RIGIDITY AND SELF-ORGANIZATION OF NETWORK GLASSES AND THE INTERMEDIATE PHASE

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1. Introduction

In these lectures, we discuss continuous random network models for glasses and their mechanical properties. We show how model systems can help us better understand glasses *via* rigidity percolation. These ideas involving rigidity percolation have been tested experimentally in bulk glasses. Some key results were obtained in the last years, which go beyond simple mean field theory or *Maxwell constraint counting.* These results, which involve a new graph theoretical approach called the *pebble game*, show that Maxwell counting is quite reliable in locating the transition from rigid to floppy. Exact constraint counting within the pebble game allows us to study the nature of the rigidity transition and how it is influenced by the peculiarities of the structure in very great detail. The pebble game also allows us to consider a crude algorithm for optimizing the network structure, which leads to the possibility of the *intermediate phase*, as described later in this paper.

The study of network structures has fascinated scientists in many areas – ranging from engineering and mechanics to the material and biological sciences. Going back more than a century, Maxwell was intrigued with the conditions under which mechanical structures made out of struts, joined together at their ends, would be stable (or unstable) [1]. To determine the stability, without doing any detailed calculations (that would have been impossible then except for the simplest structures), Maxwell used the method of *constraint counting*. This counting is an approximate method that proves to be accurate for structures where the density (of struts or joints) is roughly uniform. Maxwell's constraint counting method is exact in some cases that we will discuss in this paper. The idea of a constraint in a mechanical system goes back to Lagrange [2] who used the concept of holonomic constraints to reduce the effective dimensionality of the space. The difficult part is to determine which constraints are *linearly independent*. If the linearly independ-

ent constraints can be identified, then the problem is solved – however in most large systems this identification is not possible except using a numerical procedure on an actual realization.

The problem under consideration is a static one – given a mechanical system, how many independent deformations are possible without any cost in energy? These are the zero frequency modes, which we prefer to refer to as *floppy modes* because in any real system there will usually be some weak restoring force associated with the motion.

Sometimes it is convenient to look at the system as a *dynamical* one, and assign potentials or spring constants to deformations involving the various struts (bonds) and angles. It does not matter whether these potentials are harmonic or not, as the displacements are virtual. However it is convenient to use harmonic potentials so that the system is linear. It is then possible to set up a Lagrangian for the system and hence define a dynamical matrix, which is a real symmetric matrix having real eigenvalues. These eigenvalues are either positive or zero. The number of finite (non-zero) eigenvalues defines the *rank* of the matrix. Thus our counting problem is rigorously reduced to finding the rank of the dynamical matrix. The rank of a matrix is also the number of linearly independent rows or columns in the matrix. Neither of these definitions is of much practical help, and a numerical determination of the rank of a large matrix is difficult and of course requires a particular realization of the network to be constructed in the computer. Nevertheless the rank is a useful notion as it defines the mathematical framework within which the problem is well posed.

The genius of Maxwell [1] was to devise the simple constraint counting method that allows us to *estimate* the rank of the dynamical matrix and hence the number of floppy modes. We will discuss the application of these ideas to bulk covalent network glasses.

Until recently it has not been possible to improve on the approximate Maxwell constraint counting method, except on small systems using brute force numerical methods. Now a powerful new combinatorial algorithm, called the *Pebble Game* [3] has become available. This allows very large systems to be analyzed in two-dimensional central-force networks and in three-dimensional networks with both central-forces and bond-bending forces. Both these cases will be described in more detail later.

The layout of this article is as follows. In the next chapter we review the concept of rigidity percolation, describe the powerful yet simple ideas of constraint counting and then go on to discuss the exact algorithm – the pebble game – and the insights that it has provided into rigidity percolation. In chapter 3 we give an account of our work on self-organization of glassy networks. First we introduce our model of self-organization based on the pebble game, which leads to existence of the intermediate phase, and study the properties of this model. We also consider a similar model for random resistor networks, based on the analogy between the connectivity and rigidity per-

colation. While this model is less relevant to glasses, connectivity is much simpler to study and understand and many properties of the two models are analogous. In the last chapter we summarize our results.

Throughout much of this paper we focus on both central force networks in two dimensions and bond-bending networks in three dimensions that have central and non-central forces as these are more relevant to glasses. The reader should be aware that we do flip back and forth between these model systems, as appropriate, in order to illustrate various points.

2. Generic Rigidity Percolation

2.1. GENERAL IDEAS

The elastic properties of random networks of Hooke springs have been studied over the past 15 years [4-9]. One of the most interesting findings has been that effective medium theory describes the behavior of the elastic constants and the number of floppy modes remarkably well [6-9] except very close to the phase transition from a rigid to a floppy structure.

Early attempts to study the critical behavior in central-force networks were not very satisfactory [6-12], and the question of the universality class of the rigidity transition has only recently been resolved. This question is fundamental to understanding the nature of the rigidity transition, and may have important implications as to how the character of the glass transition is affected by the mean coordination, as has been discussed via fragile and strong glass formers [13]. We show here how substantial progress can be made in understanding the geometrical nature of generic rigidity percolation [3, 14-17].

There are two important differences between rigidity and connectivity percolation. The first difference is that rigidity percolation is a vector (not a scalar) problem, and secondly, there is an inherent long-range aspect to rigidity percolation. These differences make the rigidity problem become successively more difficult as the dimensionality of the network increases. In two dimensions, Figure 1(a) shows four distinct rigid clusters consisting of two rigid bodies attached together by two rods connecting at pivot joints. Now the placement of one additional rod, as shown in Figure 1(b), locks the previous four clusters into a single rigid cluster. This non-local character allows a single rod (or bond) on one end of the network to affect the rigidity all across the network from one side to the other.

Using concepts from graph theory, we have set up *generic networks* where the connectivity or topology is uniquely defined but the bond lengths and bond angles are arbitrary. A generic network does not contain any geometric singularities [18], which occur when certain geometries lead to null projections of reaction forces. Null projections are caused by special sym-

metries, such as, the presence of *parallel bonds* or *connected collinear bonds*. Rather than these *atypical* cases, their *generic* counterparts as shown in Figures 1(b) and (c) will be present. This ensures that all infinitesimal floppy motions carry over to finite motions [18-20].

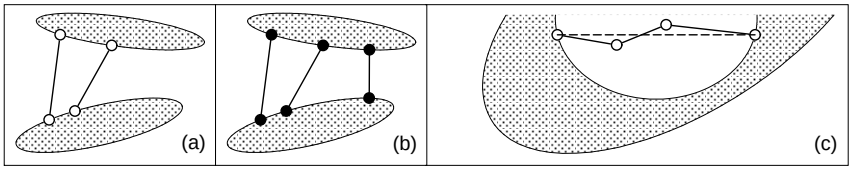

Figure 1. The shaded regions represent 2D rigid bodies. The (closed, open) circles denote pivot-joints that are members of (one, more than one) rigid body. (a) A floppy piece of network with four distinct rigid clusters. (b) Three generic cross links between two rigid bodies make the whole structure rigid. If the bonds were parallel, the structure would not be rigid to shear. (c) A set of three non-collinear connected rods connecting across a rigid body is generic and contains one internal floppy mode. If they were collinear (along the dashed line), then there would be two infinitesimal (not finite) floppy motions, and under a horizontal compression buckling would occur.

Early studies on rigidity percolation were on regular (non-generic) lattices, which as we now know inadvertently delayed a proper understanding of the rigidity transition. In non-generic (referred to as atypical) networks, geometrical singularities occur which lead to non-linear effects. For example, a diode-like problem frequently occurs in atypical networks where a string of collinear bonds can only be extended with a cost in energy but can be compressed with *no* cost in energy due to buckling [e.g. Figure 1(c)]. The diode effect complicates studies because it leads to the breakdown of linear elasticity theory, which must be reversible. A simple way to view a generic network is to take a regular lattice structure and randomly displace each site location by a small amount. This introduces local distortions throughout the lattice and is in itself a good physical model for amorphous and glassy materials. Many early studies involved the non-linear effects arising from geometrical singularities [6-12], and should therefore be regarded as a separate problem.

By considering generic networks, the diode effect and the problematic geometric singularities are completely eliminated. Therefore, the problem of rigidity percolation on generic networks leads to many conceptual advantages because all geometrical properties are robust. Moreover, real glass networks have local distortions, and are modeled better by generic networks. In two dimensions, there exist efficient, exact combinatorial algorithms allowing for the possibility of an in depth study of rigidity percolation. Similar algorithms have been extended to three dimensions, as discussed later, for some important special cases.

The rigidity of a network glass is related to how amenable the glass is to continuous deformations that require very little cost in energy. A small energy cost will arise from weak forces, which are always present in addition to

the hard covalent forces that involve bond lengths and bond angles. These small energies can be ignored because the degree to which the network deforms is well quantified by just the number of floppy modes [12] within the system. This picture of floppy and rigid regions within the network has led to the idea of *rigidity percolation* [6, 3].

Significant insights into the general phenomena of central-force rigidity percolation can be obtained by studying a random network of Hooke springs. To be specific, we start from a regular lattice (say, the triangular lattice in 2D) and consider a network of Hooke springs characterized by the potential

$$V = \frac{1}{2}\sum_{\langle ij \rangle} \alpha_{ij}\eta_{ij}\left(l_{ij} - l_{ij}^{0}\right)^2, \tag{1}$$

where the sum is over all bonds $\langle ij \rangle$ connecting sites i and j in the original lattice. A bond connecting sites i and j is present if $\eta_{ij} = 1$ with probability p and absent if $\eta_{ij} = 0$ with probability $1 - p$. The spring constants, α_{ij}, and the equilibrium bond lengths, l_{ij}^{0}, are positive real numbers but are left arbitrary. The site locations are also arbitrary, because the network is generic. Note that rigidity is a static concept, involving virtual displacements, so that while it is convenient to use harmonic potentials as done in Eq. (1), any set of pair potentials would give the same results for the geometric aspects of rigidity. A collection of sites form a *rigid cluster* when no relative motion within that cluster can be achieved without a cost in energy. Rigidity percolation occurs when a rigid cluster spans the whole network. Conversely, *floppy modes* correspond to finite motions within the system, which do not cost energy. Therefore, the geometrical properties and the number of floppy modes can be determined by an equivalent bar and joint structure [12]. Note that a *d*-dimensional system always has at least $d(d+1)/2$ floppy modes due to d global translations and $d(d-1)/2$ global rotations.

