‘Self-consistent’ phonons in amorphous Si and Ge†

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ABSTRACT

We have studied the vibrations of small clusters of atoms using self-consistent boundary conditions which simulate the infinite medium in a spirit similar to the Bethe–Peierls approximation in magnetism. The Born model for Si and Ge is used with nearest neighbour central and non-central forces. An external potential is imposed upon the surface atoms and the coefficients appearing in this potential are determined by demanding that the mean square amplitude of vibration of the surface atoms is the same as that of the interior atoms. As a simple example of this procedure we take five atoms in a tetrahedral arrangement, i.e. one interior and four surface atoms. A continuous density of states is obtained with a sharply defined optic mode peak and a broader ‘acoustic mode’ peak. These peaks occur at about the same positions as in the crystal. This calculation shows rather clearly the importance of short range order in determining the phonon density of states in solids.

§ 1. INTRODUCTION

Many elements and compounds have now been prepared in both crystalline and amorphous forms and so there has been much interest in the changes in physical properties that take place in going between these two solid states of matter. One of the physical properties that is rather convenient to investigate is the phonon density of states as it is well defined in both cases and easy to calculate in the crystal. It is also experimentally accessible; in the crystal case the dispersion curves can be measured by inelastic neutron scattering and the density of states obtained by integration over the Brillouin zone; in the amorphous form infra-red absorption and Raman scattering provide the density of states modulated by a slowly varying matrix element.

Phonon density of states have considerable structure which include peaks and discontinuities in slope (Van Hove singularities). The Van Hove singularities arise when \( \omega(k)=0 \) and are directly attributable to long range order; they will therefore be absent in the amorphous form. The peaks in the density of states can be expected to be retained however if they can be shown to result from short range order; otherwise it is extremely unlikely that they will remain. In an effort to investigate this we have studied small clusters of atoms. Unfortunately if the surface atoms are allowed to be ‘free’ the surface has a large effect on the density of states, and also a delta function spectrum is produced. We therefore introduce a new kind of boundary condition that minimizes the differences between the surface and interior atoms and also produces a continuous spectrum. Explicit calculations for Si and Ge show that whilst the two major peaks in the density of states are due to the tetrahedral coordination, other smaller ones are not.

§ 2. BOUNDARY CONDITIONS

The major difficulty in trying to understand solids in terms of small clusters (i.e. \( \lesssim 100 \) atoms) is that the number of surface atoms exceeds the number of interior atoms and so many properties are dominated by the surface. Even if one uses periodic boundary conditions, which is difficult though not impossible (Henderson and Herman 1972) for disordered systems because of the constraints the periodicity places upon the structure,

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one gets 'bogus' standing waves with wavelength related to the repeat distance introduced into the structure by the boundary conditions. We therefore use a new type of boundary condition which is illustrated in fig. 1. An amorphous cluster is divided into interior atoms (which have three neighbours in this two dimensional example) and surface atoms (which have only one neighbour). The forces inside the cluster are treated properly but an extra potential is placed upon the surface atoms. This potential is there to simulate the rest of the infinite solid in which the cluster is embedded and its size is determined by the 'self-consistency' condition that the mean square amplitude of vibration of the interior and surface atoms is the same. The effect of this boundary condition is to surround the cluster with an effective medium and so may be regarded as a coherent potential approximation (C.P.A.) for structurally disordered systems.

![Fig. 1](image)

A finite cluster with the interior atoms shown as discs and the surface atoms as circles with the dashed ellipses representing the surface potential.

This boundary condition is similar in spirit to that used in the Bethe–Peierls approximation for magnetic insulators (Bethe 1935, Peierls 1936). In this method a cluster Hamiltonian for a magnetic ion and its nearest neighbours is diagonalized with an effective magnetic field on the neighbours—the magnitude of this field being obtained by applying the self-consistency condition that the magnetization is the same at all sites. The surface potential in the present work is the analogue of the effective magnetic field in the Bethe–Peierls approximation.

§ 3. A SIMPLE EXAMPLE

As a simple example we apply the Born model (Born 1914, Smith 1948) to Si and Ge. In this model the forces are restricted to be between nearest neighbours only, with a central part \((\alpha + 2\beta)\) and a non-central part \((\alpha - \beta)\) so that the potential between a pair of atoms at \(i\) and \(j\) may be written

\[
V_{ij} = \frac{3\beta}{2} [(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{r}_{ij}]^2 + \frac{\alpha - \beta}{2} [\mathbf{u}_i - \mathbf{u}_j]^2,
\]

(1)

where \(\mathbf{u}_i, \mathbf{u}_j\) are the displacements of atoms \(i, j\) and \(\mathbf{r}_{ij}\) is a unit vector joining the two sites. The Born model gives a reasonable overall description of the phonons in the diamond cubic structure of Si and Ge except for the transverse acoustic modes which occur at too high a frequency. The reader will appreciate that it is necessary to use a simple model for the phonons or the calculation is hindered by numerical difficulties. Also in this work we are looking for rather general effects and are not concerned with detailed fitting.
A single tetrahedron with one interior atom and four surface atoms. The dashed ellipsoids represent the surface potential.

