

RIGIDITY PERCOLATION AND THE CHEMICAL THRESHOLD IN NETWORK GLASSES

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Introduction

Rigidity theory has helped in our understanding of the properties of network glasses. In 1983, Thorpe [1] considered chalcogenide glasses of the type $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$, where Ge stands for any atom that is fourfold coordinated, As any atom that is threefold coordinated and Se any atom that is twofold coordinated. We will use the terms "atom" and "site" interchangeably. An assumption is made that the most important forces between the atoms are nearest-neighbor *bond-stretching* (or central) forces and *bond-bending* (or angular) forces. Dihedral, van der Waals and other forces are neglected. This division into strong and weak forces is essential to the rigidity theory approach. Thus small displacements from the equilibrium structure can be described by a Kirkwood [2] or Keating [3] potential, which we can write *schematically* as

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

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 [4], 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 forces in (1). This means that bond lengths and/or bond angles must now 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* [5], 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. Similarly, we can 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 [6] as the composition for optimal glass formation.

Maxwell counting

We first review the rigidity approach briefly. Our network consists of atoms of coordination 2, 3 and 4, as described earlier. The total number of atoms is N , and there are n_r atoms with coordination r

$$N = \sum_{r=2}^4 n_r \quad (2)$$

and we can define the mean coordination

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

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. [7-10]. This is sometimes referred to as the *isocoordinate rule* [10,11].

The solution of the eigenmodes of the potential of Eq. (1) is a problem in classical mechanics [1,4,12], 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 these smaller terms in the potential will give these modes a small finite frequency, thus warranting the name 'floppy modes'.

The original approach [1] to describing rigidity of glass networks is known as constraint counting or *Maxwell counting*, as the idea goes back to J.C. Maxwell's 1864 paper [12]. Maxwell counting proceeds as follows. There is a single central-force constraint associated with each bond. As each bond is shared between two atoms, 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 [1]. The total number of constraints is therefore

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

As the total number of sites is given by Eq. (2) and the total number of bonds is

$$B = \sum_{r=2}^4 n_r r / 2 \quad (5)$$

Eq. (4) can be rewritten as

$$C = 5B - 3N \quad (6)$$

Then Maxwell counting assumes that the number of floppy modes F is the difference between the total number of degrees of freedom, $3N$, and the number of constraints C :

$$F = 3N - C = 3N - \sum_{r=2}^4 n_r [r/2 + (2r - 3)] = 6N - 5B \quad (7)$$

The *fraction* of zero-frequency modes is given by $f = F/3N$ which can be conveniently rewritten in the compact form

$$f = 2 - \frac{5}{6} \langle r \rangle \quad (8)$$

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 the critical $\langle r \rangle_c = 2.4$. The network then becomes rigid, as it goes through a phase transition from *floppy* to *rigid*.

Molecular framework conjecture and the pebble game

Maxwell counting is a single global count and, generally speaking, *only* approximate, for two reasons. First, not every constraint is independent; those connecting atoms already mutually rigid are *redundant*, do not change the number of floppy modes, so should not be counted - in fact, Maxwell counting gives a lower estimate of the number of floppy modes. Note that these redundant constraints introduce *stress* into the network - whenever they are present, there is stress, whereas if they are absent, there is no stress. Second, at the rigidity transition, there can still be some floppy inclusions in an overall rigid network, so the number of floppy modes is not exactly zero.

Note first that if we apply Maxwell counting and the result for the number of floppy modes is less than the 6 degrees of freedom that the rigid body has, this result cannot be right, so obviously some redundant constraints are present. Moreover, we can do constraint counting for any *subnetwork* of the network, by which we mean any set of atoms together with bonds connecting them. Again, if for at least one of such subnetworks, Maxwell counting gives less than 6 floppy modes, this is sufficient to conclude that there are redundant constraints. Subnetworks consisting of just isolated sites or dimers should be disregarded (these have just 3 and 5 degrees of freedom, respectively).

