barkema GT, Stijnman MA, Bisseling RH. Device-size atomistic models of amorphous silicon. Phys Rev B 2001;64:245214.

[20] Djordjevic BR, Thorpe MF, Wooten F. Computer model of tetrahedral amorphous diamond. Phys Rev B 1995;52:5685–9.

[21] Durandurdu M, Drabold DA, Mousseau N. Approximate ab initio calculations of electronic structure of amorphous silicon. Phys Rev B 2000;62:15307–10.

[22] Car R, Parrinello M. Unified approach for molecular dynamics and density functional theory. Phys Rev Lett 1985;55:2471–4;
Lewis LJ, De Vita A, Car R. Structure and electronic properties of amorphous indium phosphide from first principles. Phys Rev B 1998;57:1594–606.

[23] Goedecker S. Linear scaling electronic structure methods. Rev Mod Phys 1999;71:1085–123.

[24] Vashishta P, Kalia RK, Nakano A, Li W, Ebbsjö I. Molecular dynamics methods and large-scale simulations of amorphous materials. In: Thorpe MF, Mitkova MI, editors, Amorphous insulators and semiconductors, Dordrecht: Kluwer, 1997, pp. 151–213.

[25] Mousseau N, Barkema GT. Traveling through potential energy landscapes of disordered materials: The activation–relaxation technique. Phys Rev E 1998;57:2419–24.

[26] Voter AF. Hyperdynamics: accelerated molecular dynamics of infrequent events. Phys Rev Lett 1997;78:3908–11.

[27] Sorensen MR, Voter AF. Temperature-accelerated dynamics for simulation of infrequent events. J Chem Phys 2000;112:9599–606.

[28] Henkelman G, Jonsson H. Long time scale kinetic Monte Carlo simulations without lattice approximation and predefined event table. J Chem Phys 2001;115:9657–66.

[29] Geissberger AE, Galeener FL. Raman studies of vitreous SiO_2 versus fictive temperature. Phys Rev B 1983;28:3266–71.

[30] Tatsumisago M, Halfpap BL, Green JL, Lindsay SM, Angell CA. Fragility of Ge–As–Se glass-forming liquids in relation to rigidity percolation, and the Kauzmann paradox. Phys Rev Lett 1990;64:1549–52.

[31] Love SP, Sievers AJ, Halfpap BL, Lindsay SM. Effects of network topology on low-temperature relaxation in Ge–As–Se glasses, as probed by persistent infrared spectral hole burning. Phys Rev Lett 1990;65:1792–5.

[32] Senapati U, Firstenberg K, Varshneya AK. Structure–property interrelations in chalcogenide glasses and their practical implications. J Non-Cryst Solids 1997;222:153–9.

[33] Effey B, Cappelletti RL. Neutron inelastic scattering study of Se–As–Ge glasses: a test of the vibrational isocoordinate rule. Phys Rev B 1999;59:4119–24.

[34] Mousseau N, Drabold DA. Numerical studies of the vibrational isocoordinate rule in chalcogenide glasses. Eur Phys J B 2000;17:667–71.

[35] Maxwell JC. On the calculation of the equilibrium and stiffness of frames. Phil Mag 1864;27:294–9.

[*36] Thorpe MF, Jacobs DJ, Chubynsky NV, Rader AJ. Generic rigidity of network glasses. In: Thorpe MF, Duxbury PM, editors, Rigidity theory and applications, New York: Kluwer/Plenum, 1999, pp. 239–78.

[37] Boolchand P, Thorpe MF. Glass-forming tendency, percolation of rigidity, and onefold-coordinated atoms in covalent networks. Phys Rev B 1994;50:10366–8.

[*38] Duxbury PM, Jacobs DJ, Thorpe MF, Moukarzel C. Floppy modes and the free energy: rigidity and connectivity percolation on Bethe lattices. Phys Rev E 1999;59:2084–92.

[*39] Moukarzel C, Duxbury PM, Leath PL. First-order rigidity on Cayley trees. Phys Rev E 1997;55:5800–11.

[40] Jacobs DJ, Thorpe MF. Comment on 'Infinite cluster geometry in central-force networks'. Phys Rev Lett 1998;80:5451.

[**41] Thorpe MF, Jacobs DJ, Chubynsky MV, Phillips JC. Self-organization in network glasses. J Non-Cryst Solids 2000;266–269:859–66.

[**42] Thorpe MF, Chubynsky MV. Rigidity and self-organization of network glasses and the intermediate phase. In: Thorpe MF, Tichý L, editors, Properties and applications of amorphous materials, Dordrecht: Kluwer, 2001, pp. 61–96.

[**43] Thorpe MF, Chubynsky MV. The intermediate phase and self-organization in network glasses. In: Phillips JC, Thorpe MF, editors, Phase transitions and self-organization in electronic and molecular networks, New York: Kluwer/Plenum, 2001, pp. 43–64.

[**44] Boolchand P, Georgiev DG, Goodman B. Discovery of the intermediate phase in chalcogenide glasses. J Optoelectron Adv Mater 2001;3:703–20.

[*45] Selvanathan D, Bresser WJ, Boolchand P, Goodman B. Thermally reversing window and stiffness transitions in chalcogenide glasses. Solid State Commun 1999;111:619–24.

[46] Wang Y, Boolchand P, Micoulaut M. Glass structure, rigidity transitions and the intermediate phase in the Ge–As–Se ternary. Europhys Lett 2000;52:633–9.

[*47] Feng XW, Bresser WJ, Boolchand P. Direct evidence for stiffness threshold in chalcogenide glasses. Phys Rev Lett 1997;78:4422–5.

[48] Boolchand P, Feng X, Bresser WJ. Rigidity transitions in binary Ge–Se glasses and the intermediate phase. J Non-Cryst Solids 2001;293:348–56.

[49] Georgiev DJ, Boolchand P, Micoulaut M. Rigidity transitions and molecular structure of As_xSe_{1-x} glasses. Phys Rev B 2000;62:9228–31.

[*50] Wang Y, Wells J, Georgiev DJ, Boolchand P, Jackson K, Micoulaut M. Sharp rigid to floppy phase transition induced by dangling ends in a network glass. Phys Rev Lett 2001;87:185503.

[*51] Wang Y, Nakamura M, Matsuda O, Murase K. Raman-spectroscopy studies on rigidity percolation and fragility in Ge-(S,Se) glasses. J Non-Cryst Solids 2000;266–269:872–5.

[**52] Micoulaut M. Rigidity transitions and constraint counting in amorphous networks: beyond the mean-field approach. Los Alamos e-print archive, cond-mat/0201366.