2.2. CONSTRAINT COUNTING

The number of floppy modes in d dimensions is given by the total number of degrees of freedom for N sites (equal to dN) minus the number of *independent constraints*. A *dependent (redundant) constraint* can only add additional reinforcement and cause internal stress in an existing rigid body. A key quantity is the number of floppy modes, F, in the network, or normalized per degree of freedom, $f = F/dN$. By defining the total number of constraints per degree of freedom as n_c and the number of *redundant* constraints per degree of freedom as n_r, we can write quite generally,

$$f = \frac{dN - (dNn_c - dNn_r)}{dN} = 1 - n_c + n_r . \qquad (2)$$

It is straightforward to find the total number of constraints (and consequently n_c) for each given network. Neglecting redundant constraints [n_r in Eq. (2)] as first done by Maxwell [1], we come to *Maxwell counting*:

$$f \approx f_M = 1 - n_c . \qquad (3)$$

Now the idea is to associate the rigidity percolation transition with the point where f_M goes to zero. The Maxwell approximation gives a good account of the location of the phase transition and the number of floppy modes, but it ultimately fails, because some constraints are redundant and also because, as we will see soon, there are still some floppy pockets inside an overall rigid network.

We now describe Maxwell counting for specific cases.

2.2.1. *Central Force Network in Two Dimensions*

This system can be viewed as a network of Hooke springs (described in section 2.1) in 2 dimensions. It is convenient to introduce the mean coordination $\langle r \rangle$ as an average number of bonds stemming from a site. It is given by $\langle r \rangle = pz$, where p is the probability of the bond being present (as in section 2.1), z is the coordination of the underlying regular lattice (6 for the triangular lattice, for example). If the total number of sites is N, the number of bonds is $N_B = N\langle r \rangle / 2$. Each of these bonds represents one constraint, as always in central force networks, and therefore the number of constraints per degree of freedom is given by

$$n_c = \frac{N_B}{2N} = \frac{\langle r \rangle}{4} . \qquad (4)$$

Therefore, according to Eq. (3), Maxwell counting gives

$$f \approx f_M = 1 - \frac{\langle r \rangle}{4} . \qquad (5)$$

This quantity goes to zero at $\langle r \rangle_c = 4$, which we associate with the rigidity percolation transition. For the triangular lattice this corresponds to $p_c = 2/3$.

2.2.2. *Bond-Bending Glassy Networks in Three Dimensions*

We start by examining a large covalent network that contains no dangling bonds or singly coordinated atoms. We can describe such a network by the chemical formula $Ge_xAs_ySe_{1-x-y}$, where the chemical element, Ge, stands for *any* fourfold bonded atom, As for *any* threefold bonded atom and Se for *any* twofold bonded atom. Each atom has its full complement of nearest neighbors and we consider the system in the thermodynamic limit, where the number of atoms $N \to \infty$. There are no surfaces or voids and the chemical distribution of the elements is not relevant, except that we assume there are no isolated pieces, like a ring of Se atoms. The total number of atoms is *N* and there are n_r atoms with coordination *r* ($r = 2$, 3 or 4), then

$$N = \sum_{r=2}^{4} n_r \tag{6}$$

and we can define the mean coordination

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} = 2 + 2x + y\,. \tag{7}$$

We note that $\langle r \rangle$ (where $2 < \langle r \rangle < 4$) gives a partial but very important description of the network. Indeed, when questions of connectivity are involved the average coordination is the key quantity.

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 [21] or Keating [22] potential, which we can write *schematically* as

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta l}{2}(\Delta\theta)^2\,. \tag{8}$$

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. For more details see Ref. [4]. If the modes already have a

finite frequency, these extra small terms will produce a small, and rather uninteresting, shift in the frequency. This division into *strong* and *weak* forces is essential if the constraint counting approach is to be useful. It is for this reason that it is of little, if any, use in metals and ionic solids. It is fortunate that this approach provides a very reasonable starting point in many covalent glasses.

To estimate the total number of zero-frequency modes, Maxwell counting was first applied by Thorpe [4], following the work of J.C. Phillips [23, 24] on ideal coordinations for glass formation. It proceeds as follows. There are a total of $3N$ degrees of freedom. There is a single central-force 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. (8). 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. The total number of constraints is therefore

$$\sum_{r=2}^{4} n_r \left[r/2 + (2r-3) \right]. \tag{9}$$

Using Eqs. (6) and (7), their fraction n_c can be rewritten as

$$n_c = \tfrac{5}{6}\langle r \rangle - 1, \tag{10}$$

thus, according to Eq. (3),

$$f \approx f_M = 2 - \tfrac{5}{6}\langle r \rangle . \tag{11}$$

Note that this result only depends upon the combination $2x + y = \langle r \rangle$, which is the relevant variable. When $\langle r \rangle = 2$ (e.g. Se chains), then $f_M = 1/3$; that is, one third of all the modes are floppy. As atoms with higher coordination than two are added to the network as cross-links, f_M drops and goes to zero at $\langle r \rangle_c = 2.4$, and network goes through the rigidity percolation transition. This mean field approach has been quite successful in covalent glasses and helps explain a number of experiments. Also in later sections, we discuss the results of computer experiments and show that they are rather well described by the results of this subsection.

We note that Eq. (9) holds only when there are no 1-fold coordinated atoms. Their presence leads to the threshold being shifted down [25-27].

2.3. THE PEBBLE GAME

We will focus on the geometrical aspects of rigidity percolation. Previous studies have used numerical methods on networks containing $N \sim 10^4$ sites, but were faced with difficult challenges. For example, relaxation methods are well suited for calculating elastic constants, but not for characterizing the geometric structure of the network. This is because numerically one cannot identify which bond has exactly zero stress or if a bond accidentally has zero stress. However, this was the only approach available in determining the stress carrying backbone.

We have been able to study networks containing more than 10^6 sites, using an integer algorithm, which gives exact and unique answers to the geometric properties of generic rigidity percolation. Because of the non-local characteristic of rigidity percolation, [e.g. Figs. 1(a), 1(b)] burning-type algorithms [28] commonly used in connectivity percolation are useless. This implies that the entire structure needs to be specified (stored in memory) since rigidity in a given region may depend on bonds far away.

A very efficient combinatorial algorithm, as first suggested by Hendrickson [18], has been implemented to (i) calculate the number of floppy modes, (ii) locate over-constrained regions and (iii) identify all rigid clusters for 2D generic bar-joint networks. The crux of the algorithm is based on a theorem by Laman [19] from graph theory.

Theorem: *A generic network in two dimensions with N sites and B bonds (defining a graph) does not have a redundant bond if and only if no subset of the network containing n sites and b bonds (defining a subgraph) violates* $b \leq 2n-3$.

By simple constraint counting it can be seen that there must be redundant bond(s) when Laman's condition is violated. This necessary part generalizes to all dimensions such that if $b > dn - d(d+1)/2$ then there is a redundant bond for $n \geq d$. For $n < d$ it follows that if $b > n(n-1)/2$ then there is a redundant bond. Note that $n = 1$ is an excluded case in Laman's theorem, because two sites are required for a bond to be present. The essence of Laman's theorem is that in two dimensions finding $b > 2n-3$ is the only way redundant bonds can appear. This sufficient part *does not* generalize to higher dimensions [18].

The basic structure of the algorithm is to apply Laman's theorem recursively by building the network up one bond at a time. Only the topology of the network is specified, not the geometry. Because of the recursion, only the subgraphs that contain the newly added bond need to be checked. If each of these subgraphs satisfy the Laman condition, $b \leq 2n-3$, then the last bond

placed is independent, otherwise it is redundant. By counting the number of redundant bonds, the exact number of floppy modes is determined.

Searching over the subgraphs is accomplished by constructing a pebble game [3, 14]. Each site in the network has two pebbles tethered to it. A pebble is either *free* when it is on a site or *anchored* when it is covering a bond. A free pebble represents a single motion that a site can undertake. Consider a single site having two free pebbles, representing two translations. If two additional free pebbles can be found at a different site, then the distance between this pair of sites is not fixed. Placing a bond between this pair of sites will constrain their distance of separation. To record this constraint, one of the four free pebbles is anchored to the bond. Once the bond is covered, only three free pebbles can be shared between that pair of sites. After a bond is determined to be independent, it will always remain independent and covered.

We begin with a network of N isolated sites each having two free pebbles. The system will always have $2N$ pebbles; initially two free pebbles per site. We place one bond at a time in the network connecting pairs of sites. The topological placement of either the sites or bonds will depend on the model under study such as the diluted generic triangular lattice described here. Only independent bonds are covered by pebbles. Therefore, before a bond can be covered it must be tested for independence. For each bond placed in the network, four pebbles (two on each site at the ends of the bond) must be free for the bond to be independent. When a bond is determined to be independent, any one of the four pebbles can be anchored to that bond. In general, not all four pebbles across an added bond will be free because they are already anchored to other bonds. These anchored pebbles may possibly become free at the expense of anchoring a neighboring free pebble while keeping a particular independent bond covered. In other words, pebbles may be shuffled around the network provided all independent bonds remain covered.

It is always possible to free up three pebbles across a bond, since they correspond to its rigid body motion. When a fourth pebble across a bond cannot be found, then that bond is redundant and it is not covered. In Figure 2, an example of how pebbles are shuffled is schematically shown on a small generic structure. Two distinct pebbles are associated with each site for which each pebble is either used to cover a bond or free to cover a bond. As schematically drawn in Figure 2, the two pebbles closest to a given site are the pebbles that are tethered to that site. Thus a pebble may either be on a site (free pebble) or on a bond (anchored pebble) but it always remains tethered to a given site regardless of how the pebbles are shuffled. Note that a bond may be covered by a pebble from either of its end sites. Therefore, free pebbles can be moved across the network by exchanging the site from which a pebble is used to cover a bond.

