MECHANICAL PROPERTIES OF GLASSY MATERIALS

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1. ABSTRACT
In this talk we discuss how concepts from rigidity percolation can be used to understand the mechanical and elastic properties of network glasses like Ge$_x$As$_y$Se$_{1-x-y}$. When the mean coordination $\langle r \rangle = 2 + 2x + y$ is low, these materials are soft and their properties are strongly influenced by low frequency phonons. We review explicit calculations of the elastic properties, and present new results from model calculations for the density of states and the Debye-Waller factor.

2. 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$_x$As$_y$Se$_{1-x-y}$. If the total number of atoms is $N$ and there are $n_r$ atoms with coordination $r$ ($r = 2, 3$ or $4$) then

$$N = \sum_r n_r$$  \hspace{1cm} (1)
and we can define the mean coordination \( <r> \) by

\[
<r> = \sum_r \frac{n_r}{r} \sum_r n_r
\]

\[
= 2 + 2x + y
\]  

(2)

We note that \( <r> \) [where \( 2 < <r> < 4 \)] gives a partial, but very important, description of the network. We will also see that the elastic properties depend sensitively on \( <r> \).

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 if suitable modifications are made. The ideas developed in the talk on Rigidity Percolation \(^3\) can be applied with suitable modifications to the network structures of interest here. The main new feature to include are the angular forces.

3. CONSTRAINT COUNTING

In covalent networks like Ge\(_x\)As\(_y\)Se\(_{1-x-y}\), the bond lengths and angles are well defined and small displacements from a (supposed) equilibrium structure can be described by the potential\(^4\)

\[
V = \frac{\alpha}{2} \sum_{i,j} \left( \vec{u}_i - \vec{u}_j \right) \cdot \hat{r}_{ij}^2 + \frac{\beta}{2} \sum_{i,j,k} l_{ij} l_{jk} [\Delta \theta_{ijk}]^2
\]  

(3)

Here \( \vec{u}_i \) is the displacement of the atom \( i \) and \( \hat{r}_{ij} \) is a unit vector connecting nearest neighbor sites \( i, j \); \( l_{ij} \) is the length of the bond \( ij \) and \( \theta_{ijk} \) is the angle between the bonds \( ij \) and \( jk \). The bond stretching force constant \( \alpha \) and the bond bending force constant \( \beta \), are the largest forces in covalent glasses. 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 not important in what follows in this section as we shall be making small virtual displacements. The detailed form of the potential will be important when we come to calculate spectral responses later.

We will regard the solution of the eigenmodes of the potential (3) as a problem in classical mechanics\(^5\). The dynamical matrix has a dimensionality \(3N\) which corresponds to the \(3N\) degrees of freedom. In a stable rigid network we would expect all the squared eigenfrequencies \(\omega^2 > 0\) 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 additional 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 assign as \(r/2\) 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 are a total of \(2r - 3\) angular constraints\(^6\). The total number of constraints is equal to the number of finite frequency modes which are therefore

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

(4)

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

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

(5)

which can be rewritten as

\[
f = 2 - \frac{5}{6} \langle r \rangle
\]

(6)
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 all 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 while 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.R.N., bonds were removed at random from a series of diamond lattices in such a way that sites with 2, 3 and 4 fold coordination were produced. If removing a bond would result in a dangling bond that move was not allowed. Using this technique, networks with \( \langle r \rangle \) as low as 2.15 can be produced. The potential (3) is rewritten to apply to this situation as \(^4\),

\[
V = \frac{1}{2} \sum_{i,j} p_{ij} \left[ \hat{u}_{ij} \cdot \hat{r}_{ij} \right]^2 + \frac{8}{8} \sum_{i,j,k} \left[ \hat{u}_{ij} \cdot \hat{r}_{ik} + \hat{u}_{ik} \cdot \hat{r}_{ij} \right]^2
\]  

