CONTINUOUS DEFORMATIONS IN RANDOM NETWORKS

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We examine some current ideas concerning the differences between covalent random networks with high and low average coordination. These ideas can be made rigorous by considering the number of continuous deformations (i.e. zero frequency modes) allowed within the network. In the transition from one kind of network to another, rigidity percolates through the system. This leads to a picture in which random networks with low average coordination (polymeric glasses) have large floppy or spongy regions with a few rigid inclusions. On the other hand in random networks with high average coordination (amorphous solids) the rigid regions have percolated to form a rigid solid with a few floppy or spongy inclusions.

1. Introduction

It is quite reasonable to consider a network consisting of long polymer chains with a few cross links [1] to be quite different in terms of its rigidity from a random network describing an amorphous solid [2] like Si. The former can be deformed easily whereas the latter is rigid. Ideas somewhat along these lines have led Phillips [3–6] to postulate the notion of “overconstrained” and “underconstrained” glasses. His arguments attempt to relate the entropy and strain at the glass forming temperature $T_g$ with the average coordination. While we have found his general ideas to be insightful and physically appealing, two objections must be raised.

The first is that any discussion of entropy and strain at $T_g$ is bound to be imprecise as the processes taking place are complex and poorly understood. However the important physical insights of Phillips can be incorporated into arguments that are rigorous if the following viewpoint is adopted. Given a network structure at some reasonably low temperature ($\leq T_D$, where $T_D$ is the Debye temperature and $T_D < T_g$), let us enumerate the number of ways $M_0$ in which the network can be continuously deformed with no cost in energy. This is equivalent to asking for the number of zero frequency modes and is a well posed mathematical problem. In this paper we argue that for low mean coordination $\langle r \rangle$ the network is a polymeric glass in which the rigid regions are isolated as

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sketched in fig. 1. As the mean coordination \( \langle r \rangle \) increases, these rigid regions increase in volume until \( \langle r \rangle = r_p \) when a percolation transition takes place to a rigid network or amorphous solid also sketched in fig. 1. Although this may seem at first sight to be just another simple variant of the percolation problem, albeit with a rather unusual quantity (rigidity) doing the percolating, in fact the situation is rather more subtle and complex. This is because the floppy regions contain both rigid and floppy modes. Indeed the rigidity, associated with finite frequency modes, and the floppiness, associated with zero frequency modes, have many similarities with extended and localised modes found in Anderson localisation [7]; the finite frequency modes being extended and the zero frequency modes localised. However, we prefer to focus on the percolation aspects of the problem as it is the percolation of rigidity that drives the transition. In the next section we develop a mean field theory which leads to the transition taking place at

\[
r_p = 2.4
\]  

(1)

as previously obtained by Döhler et al. [8].

The second objection is that whilst these ideas lead inevitably to the concept of floppy and rigid regions and rigidity percolation, they do not lead inevitably to the formation of molecular clusters [3–6]. What we are saying is that, ideas based on constraints cannot be used as an argument to support the existence of molecular clusters. On the other hand, the existence of such clusters is not inconsistent with these ideas either.

The layout of this paper is as follows. In the next section we focus attention on the number of zero frequency modes and rederive the result \( r_p = 2.4 \). We note that this same result can also be derived from a mean field theory of the cross linking of polymer chains. In §3 we argue that this is really a percolation problem and note that two corrections must be made to a mean field estimate of \( r_p \). One is that the number of zero frequency modes is not zero at \( \langle r \rangle = r_p \) because floppy inclusions still exist. These are fluctuation effects and as such go beyond mean field theory. The other correction is for the overcounting of constraints due to rings, rings of rings etc., which become increasingly important for \( \langle r \rangle < r_p \). We show that rings with 6 or less atoms are rigid whereas isolated rings with 7 or more atoms are floppy. This also implies that a

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**Fig. 1.** The Rigid and Floppy regions in networks of type I (polymeric glass) and Type II (amorphous solid).
"bridge" containing 6 or more atoms is floppy. Throughout this work, the counting of linearly independent constraints is crucial and not always easy. In section four we show how the ring constraints may be incorporate to yield an exact (though trivial) answer in two dimensions and an improved approximation in three dimensions. In section five we set up a simple soluble model, that contains more some of the features of interest. We show that a third order phase transition takes place in this model.

