ELASTIC PROPERTIES OF GLASSES

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ABSTRACT

It is shown that the elastic properties of covalent networks are very sensitive to coordination. High coordination networks are relatively hard and the elastic constants are determined by the covalent forces. Low coordination networks are relatively soft and the elastic constants are determined by longer range forces.

INTRODUCTION

Many network glasses are well described by the Continuous Random Network (C.R.N.) model first discussed by Zachariasen[1] more than 50 years ago. Examples are Si and Ge that like to make 4 bonds in a tetrahedral arrangement; As that makes 3 bonds; and S, Se and O that make 2 bonds. A C.R.N. can be described by a chemical formula like Ge$_4$As$_3$Se$_{4-x}$O$_x$. If the total number of atoms is $N$ and there are $n_r$ atoms with coordination $r$ ($r = 2, 3$ or $4$) then

$$N = \sum_r n_r$$

(1)

and we can define the mean coordination $\langle r \rangle$ by

$$\langle r \rangle = \sum_r \frac{r n_r}{N}$$

$$= \bar{z} + \bar{y} + 2\bar{x}$$

(2)

We note that $\langle r \rangle$ (where $2 < \langle r \rangle < 4$) gives a partial, but very important, description of the network. We will see that the elastic properties are very sensitive to $\langle r \rangle$.

We regard a perfect C.R.N. with no dangling bonds as being analogous to the perfect crystal. In practice one can approach a perfect C.R.N. by careful preparation techniques in which the number of dangling bonds is kept to a minimum. In some circumstances the C.R.N. model is inappropriate and the network has effectively lower dimensionality and may be better thought of as a spaghetti of twisted ribbons.[2] The ideas that we are discussing in this paper also apply to such networks, but with some modifications that will be discussed later.

CONSTRAINT COUNTING

In covalent networks like Ge$_4$As$_3$Se$_{4-x}$O$_x$, the bond lengths and angles are well defined and small displacements from a (supposed) equilibrium structure can be described by the potential

$$V = \frac{a}{2} \sum_{i<j} \left( \hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j \right) \cdot \left( \hat{r}_{ij} \right)^2 + \frac{b}{2} \sum_{i<j<k} k_{ij} k_{ik} \left( \delta \theta_{ijk} \right)^2$$

(3)

Here $\hat{\mathbf{u}}_i$ is the displacement of the atom $i$ and $\hat{r}_{ij}$ is a unit vector connecting nearest neighbor sites $i,j$; $k_{ij}$ is the length of the bond $ij$ and
\[ \theta \] is the angle between the bonds \( ij \) and \( k \). The bond stretching force constant \( a \) and the bond bending force constant \( b \), are the largest forces in covalent glasses and typically \( a > 5b \). Other forces are much smaller as would be expected from the nature of the covalent bond. The potential (3) has been written as harmonic but this is really not important in what follows as we shall be making small virtual displacements.

We will regard the solution of the eigenmodes of the potential (3) as a problem in classical mechanics.\(^3\) The dynamical matrix has dimensionality \( 3N \) which corresponds to the \( 3N \) degrees of freedom. In a stable rigid network we would expect all the squared eigenfrequencies \( w^2 > 0 \) with precisely \( 6 \) modes at zero frequency. These \( 6 \) modes are just the \( 3 \) rigid translations and the \( 3 \) rigid rotations. However we will find that in some covalent networks described by the potential (3), there are a significant number of extra zero frequency modes which correspond to internal deformations of the network. The number of such modes can be determined by counting the constraints in the system. There is one constraint associated with each bond which we can reassociate as \( 2/r \) constraints associated with each \( r \) coordinated atom. In addition there are constraints associated with the angular forces in (3). For a \( 2 \) coordinated atom there is one angular constraint, for a \( 3 \) coordinated atom there are three angular constraints and for an \( r \) coordinated atom there is a total of \( 2r - 3 \) angular constraints. The total number of constraints is equal to the number of finite frequency modes which are therefore

\[
\sum_r n_r [r/2 + (2r - 3)]
\]

The fraction \( f \) of zero frequency modes is given by

\[
f = (3N - \sum_r n_r [r/2 + (2r - 3)]) / 3N
\]

which can be rewritten as

\[
f = 2 - \frac{5}{2} \langle r \rangle
\]

where \( \langle r \rangle \) is defined in (2). When \( \langle r \rangle = 2 \) (e.g. Se chains), then \( f = 1/3 \); that is one third of the modes are at zero frequency. As atoms with higher coordination than 2 are added to the network, \( f \) drops and goes to zero at \( \langle r \rangle = 2.4 \).

What is the interpretation of this result? Networks with \( \langle r \rangle < 2.4 \) are unstable under covalent forces whilst networks with \( \langle r \rangle > 2.4 \) are stable. This can be demonstrated from numerical simulations performed by He and Thorpe\(^4\) shown in Fig. 1. In order to simulate a C\( \in \)N bonds were removed from a series of diamond lattices in such a way that sites with 2, 3 and 4 fold coordination were produced. It can be seen from Fig. 1 that the number of zero frequency modes \( f \) and the elastic constant \( C_{11} \) go to zero around \( \langle r \rangle = 2.4 \). Similar results are obtained for the shear modulus\(^8\) \( C_{44} \). Thus we can divide network glasses into two types as first suggested by Phillips\(^5\).