(7)

where the probability that the bond \( ij \) is present or missing is included by letting \( p_{ij} \) be either one or zero. Here all the bond lengths \( l \) are the same and \( \hat{u}_{ij} = \hat{u}_i - \hat{u}_j \). The angular force involving \( \beta \) is not quite the same in (7) as in (3) but we have found (7) a little easier to use in numerical calculations. As most of the effects that we are discussing depend on the mean coordination, we believe that our results for these randomly diluted crystals will be very similar to those that would be obtained for glasses with the same \( \langle r \rangle \). It can be seen from Fig. 1 that the number of zero frequency modes \( \delta \) and the elastic constant \( C_{11} \) go to zero around \( \langle r \rangle = 2.4 \). Note however upon closer examination that there is a Lifshitz like tail for \( \delta \) above \( \langle r \rangle = 2.4 \). This corresponds to small isolated floppy islands in the rigid matrix. Such an effect must also occur in random central force networks \(^3\) but it is much larger in the glassy networks we are discussing here. Similar results are obtained for the shear modulus \(^4\) \( C_{44} \). Thus we can divide network glasses into two types as first suggested by Phillips \(^7\).
Fig. 1. The elastic modulus $C_{11}$ with $a = 58$ as a function of the mean coordination $\langle r \rangle$. The three symbols are for three different series of random networks. The inset shows the fraction of zero frequency modes (averaged over the three series of networks) compared to Eq. (6). Reproduced from reference 4.

For $\langle r \rangle > 2.4$, the network is mechanically stable and the elastic properties are determined by the covalent forces $\alpha, \beta$. 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 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 $\alpha, \beta$ (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 crystallize when heated but rather return directly to the liquid phase.
We thus regard a covalent network glass as consisting of floppy and rigid regions. 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 \( r = 2.4 \).

The key ingredient in understanding the nature of the transition is constraint counting which also serves to locate the transition. 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.

4. DENSITY OF STATES

We must now concern ourselves with making contact with experiment. The first experiments determined the elastic constants \( c_{11} \) and \( c_{44} \) using ultrasonic techniques. These measurements do show a rather sharp rise in the elastic constants above \( r = 2.4 \) in some cases. Other results put this rise at larger values of \( r \). It has been suggested that anelastic effects are important in these materials and more work on the time dependence of the elastic constants would be useful.

More complete information about these systems is contained in the complete phonon density of states as a function of frequency. Such experiments have recently been done for Ge-Se \(_{1-x}\) glasses. Previously a density of states for a-Se had been obtained by Gompf which showed a sharp low frequency peak at around \( \omega/\omega_{\text{max}} = 0.15 \) that contains about 1/3 of the total weight. Here \( \omega_{\text{max}} \) is the top of the phonon band which is rather insensitive to \( x \). Similar densities of states are obtained for the crystalline forms of Se where these low frequency modes can be associated with the torsional vibrations of the chains. In the amorphous material we prefer to think of these modes as the zero frequency modes that are shifted to higher frequencies when additional terms are added to the potential. Inelastic neutron scattering measurements of the density of states in...
Ge$_x$Se$_{1-x}$ glasses follow this low frequency peak as a function of composition. The frequency of the peak position does not shift much with $x$ but the weight in this peak rapidly decreases as $x$ increases so the the anomalous modes have vanished by about $x = 0.2$ which corresponds to $\langle r \rangle = 2.4$. This is the behavior we would expect. The zero frequency modes produced by the potential (7) are moved to low frequency by adding additional terms. However the weight in the floppy modes is still given approximately by (6) and decreases from 1/3 for Se to 0 for Ge$_x$Se$_{1-x}$. In order to better understand these results, we have extended our model based on the bond depleted diamond lattice discussed in the previous section.

Using the equation of motion technique$^{15}$ for a $8 \times 125 = 1000$ atom sample with periodic boundary conditions, we have calculated the density of states for various values of $x$. The $a$ component of the displacement for the $i$th atom $u_{ia}(t)$ is computed using the equation of motion$^{16}$ that results from the potential (7). The density of states $\rho(\omega)$ can be written,

$$\rho(\omega) = \frac{2}{\pi} \int_0^T dt \cos(\omega t) e^{-3(t/T)^2} \sum_{i,a} A_{ia} u_{ia}(t)$$

where choosing the truncation time $T$ determines the frequency resolution of the result. The exponential factor in (8) helps with convergence. All the atoms have the same mass $M$. Here the appropriate starting conditions for the density of states are,

$$u_{ia}(0) = A_{ia} = \sqrt{2} \cos \Theta_{ia}$$

where $\Theta_{ia}$ is a random angle uniformly distributed in the range $0 < \Theta_{ia} < 2\pi$. We also set the velocities $u_{ia}(0) = 0$. Results are shown in Fig. 2 for various values of $x$. At small values of $x$ the zero frequency modes are broadened by the resolution function. It can even be seen that there are still a few states with zero frequency beyond $x = 0.2$ as discussed previously. In order to stabilize the
lattice and move the floppy modes away from zero frequency, we add a stabilizing potential $V_s$ to the potential $V$ given in (7),