In the conclusion we make some speculative comments concerning the relationship of this work to physical observables such as the shear modulus and the anomalous low temperature properties of glasses.

2. Zero frequency modes

Imagine that a particular network with \( N \) atoms has been constructed with \( n_r \) atoms having \( r \) bonds

\[
\sum_r n_r = N. \tag{2}
\]

Small vibrations about this (equilibrium) structure are described by a potential.

\[
V = \frac{1}{2} \sum_{\langle ij \rangle} \alpha_{ij} (\Delta r_{ij})^2 + \frac{1}{2} \sum_{\langle ik \rangle} \beta_{ijk} (\Delta \theta_{ijk})^2, \tag{3}
\]

where \( \Delta r_{ij} \) is the change in the nearest neighbour bond length between atoms \( \langle ij \rangle \) and \( \Delta \theta_{ijk} \) is the change in the bond angle between two adjacent bonds \( \langle ij \rangle \) and \( \langle jk \rangle \). The \( \alpha_{ij}, \beta_{ijk} \) are force constants whose precise value will not concern us (an alternative form for the angular part of eq. (3) such as that used by Keating [9] would not affect the argument). These forces are known to be the most important in covalent molecules and solids [10] and all the comments up to the end of section four assume that the network is described by the potential (3). We seek to calculate the number \( M_0 \) of vibrational modes with zero frequency. These correspond to ways in which the network can be continuously deformed at no cost in energy.

In general the number of modes with zero frequency \( M_0 \) is given by the difference between the number of degrees of freedom \( 3N \) and the number of linearly independent constraints \( N_c \)

\[
M_0 = 3N - N_c. \tag{4}
\]

These constraints are just the number of eigenvectors of the dynamical matrix formed from eq. (3) that correspond to non-zero frequencies. Put another way \( N_c \) is the rank of the dynamical matrix [11]. The number of zero frequency modes \( M_0 \) could be ascertained directly by diagonalising the dynamical matrix or by determining its rank. Another way is to estimate the number of
constraints*. These are:

(A) one per bond that is associated with the first term in eq. (3) and
(B) for a 2 coordinated atom there is a single angular constraint associated
with the second term in eq. (3). Adding each additional bond gives two more
constraints because the angles with two existing bonds must be specified. As we
are only concerned with continuous deformations, other discrete possibilities
are ignored. This gives a total of 2r − 3 linearly independent constraints
around an atom with r ≥ 2 bonds [8]. This has previously been overestimated
[3,8] to be r(r − 1)/2 which gives 1, 3, 6 for r = 2, 3, 4 rather than the correct
values 1, 3, 5.

Using the constraints associated with both terms in the potential (3) we have

\[ M_0 = 3 \sum r_n - \sum n_r \left[ r/2 + (2r - 3) \right]. \]  \hspace{1cm} (5)

which setting \( M_0 = 0 \) yields

\[ r_p = \langle r \rangle = \frac{\sum r n_r}{\sum n_r} = 2.4. \]  \hspace{1cm} (6)

Note that in applying eq. (6) dangling bonds (r = 1) are excluded. They take
no part in the connectivity of the network and can be progressively removed
until no more exist. They are relevant in reducing the average co-ordination of
the remaining network (e.g. H in amorphous Si, see for example ref. 13).

For \( \langle r \rangle > r_p \), the network is rigid and we refer to it as an amorphous solid;
whereas for \( \langle r \rangle < r_p \), the network is not rigid and can be macroscopically
deformed. This is referred to as a polymeric glass.

It is simple to apply these ideas to a network like Ge_xAs_ySe_1-x-y, where Ge
has \( r = 4 \), As has \( r = 3 \) and Se has \( r = 2 \). Using eq. (1) we find that the
boundary is given by

\[ 4x + 3y + 2(1 - x - y) = 2.4, \]

that is

\[ 2x + y = 0.4, \]  \hspace{1cm} (7)

which is shown in the phase diagram of fig. 2.