An important proposition is that for networks, in which all angular constraints are present - which is exactly the case we consider here - checking all subnetworks should suffice to establish whether a given network has redundant constraints or not. This can be formulated as follows:

A generic network in three dimensions, with angular constraints between every pair of bonds that share a common site, has no redundant constraints

if no connected subnetwork of the network containing N_s sites and B_s bonds violates $5B_s \leq 6N_s$.

This statement is a part of the *molecular framework conjecture* proposed by Tay and Whiteley [13]. In its full form, this conjecture also allows finding the exact number of floppy modes. It has not been proved rigorously, however, no counterexamples have been found in many years of extensive studies. Note that the situation is quite different for networks when angular constraints are not present everywhere, with counterexamples for cases in which some bond angles can change freely. Also note that an analogous statement in two dimensions was proved rigorously in 1970 by a Dutch mathematician G. Laman even for networks without angular constraints and is known as the Laman's theorem [14].

This approach of exactly determining the presence or absence of redundant constraints is the basis for a numerical algorithm for exact constraint counting called the *Pebble Game* [15] and based directly on Laman's theorem in two dimensions and on the molecular framework conjecture in three dimensions. The idea is to start from a network without constraints and then place all constraints one by one. Every new constraint is checked for redundancy by an ingenious algorithm checking all subnetworks simultaneously; if the constraint is redundant, it is rejected and not counted. Besides counting floppy modes, this algorithm can find the rigid clusters. It can also find the *stressed regions*, which are defined as subnetworks that are stressed and deformed in a correlated fashion.

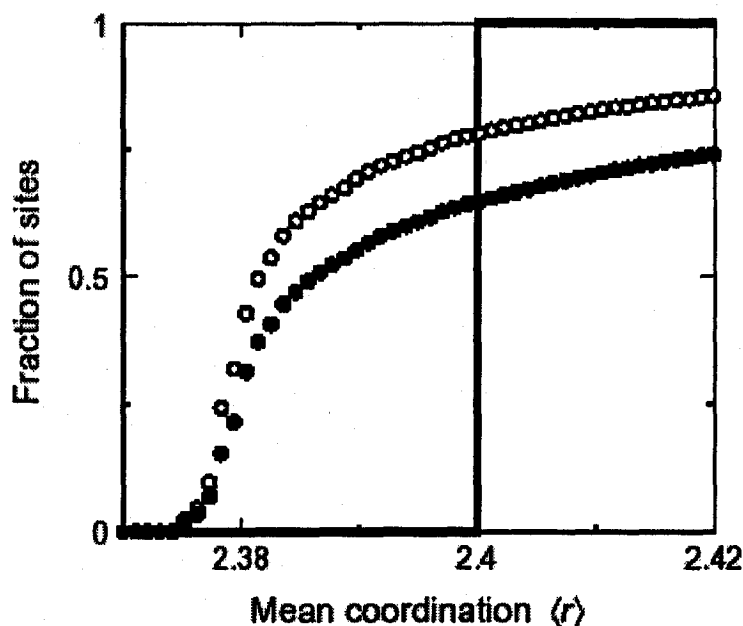


Fig. 1. The fractions of sites belonging to the percolating rigid cluster (open circles) and the percolating stressed region (filled circles) as functions of the mean coordination for the case of random dilution of the diamond lattice. The transition is second order in this case, with rounding due to finite size effects. The results are averages over 11 networks of 125000 sites each. The solid line shows these fractions for chemically ordered networks, as described later in the text. In the latter case, both quantities jump simultaneously from 0 to 1 at 2.4, and the transition is first order.

The Pebble Game was applied to sequences of networks obtained by removing bonds one by one from initially fully 4-coordinated networks in such a way that no sites with coordination less than 2 are formed. As the initial network, both the diamond lattice and an amorphous network obtained by the WWW procedure [16,17] were used. The size of the percolating rigid cluster can be used as the order parameter. Another possible order parameter is the size of the percolating stressed region. Both these quantities are zero below the transition and non-zero above (Fig. 1). Their behavior indicates that the transition is second order. In both cases, the rigidity percolation transition occurs very close to $\langle r \rangle = 2.4$ (at 2.375 and 2.385, respectively). The number of floppy modes F as a function of $\langle r \rangle$ (Fig. 2) exhibits a singularity in the second derivative at the transition and $-F$ can be regarded as a *free energy* [18].

