PHONONS IN METALLIC GLASSES*

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ABSTRACT

The vibrational spectrum of a dense packed metallic glass is discussed in terms of a simple but realistic force constant model. The spectrum of an 87 atom model is found by direct diagonalization and the spectrum of an 888 atom model is calculated by a molecular dynamics method. The results show that the shape of the spectrum is largely determined by short range order.

In this paper we present calculations of the vibrational density of states of elemental metallic glasses. Metallic glasses that exist at room temperature all have at least two components. However, it is possible to make metallic glasses with up to 80% of a single element - such as for example Fe$_{80}$P$_{13}$C$_{7}$, Co$_{78}$P$_{22}$, and Ni$_{76}$P$_{24}$. At low temperatures amorphous metallic thin films of single elements such as Fe, Co, and Au have been prepared.

To calculate the vibrational density of states a description of a) the structure, and b) the interatomic forces is needed. As a first approximation the structure is similar to a snapshot of a liquid although the radial distribution function (RDF) of the simple metallic glasses show more structure at large r than

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the RDF of simple liquids. A better representation is given by a Bernal\textsuperscript{2} type structure which we used in our calculations.

To find an expression for the interatomic forces, it is useful to study the crystalline state first. The interatomic forces in metals are complicated because they are, in principle, both long range and non-central. Over the past decade the phonon spectra of a number of crystalline close packed metals have been studied by inelastic neutron scattering and, in particular, the dispersion relations $\omega(k)$ have been measured along symmetry directions.\textsuperscript{3,4} When these dispersion curves are fitted with a rigid ion model, it is found that the nearest neighbor central force dominates with the next largest force down by an order of magnitude.\textsuperscript{3,4} When the density of phonon states is calculated using the fitted force constants, (as shown for f.c.c. Ni in Fig. 1) it is very close to the density of states that we have calculated for an f.c.c. lattice with nearest neighbor central forces only (also shown in Fig. 1). It is surprising that the effect of longer range forces is not more pronounced in these metals. Calculations which attempt to include the conduction electrons do not modify this conclusion.\textsuperscript{5} The situation in h.c.p. metals appears to be similar, although less well documented.\textsuperscript{6} The density of states for the h.c.p. lattice has also been calculated with nearest neighbor forces only and is shown in Fig. 1. It can be seen that there are more Van Hove singularities because of the larger unit cell and lower symmetry. More importantly, while both spectra have a spike near the highest frequency, and very similar low frequency elastic behavior, the middle parts of the spectra are different. This may be attributed to the different near neighbor configurations in f.c.c. and h.c.p.; three of the f.c.c. nearest neighbors would have to be displaced to get the h.c.p. nearest neighbors.

In order to study the effects of structural disorder on the phonon spectrum, it is necessary to have a simple model and fortunately, as discussed above, a
one parameter model with a nearest neighbor central force constant $k$ is realistic. The harmonic potential energy $V$ is given by

$$V = \frac{k}{4} \sum_{n, n'} \left[ \left( u^{n'}_{\alpha}(t) - u^0_{\alpha}(t) \right) r^{n'}_{\alpha}(n, n') \right]^2$$  \hspace{1cm} (1)

where $u^{n'}_{\alpha}(t)$ is the $\alpha$-component of the displacement of atom $n$ at time $t$ and $r^{n'}_{\alpha}(n, n')$ is the $\alpha$-component of a unit vector joining the equilibrium positions of nearest neighbors at sites $n$ and $n'$. The equation of motion is

$$m \ddot{u}^{n'}_{\alpha}(t) = -\sum_{n' \alpha} \phi^{n'}_{\alpha}(n, n') u^{n'}_{\alpha}(t)$$  \hspace{1cm} (2)

where the dynamical matrix is given by:

$$\frac{1}{m} \phi^{n'}_{\alpha}(n, n') = \frac{\partial^2 V}{\partial u^n_{\alpha}(t) \partial u^{n'}_{\alpha}(t)}$$  \hspace{1cm} (3)

The atomic mass is denoted by $m$. The general solution of the equation of motion can be written as

$$u^{n'}_{\alpha}(t) = \sum_i A_i e_i^{n'}_{\alpha} \cos(\omega_i t + \phi_i)$$  \hspace{1cm} (4)

with eigenfrequencies $\omega_i$ and eigenvectors $e_i^{n'}_{\alpha}$. The amplitudes $A_i$ and phase factors $\phi_i$ are specified by the initial conditions.