![Graphs showing density of states for various values of x](image)

**Fig. 2.** Showing the density of states for various values of $x$. The dotted curve is using the potential (7) and the solid curve is with the additional terms (10) added. The maximum frequency $\omega_{max}$ is given by $\omega_{max}^2 = 8(a + b)/3$. The frequency scale is in units where $\omega_{max} = 1$ and the full width of the frequency resolution function is $\Delta \omega = \omega_{max}/20$. 
\[ V_s = \frac{Y}{2} \sum_{ij} \left[ p_{ij} p_{jk} p_{kl} [\Delta \phi_{ij}, kl']^2 + \frac{a_i}{2} \sum_{i,j} (1 - p_{ij}) \left[ \vec{u}_{ij} \cdot \vec{r}_{ij} \right]^2 \right] \quad (10) \]

The first term in (10) involving \( Y \) is the dihedral angle force involving the dihedral angle \( \phi_{ij}, kl \) which by itself is sufficient to stabilize all the zero frequency modes. However we found it convenient to add a small "interchain" term \( a' \). This was so that we could position the two major bands shown in Fig. 2 in roughly the correct places to agree with the experimentally determined density of states\(^{13}\)). This led to \( a : b : y : a' = 1 : 0.3 : 0.1 : 0.03 \) and the overall magnitude of the force constants was chosen to get the maximum frequency correct. No attempt was made to fit the elastic constants. The results of this calculation are also shown in Fig. 2. It can be seen that the floppy modes are moved into the low frequency peak and the weight is shuffled about within the spectrum. The maximum frequency was taken to be still given by \( \omega_{\text{max}}^2 = 8(a + b)/3 \) as the top of the band hardly moved with the inclusion of \( V_s \).

5. **DEBYE-WALLER FACTOR**

The Debye-Waller factor \( \exp[-(k \cdot \vec{u})^2] \) modifies the intensity in many scattering type experiments. Here \( k \) is the momentum transferred to the sample. A measurement of this quantity allows the mean square displacement to be extracted. The mean square displacement in a particular direction for a single frequency is given by \( \langle x^2 \rangle \) where

\[ \langle x^2 \rangle = \frac{\hbar}{M \omega} \left[ \bar{n} + 1/2 \right] \quad (11) \]

and \( \bar{n} \) is the Planck function\(^{16}\)). At low temperatures, this becomes

\[ \langle x^2 \rangle = \frac{\hbar}{2M \omega} \quad (12) \]

and at high temperatures in the classical limit,

\[ \langle x^2 \rangle = \frac{k_B T}{M \omega^2} \quad (13) \]
where $k_B$ is Boltzmann's constant. For many harmonic oscillators we must average over the modes in the system. We define

$$
\langle \omega^r \rangle = \int_0^\infty \rho(\omega) \omega^r \, d\omega / \int_0^\infty \rho(\omega) \, d\omega.
$$

(14)

At low temperatures, we may extract the $r = -1$ moment and at high temperatures we may extract the $r = -2$ moment. At these two extremes the Debye-Waller factor is very sensitive to the low frequency part of the spectrum. Indeed this is true at all temperatures.

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**Fig. 3.** Showing $\rho(\omega)/\omega$ as a function of the frequency $\omega/\omega_{\text{max}}$ for various values of $x$. 
It is very dangerous to use the computations reported in Fig. 2 to calculate these moments as the density of states has a small finite value at $\omega = 0$ due to the resolution function and the cosine factor in Eq. (8). We therefore compute the quantity

$$\rho(\omega) = \frac{2}{\pi} \int_0^T dt \sin(\omega t) e^{-3(t/T)^2} \sum_{i,\alpha} A_{i\alpha} u_{i\alpha}(t)$$  \hspace{1cm} (15)$$

with the initial conditions

$$\dot{u}_{i\alpha}(0) = A_{i\alpha} = \sqrt{2} \cos \Theta_{i\alpha}$$  \hspace{1cm} (16)$$

where $\Theta_{i\alpha}$ is a random angle uniformly distributed in the range $0 < \Theta_{i\alpha} < 2\pi$. We set the displacements $u_{i\alpha}(0) = 0$. In Fig. 3 we show results from this procedure.