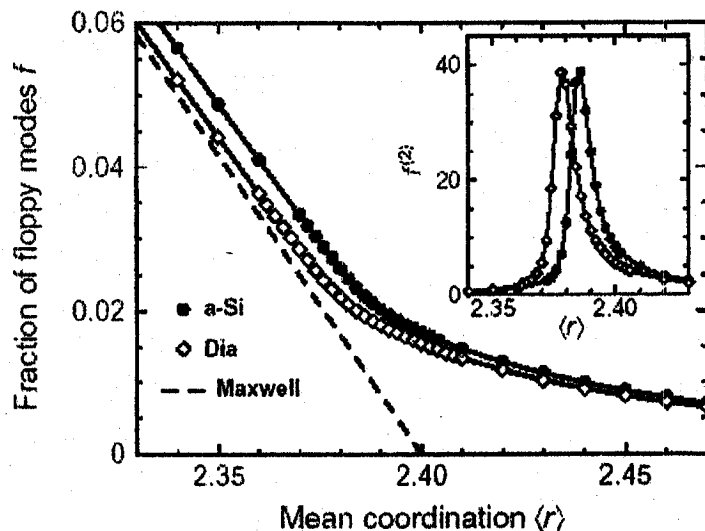


Fig. 2. The number of floppy modes per degree of freedom f for randomly diluted amorphous silicon and diamond networks. The Maxwell counting result is shown dashed. The insert shows the second derivative of f with respect to $\langle r \rangle$.

Obtaining networks by random removal of bonds is certainly not the only possibility. In real glass networks various correlations are possible. We considered a model of *self-organized networks* [19], which were built from scratch (no bonds present) with bonds being added in such a way that no stress appears for as long as possible. In this case an *intermediate phase* appears that is rigid, but unstressed [19], so there are two transitions instead of one: at the first transition, the percolating rigid cluster appears, at the second transition, the percolating stressed region appears.

Chemically ordered networks

Here we consider another construction that models the consequences of the presence of *chemical ordering*. Consider a network, all sites of which are

3-fold coordinated. In Fig. 3 we show an example of a piece of such a network. This particular example was obtained in [20] by starting from a honeycomb lattice and amorphizing it by a procedure similar to the WWW method [16]. The network is constructed with *periodic boundary conditions*, this results in connections between sites at opposite boundaries and ensures that there are no free boundaries and all atoms are 3-coordinated even in a finite sample. The network is planar, but it is assumed that atoms can move in all 3 dimensions and thus have 3 degrees of freedom each. Our further consideration applies to networks with a fully 3-dimensional structure as well. Now we start decorating bonds with atoms, so that 2-coordinated atoms appear. At this stage, we do not allow more than one 2-coordinated atom to be placed between 3-coordinated atoms. In this way, we can reach $\langle r \rangle = 2.4$ that corresponds to the As_2Se_3 composition. At this point all bonds of the original 3-coordinated network are decorated with exactly one atom and the network is fully chemically ordered: there are only 2-coordinated atoms next to 3-coordinated atoms and vice versa. We continue the process of atom insertion further, by decorating the original bonds one by one with a second atom; this way we can go below 2.4 and reach $\langle r \rangle = 2.25$.