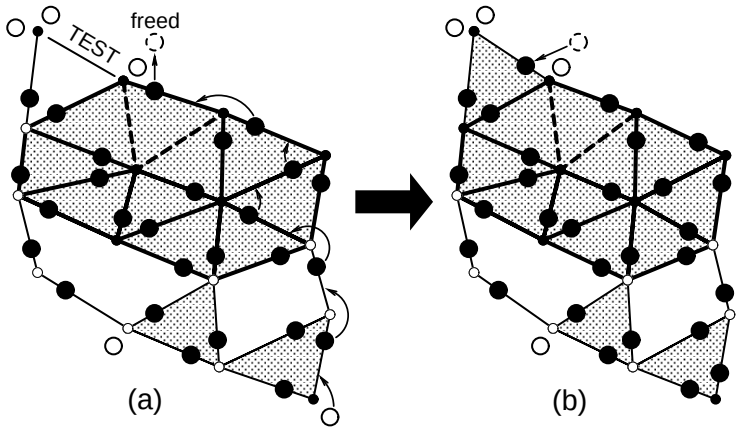

Figure 2. A demonstration of the pebble game on a generic network. Independent (redundant) bonds are shown with solid (dashed) lines which are (are not) covered by a pebble. Large (filled, open) circles denote (anchored, free) pebbles on (bonds, sites). The two closest pebbles to a given site are tethered to that site. Small (filled, open) circles denote sites belonging to (one, more than one) rigid cluster. Over-constrained bonds are shown with heavy dark lines. Shaded regions denote 2D rigid bodies. (a) There are seven rigid clusters and the five free pebbles indicate 5 floppy modes until a new bond is added and tested for independence. (b) The added bond is independent and thus covered. There are now six rigid clusters and four floppy modes.

Over-constrained regions are recorded each time a dependent bond is found. These regions correspond to the set of bonds that were searched in trying to free the fourth pebble but failed. These regions, called *Laman subgraphs*, violate the condition $b \leq 2n-3$. A bond added to a Laman subgraph will be redundant.

We identify all the rigid clusters after the network is completely built. First, we identify isolated sites. Then the rigidity of all other sites is tested with respect to a reference bond. If a test bond between either one of the pair of sites forming the reference bond and the site in question is found to be (dependent, independent) then that site (is, is not) rigid with respect to the reference bond. The test bond is actually never added to the network. Since a bond can only belong to one cluster (unlike sites), all the bonds within a rigid cluster are ascribed to a particular reference bond. A systematic search is made to map out all rigid clusters.

We show in Figure 2(b) the end result of the pebble game applied to a simple structure. Many aspects of rigidity are displayed. It can be seen that:

(1) The exact number of floppy modes is determined by the number of free pebbles remaining. A depletion or excess of pebbles to cover a set of bonds distinguishes the over-constrained regions from the floppy regions, unlike the approximate global counting of Maxwell;

(2) This network is uniquely decomposed into a set of six distinct rigid clusters, although the clusters are not disconnected;

(3) The free pebble along the bottom edge cannot be shuffled over to the rigid body at the top, which already has three free pebbles. This free pebble is shared among three bars and two triangles. Generally, free pebbles get trapped in floppy regions consisting of many rigid clusters giving rise to complex collective floppy motion;

(4) The number of redundant bonds is unique, whereas their locations are not unique since this depends on the order of placing the bonds. Nevertheless, each redundant bond belongs to a unique over-constrained region (Laman subgraph). For example, there are 19 over-constrained bonds in the rigid cluster at the top of the structure in Figure 2(b), while having only two redundant bonds;

(5) A rigid cluster will generally have sub-regions that are over-constrained. If any bond that is over-constrained is removed, the rigidity of the network is unchanged.

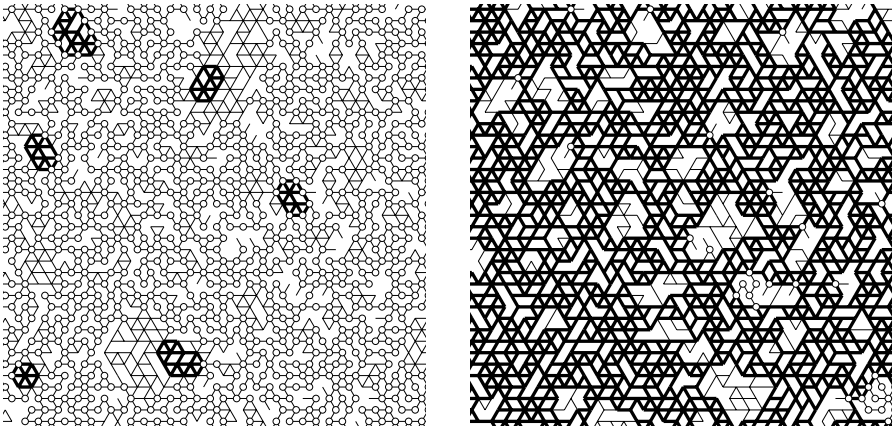

Figure 3. The topology of a typical section from a bond-diluted generic network at $p = 0.62$ (below percolation) and at $p = 0.70$ (above percolation). A particular realization would have local distortions (not shown), thus making the network generic. The heavy dark lines correspond to over-constrained regions. The open circles correspond to sites that are acting as pivots between two or more rigid bodies.

Sections of a large network on the bond-diluted generic triangular lattice are shown in Figure 3 after the pebble game was applied. Below the transition the network can be macroscopically deformed as the floppy region percolates across the sample. Above the rigidity transition, stress will propagate across the sample. However, below the transition there are clearly pockets of

large rigid clusters and over-constrained regions, while above the transition there are pockets of floppy inclusions within the network.

2.3.1. *Two Dimensional Central Force Networks*

In this subsection, we review some results for central-force generic rigidity percolation on the triangular net. A more detailed account can be found in Ref. [14].

We begin by finding the number of floppy modes and comparing it to the Maxwell counting result. This is shown in Figure 4. The exact value of f is very close to f_M far enough below the mean-field estimate for the rigidity transition $\langle r\rangle_c^M = 4$, but then starts to deviate significantly and does not reach zero (until full coordination, $\langle r\rangle = 6$, is reached). The quantity f looks quite smooth, but the second derivative of it with respect to $\langle r\rangle$ (shown in the insert) does in fact have a singularity. This singularity corresponds to the rigidity percolation threshold, as can be checked by detecting the percolating rigid cluster directly. Using finite-size scaling, the position of the transition was found to be $\langle r\rangle_c = 3.961 \pm 0.002$. This is amazingly close to the mean-field value of 4.

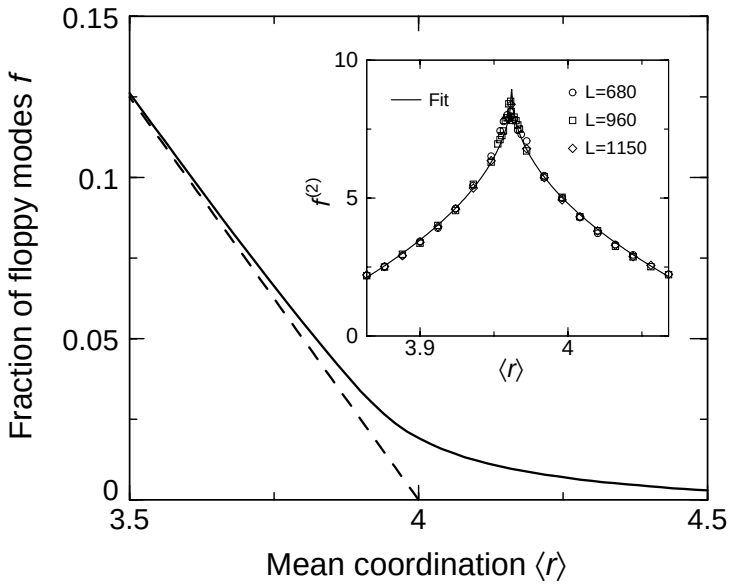

Figure 4. Simulation results on the triangular net for the fraction of floppy modes *f* (solid line) compared to the Maxwell prediction (dashed line). The insert shows the second derivative of *f* with respect to $\langle r\rangle$.

The behavior of the second derivative suggests that the number of floppy modes is an analogous quantity for rigidity and connectivity percolation. In

the case of connectivity percolation, the number of floppy modes is simply equal to the total number of clusters, which corresponds to the free energy [4, 29-31]. It would be nice if a similar result holds for rigidity percolation. It turns out that the second derivative of the total number of clusters changes sign across the transition, thus violating convexity requirements. Noting that typically rigid clusters are not disconnected, it was suggested that the number of floppy modes generalizes as an appropriate free energy [4, 29-31]. With this assumption, the exponent α is estimated in the usual context of a *heat capacity* critical exponent, even though no temperature is involved here.

Again analogously to connectivity percolation, the fraction of bonds in the percolating rigid cluster P_∞^r serves as the order parameter for this system. The critical exponent β is defined as the rigid cluster size critical exponent. Another order parameter is also possible, namely, the fraction of bonds P_∞^s in the percolating *stressed* cluster, which is defined as a percolating stressed subset of the percolating rigid cluster. It was found (and this is an important point) that both P_∞^r and P_∞^s go to zero at the same point – the percolation transition. This will be different in the next chapter on self-organization and will lead to the existence of the *intermediate phase*, and two phase transitions.

The results of study of this model [14] lead to the conclusion that the rigidity transition in this system is second order, but in a different universality class than connectivity percolation, with the exponents: $\alpha = 0.48 \pm 0.05$, $\beta = 0.175 \pm 0.02$ and $\nu = 1.21 \pm 0.06$ (the last exponent defines the scaling of the average rigid cluster size, when the transition is approached). The fractal dimension of the percolating rigid and stressed clusters at the threshold is $d_r = 1.86 \pm 0.02$ and $d_s = 1.80 \pm 0.03$ respectively.