The smallest non-trivial cluster that may be taken to be representative of the structure is shown in fig. 2. This is a single tetrahedral unit with one interior and four surface atoms. The potential (1) is applied to the four bonds shown in the figure and additional potentials are placed upon the four surface atoms. By symmetry these potential wells must be ellipsoidal in shape with axes along the bond directions. There are thus two parameters in this potential to be determined. The mean square amplitude of vibration is isotropic for the central atom and we demand that it be exactly the same for the four surface atoms at each frequency. This condition determines the two parameters in the surface potential as functions of the frequency. The potential wells are thus frequency dependent. Full mathematical details may be found in a forthcoming publication (Thorpe 1973). The local density of states at the central atom is given by \(- (2m \nu / \hbar) \text{Im } g\), where \(g\) obeys the self-consistent equation

\[
4/3 \sqrt{(1 + [2(\alpha - \beta)g]^3) + 2/3 \sqrt{(1 + [2(\alpha + 2\beta)g]^3)}} = 1 + g(m \nu^2 - 4\alpha). \tag{2}
\]

In order to discuss the results we first consider the case of the tetrahedron in fig. 2 with no surface potential. Choosing a value of \(\beta/\alpha = 0.6\) which is reasonable for Si and Ge (the crystalline phonon dispersion curves can be reasonably well fit except of course for the transverse acoustic modes) we show the modes of the single tetrahedron in fig. 3. The notation is that of Koster et al. 1963 for the point group \(T_d\). These modes bear little resemblance to the density of states for the crystal as shown in fig. 4 by the dotted line (von Heimendahl 1973). This is because the 'free surface' has an enormous effect on the spectrum.

It is useful to remark at this point that the Born model is not an unreasonable description of the phonons in Si and Ge (see the recent 'experimentally determined' density of states of Nilsson and Nelin 1972). The two large peaks and the two smaller peaks in the centre are reproduced by the Born model although the precise positions and shapes are not correct. The most serious error is that the lower peak due to the transverse acoustic modes occurs at too high a frequency; this is believed to be due to the omission of high frequency harmonics in the dispersion curves such as can be described by either long range Coulomb effects or by various shell models (see for example Cochran 1959).
The density of states for a single tetrahedral unit with no surface potential and with $\beta/a = 0.6$. The height of the lines represents the weight in the delta functions. The frequency $\omega_{\text{max}}$ is given by $\omega_{\text{max}} = \sqrt{(8\pi/m)}$.

The density of states for the Born model with $\beta/a = 0.6$. The dashed line is for the diamond cubic structure (Von Heimendahl 1973) and the solid line is for the tetrahedral cluster shown in fig. 2 with a self-consistently determined surface potential. The frequency $\omega_{\text{max}}$ is given by $\omega_{\text{max}} = \sqrt{(8\pi/m)}$.

In fig. 4 we also show the density of states obtained by solving eqn. (2) numerically. The broad transverse acoustic mode peak and the sharper transverse optic mode peak are well reproduced both in position and width. The two sharp peaks in the centre are completely absent however. Also there are no modes at very low and very high frequencies where we would have expected some using the crystal as a guide. These are long wavelength modes however which do not emerge for the cluster. It can be seen that the relative weight in these modes is rather small.

Thus with only five atoms and boundary conditions that simulate the infinite solid we are able to reproduce the two most prominent peaks in the density of states. Experimentally (Lurio and Brodsky 1972, Smith et al. 1971) these two peaks are the largest features in the spectra of both amorphous Si and Ge. The two sharp peaks in the centre of the spectrum do not come solely from the tetrahedral coordination and must result from the vibrations of rings of atoms or even larger units if the point of view adopted in this
paper is correct. The same experiments show that the one phonon density of states would appear to have some structure at these intermediate frequencies.

§ 4. Conclusions

We have shown that continuous density of states can be obtained from small clusters if ‘self-consistent’ boundary conditions are applied. In a simple example with only five atoms the two most prominent features in the density of states of Si and Ge are reproduced. It is not clear at this time whether this technique will be practicable for treating clusters of the size shown in fig. 1, because of the numerical problems involved. However it is extremely useful in elucidating the role of short range order on phonon density of states as is shown in the simple example of this paper.

References