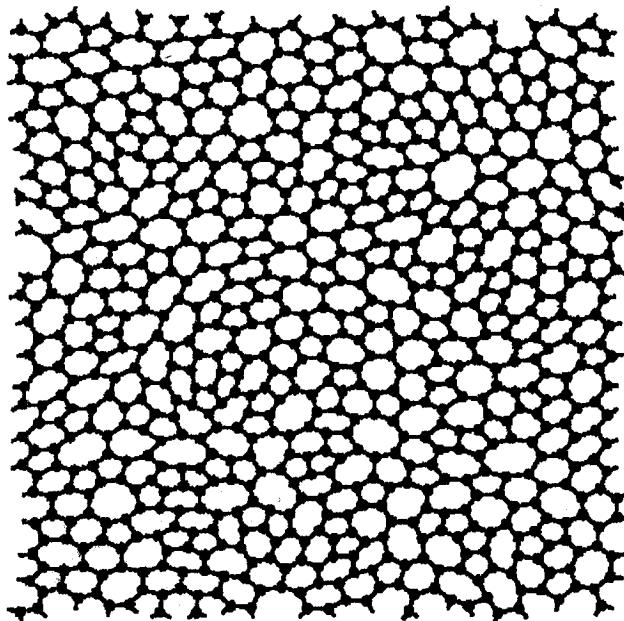


Fig. 3. The supercell of a fully 3-coordinated network consisting of 1800 sites used for simulations of chemically ordered networks described in the text.

We now apply the Pebble Game algorithm to study this sequence of networks. We find that in this case Maxwell counting is *exact*. Namely, below $\langle r \rangle = 2.4$ there are no redundant bonds and the dependence of the number of floppy modes on the mean coordination (Fig. 4) is linear and exactly as given by Maxwell counting, Eq. (8); at $\langle r \rangle = 2.4$ the rigidity transition occurs and above this point the whole network becomes rigid and stressed and there are no floppy modes at all (see Fig. 1).

Looking more carefully at the finite size effects, we find, first of all, that the number of floppy modes F is at least 6, of course, as the rigid body motions

should be counted. Interestingly, F stays exactly at 6 all the way down to the point of crossing with the Maxwell counting line (Fig. 5(a)). This crossing corresponds to a network with all bonds decorated with one atom, except for six bonds that are decorated with two atoms. In the thermodynamic limit, these six extra atoms are, of course, negligible, and the crossing is at $\langle r \rangle = 2.4$ exactly. Looking at rigidity and stress percolation (Fig. 5, (b) and (c)), we find that when all bonds are decorated with one site, except five that are decorated with two sites, the whole network is stressed; when one more site is added, stress disappears completely, but still the whole network is rigid. Finally, when yet one more site is added, the percolating rigid cluster disappears and in fact, there are no rigid clusters, except for trivial ones consisting of just one site with its neighbors. Thus the transition is *first order* now; in fact, it is extremely sharp: rigidity is completely destroyed with just a few sites added. The first order character of the transition is also reflected in the fact that now the *first* derivative of the number of floppy modes has a jump at the transition.

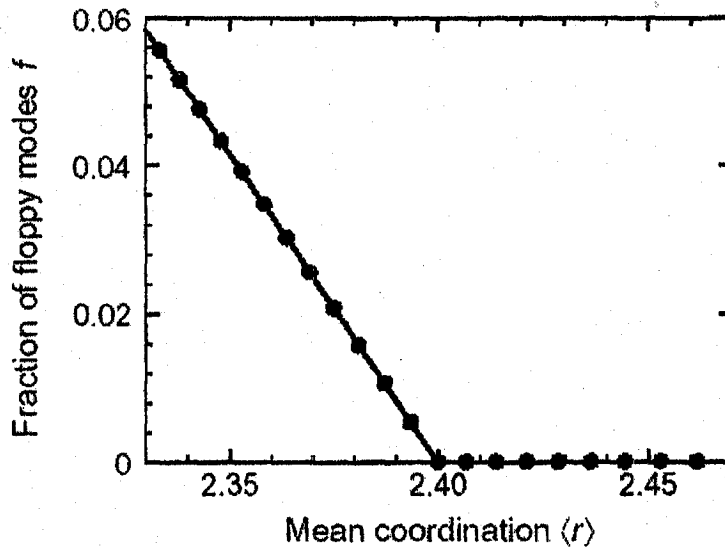


Fig. 4. The fraction of floppy modes as a function of mean coordination for chemically ordered networks obtained by decorating a 3-coordinated network of 3×3 supercells shown in Fig. 3.