It has been suggested by Duxbury and co-workers [16] that the rigidity transition might be weakly first order on triangular networks. While we think this is unlikely, it cannot be completely ruled out at the present time.

2.3.2. *Three Dimensional Bond Bending Networks*

Unfortunately it is not possible to extend the pebble game in full generality to three dimensional central-force networks, as this algorithm is based on Laman's theorem which does not generalize to three dimensions. This is because of the existence of banana graphs, as shown in Figure 5.

While the pebble game described in this paper is only applicable in 2D, the rules were generalized for a certain class of three-dimensional networks. Although the Laman condition is not generally sufficient [18-20, 32] in three dimensions, it was recently shown [33] that it can be generalized within bond bending networks. While we do not have a rigorous mathematical proof, we do explain why bond-bending networks can almost certainly be treated with pebbles, based on a Laman type theorem. The problem of the Laman ba-

nanas, as shown in Figure 5, is conveniently eliminated once angular forces are included as in a Kirkwood or Keating potential [Eq. (8)]. As a result, we are able to construct a three dimensional pebble game for the bond-bending model, having nearest and next nearest neighbor forces. Fortunately, the bond-bending model is precisely the class of models that is applicable to the study of many covalent glass networks.

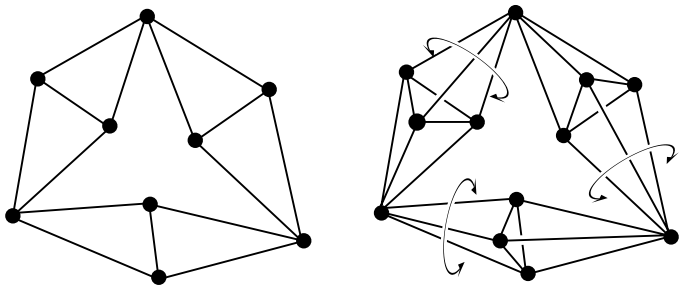

Figure 5. (Left panel) A single rigid cluster in two dimensions. (Right panel) 3 bananas in a three dimensional network. There are four rigid clusters here – three bananas plus an additional rigid cluster consisting of the three sites at the corners, which are connected by implied bonds. Such non-contiguous rigid clusters cannot occur in two dimensional networks, and are responsible for the breakdown of Laman's theorem in three dimensions.

For the most part, the three dimensional pebble game rules come from naively generalizing the 2D rules (such as using three pebbles per site instead of two). However, there are some subtle differences caused by restricting the three dimensional networks to be in a certain class. The order of bond placement in building a network now becomes important, so that the bond-bending model at each step of the process is preserved and thereby insuring that at no time will banana structures form. A somewhat longer discussion of the three dimensional pebble game is given in Refs. [33, 34].

It can be shown [33] that the only floppy element in a three dimensional bond-bending network is a hinge joint. Hinge joints can only occur through a central-force (CF) bond and are always shared by two rigid clusters – allowing one degree of freedom of rotation through a dihedral angle. Note that in two dimensional central force generic networks, sites that belong to more than one cluster act as a pivot joint, and more than two rigid clusters can share a pivot joint. Because of this difference between CF and bond-bending networks, the order parameters analogous to P_∞^r and P_∞^s of the previous subsection, have to be defined as a fraction of sites in respective percolating clusters and not bonds, as bonds can be shared between a percolating and a non-percolating clusters.

For purposes of testing rigidity in generic three-dimensional bond-bending networks, it is only necessary to specify the network topology or connectivity of the CF bonds, since the second nearest neighbors via CF bonds define the associated bond-bending constraints. Here, we have consid-

ered two test models. In the first model, a unit cell is defined from our realistic computer generated network of amorphous silicon [35] consisting of 4,096 atoms having periodic boundary conditions. Larger completely four-coordinated periodic networks containing 32,768, 262,144 and 884,736 atoms are then constructed from the amorphous 4,096-atom unit cell.

The four-coordinated network is randomly diluted by removing CF bonds one at a time with the constraint that no site can be less than two-coordinated. That is, a CF bond is randomly selected to be removed. If upon removal either of its incident atoms becomes less than two coordinated, then it is not removed and another CF bond is randomly selected from the remaining pool of possibilities. The order of removing CF bonds is recorded. This process is carried out until all remaining CF bonds cannot be removed, leading to as low an average coordination number as possible. All CF bonds that were successfully removed are marked. This method of bond dilution gives a simple prescription for generating a very large model of a continuous random $Ge_xAs_ySe_{1-x-y}$ type of network. For comparison, a second test model, a diamond lattice, was diluted in the same way and contained 32,768, 262,144 and 10^6 atoms.

In the application of the three dimensional pebble game, the network is built up one constraint at a time. The first step is to place all the unmarked CF bonds in the network. Once a CF bond is placed in the network, all its associated bond-bending constraints must also be placed before the next CF bond can be considered. Then the marked CF bonds (including their associated bond-bending constraints) are placed in the network in the reverse order from that when they were removed as the network was randomly diluted. In this way, the rigidity properties of the network can be monitored as a function of the average coordination number, which typically ranges from $\langle r \rangle =$ 2.2 to 4.0, and the network type is always like that of $Ge_xAs_ySe_{1-x-y}$.

The ensemble average over many realizations of bond dilution for the fraction of floppy modes and its derivatives have been numerically obtained for different size networks. The fraction of floppy modes is calculated exactly for each realization, its first derivative is obtained by Monte Carlo sampling and the second derivative is determined by one numerical differentiation. The fraction of floppy modes and its second derivative for both the bond diluted amorphous silicon and diamond lattices are shown in Figure 6. The bond-diluted generic diamond lattice behaves in nearly the same way as the bond-diluted amorphous silicon. They both have a rigidity transition slightly below the simple Maxwell constraint counting estimate of 2.4. The rigidity transition can be accurately found from the sharp peak in the second derivative in the fraction of floppy modes. In particular, for the diamond lattice $\langle r \rangle_c = 2.375 \pm 0.003$ and for a-Si, $\langle r \rangle_c = 2.385 \pm 0.003$. Remarkably, the Maxwell constraint counting estimate is accurate to about 1% in locating the threshold in both cases.

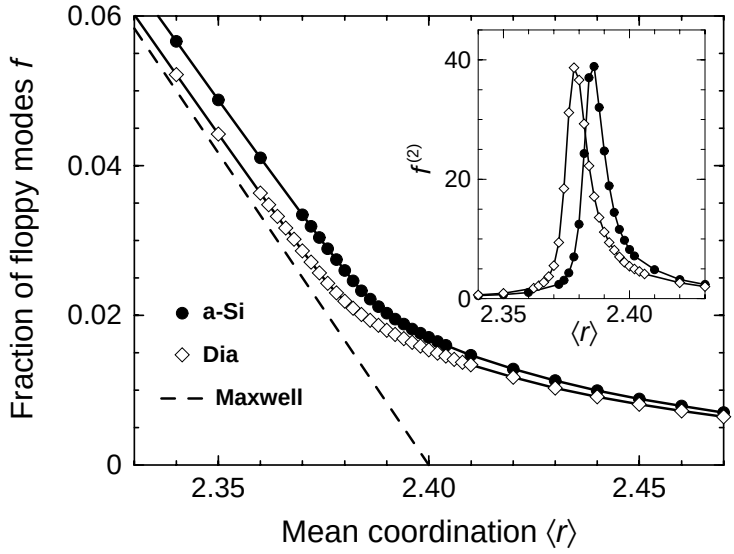

Figure 6. The number of floppy modes per degree of freedom f for two bond diluted models: based on the diamond lattice and on amorphous Si. The insert shows the second derivative of f with respect to $\langle r \rangle$ for the same models.

Just 1% below the rigidity transition, a-Si is still very floppy with small over-constrained regions scattered throughout the network – mostly due to the presence of five-fold rings. Unlike in two dimensions, large isostatic regions are not seen. Although most of the CF bonds are acting as hinge joints, it is worth noting that the average number of hinge joints per floppy mode is rather large, indicating that these modes are not localized on just one or two bonds. Above the rigidity threshold, where a spanning over-constrained region forms, there are still very few isostatic rigid regions, although many floppy inclusions remain. The average number of hinge joints per floppy mode passes through a maximum at the rigidity transition. A figure showing typical sections of the network above and below the transition and illustrating these conclusions can be found in Ref. [36]. Note that the rigidity transition discussed in this section is always second order.

3. Self-Organization and Intermediate Phase

So far in these lectures, we have dealt with networks built by inserting bonds completely at random. However, realistic glassy networks will have non-random features. Even though bulk glasses form at high temperatures where entropic effects are dominant, it is clearly not correct to completely ignore energy considerations that can favor particular local structural arrangements over others. A simple example of this is local chemical ordering, where, for

example, bonding between certain same-type atoms is unfavorable. This can lead to chemical thresholds that appear at certain concentrations, at which unfavorable bonding can no longer be avoided. This kind of non-randomness can also influence rigidity percolation thresholds, as was shown in [36]. A more interesting and subtle effect of interest to us here is how the structure itself can incorporate non-random features in order to minimize the free energy at the temperature of formation. 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, as discussed in the lectures of Boolchand. Here we focus on the mechanical properties and critical mechanical thresholds, as this is where it is easiest to make theoretical progress at this time.

How can such an idea be developed theoretically? A proper procedure might be to consider a very large supercell and use a first principles quantum approach, like that of Car and Parrinello [37], to form the glass. The problem with this is that the relaxation times at the appropriate temperatures are very large, so full equilibration is impossible. The structure thus obtained would be unreasonably strained. This situation is made worse as only small supercells with about 100 atoms can be used at present and in these the periodic boundary conditions produce unacceptably large internal strains. Using the fastest linear-scaling electronic structure methods (see Ordejón's lectures in this volume) or even molecular dynamics with empirical potentials is still much too slow. We therefore need to look at other ways of generating self-organizing networks. One promising approach is that of Mousseau and Barkema [38] who explore the energy landscape of a glass by moving over saddle points. In network terms, this corresponds to selective (thus non-random) bond switching. In these lecture notes, we look at even more simplified approaches that show what kinds of effects self-organization, and the resulting non-randomness, can lead to.