These ideas must not be used indiscriminantly. For example in Si_xO_1-x, eq.
(7) leads to the boundary being at \( x = \frac{1}{2} \) whereas because the Si–O–Si bond
angle is known to take on a range of values [14], it is reasonable not to count
the angular force at the oxygen atoms, leading to a boundary at \( x = \frac{1}{2} \) which is
more reasonable as SiO_2 is a good bulk glass.

Because \( r_p \) is not too much greater than 2, it is instructive to re-examine the

* Similar arguments have been used before. In the context of random networks these go back to
Weaire and Thorpe [12a], as applied to the vibrational problem see Weaire and Alben [12b] and
Sen and Thorpe [12c] and particularly Thorpe and Galeener [12d] where it was shown that
\( M_0 = 3N - N_b \) for nearest neighbour central forces only in networks with \( r = 2, 3 \) and 4 where
\( N_b \) is the number of nearest neighbour bonds.
derivation of eq. (1) by progressively cross-linking polymer chains as shown in fig. 3. A single polymer chain with \( s \) atoms has \( 3s - (s - 1) - (s - 2) = s + 3 \) zero frequency modes, so that if the total number of atoms in an assembly of isolated polymer chains is \( N_a \), we have

\[ M_0 = N_a + 1.5n_e, \quad (8) \]

where \( n_e \) are the number of ends \( (\text{two/chain}) \). We can imagine a \( \text{(mathematical)} \) cross-linking in which 3 and 4 co-ordinated sites are formed by \textit{fusing together} pairs of atoms as indicated in fig. 3. In order not to have any free ends, the number of 3 co-ordinated atoms \( n_3 = n_e \). Each time a 3 co-ordinated atom is made, the total number of atoms is reduced by one \( \text{(costing 3 constraints to coalesce the atoms)} \) and 2 additional angular constraints are required. The situation is similar when a 4 co-ordinated atom is made, except that 3 rather than 2 additional angular constraints are required. If there are \( N \) atoms when this process is complete

\[ N = N_a - n_3 - n_4, \quad (9) \]

and

\[ \langle r \rangle = \left[ 4n_4 + 3n_3 + 2(N - n_3 - n_4) \right]/N, \quad (10) \]

and \( M_0 \) given in eq. (8) has been reduced to

\[ M'_0 = N_a + 1.5n_3 - (3 + 2)n_3 - (3 + 3)n_4. \quad (11) \]

Fig. 2. Triangular phase diagram for the ternary compounds Ge, As, Se, which are known to form glasses \( \text{[3]} \) all over region 1.

Fig. 3. Isolated polymer chains can be cross-linked to form 3 and 4 co-ordinated atoms by \textit{fusing} pairs of atoms together.
At this point it is convenient to introduce the quantity $f$, which is the fraction of zero frequency modes in the system

$$f = \frac{M_0}{3N}$$

and from eqs. (9)–(11) we find that

$$f = \frac{(12 - 5\langle r \rangle)}{6},$$

which is shown as the dashed line in fig. 4. The quantity $f$ goes to zero at $\langle r \rangle = r_p = 2.4$ as before. Of course $f$ cannot be negative and so within this simple mean field scheme we have $f = 0$ for $\langle r \rangle > r_p$. This particular way of achieving the final result is somewhat arbitrary and other schemes could be used. Using polymer language, $\langle r \rangle = 2.4$ implies that 40% of all atoms are cross linked if the cross linkages are all of the type 3 shown in fig. 3 whereas only 20% are cross linked if they are all of the type marked 4.

3. Rigidity percolation

The ideas of the previous section argue that covalent networks can be divided into two classes. Those of type I for which $f > 0$ (polymeric glasses) and those of type II for which $f = 0$ (amorphous solids). It is clear that by definition $f$ cannot be negative. If, in attempt to count the number of constraints, $f$ should appear to become negative, then the constraints are not all linearly independent. It is only linearly independent constraints that reduce the number of zero frequency modes.

