PHONONS IN AMORPHOUS CLUSTERS

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ABSTRACT

Recent work has shown that the vibrational properties of solids may be calculated to some approximation by using small clusters such that the surface atoms have an additional potential upon them. This potential, which is complex and frequency dependent, is determined by demanding that the average mean square displacements of the surface and bulk atoms is the same.

In this paper, the work is extended from the basic tetrahedral unit of Si/Ge to larger structural units - pentagonal and hexagonal rings. These yield characteristic densities of states which are not very different from those obtained previously for the tetrahedral unit. The implications of this result are discussed.

INTRODUCTION

In order to understand the properties of amorphous solids, the most satisfying and rewarding calculations do not involve making a quasi-crystalline approximation at some stage. There are two techniques in this category that have been pursued recently and applied to the problem of vibrations in tetrahedrally bonded semiconductors. One of these has already been described by R. Alben and involves the diagonalization of the dynamical matrix for random networks containing up to about 100 atoms, with some simple boundary conditions such as free surface atoms. This technique was pioneered by Bell and Dean1 for SiO2 type glasses and has been applied to Si/Ge by Alben et al.2

Another technique3 is to isolate small clusters from the solid and calculate the vibrational spectrum using more sophisticated boundary conditions that attempt to simulate the embedding of the cluster in the infinite solid. This method may not be as useful in comparing with experiment as numerical diagonalization, but, making fewer structural assumptions, can lead to a better understanding of the role of short range order and allow certain general conclusions to be drawn.

As in previous work,4 we use the Born model with forces restricted to nearest neighbors only, with a central part (α + 2β) and a non-central part (α - β) so that the potential between a pair of atoms at i and j may be written:

$$V_{ij} = 3\beta/2 \left[ (\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{e}_{ij} \right]^2 + (\alpha - \beta) / 2 \left[ \mathbf{u}_i - \mathbf{u}_j \right]^2$$  (1)

* Work supported in part by the National Science Foundation.
where $\hat{u}_i$, $\hat{u}_j$ are the displacements of atoms $i$, $j$ and $\hat{r}_{ij}$ is a unit vector connecting the two sites. The ratio $\beta/a = 0.63$ gives a reasonable fit to the known crystalline density of states for Si/Ge and is shown in Fig. 1 by the dashed curve.

Fig. 1 The dashed curve is the density of states for the diamond cubic structure and the solid curve is for the single tetrahedral unit (from Ref. 3).

CLUSTER CALCULATION

Because the cluster is embedded in an infinite solid it is necessary to put an additional potential upon the surface atoms of the cluster. This potential is complex and frequency dependent and is determined by demanding that the mean square amplitude of vibration of the interior and surface atoms is the same at each frequency. Previously this was applied to a single tetrahedral unit and the result is shown in Fig. 1 by the solid curve. It is noticeable in examining Fig. 1 that the two sharp peaks in the center of the spectrum for the crystal are completely absent from the cluster calculation, whereas the two major peaks due to the TA and TO modes are well reproduced in the cluster. It is tempting to speculate that the two sharp peaks might be displayed by slightly larger structural units where the ring structure of the bonds may play a role. We have therefore studied the spectrum of a hexagonal ring in the chair configuration (Fig. 2), as found in the diamond cubic structure, and a planar pentagon which is thought to occur in amorphous Si/Ge.

The hexagon has 6 interior atoms and 12 surface atoms. We place a potential on the surface atoms that has axial symmetry about the bond and so contains two parameters, one for motion parallel to the bond and the other for motion perpendicular to the bond. This potential is represented by the open circles in Fig. 2 and has the same form as that used for the tetrahedral unit.3 This potential simulates the homogeneous medium in which the cluster is embedded and so the axial symmetry is necessary. In the case of the tetrahedral cluster, the two parameters in the potential were determined by the two independent constraints that are obtained by demanding...
that the mean square amplitudes of vibration be isotropic everywhere at each frequency. In the present case, because of the reduced symmetry, this leads to many more than two independent constraints and consequently the parameters in the surface potential are overdetermined. However, as the purpose of the surface potential is to reduce the amplitude of vibration of the surface atoms so that it is similar to the interior; the precise way in which this is done is not very important and we select any two reasonable independent constraints. We have used two boundary conditions to convince ourselves that the differences between them are indeed small. The complex $3 \times 3$ matrix:

$$M_{\alpha \beta} = \langle u_i^\alpha u_i^\beta \rangle$$

(2)

is calculated for all atoms in the cluster at each frequency.