3.1. SELF-ORGANIZATION IN RIGIDITY PERCOLATION

3.1.1. *Description of the Model*

We have seen in chapter 2 that starting from an "empty" lattice (without bonds) and adding one bond at a time, we can use the pebble game to analyze whether the bond we are adding is independent of those already in the network or redundant. We also know that redundant bonds cannot be accommodated without changing the natural bond lengths and angles of the network and so stressed (over-constrained) regions would be created. Thus within the present approach we have a rather unique opportunity to construct stress-free networks without a huge computational overhead.

The idea is to start, as before, from an "empty" lattice and add one bond at a time to it, applying the pebble game at each stage. If adding a trial bond would result in that bond being redundant and hence create a stressed region,

then that move is abandoned. Thus the network self-organizes in such a way that there is no stress in it at all. Note that the pebble game now serves not only as a tool to analyze the network, as before, but also as a decision-making mechanism when building the network.

It is not possible to keep adding bonds beyond a certain point, without introducing stress (this is considered in more detail below). How should we proceed then? While going on with some sort of self-organization would be reasonable (as some bonds would create less stress than others), it is impossible to analyze this within our model, so we start inserting bonds completely at random, once avoiding stress becomes impossible.

3.1.2. *General properties*

First of all, how long is it possible to keep adding bonds to a network without introducing stress? It is certainly impossible to have more independent constraints then there are degrees of freedom in the network. Now recall that in the Maxwell counting approximation, the rigidity transition occurs when the numbers of constraints and of degrees of freedom balance. Thus it is certainly not possible to have an unstressed network with the mean coordination above where Maxwell counting predicts the transition (that is, above $\langle r \rangle = 4$ for central-force networks in 2D and $\langle r \rangle = 2.4$ for glassy networks in 3D). This provides an upper limit (still not always reachable, as we will see) for the unstressed networks. Note, though, that since the Maxwell counting percolation limit is not exact, this does not mean that rigid networks are necessarily stressed! The actual rigidity transition may occur below the point where Maxwell counting puts it. This is a very important point that leads to possibility of an *intermediate phase*, as described below.

Secondly, we know that the Maxwell counting result for the number of floppy modes would be exact if all constraints in the network were independent. But this is exactly what we have in our case! Thus the number of floppy modes in Maxwell counting is *exact* for as long as we are able to keep the network unstressed. Hence we follow the Maxwell result for the number of floppy modes in the floppy and intermediate phases.

We now analyze some specific cases in more detail.

3.1.3. *Intermediate Phase in 2d Central-Force Networks*

Let us first prove that it is indeed possible to reach the Maxwell counting limit without any stress in this case (and for any CF networks), provided that the fully coordinated (undiluted) network has no floppy modes (which is the case for triangular networks). As we have seen before (e.g., in subsection 2.2.2), generally speaking, we should distinguish carefully between constraints and bonds. A constraint can be thought of as one algebraic relation for the coordinates of atoms; stress appears whenever one or more of such relations are not satisfied. A bond can have several associated constraints, as in bond-bending networks. In the case of CF networks, though, each bond

has only one associated constraint (the distance between the sites it connects), so "bonds" and "constraints" are identical. Recall once again that every single constraint can be either independent (in which case it reduces the number of floppy modes of the network by 1), or redundant (so it does not change the number of floppy modes). Now, assume the opposite of our statement. This means that at some $\langle r \rangle_0 < \langle r \rangle_c^M$ we have an unstressed network, but any trial bond would cause stress (be redundant). So any bond would not change the number of floppy modes, as is always the case with redundant constraints. We know that since the network is unstressed the number of floppy modes given by Maxwell counting is exact, thus $f > 0$. If we try a constraint at some point and it turns out to be redundant, it will certainly remain redundant upon trials at any later point (i.e., after some other bonds are inserted). Therefore even inserting all of the remaining bonds would not change the number of floppy modes compared to their number at $\langle r \rangle_0$, so it will remain greater than zero even for a fully coordinated network, which is not true, so we come to a contradiction. Thus the exact limit for stressless networks $\langle r \rangle_0 = \langle r \rangle_c^M$ ($= 4$ in 2D) is established. We would like to emphasize that equivalence of "bonds" and "constraints" was essential for this proof (we used these terms interchangeably). See the next subsection for comparison.

Secondly, it is possible to establish a relation between the self-organized networks and those obtained by usual completely random insertion (to which we for simplicity refer as "random" in contrast to "self-organized" in what follows). Indeed, assume we are using the same random list of M bonds to build a random network and a self-organized one, trying to insert bonds as they are listed. For the random network, all the M bonds will get in; for the self-organized network, some of them will be, generally speaking, rejected, so that $M_0 \le M$ will be inserted. The bonds rejected in the self-organized network will be redundant in the random one; they do not influence the number of floppy modes, the configuration of rigid clusters (and thus whether or not rigidity percolation occurs) and the redundancy or independence of all the subsequently inserted bonds. Thus all these characteristics will be identical for the two networks. The consequence is that there is a correspondence between self-organized and random networks having the same number of floppy modes; in particular, rigidity percolation occurs at the same number of floppy modes.

This analysis allows us to make a very important conclusion. Since in random networks rigidity percolates at a non-zero f and the same has to be true for self-organized networks (because of the just mentioned consequence), yet stress appears exactly at $f = 0$, we conclude that there exists an *intermediate phase*, which is rigid (i.e. the infinite rigid cluster exists), but unstressed (so, evidently, there is no stress percolation). This is different

from the situation with random insertion, where the rigidity and stress percolation thresholds always coincide (see Figure 7).

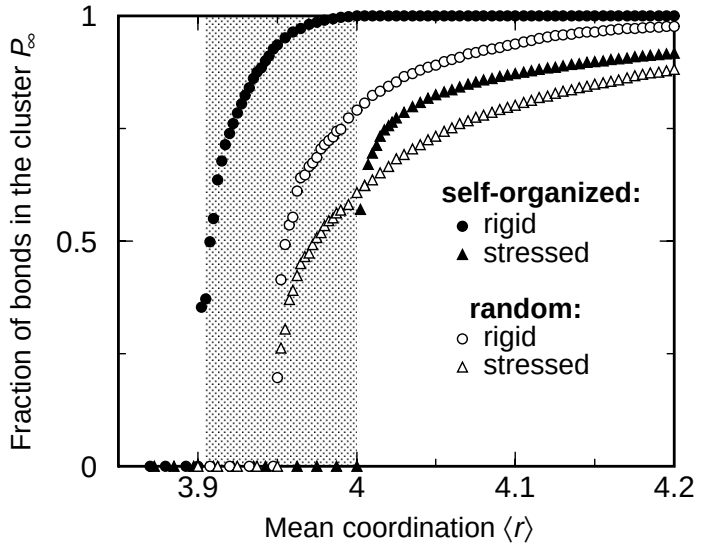

Figure 7. Order parameters P_∞^r and P_∞^s for self-organized and random triangular networks. It is seen that the intermediate phase (shaded) is formed in the self-organized case, extending from 3.905 to 4, while in the random case the two thresholds coincide and there is no intermediate phase. All results are averages over two realizations on 400×400 networks.

It could be possible that stress does not percolate immediately after it is introduced; we will see from simulation results that this is not the case, so the upper boundary of the intermediate phase (the *stress transition*) may be defined as either the point where stress first appears, or equivalently, the point where it percolates. As is seen from our consideration, it lies at $\langle r \rangle_0 = 4$.

As we have mentioned in subsection 2.3.1, the fractions of bonds in percolating rigid and stressed clusters (denoted P_∞^r and P_∞^s respectively) can serve as order parameters. Now, since there is an intermediate phase where rigidity percolates, while stress does not, these two parameters turn zero at *different* points, between which the intermediate phase lies. Besides, since the number of floppy modes is zero above the stress transition, the whole network is rigid, and thus P_∞^r is identically 1. These facts are illustrated in Figure 7.

Given the discussion of the floppy modes in the random and self-organized networks, it is tempting to suggest that the same relation holds for the just defined rigidity order parameter. The subtlety is that the relation is defined in terms of sites (i.e., same sites are in the percolating cluster and same sites are pivot joints on its border), while the order parameter is defined in terms of bonds. Of course, there is no direct correspondence between

bonds, as there are different numbers of bonds in related random and self-organized networks. Still it might be safely assumed that the rigid cluster size critical exponents are the same for rigidity percolation in random and self-organized networks. Other critical exponents may be different, though.

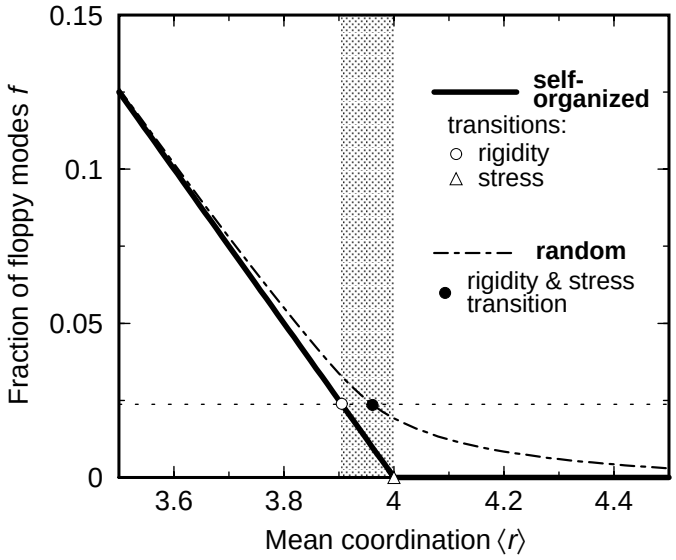

Figure 8. Number of floppy modes per degree of freedom for self-organized and random triangular networks. Thresholds are shown with different symbols. The intermediate phase in the self-organized case is shaded. Note that rigidity percolation occurs at the same f in the random and self-organized cases. The self-organized plot is strictly linear up to $\langle r \rangle = 4$ and coincides with Maxwell counting.