We now prove that the above observations are true for a rather broad class of networks. Our proof even applies to finite networks, as long as all atoms of the starting network are still 3-coordinated. In the case that we treated with numerical simulations, this was ensured by using periodic boundary conditions; but even with free boundaries, this can be achieved; this is a minor issue, of course, as we are mostly interested in the thermodynamic limit. The only other assumption we make is that every subnetwork of the original network is connected to the rest of the network with at least four bonds (except, of course, those subnetworks consisting of just a single site, or vice versa, lacking just a single site – a site is connected with just three bonds, of course). This is a rather weak assumption that the network in Fig. 3 certainly satisfies; note, however, that the initial network should certainly contain no triangles (note that in Fig. 3 the smallest ring is a pentagon).

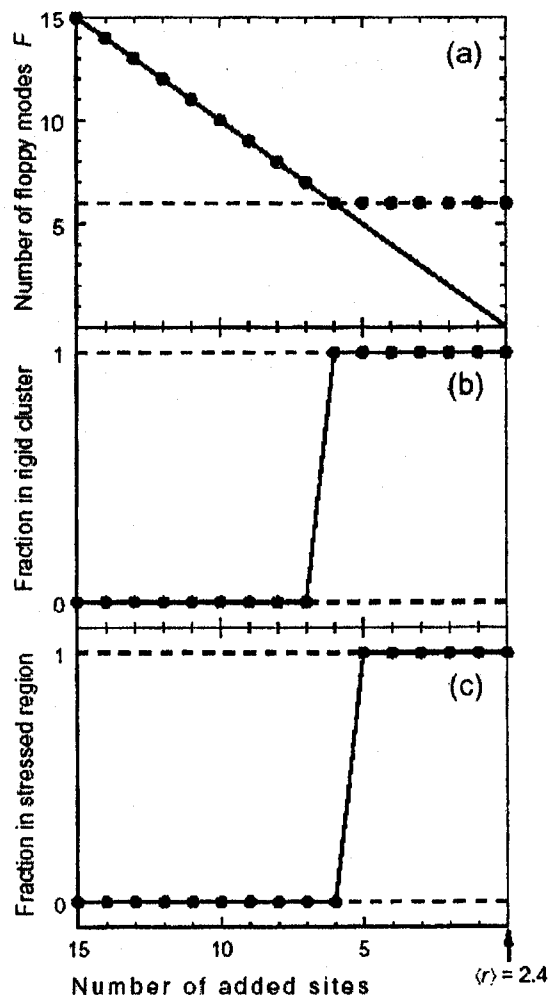


Fig. 5. A set of panels illustrating finite size effects for chemically ordered networks. Moving along the horizontal axis corresponds to changing the number of decorating sites. The right border of the plot corresponds to a network with one atom decorating each bond, which is exactly $\langle r \rangle = 2.4$. Moving to the left corresponds to adding second sites to bonds one by one; the number of added sites is specified. Panel (a) shows the number of floppy modes F . The solid line is Maxwell counting. Panels (b) and (c) show the fractions of sites in the percolating rigid cluster and in the percolating stressed region, respectively.

We first note that a network with one atom decorating each bond of the original network has the mean coordination of exactly 2.4. Consider now networks obtained from such a network by adding an extra atom to (a) 5 more bonds; (b) 6 more bonds; (c) 7 more bonds. Then in such a network all of the original bonds are decorated with one atom, except (a) 5; (b) 6; and (c) 7 bonds are decorated with two atoms. In the thermodynamic limit, these few extra atoms are negligible and all these networks still have $\langle r \rangle = 2.4$.

Now we apply the molecular framework conjecture to networks corresponding to these three cases, (a), (b), and (c), i.e. we apply constraint counting to the whole network and all subnetworks.