For a single long polymer chain, there is one bond and one angle constraint per site so that $f = \frac{1}{2}$ for $\langle r \rangle = 2$. Note that dangling bonds, if they ever existed, are removed by progressive elimination as mentioned in the previous section. For $\langle r \rangle$ close to 2, the initial slope $\frac{df}{d\langle r \rangle} = -\frac{5}{3}$ as $\langle r \rangle \to 2$ is also given correctly by mean field theory. However as $\langle r \rangle$ increases, mean field theory become increasingly unreliable as $\langle r \rangle$ approaches $r_p$. This is because, mean field theory overestimates the number of linearly independent constraints.

In fig. 4 we show in the solid curve the conjectured behaviour of $f$ against $\langle r \rangle$. As $\langle r \rangle$ is increased from 2, the small rigid regions grow in size until they percolate [15] at $r_p$. The quantity $f$ is not zero at $r_p$ because small floppy inclusions exist in the percolated rigid region. The whole solid is rigid for $\langle r \rangle > r_p$. The behaviour for $\langle r \rangle = r_p$ is harder to conjecture and for this we rely heavily on the simple soluble model described in section five. This would suggest that $f$ and its first two derivatives are continuous at $r_p$ but the third derivative is discontinuous,

$$\frac{d^3f}{d\langle r \rangle^3} \text{ discontinuous at } \langle r \rangle = r_p.$$  

One of the main deficiencies of the simple model in §5 is that it is
completely random, whereas the network situation is much less so especially when chemical ordering is taken into account (i.e., 2 co-ordinated atoms avoiding each other, etc.). It is harder to say where the tail terminates and $f$ may well be zero for $\langle r \rangle > 3$. This tail is somewhat akin to a Lifshitz tail [16] depending upon how random the configurations are above $r_p$.

In order to illustrate how small floppy regions could occur for $\langle r \rangle > r_p$, we consider a bridge made up of $s$, 2 co-ordinated atoms attached to the rest of the (rigid) network as shown in fig. 5. If the 3 co-ordinated atoms are anchored into the rigid parts of the network, then for the bridge shown

$$M_0 = 3s - ((s + 1) + s + 4) = s - 5,$$

which means this forms a floppy region if $s \geq 6$. For $s \leq 4$, the constraints are not linearly independent and the result (15) is invalid. This will be clearer after the discussion on rings that follows in the next section. There are other more likely, but less simple, ways to construct floppy regions.

Because the transition takes place when the network is rather open, we

Fig. 4. The fraction of zero frequency modes $f$ versus mean co-ordination $\langle r \rangle$. Rigidity percolation occurs at $r_p$. The dashed curve is a result of a mean field calculation and the solid curve is a sketch of the conjectured behaviour with the transition taking place at the cross.

Fig. 5. A bridge of length $s = 5$ with 2 co-ordinated atoms lying between two other atoms with co-ordination greater than 2.
believe that the mean field result \( r_p = 2.4 \) is probably a very good estimate of where the transition takes place. Also the two corrections, the constraints due to rings etc. and floppy regions still existing at \( r_p \), go in opposite senses and will tend to cancel. In the next section we make a crude estimate of the ring corrections. We note that it is only within mean field theory that the network is completely characterised by \( \langle r \rangle \) and in reality other structural quantities like the ring statistics will be involved [17].

4. Ring corrections

The existence of small rings of bonds means that not all the constraints specified in §2 are linearly independent. Using arguments from the previous section applied to a ring with \( s \) atoms

\[
M_0 = 3s - (s + s) = s.
\]  

However for \( s \geq 3 \), \( M_0 \) must be at least 6 for the three rigid translations and three rigid rotations. The argument leading to eq. (16) is correct for \( s \geq 6 \) leading to

\[
M_0' = s - 6
\]