It is interesting to note that since f given by Maxwell counting is exact in the whole unstressed region, in both the floppy and the intermediate phase f is a perfect *straight line* and the rigidity transition *does not show up* in f.

Results of our simulations of this model are shown in Figures 7 and 8. The simulations were done for networks with periodic boundary conditions in both directions. There are several facts to be inferred (besides confirming all the results we have obtained so far). We see that stress percolates immediately after it appears at $\langle r \rangle = 4$ (this fact was mentioned above). Second, the cluster size critical exponent for the *stressed* cluster is quite small (smaller than the one for the rigid cluster). In random networks, the stressed cluster exponent is *larger* than the rigid cluster exponent, which is because the stressed percolating cluster is *smaller* than the rigid cluster (the former being a subset of the latter) and the two thresholds coincide.

3.1.4. *Intermediate phase in 3d Bond-Bending Networks*

In case of glassy networks there is a slight problem with implementing our general algorithm of self-organization. In the CF case we were starting from an empty lattice to ensure that it had no stress initially. In the present case the initial dilution can only go as far as to the point where any further dilution would create a 1-coordinated site. At this limit there are no bonds with both ends being sites of coordination 3 and higher, so that further dilution is impossible. It is generally not true that this final network is unstressed. For smaller networks (~10^4 sites and less), it is possible to pick those that are unstressed; for larger ones such cases are rare, and it is reasonable to assume that the fraction of constraints that are redundant is a constant in the thermodynamic limit. This constant seems to be very low, though (in our simulations, typically about 0.05% of constraints were redundant). Besides, the number of redundant constraints does not grow when new bonds are inserted according to our algorithm (up to the stress transition), so this problem is largely irrelevant.

Unlike the case of CF networks, BB networks have more than one constraint associated with each bond. When a new bond is added, not only the distance between the sites it connects is fixed, but the angles between the new bond and those stemming out of the two sites at either end of that bond are fixed as well. Any bond that has at least one redundant constraint associated with it would cause stress. Some of the stress-causing bonds have only part of the associated constraints redundant and the rest independent, and such a bond will change the number of floppy modes. This makes some of our conclusions made for CF networks invalid in this case.

Firstly, this invalidates the proof of the reachability of the Maxwell counting limit ($\langle r \rangle = 2.4$ in this case). This is because even when at the upper reachable limit all the as yet uninserted bonds would cause stress, some of these bonds may further decrease the number of floppy modes and thus this number is not necessarily zero at this point.

Secondly, the nice relation between random and self-organized networks no longer holds, because out of the redundant bonds by which the two differ, some (namely, the partially redundant ones) change f, rigidifying the network and changing the configuration of rigid clusters. Still the equality of critical exponents β for rigid cluster sizes in random and self-organized cases probably holds.

At the same time, some facts are unchanged. In particular, f given by Maxwell counting is still exact in the unstressed region. Most importantly, the intermediate phase still exists.

The results of simulations done for the diluted diamond lattice are given in Figures 9 and 10. As in the previous subsection, we use periodic boundary conditions in all directions. We note in addition to the graphs that, as in the CF case, stress percolates immediately after it appears. The intermediate

phase extends from $\langle r \rangle = 2.376$ to 2.392 (not reaching 2.4). Again, the stress transition is sharper than the rigidity transition. Our results are consistent with the second order transition with the very small critical exponent $\beta_{str} \approx 0.1$, or a first order transition is more likely.

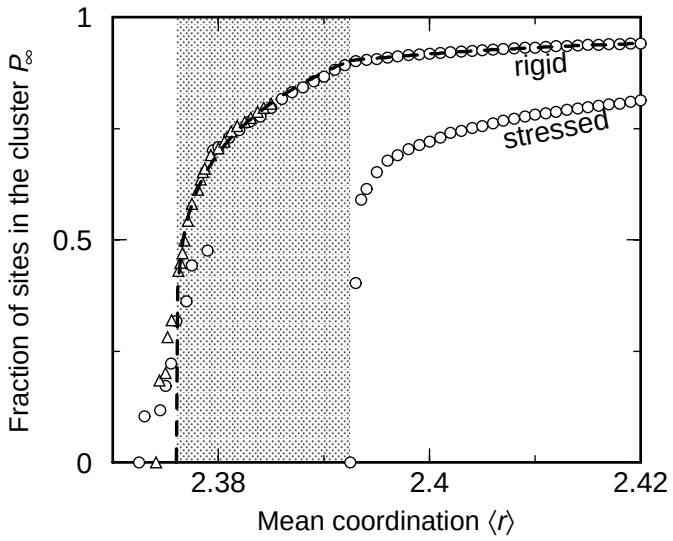

Figure 9. The order parameters P_∞^r and P_∞^s for the self-organized diluted diamond lattice. The intermediate phase is shaded. Circles are averages over 4 networks with 64,000 sites, triangles are averages over 5 networks with 125,000 sites. The dashed lines are the power law fit below the stress transition and for guidance of the eye above. Note the break in the slope at the stress transition.

Another feature of the plot in Fig. 9 is that the rigidity order parameter is not exactly unity in the stressed phase (which is expected, as some floppy modes remain in the stressed phase) and the second transition shows up as a kink in the rigidity order parameter.

In conclusion to this section, we would like to mention that it is possible within our approach to establish a hierarchy of stress-causing bonds (by the number of associated redundant constraints) and when stress becomes inevitable, first put those having one redundant constraint, then those having two, and so on. Exactly at $\langle r \rangle = 2.4$ only those bonds having no associated *independent* constraints will remain uninserted. It is unlikely, though, that there is a good correlation between the number of redundant constraints and the actual increase in stress energy, as the distribution of stresses caused by different bonds is quite wide, so this complication seems unreasonable.

3.1.5. *Elastic Properties of Self-Organized Networks*

So far our study of self-organized networks was limited to their geometrical properties. Of course, this work becomes really meaningful when we turn to

what the physical consequences of self-organization are. The simplest quantity to look at is the elasticity of the networks of springs. Unfortunately, the pebble game, being concerned with the geometric properties only, is unable to help us find the numerical values of elastic constants, so we have to do a usual relaxation using, for example, the conjugate gradient method [39] and consider particular configurations, and not just the connectivity. So far in this preliminary study, we have only considered the 2D case.

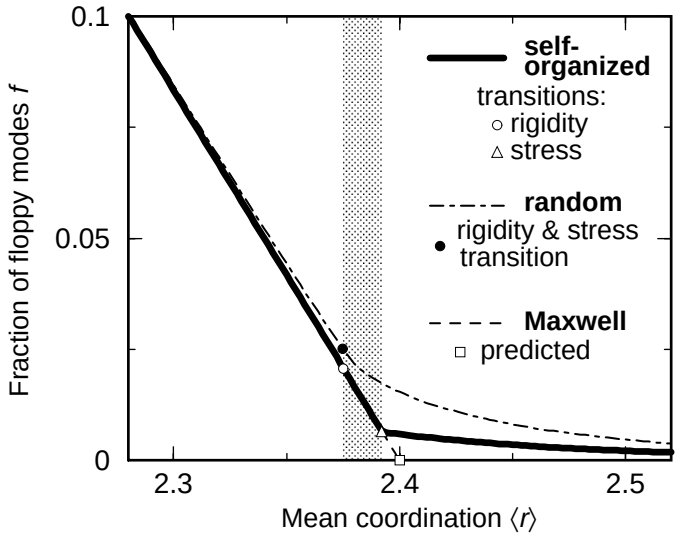

Figure 10. The fractions of floppy modes per degree of freedom for the diluted diamond lattice (both self-organized and random cases). Different thresholds and the Maxwell prediction for the rigidity threshold are shown with different symbols. The intermediate phase in the self-organized case is shaded. The Maxwell counting line is seen only above the stress transition point in self-organized networks, as below this point it coincides with the self-organized line. Note that the rigidity transition in the two cases no more occurs at the same f. Instead, the values of $\langle r \rangle$ are close, which is probably coincidental.

The first and quite surprising fact is that in case of periodic boundary conditions in all directions the elastic constants are *exactly zero* in the intermediate phase, regardless of the size of the supercell and despite the existence of the percolating rigid cluster. Indeed, periodic boundary conditions mean that positions of images of same site in different supercells are fixed with respect to each other. The network is built stressless with these additional constraints taken into account. The exact specification of these constraints beyond stating what sites are involved is determined by the particular size and shape of the supercell, but is never taken into account (just as particular bond lengths never matter in determination of stressed regions). So straining the network by changing this size and shape leaves it stressless. The important thing here is that straining does not add any new constraints. We

confirmed this result numerically by doing exact diagonalization of the dynamical matrix (similar to [40]), rather than by relaxation, which ensures better precision.