For \( \langle r \rangle > 2.4 \), the network is mechanically stable and the elastic properties are determined by the covalent forces \( a,b \). Other forces are small and can be neglected. We will refer to this as an amorphous solid. It roughly corresponds to the amorphous thin films that must be rapidly cooled and which upon heating crystallize before melting.

For \( \langle r \rangle < 2.4 \), the network is mechanically unstable and we must include the other weaker forces to stabilize the structure. The most important of these are the dihedral angle forces. The elastic constants are determined by this force as there is no contribution to the elastic constant from \( a,b \) (see Fig. 1). We refer to this phase as a polymeric glass. It roughly
corresponds to the bulk glasses that can be cooled slowly from the melt and do not crystalize when heated but rather return directly to the liquid phase.

We thus regard a covalent network glass as consisting of floppy and rigid regions\[6\] as shown in Fig. 2. In the low coordination network or polymeric glass, there are small rigid inclusions in a floppy matrix. As the coordination is increased the rigid regions grow until they percolate at \(\langle r \rangle = 2.4\).

The key ingredient in understanding the nature of the transition is constraint counting which also serves to locate the transition. In what follows we will illustrate these ideas by applying them to a few systems. All are well known examples, except for the last which appears here for the first time. Note that constraints are either counted or not—there is no such thing as a partial constraint. Thus these ideas work best when the forces can be divided into two groups, strong and weak. The constraints associated with the strong forces are counted and the rest ignored.

Example 1

We consider\[7,8\] Si\(_2\)O\(_4\). It is known from diffraction studies that the distribution of Si-O-Si angles is quite broad.\[8\] We will therefore only count the constraints associated with the Si-O bond lengths and the O-Si-O bond angles. If there are a total of \(N\) atoms, we have

\[3N - 3N - 7N - N(1 - x)\]

\[f = \frac{2}{3} - 2x\]  

(7)

which goes to zero at \(x = \frac{1}{4}\) which corresponds to vitreous silica SiO\(_2\). Thus the elastic properties of vitreous silica are determined by the weak Si-O-Si angular forces.
Another interesting application is to a model of SiO₂ proposed by Phillips[9] in which SiO₂ clusters are terminated with with Si = O double bonds. If there are N₆ surface oxygen atoms, then the number of zero frequency modes is 3N₆ (or 4N₆ if the surface Si atom is in a plane with its three oxygen neighbors). This qualitatively explains the zero frequency (or cyclic) modes found in calculations using such clusters.[10,11]

Another example is provided by a model for SiO₂, in which SiO₂ clusters are connected by "peroxyl" groups so that Si-O-O-Si bonds are formed between the clusters.[12] The number of zero frequency modes is reduced by 1/2 per surface oxygen atom from the previous case of oxygen double bonds leading to 5/2 N₆ zero frequency modes (as N₆ must be even in this case). We may regard this as 5 zero frequency modes per peroxyl group. If all the surface Si atoms have three oxygen atoms in a plane as neighbors, this number is increased to 7 zero frequency modes per peroxyl group.

In these examples, the floppy modes are associated with "surfaces" although the eigenvectors may penetrate far into the clusters. The picture is still similar to Fig. 2, except that the location of the floppy regions is determined by the "surface" oxygens. We may refer to floppy regions as being pinned rather than just determined by the statistical properties of the C.R.N.

Example 2
When hydrogen is introduced into amorphous Si it serves to tie off dangling bonds. However it also degrades the mechanical properties of the network and the elastic properties are expected to soften. If there are N atoms in Si₄N₁₋ₓ and if the hydrogen is singly bonded to silicon, then we can show that there are 3N = 7Nx - N(1-x)/2 = N(5-13x)/2 zero frequency modes. Thus the network becomes unstable when x = 5/13 which corresponds to 62% hydrogen.[8] This assumes that silicon can have 1, 2 or 3 hydrogens
bonded to them. If some H goes in as silane SiH₄, even more hydrogen can be
taken up as the silane molecules should not be counted as part of the
network. Note that polysilane chains SiH₂ correspond to 67% hydrogen and
would be mechanically unstable. By unstable we mean that the network would
be very soft and have its properties determined by forces other than the
strong covalent forces.

Example 3

Consider a metallic glass like Co₆Pₓ and suppose that we regard this
as a closely placed structure where every atom has exactly 12 neighbors
(either Co or P). Suppose the P goes in randomly and that the elastic
properties of such a network are described by strong nearest neighbor
central forces between pairs of Co atoms and that we can neglect all other
forces to a first approximation. If there are N atoms, the fraction of zero
frequency modes f is given by

\[ 3f = 3 - 6N \]

\[ f = 1 - 2x \] (8)

which goes to zero at x = 1/2. We have excluded the zero frequency modes
associated with P atoms as these are not part of the network. Thus as P is
introduced into the Co network, the elastic properties would be expected to
soften and the network become unstable at about 50% of metalloid P. Again
by unstable we mean that the elastic constants are determined by other
weaker forces. It is interesting to note the many metallic glasses contain
up to ~20% metalloid and we might speculate that this number is correlated
with the approach to the elastic instability.

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