*internal* zero frequency modes. A 6 sided ring is just rigid. Triangles, quadrilaterals and pentagons are also rigid but the constraints given in §2 are overcounted by 3 for a triangle, 2 for a quadrilateral and 1 for a pentagon. This is easily seen for a triangle where specifying the lengths of the sides automatically determines the three angles. Similar arguments can be given for the quadrilateral and pentagon. We thus reach the important conclusion that all isolated rings with less than 6 sides are *rigid* and all isolated rings with 7 or more sides are *floppy*. Of course when such rings are part of a network the rigid rings remain rigid but the floppy rings can become rigid by proximity to rigid rings and hence rigidity percolates through the network. An example of this is shown in fig. 6. Starting with a single rigid 6 sided ring, a bridge of 5 atoms is added. As argued earlier bridges with less than or equal to 5 atoms are rigid, so that the 7 sided ring formed is rigid when attached to the 6 sided ring. In other words the single degree of freedom of an isolated 7 sided ring has been *quenched* by contact with a 6 sided ring. In a similar way the 4 and 5 atom bridges can be added to form rigid 8 and 9 sided rings as shown. Although it is convenient to think of rigidity as spreading outwards from a rigid seed, in this case the 6 sided ring; this is not necessary and floppy rings can become rigid if they are near other floppy rings and are not too large.

Rigidity does not always “flow” from the rigid seed if it is surrounded by enough large floppy rings, as illustrated in fig. 7. This is an extreme situation with the central ring surrounded by rings with 15 and more sides but does serve to illustrate the point that isolated rigid regions can exist.

The reader may be struck by the fact that some of the floppy rings in the
above arguments are very large. This is as it should be when considering that
the transition with takes place at $r_p \approx 2.4$ when 2 co-ordinated atoms are in the
majority. For example, in $\text{As}_y \text{Se}_{1-y}$, the transition takes place when $y = 0.4$
(i.e. $\text{As}_2\text{Se}_3$). One example of such a (crystalline) network would be a puckered
two-dimensional honeycomb lattice with a Se atom inserted between each of
the 3 co-ordinated As atoms. All the elementary rings in this network are 12
sided. In a random structure there will be a distribution of ring sizes of course
but the point is that at $r_p = 2.4$, there are not many small rings so that the mean
field theory of §2 should give a good estimate of $r_p$.

In two dimensions a network can be dissected into elementary polygons as
shown in fig. 8. If we constrain all motion to be within the plane, then the
network cannot be deformed continuously when controlled by the potential (3),

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Fig. 6. A single rigid ring (6) and three floppy rings (7, 8, 9). The final unit shown is rigid because
the rigidity of the 6 sided rigid ring propagates through the network as shown.

Fig. 7. A rigid ring surrounded by floppy rings so that the rigidity does not percolate away.
We use this to check that we do indeed understand how to count the constraints.

In two dimensions, there are $2N$ degrees of freedom and only $r-1$ angular constraints associated with each $r$ co-ordinated site as only one additional angle need to be specified each time a bond is added at a site. Eq. (5) must be modified accordingly. In addition, every time a polygon is closed, the position of the last bond and its associated two angles are determined by the previous constraints as indicated in fig. 8. Thus 3 constraints per polygon must be removed so as not to overcount the constraints and eq. (5) is modified to become

$$M_0 = 2\sum_r n_r - \sum_r [r/2 + (r - 1)] + 3F,$$

where $F$ is the number of polygons (Faces). The number of Edges $E = 1/2\sum_r r n_r$, and the number of Vertices $V = \Sigma_r n_r$, so that

$$M_0 = 3(V - E + F) = 3$$

where we have used Euler’s theorem*. These three modes are just the two uniform translations and one rotation of the whole system with free boundaries which is rigid as expected.

The overcounting of constraints due to rings is much more serious in two dimensions, where three constraints must be removed for each polygon formed, than in three dimensions, where three constraints must be removed for a triangle, two for a quadrilateral, one for a pentagon and none for larger rings.