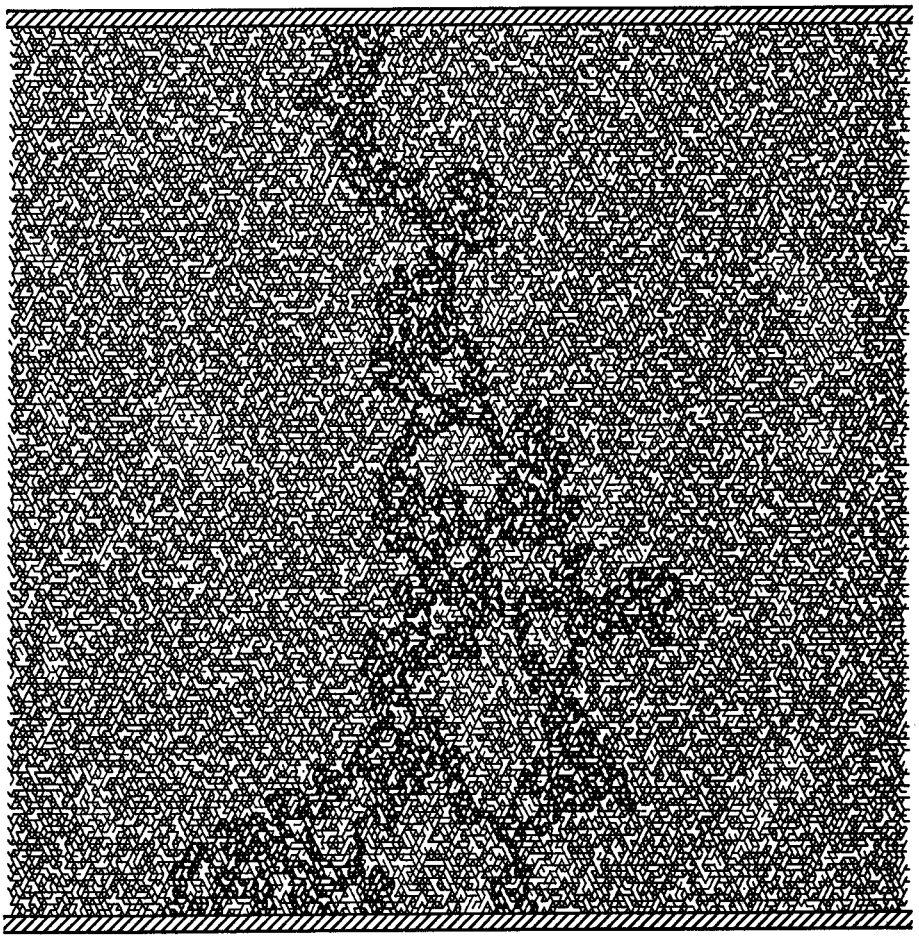

Figure 11. An example of the triangular self-organized network 150×150 in the intermediate phase (at $\langle r \rangle = 3.95$). The thickest bonds belong to the applied-stress backbone, those of medium thickness are in the percolating rigid cluster (but not in the backbone), the thinnest ones are not in the percolating cluster. The busbars are shown schematically.

Of course, for different boundary conditions the elastic constants may be non-zero for finite samples, but are expected to vanish in the thermodynamic limit. We consider the *busbar geometry*, in which busbars are applied to two opposite sides of the network and it is strained perpendicular to the busbars. The network is built assuming open boundaries at the busbars and periodic boundary conditions parallel to the busbars. The first and the last rows of sites are assumed belonging to the respective busbar (i.e., attached rigidly to it). In addition, when building the network, we consider the sites belonging to

each busbar as being fixed with respect to each other, connecting them with fictitious bonds and considering these bonds as belonging to the network. This makes the open boundaries "less open" and eliminates certain boundary effects, as will be clear from an analogy in the next section with connectivity percolation. The arguments of the previous paragraph do not apply here, as the network is built not assuming a fixed distance between the busbars (as if it is allowed to relax) and straining changes and fixes it thus imposing an additional constraint.

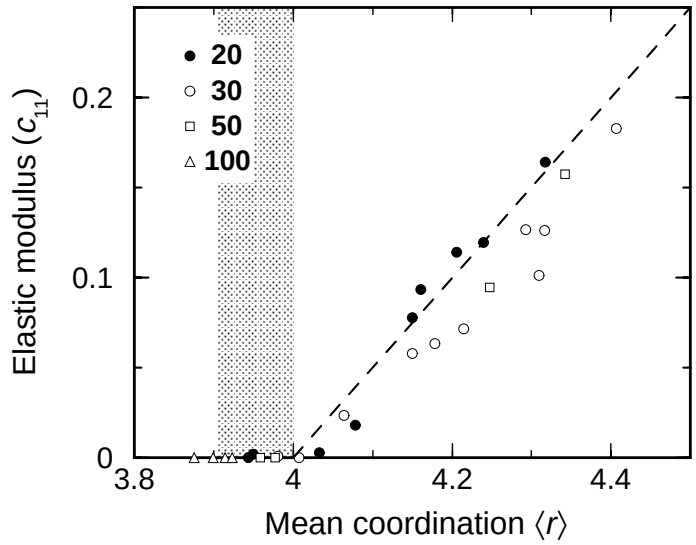

Figure 12. The elastic modulus c_{11} for self-organized triangular networks. Each point corresponds to one sample (their linear sizes are specified by different symbols). The intermediate phase is shaded. The dashed line is the mean-field linear dependence, reaching 1 at the full coordination.

When introducing the boundary conditions as described above, we will have non-zero stress when an external strain is applied, and some of the bonds will be stressed. These bonds are said to belong to the *applied stress backbone* [16] (which we refer to as simply backbone in what follows). It can be found easily by the pebble game using a method proposed by Moukarzel [41], which in our case consists in putting an additional bond across the network emulating the external strain, and finding those bonds in which stress is induced. A typical result is shown in Figure 11, in which it is seen that the backbone has filamentary structure. We note that stress in this backbone was created by putting just one extra bond and thus it is enough to take any one bond out of the backbone for it to be destroyed, so it is extremely fragile. Also, since the backbone always has only one redundant bond (when the bond across is added), it does not grow throughout the intermediate phase after it appears at the rigidity transition, because growth can only occur by

adding new redundant bonds. This means that for any given sample the elastic constants are the same throughout the intermediate phase (here we mean finite samples, of course, as in the infinite limit the elastic constants are zero).

We found the elastic modulus c_{11} numerically in both the intermediate and stressed phases. The triangular lattice was distorted by random displacement of atoms. For displacements along each axis uniform distribution on an interval $(-0.1; 0.1)$ in units of the lattice constant was chosen, but the results are only slightly sensitive to the width of the distribution. Equilibrium lengths of springs were chosen equal to the distance between the atoms they connect, so the initial network is unstressed. Thus subtraction of two large energies when finding elastic constants is avoided. The results are shown in Fig. 12. Pre-determining the applied stress backbone speeds up the relaxation greatly, as was first pointed out in Ref. [16]. Still, we were unable to reach full relaxation in the intermediate phase in all but the smallest samples (up to 30×30). The values in the intermediate phase are very low and are assumed to go to zero in the limit of large samples. We are currently doing finite size scaling to test this. Above the stress transition, the modulus seems to grow linearly, but, of course, it is hopeless to try and determine the critical exponent with reasonable precision from our data.

3.2. SELF-ORGANIZATION IN CONNECTIVITY PERCOLATION

3.2.1. *The model*

It is interesting and useful to see if similar phenomena are possible in the more familiar case of connectivity percolation, especially as connectivity percolation is easier to study and understand.

The essence of our algorithm of building self-organized networks in the rigidity case is rejecting stress-causing bonds (or those having redundant constraints). As we have seen, in the CF case, when "bonds" and "constraints" are the same, we may equivalently formulate this as rejecting redundant or irrelevant bonds. In bond connectivity percolation we also can build the networks by inserting bonds one by one; most importantly, there is a clear analog to redundant bonds. The relevant property now is connectivity, by which we mean the presence or absence of paths connecting any two sites of the network. Redundant bonds are those which connect sites already connected, that is would close a loop in the network. Thus the analog of self-organization is building *loopless networks*.

There are other equivalent ways to draw this parallel. The first is based on the fact that connectivity percolation can be considered as rigidity percolation with the sites having one degree of freedom regardless of the lattice dimensionality. Each site thus has one coordinate and each bond is a relation between the coordinates of the sites it connects. Then the concepts of rigid clusters and clusters in the usual connectivity sense coincide. The number of

floppy modes f is now the number of clusters. A redundant bond in the rigidity sense is the one that does not change f, it is also stress-causing, as it would introduce a relation between coordinates that cannot generally be satisfied. On the other hand, viewed from the connectivity perspective, such a bond connects the sites belonging to the same cluster and closing a loop, and our model is again recovered. Yet another way is to recall that rigidity percolation with angular constraints in 2D (or with angular and dihedral constraints in 3D) is equivalent to connectivity percolation. Then stresslessness is equivalent to looplessness.

Connectivity percolation and related phenomena were studied so extensively in all imaginable flavors that it would be strange if this and similar models were not studied before. Indeed exactly this model was proposed as far back as 1979 [42] and rediscovered in 1996 [43]. Besides, there was an extensive study of loopless graphs (trees) in relation to various phenomena ranging from resistance of a network between two point contacts (considered by Kirchhoff in mid nineteenth century [44]) to river networks [45] to certain optimization problems [46,47]. In many of these and other papers the algorithm for building trees was equivalent to ours. Still, we consider this model from a different perspective.

Given that connectivity percolation can be considered as rigidity percolation with one degree of freedom per site, we can apply the usual two-dimensional pebble game with the following modifications:

1) there is one pebble per site instead of two;
2) for a trial bond to be independent, it must be possible to free two pebbles at its ends (one pebble can always be freed).

As before, the number of free pebbles equals the number of floppy modes (which for connectivity is the number of clusters). We emphasize that this algorithm is absolutely independent of the actual dimensionality of the network.

Of course, the essence of our self-organization algorithm is still the rejection of bonds that are not independent. The pebble game allows the determination of all analogs of the quantities considered for rigidity.

3.2.2. *The Intermediate Phase*

In this section we carry out the same kind of analysis as was done for rigidity percolation.

First of all we describe Maxwell counting, as this, although simple, is rarely discussed in relation to connectivity percolation. For a network with *N* sites the number of degrees of freedom is now simply *N*, the number of constraints is, as before, $N\langle r\rangle/2$, so the number of floppy modes per site is $f = 1-\langle r\rangle/2$ and this becomes zero at $\langle r\rangle_c = 2$.

Since, as we have seen, connectivity percolation is nothing but a kind of rigidity percolation on a CF network with 1 degree of freedom per site, all of the general analysis for CF networks in the previous section is valid. Specifically, Maxwell counting is exact in the "unstressed" (this now means loopless) phases; the limit $\langle r \rangle_c = 2$ is reachable without creating loops; the relation between random and self-organized networks also holds.

The order parameters are defined analogously to the rigidity case. The first parameter is (by analogy) the size of the percolating (connectivity) cluster. However, the difference is that now the clusters (including the percolating one) can be defined in terms of either bonds or sites (there are no "pivot joints" that would be shared between several clusters). Therefore, there is a possibility to define this order parameter as the fraction of *sites* (instead of bonds) in the percolating cluster. This makes the relation between the order parameters of self-organized and random networks with the same number of "floppy modes" (clusters) exact. Yet, to be consistent, we ignore this possibility and define all the order parameters as a fraction of bonds, not sites, throughout this paper. The second order parameter is, logically, the fraction of "stressed" bonds (bonds in loops).