We first apply constraint counting to whole networks, i.e., do the usual Maxwell counting. If the number of atoms in the original 3-coordinated network was M , the number of 2-coordinated atoms is (a) $(3/2)M+5$; (b) $(3/2)M+6$; (c) $(3/2)M+7$. The number of 3-coordinated atoms is still M , the total number of sites is thus (a) $N = (5/2)M+5$; (b) $N = (5/2)M+6$ and (c) $N = (5/2)M+7$. The total number of bonds is (a) $B = 3M+5$; (b) $B = 3M+6$; (c) $B = 3M+7$. Then Maxwell counting gives (a) $F = 6N - 5B = 5$; (b) $F = 6$; (c) $F = 7$.

We now do constraint counting for subnetworks smaller than the full network. We are going to prove that in all three cases, (a), (b), and (c), constraint counting always gives more than 6 floppy modes for such networks. In view of this, it is clear that we need not consider subnetworks having dangling pieces. Indeed, if a subnetwork consists of two smaller subnetworks connected with a chain and each of the smaller subnetworks has $F > 6$, then the whole big subnetwork will always have $F > 6$ as well. We now consider three kinds of subnetworks separately.

1. Subnetworks obtained by removing just a single chain going between two 3-coordinated atoms from the full network. Such a chain will contain one or (very rarely) two 2-coordinated sites and 2 or 3 bonds, respectively. Then the number of atoms in the subgraph is $N-1$ or $N-2$, respectively, and the number of bonds is $B-2$ or $B-3$, respectively, and by checking explicitly each of the cases (a), (b), and (c), we can see that the number of floppy modes is always bigger than 6 (the least favorable case is (a) with the number of atoms $N-2$ and the number of bonds $B-3$, which gives 8 floppy modes).
2. Subnetworks obtained by removing a single 3-coordinated site with three adjacent chains. Here the lowest number of floppy modes is in the case (a) and when all the three chains happen to have two sites. In this case the number of floppy modes given by constraint counting is $8 > 6$.
3. All other subnetworks not having any dangling parts. By our assumption, such subnetworks are separated from the rest of the network by cutting 4 or more bonds. Cutting each of these bonds converts a 3-coordinated site into a 2-coordinated site. Each of the remaining 3-coordinated sites has three adjacent chains, each of them having at least one 2-coordinated site. Each of the chains is shared between two 3-coordinated sites, so if the number of 3-coordinated sites in the subnetwork is M_1 , the number of chains is $(3/2)M_1$. Moreover, since at least four 3-coordinated sites became 2-coordinated, then at least either 4 of all chains consist of 3 sites each, or 2 of all chains consist of 3 sites each and 1 chain consists of 5 sites, or 2 chains consist of 5 sites each, or 1 chain consists of 7 sites and 1 chain consists of 3 sites, or 1 chain consists of 9 sites. Then the number of 2-coordinated sites is at least $(3/2)M_1+8$ and the number of floppy modes is at least 8 – more than 6.

Thus in case (a), for the whole network $F=5$, so there must be redundant bonds and stress, but any subnetwork has no redundancy and no stress when isolated from the rest of the network. The conclusion is that the whole network is stressed; if only a part was stressed, we could have considered this part alone as a subnetwork, and it would have been stressed alone. Of course, if there are even fewer decorating sites, all the more the whole network will be stressed. In case (b), for the whole network $F=6$, for all subnetworks the number of floppy modes is bigger than 6. Then there are no redundant bonds, so no stress, but the whole network is rigid – a smaller subnetwork cannot be rigid by itself. Finally, in case (c), there are no redundant bonds still, and also, since now the number of floppy

modes is more than six for all subnetworks *and* for the full network, there is no percolating rigid cluster and in fact, no rigid clusters at all, except trivial ones represented by a single site with all its neighbors. When the number of decorated sites is higher, this conclusion is still going to hold, of course, and since there are no redundant bonds, Maxwell counting is exact. Thus the proof is complete.