A) The trace of this matrix is averaged over the surface atoms, and separately over the interior atoms. The two averaged traces are equated. The same procedure is followed for the determinant. This leads to two constraints that determine the two parameters in the potential. (N.B. there are really four unknowns as both constraints and parameters are complex.) Schematically we represent the boundary conditions:

$$\text{Tr } M, \text{ Det } M$$

B) The same as A) except that instead of the determinant, we use the trace of the squared matrix, schematically:

$$\text{Tr } M, \text{ Tr } M^2$$

Although the problem has 54 degrees of freedom, it can be greatly simplified by exploiting the symmetry and "folding back" the 12 surface atoms onto the hexagon. We calculate the surface potential at each frequency by applying the self consistency conditions above, and then calculate the Greens function for the interior atoms and so obtain the characteristic density of states for the ring. The result is shown in Fig. 3 and results of a similar calculation for the planar pentagonal ring in Fig. 4. The spurious root is rejected on physical grounds – there is no problem when the roots cross as by
Fig. 3 The density of states calculated for a hexagonal chair unit with boundary conditions A as described in the text. The dashed line is a spurious root with no physical significance. The solution for boundary condition B is indistinguishable from the above on the scale of this drawing although no spurious root was found in this case. Examining the eigenvectors it is easy to follow either one.

CONCLUSIONS

It is immediately apparent from the results that the sharp peaks in the center of the crystal spectrum are not present in Figs. 3 and 4 and indeed there is very little change from the spectrum for the tetrahedral unit shown in Fig. 1. In the hexagonal case, a sharpening of the structure around \( \omega/\omega_{\text{max}} = .44 \) and .89 is apparent and in both Figs. 3 and 4 a feature is beginning to develop around \( \omega/\omega_{\text{max}} = .3 \), which corresponds to the \( P_1 \) type critical point due to phonons at the L point in the crystal. The pentagonal ring spectrum lacks the symmetry about the mean frequency when plotted as a function of frequency squared, and indeed there is a narrowing of the sharp upper peak with little change in the broad lower peak. It is therefore clear that we will have to proceed to much larger clusters to get any significant change from the spectrum as produced by the basic tetrahedral unit. This is not to say that the rings are unimportant: in a true three dimensional solid there are between 5 and 12 pentagonal and hexagonal rings through each atom whereas we have only one.

It therefore seems that the peaks in the crystal spectrum are of rather distinct character - some coming from short range effects...
Fig. 4 The density of states calculated for a planar pentagonal unit using boundary conditions A and B as described in the text. A spurious root similar to that in Fig. 3 was also found for A but is not shown. The differences due to boundary conditions are greater than for the hexagon - probably due to the planar nature of the pentagon.

and others relying on longer range structural correlations. There will in general be intermediate cases but not in the present example. This conclusion gains support if we examine the origin of the peaks in the crystal. The broad lower peak and the sharper upper peak come from the TA and TO branches and contain contributions from all over the Brillouin zone - whereas the sharp peaks in the middle of the spectrum come from states extremely close to the hexagonal faces on the Brillouin zone boundary for the f.c.c. structure. It is therefore reasonable to associate this kind of peak with the long range structural periodicities in the crystal and we expect it to be substantially absent in the amorphous density of states. This point of view appears to be consistent with experiment (for a discussion and references, see Ref. 3).
REFERENCES

1. For a review see: P. Dean, Rev. Mod. Phys. 44, 127 (1972).
2. For a review see: R. Alben, this conference.
DISCUSSION AND COMMENTS

S. MOSS: The hexagonal zone faces are perpendicular to <111> and it has been suggested that the random network has periodic planar features normal to this same direction. Can the central peak structure possibly rise therefore from this longer range feature?

M. THORPE: It is possible that such a planar structure would have a central peak.

J. JOANNOPoulos: I would like to mention that we have recently developed new methods to study the electronic densities of states of small clusters of atoms which will be presented at this conference. The method involves using the Bethe lattice as a boundary condition. I wonder if you have considered something similar in your work?

M. THORPE: Yes. In fact in order to solve the self consistent equations for the cluster I put Bethe lattices on the surface atoms to get a first approximation and then use Newton's method of iteration to solve the self consistent equations.

A. BIENENSTOCK: I think it would be quite advantageous to use larger clusters. By using an average potential on the surface atoms, you are not likely to see modes whose frequencies are strongly determined correlations in the motion of a number of atoms.

M. THORPE: Of course, but the improvement is slow as the cluster gets bigger and I am not convinced that it would be worthwhile.

M. SCHLUTEr: Do you have a physical explanation, other than the location in k-space, why longitudinal optical mode peaks do not appear in your calculation?

M. THORPE: No.