In three dimensions, networks cannot be divided up into elementary rings in any natural way and so there are no rigorous results. If we count all the rings in the network with five sides and less and if there are $Nm^3$ triangles,

* See for example Hammermesh [18]. Note that $E - V + F = 2$ if the network is embedded in the surface of a sphere and $V - E + F = 1$ with free boundaries as in fig. 8.
$N m_4$ quadrilaterals and $N m_5$ pentagons, we must modify eq. (6) to give

$$r_p = 2.4 + 1.2 m_3 + 0.8 m_4 + 0.4 m_5.$$  \hspace{1cm} (20)

This equation needs still further corrections due to rings of rings etc. In order to get a feeling for how large the effect of rings is, we consider that a fraction $f'$ of the Se atoms in Ge$_x$Se$_{1-x}$ are in edge sharing tetrahedra (see ref. 19 and also see comments in ref. 3, Vol. 43, p. 49); then $m_4 = (1 - x) f'/2$ and

$$r_p = 2.4 + 0.4(1 - x) f',$$  \hspace{1cm} (21)

which using $r_p = \langle r \rangle = 4x + 2(1 - x)$ leads to $x = (1 + f')/(5 + f')$ so that as $f'$ goes from 0 to 1; $x$ goes from $\frac{1}{5}$ to $\frac{1}{3}$. Thus we see that $r_p$ does depend upon the topology of the network and not just the mean co-ordination. However the example above is somewhat extreme and for most networks without large numbers of small rings these corrections are probably small. In addition the non-zero value of $f'$ at $r_p$ will reduce the shift in $r_p$ away from the value 2.4. The above example with $f' = 1$ corresponds to the polymer chain GeSe$_2$ which is just rigid as long as the ring constraints are included properly as above.

$$\text{Se} < \text{Ge} < \text{Se} < \text{Ge} < \text{Se} < \text{Ge}.$$ \hspace{1cm} (22)

This can be seen directly. If there are $N$ formula units then,

$$M_0 = 9N - (4N + 5N + 2N) + 2N = 0,$$

where the last term is the ring correction.

5. A simple soluble model

In order to understand better how the effects that we have been discussing occur, consider the following simple model system. Mass points $m$ are placed at the sites of a (crystalline) lattice and their motion is described by the Lagrangian

$$L = 1/2 \sum_i m(z_i)^2 - 1/2 \sum_{\langle ij \rangle} a(z_i - z_j)^2 p_{ij}.$$  \hspace{1cm} (23)

where $z_i$ is the displacement from equilibrium of the mass at site $i$ in a direction orthogonal to the dimensions that define the lattice geometry. The sum over $\langle ij \rangle$ is over nearest neighbour pairs. The quantities $p_{ij} = 1, 0$ with probability $p, 1 - p$ so that we have a bond percolation problem $[15]$. Note that every site is always occupied by a mass point. An example would be a square lattice defined in the $xy$ plane with particle motion in the $z$ direction. Again we ask for the number of zero frequency modes $M_0$. It is easy to see that there is exactly one such Goldstone mode associated with each isolated cluster $[20-21]$ so that

$$M_0 = N_0 \text{tr}(\gamma_e(p)) + N(1 - p)^z,$$  \hspace{1cm} (23)
where $\langle \gamma_c(p) \rangle$ is the average number of distinct connected clusters per bond for bond percolation, $N_b$ is the number of bonds and $N(1-p)^z$ is the number of isolated sites. Therefore we have

$$f = z/2\langle \gamma_c(p) \rangle + (1-p)^z$$  \hspace{1cm} (24)

and the problem of finding $f$ is reduced to that of knowing $\langle \gamma_c(p) \rangle$ for this simple model. An identical result to eq. (24) would be obtained for the fraction of zero frequency spin wave modes in a bond dilute Heisenberg ferromagnet.

In order to link up with our previous notation, we will define

$$\langle r \rangle = z p.$$  \hspace{1cm} (25)

The quantity $\langle \gamma_c(p) \rangle$ is not known analytically for any real lattice although excellent numerical simulations exist [21] and its overall behaviour and critical behaviour is well understood. $\langle \gamma_c(p) \rangle$ plays the role of a free energy [20,21] for the percolation problem and so $f$ defined in eq. (24) also behaves like a free energy analogue although of course there is no temperature defined in this problem. In general $f$ and its first two derivatives are continuous at $p_c$ so we may regard the transition at $p_c$ as being third order [23] (in the Ehrenfest sense) with

$$d^2f/d\langle r \rangle^2 \text{ discontinuous at } r_p.$$  \hspace{1cm} (26)

Put another way, a “specific heat” that can be formed from $\langle \gamma_c(p) \rangle$ by taking two derivatives is continuous but its derivative is discontinuous. The specific heat has critical exponents [21],

$$\alpha = \alpha' = -0.60 \pm 0.1 \text{ in two dimensions},$$  
$$\alpha = \alpha' = -0.58 \pm 0.11 \text{ in three dimensions},$$  \hspace{1cm} (27)

which correspond to a cusp.