These considerations are also applicable to a similar model, in which in the starting lattice all sites are 4-coordinated. Similarly, bonds are first decorated one by one with one atom, then, after all bonds are decorated, by the second atom, then by the third atom, etc. At $\langle r \rangle = 2.4$, there is again chemical order: all original bonds are decorated with exactly two atoms. All considerations can be repeated and the same conclusions are arrived at: there is a sharp rigidity and stress transition at $\langle r \rangle = 2.4$ and Maxwell counting is exact below the transition point. The result will also remain unchanged, if, for example, atoms are placed in pairs, i.e., bonds are decorated with two atoms at once.

Finally, we can consider networks of the Si-O type, in which angular constraints associated with the oxygen atoms are weak and generally assumed to be broken. We cannot approach such situations with the molecular framework conjecture, but there is an assumption [21] that in terms of rigidity, this is equivalent to replacing each bridging oxygen with two 2-coordinated atoms and restoring all angular constraints. Then, a chemically ordered SiO₂ network, with an O atom between every two Si atoms, corresponds to an initially 4-coordinated network with each bond decorated with two 2-coordinated atoms with angular constraints present everywhere, just like in our model. If we consider starting from a Si network and decorating bonds with O atoms, this will correspond to decoration with pairs of 2-coordinated atoms with angular constraints, and the rigidity transition will correspond exactly to the SiO₂ composition, with $\langle r \rangle = 2.67$.

We note that in all considered cases, the networks were fully chemically ordered at the threshold. Indeed, it is this absence of fluctuations in the chemical order that gives rise to the described behavior. If, for example, we start with a network that has both 3- and 4-coordinated sites and decorate it, then at $\langle r \rangle = 2.4$ there will be no order, as the number of 2-coordinated atoms per original bond will be between 1 and 2 on average, so this number will vary from bond to bond, and because of these variations, Maxwell counting will no longer be exact.

Discussion

We note that our results apply to systems with planar topology, such as that shown in Fig. 3, as long as atoms are still able to move in 3 dimensions and all angular constraints are present. This returns us to the suggestion by Tanaka [22] that planar systems undergo the rigidity transition at $\langle r \rangle = 2.67$ and because of this, between $\langle r \rangle = 2.4$ and $\langle r \rangle = 2.67$ networks can avoid stress being in a planar configuration; then at $\langle r \rangle = 2.67$ a transition to a 3-dimensional topology happens. We now see that in fact, topologically planar systems also have the rigidity threshold at $\langle r \rangle = 2.4$, so the explanation in terms of rigidity is incorrect. We can see the reason of its failure. Tanaka assumes that atoms still move in 3 dimensions, so there are 3 degrees of freedom per atom; the number of central-force constraints is still $r/2$ per atom of coordination r ; but the number of angular constraints is $r-1$ (rather than $2r-3$), because the configuration is now planar, so only $r-1$ angles are independent. The last statement is not true, as since atoms are allowed to move out

of the plane, the configurations will not be strictly planar and the number of angular constraints remains. If the atoms are only allowed to move in the plane, so the number of degrees of freedom per atom is reduced to 2, then indeed, the number of independent angular constraints per atom becomes $r-1$, but this leads to the transition being at $\langle r \rangle = 2.0$ (that is being connected is equivalent to being rigidly connected) instead of 2.67. Then the Tanaka transition should have another explanation. We notice that there is increasing evidence that all observed transitions around 2.67 can be explained as being due to various chemical thresholds. In particular, Tichý *et al.* [23] note that many of the observed peculiarities are located at the obvious threshold where all of the bonds are between a 2-coordinated chalcogen and a 3- or 4-coordinated atom; for the mean coordination above this threshold, there have to be bonds between 3-coordinated and/or 4-coordinated sites; below this threshold, there are bonds between 2-coordinated sites. For glasses of composition $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$, the position of the threshold is given by an equation

$$2(1-x-y) = 4x + 3y \quad (9)$$

Using Eq. (3), the mean coordination at the chemical threshold is

$$\langle r \rangle = 4(1-x-y) \quad (10)$$

i.e., it is 4 times the fraction of 2-coordinated atoms. This threshold is located between 2.4 (for $x = 0$) and 2.67 (for $y = 0$). The actual interplay between the rigidity and chemical thresholds may be more complex for some networks and needs further study.

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