We do not show the results of simulations (which were done for the square lattice) as they are very similar to those in rigidity case, except that the "stressed" cluster critical exponent is larger, not smaller than the connected cluster exponent. Existence of the intermediate phase is confirmed in the range from $\langle r \rangle = 1.805$ to 2 for the square net. The lower transition coincides with the result obtained in Ref. [43].

3.2.3. *Conductivity*

Similarly to the elasticity case, we consider the busbar geometry here. We consider two variants, with and without fictitious bonds making sites at the busbars rigid with respect to each other (we refer to these two cases as boundary conditions A and B respectively). As in rigidity, it is possible to find the conductivity backbone by Moukarzel's method [41] (for B all the fictitious busbar bonds have to be put prior to placing the bond across, while they are already in the network in case A). Two examples corresponding to A and B are shown in Fig. 13. For A the backbone consists of just one path, while for B it is tree-like with branching near the busbars. Analog of these "boundary effects" in B is what was eliminated in study of elasticity (subsection 3.1.5), when the boundary conditions analogous to A were chosen.

The simulations for conductivity in 2D can be done very efficiently with the Frank-Lobb algorithm [48], whose only limitation is that it is applicable for the open boundary conditions only.

It is known from work on a river network model built in the same way as our network [45] that the backbone branches (in fact, all network branches) are fractal and the fractal dimension is $d_l \approx 1.22$. The only essential difference between the river network model and our one is that they consider

spanning trees (i.e., all sites are in the connecting cluster), which in our case corresponds only to $\langle r \rangle = 2$. This should not matter, though, since it is the dimensionality of the network that the cluster actually spans (i.e., of the connecting cluster) that is important and this dimensionality is 2 everywhere in the intermediate phase. Thus we come to a conclusion that the fractal dimension of backbone branches is the same throughout the intermediate phase and equals 1.22. We confirm this fact in our simulations. We note that this differs from both the random walk result ($d = 2$) and that for self-avoiding random walks ($d = 4/3$) – in our case branches are more "straight" than both of these walks. Then for boundary conditions A it is obvious that the fraction of bonds in the backbone is $\sim L^{d_l - 2} = L^{-0.78}$ and the conductance is $\sim L^{-d_l}$. Our simulations confirm this result, for both geometries. The effective conductivity in 2D is equal to the conductance. Thus we come to the conclusion that the conductivity does indeed go to zero in the thermodynamic limit for the intermediate phase.

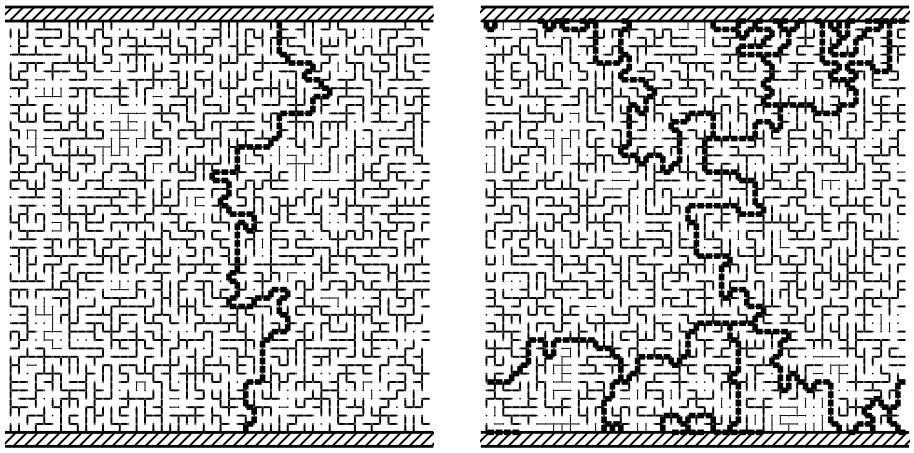

Figure 13. Examples of self-organized square networks in the intermediate phase with boundary conditions A (left panel) and B (right panel), as described in the text. The thickest bonds are in the conducting backbone, those of medium thickness are in the percolating cluster (but not in the backbone), the thinnest are not in the percolating cluster. The busbars are shown schematically.

The results in both the intermediate and the stressed phase are shown in Fig. 14. Just as for elastic constants, the dependence in the stressed phase is linear, but now much larger sizes are available, so this linearity may be exact, but we know of no reason for this to be so. Note the finite value of the conductivity in the intermediate phase, which is a finite size effect. This value would be constant for boundary conditions A, as the conducting backbone consists of just one stem not changing across the intermediate phase. Here this value changes slightly across the intermediate phase.

3.2.4. *Superconducting Networks*

We have seen that in the thermodynamic limit the conductivity σ is zero in both the disconnected and intermediate phases (just as elastic constants were zero in both the floppy and intermediate phases in the rigidity case). These results make us wonder if the lower transition shows up in any physical quantities for infinite networks. One possibility is to consider superconductor networks instead of resistor networks. In this model all the existing bonds are replaced with conductors of zero resistance ("superconductors"), while all the absent bonds are equal resistors with finite resistance.

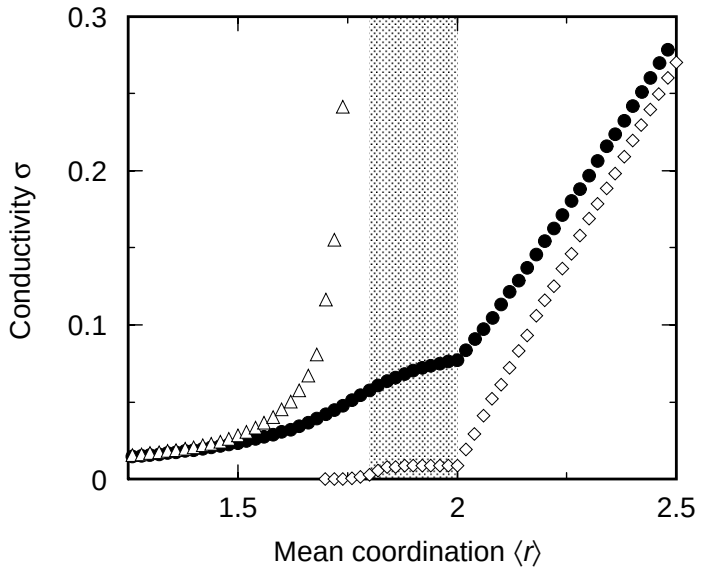

Figure 14. Conductivity for resistor networks with present bonds having resistance $R_1 = 1$ and missing having resistance $R_2 = \infty$ (diamonds); superconducting networks ($R_1 = 0$, $R_2 = 200$, circles); mixed networks ($R_1 = 1$, $R_2 = 200$, triangles). All results are averages over 10 square networks 100×100 with open boundary conditions parallel to the busbars, the busbar sites are treated as in case B (see text).

It turns out that the same kind of correspondence between random and self-organized networks with the same f we had for clusters is valid for the conductance in this case. Indeed, these networks differ by redundant bonds that connect sites already connected. All the connected sites have zero potential difference (as they are connected with superconductors), so putting redundant bonds does not change the distribution of the potential and thus does not influence the conductance.

It is known [28] that in the random case the *resistivity* is zero above the threshold and non-zero below it, with the critical exponent the same as for the *conductivity* of resistor networks (1.30). Thus in the self-organized case

the resistivity will turn zero in the point related to the percolation threshold of random networks by the above relation, i.e., at the *lower* transition. The critical exponent will be the same as in the random case (1.30), but this is now *different* from the value for σ of resistor networks (≈ 1).

3.2.5. *Mixture of Two Sorts of Resistors*

We can now "combine" the resistor and superconductor models by introducing two sorts of resistors, with resistances R_1 and R_2, $R_1 < R_2$, and putting R_1 resistors in place of present bonds and R_2 resistors in place of missing bonds. Assume now that $R_1 << R_2$. Below the lower transition there are no lower resistance percolating paths, thus essentially all the potential drop is on the higher-resistance bonds connecting lower-resistance clusters. This means the potential is almost constant within these clusters, and they may be considered as consisting of superconducting bonds. Thus we will have a smeared near-singularity in the conductivity at the lower transition. There will be a monotonic rise in conductivity throughout the intermediate phase, but it will remain low, as the low-resistance filaments are irrelevant by themselves in the thermodynamic limit. Above the second transition the low-resistance backbone by itself gives finite conductivity, so the high-resistance part of the network is irrelevant. Unlike the first transition, the second one is sharp, which is an artifact of change in the bond-insertion algorithm. Figure 14 shows the result for this model for $R_2/R_1 = 200$.

3.3. STABILITY

We have already mentioned the extreme fragility of the backbone and thus of the very fact of percolation in the intermediate phase: removal of a single bond from it can destroy it. In fact, if at some point in the intermediate phase we start *removing* bonds at random, then since there are more than O(1) bonds in the backbone, percolation will be destroyed immediately. We can ask the following question. Our networks turn out to be strongly biased [49]: at any given $\langle r \rangle$ not all networks satisfying the condition of stresslessness are equiprobable. What if we build the networks, which are truly random with the only constraint of stresslessness? This question was studied for connectivity by variety of methods [49-51], and, formulating the result in our terms, regrettably, the intermediate phase is destroyed. We did not study this question in rigidity case yet, but it is clearly important and more work needs to be done on this issue.

4. Summary

In these lectures we have discussed the rigidity of random and self-organized networks. We find that there is a single transition from floppy to rigid in random networks, but an intermediate phase intervenes in the self-organized networks. This intermediate phase is rigid but contains no redundant bonds and so is stress-free.

These idealized models of glassy networks can give us insights into real glasses, and this is discussed at length by P. Boolchand in his lectures. It should be remembered that adding the weaker interactions that we have ignored will round out any second order phase transitions.

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