In order to have an analytic expression for $f$ for this model we have examined it on a Bethe lattice. Using the formalism of Fisher and Essam [24] we find that for $p < p_c$ (i.e. $\langle r \rangle < r_p$)

$$f = 1 - \langle r \rangle/2,$$  \hspace{1cm} (28)

where $z p_c = r_p = z/(z-1)$. The form (28) is universal for all $z$. For $p > p_c$ (i.e. $\langle r \rangle > r_p$) the result depends on $z$. For $z = 3$,

$$f = [(3 - \langle r \rangle)/\langle r \rangle]^2 (\langle r \rangle - 1)/2$$  \hspace{1cm} (29)

and for $z = 4$,

$$f = [(4 - \langle r \rangle)/\langle r \rangle]^4 (\langle r \rangle - 4 + [\langle r \rangle(16 - 3\langle r \rangle)]^{1/2})/2.$$  \hspace{1cm} (30)

These results are shown in fig. 9, where the values of $r_p$ are marked by crosses as a discontinuity in the third derivative is not apparent to the eye!

* Another interpretation for $f$ is that it is the ratio of the entropy at zero temperature to that at infinite temperature for a dilute bond spin $\frac{1}{2}$ Ising model [22]. Each cluster behaves like a spin with two orientations at zero temperature.
Fig. 9. The behaviour of $f$ with $\langle r \rangle$ for the simple model of §4. The dashed line is for the linear chain. The transitions in the solid curves take place at the crosses. The Bethe lattice results are exact and the result for the square lattice is estimated (see text).

For a real lattice with rings etc. like the square net, it is possible to count the small clusters and show that for $\langle r \rangle < r_p$

$$f = 1 - \langle r \rangle / 2 + (nz / 2z)(\langle r \rangle / z)^2 + O((\langle r \rangle / z)^3), \quad (31)$$

where the first two terms are universal and the leading corrections depend on the size of the smallest rings which have $s$ bonds with $n$ of them through each edge (2 for the square net). For $\langle r \rangle \leq z$, we have

$$f = [(z - \langle r \rangle) / \langle r \rangle]^z, \quad (32)$$

which is obtained by isolating a single site by removing the $z$ bonds around it. For the square net the value of $\langle \gamma_k (p) \rangle$ at the critical point is known [25] and from eq. (24) leads to $f = 0.16$ at $r_p$. We have used this and the results (31) and (32) to sketch the result for the square net shown in fig. 9.

Adding the next bond may either reduce the number of zero frequency modes by 1 or 0. For small $\langle r \rangle$, it will almost always be 1 but as the density of bonds gets larger it may be 0 if the two sites, associated with the bond, already belong to a connected cluster. This means that

$$-\frac{1}{\langle r \rangle} \leq \frac{df}{d\langle r \rangle} \leq 0, \quad (33)$$

where the lower value $(-\frac{1}{\langle r \rangle})$ is attained for small $\langle r \rangle$ and the slope gradually goes to 0 as $\langle r \rangle \to z$. 
The important aspect of this simple model is that there is a phase transition of the percolation kind [15]; that this phase transition is third order; and that the behaviour of \( f \) with \( \langle r \rangle \) is rather universal. It is interesting to note that the result for the linear chain, eq. (28) for \( \langle r \rangle < 2 \), is linear all the way like the mean field result of §2 whereas the Bethe lattice results show more curvature as \( z \) increases. The value of \( f \) at \( r_p \) lies between 0.16 and 0.33 for the two-dimensional networks shown in fig. 9.