**Fig. 4.** Showing $\rho(\omega)/\omega^2$ as a function of the frequency $\omega/\omega_{\text{max}}$ for various values of $x$. 
It can be seen that there is no divergence at low frequency and the area under the curves in Fig. 3 can easily be used to give the \( r = -1 \) moments. Indeed as a lucky bonus, at low frequency the result (15) gives \( \rho(\omega) \sim \omega^2 \) as can be seen by expanding the sine inside the integrand. Thus the resolution function does not the fight the expected \( \omega^2 \) behavior at low frequency and we get well behaved results. In Fig. 4 we show the quantity \( \rho(\omega)/\omega^2 \) which has a finite intercept at \( \omega = 0 \) as expected. This was obtained by dividing the data in Fig. 3 by \( \omega \).

We have used the measured values \(^{10}\) of the density and \( c_{11} \) and \( c_{44} \) to calculate the coefficient of the \( \omega^2 \) term in the density of states for \( x = 0.2 \) and obtain reasonable agreement. The intercept scales as \( [c_{44}]^{-3/2} \) as the density is roughly constant and the transverse excitations dominate the low frequency density of states. There is an inconsistency here as our results would predict that \( c_{44} \) would fall as \( x \) is reduced from 0.2 whereas in the experiment \( c_{44}^{10} \) is rather constant in this region.

Rather than find the area under the curves in Figs. 3 and 4, we can integrate the expression (15) over frequency directly to give

\[
\langle 1/\omega \rangle = \frac{2}{\pi} \int_0^T dt \sum_{i, \alpha} A_{i\alpha} u_{i\alpha}(t)/t
\]

where we have omitted the exponential convergence factor as the factor \( 1/t \) makes this integral well behaved at large \( t \). There is no problem at small \( t \) as \( u_{i\alpha}(0) \sim 0(t) \) for small \( t \). The results obtained from (17) agree very well with those obtained by direct integration of the area under the curves in Fig. 3. However using (17) is a much more straightforward procedure. The results are shown in Fig. 5.

We can also obtain the \( r = -2 \) moment by directly integrating (15). The result is

\[
\langle 1/\omega^2 \rangle = \int_0^T dt e^{-3(t/T)} \sum_{i, \alpha} A_{i\alpha} u_{i\alpha}(t)
\]
where we must now keep the exponential convergence factor in order to get reasonable results that agree with a direct integration of the area under the curves in Fig. 4. In practice we have found the direct integration of the area under the curve in Fig. 4 to be more satisfactory in this case because of the poor convergence of (18) at large $t$. The results are shown in Fig. 6.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Showing the $r = -1$ moment $\langle \omega_{\text{max}} / \omega \rangle$ as a function of the composition parameter $x$. The lines are for the guidance of the eye.}
\end{figure}

The results in Fig. 5 show that most of the contribution to the $r = -1$ moment comes from the floppy modes in the low frequency peak making the low temperature measurement of the Debye-Waller factor a sensitive probe of the floppy modes. The $r = -2$ moment probes even lower parts of the frequency spectrum and is sensitive to both the floppy modes and the acoustic modes as can be seen from Fig. 4.
Fig. 6. Showing the $r = -2$ moment $\langle (\omega_{\text{max}}/\omega)^2 \rangle$ as a function of the composition parameter $x$. The lines are for the guidance of the eye.

In Fig. 5 we see that the $r = -1$ moment increases with lower $x$ as expected and has a small break in the slope at around the threshold for rigidity percolation. A similar situation holds for the $r = -2$ moment shown in Fig. 6 more clearly. This moment relates to the high temperature behavior of the Debye-Waller factor and it may be that a harmonic theory as given here is suspect, especially for low $x$. A preliminary analysis of Mössbauer results \cite{17} seem to show behavior in qualitative agreement with these results and will be reported on in a subsequent publication \cite{18}. Note that the masses and force constants are sufficiently similar that $\langle x^2 \rangle$ would not be expected to vary significantly from site to site. Our calculations involve an average over all sites. It may be that regions of the sample that are denser in floppy modes have larger $\langle x^2 \rangle$, but that remains to be seen.
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7. REFERENCES

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