6. Conclusions

We have presented a new framework from which to look at the differences between random networks with high and low mean co-ordination. The original ideas of Phillips [3–6] focused on the free energy \( F = E - TS \) at the temperature \( T = T_c \) at which the network is formed. This is an extraordinarily complex quantity involving both the energy \( E \) and the entropy \( S \). We have adopted a different and simpler viewpoint in this paper. Given a network at some temperature, we do not worry about how it was formed or what is its energy or entropy. We ask only if it can be continuously deformed. This is a well posed mathematical problem.

We have shown that a mean field theory of rigidity percolation leads to a linear dependence of \( f \) on \( \langle r \rangle \) and gives \( r_p = 2.4 \). The network is divided into two kinds of regions that are designated rigid and floppy as shown in fig. 1. For \( \langle r \rangle < r_p \), we have a polymeric glass whereas for \( \langle r \rangle > r_p \) we have an amorphous solid.

We have shown that the key quantity is \( f \), the fraction of zero frequency modes. This can never be negative and avoids the mathematically undefined notion of an “overconstrained network” [3]. Instead the apparent constraints become more and more linearly dependent as \( r_p \) is approached from below. Indeed it is untrue [3] to say that strain builds up like \( R^2 \) (where \( R \) is the radius) when hand built models are constructed [17]; instead the strain is held within the small rings and does not propagate. Thus it is possible for both a polymer with a few cross links and a tight random network like amorphous Si to exist. The discussion then passes to the zero frequency modes. Whether or not such infinite random networks do actually exist is beyond the scope of the arguments given in this paper.

We have examined a simple model for which \( f \) can be calculated as a function of \( \langle r \rangle \). The model shows that there is indeed a phase transition but that it is the third derivative of \( f \) that is discontinuous. If this result transfers to random networks, it means that attempts to locate \( r_p \) by numerically diagonalising dynamical matrices, or by finding their rank, are doomed. It will probably be necessary to examine other quantities such as the elastic constants that are expected to be more singular at \( r_p \).

To conclude this paper, we indulge in some speculations because they have important experimental implications. In real covalent networks, there are
additional terms that occur in the potential (3). These are usually quite small [10] (say $\leq T_D/30$) but are important for the zero frequency modes, which will acquire a small finite frequency from harmonic interactions between more distant neighbours. Some of the zero frequency modes may become tunnelling modes [27] when the effects of more distant harmonic interactions and anharmonicity are turned on. We stress that although these additional interactions are small compared to $T_D$, they are large compared to the temperatures below $\leq 2$ K where affects due to tunnelling are usually observed. These effects result in anomalous low temperature properties for the specific heat, thermal conductivity, ultrasonic attenuation etc.

Our picture is that the potential for the zero frequency modes becomes a weak, slowly varying, function of the normal co-ordinate that can produce low frequency harmonic modes and tunnelling modes. Instead of using the word floppy to describe these regions in the network, the word spongy is probably more appropriate. These spongy regions do not imply a two phase material; they are just the inevitable consequence of the random nature of the network.

Given this viewpoint, it would obviously be very interesting to measure properties like shear modulus; specific heat, thermal conductivity and ultrasonic attenuating at low temperatures, against $\langle r \rangle$. We would expect them all to contain a part that tracks the behaviour of $f$ as sketched in fig. 4. In particular we would expect the coefficient of the linear term in the specific heat to decrease rapidly as $\langle r \rangle$ increases, going to zero as $\langle r \rangle \to 4$. It is interesting that no linear specific heat term has been observed in amorphous Si or Ge [25]. This model also potentially provides an explanation for the increase in the coefficient of the $T^3$ term in the specific heat compared to that expected from sound velocities and/or elastic moduli. The increase would be associated with the localized low frequency modes in the spongy regions that take no part in sound propagation but would contribute to the density of states and hence to the specific heat.

As we have said these final remarks are quite speculative and it is unclear if the effects mentioned here can be separated from other effects, like chemical impurities [27], that have a large effect on the anomalous low temperature properties of glasses.

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References

M.F. Thorpe / Continuous deformations in random networks