The most direct approach to calculate the density of states of an amorphous cluster consists of a direct numerical diagonalization of the dynamical matrix for as large a cluster as possible. In a first approach we diagonalized the dynamical matrix of an 87 atom cluster. However, rather than use one of the Bernal structures in the literature, where the concept of "nearest neighbors" is not directly applicable, we have in this first approach adapted a random network built at Harvard by Connell and Temkin\textsuperscript{7} for tetrahedrally bonded structures. This model has only even rings. Half the atoms can be removed so that every remaining atom has exactly 12 nearest neighbors. We used the coordinates of 87 atoms selected in this way from the Harvard model to generate the $261 \times 261$
dynamical matrix. This cluster has only 19 fully bonded atoms, so that the influence of the surface on the spectrum is still rather strong. We used a projected density of states

$$\rho_\alpha(\omega) = \sum_{i} \left[ e_i^Q \right]_\alpha^2 \delta(\omega - \omega_i)$$  \hspace{1cm} (5)

to suppress the influence of the surface on the spectrum. If \( \rho_\alpha(\omega) \) is summed over all \( \alpha \), the unprojected density of states is obtained, because of the orthonormality condition

$$\sum_{\alpha, \alpha'} e_i^\alpha e_i^{\alpha'} = \delta_{\alpha \alpha'}.$$  \hspace{1cm} (6)

However, if \( \rho_\alpha(\omega) \) is summed over inner atoms only — in our calculations over the 19 inner fully bonded atoms — modes with particularly large amplitudes on surface atoms are suppressed and the influence of the surface on the spectrum is reduced. The result of our calculations is shown in Fig. 2. It is interesting to note that a well defined separate peak remains at the top of the spectrum and that the overall shape is similar to the crystalline spectra shown in Fig. 1. This peak can be shown to be related to the existence of triangles of near neighbor bonds. 8

Although this calculation already gives a fair impression of how the spectrum of a metallic glass should look, it is desirable to calculate the frequency spectrum of a substantially larger cluster. This would reduce further the influence of the surface and would give a better representation of the possible near neighbor configurations present in the bulk. However with present computers it is not possible to diagonalize matrices very much larger than 300 x 300 which correspond to 100 atoms. The methods employed earlier by Bell and Dean 9 were mainly used for very large one dimensional systems. It has been used for large three dimensional systems too (< 500 atoms), but loses many of its attractive features. We used molecular dynamics methods similar to those
discussed by Rahman and Dickey and Paskin, i.e. a direct numerical integration of the equations of motion. This method is simple to apply to very large systems.

As a structure we choose an inner section of 888 atoms of the 3999 atom Bennett model. This is a computer generated close packing of hard spheres. Cargill pointed out the resemblance of the RDF of these close packed hard sphere structures and the experimental RDF of alloy glasses. We relaxed the Bennett structure using a Lennard Jones potential to avoid the rather unphysical consequences of the hard sphere contact. As a result of the relaxation especially the second split peak in the RDF is much more similar to the peak in the experimental curves. We defined as interacting neighbors all atoms at distances smaller than the distance of the minimum following the first maximum in the RDF. The integrated area of the curve out to this distance gives a number very close to the coordination number 12 of the close packed crystal structures.

In the numerical integrations of the equation of motion we iterated

\[
u_i^{(n+1)} = 2u_i^{(n)} - u_i^{(n-2)} + \frac{(\Delta t)^2}{m} \sum_{n,n'} \phi_{n,n'}^{(n)} u_{n,n'}^{(n)} t_i^{(n)}
\] (7)

where \(t_i = \ell \cdot \Delta t\) and \(\Delta t\) is the time step of the iteration. As initial condition we chose

\[
u_i^{(n)} = \delta_{n,n'} \delta_{n,n'}^{(n)} a_i^{(n)} \quad \text{and} \quad \dot{u}_i^{(n)} = 0
\] (8)

which leads to

\[
A_i = e_i^{(n)}, \quad \phi_i = 0
\] (9)

and

\[
u_i^{(n)} = \sum_i \left[ e_i^{(n)} \right] \cos(\omega_i t)
\] (10)

The density of states projected onto the \(a_i\) component of atom \(n_i\) is obtained by Fourier transforming \(u_i^{(n)}\)

\[
\int_0^\infty \frac{\omega}{2} d\omega u_i^{(n)} \cos \omega t = \frac{1}{\ell} \sum_i \left[ e_i^{(n)} \right] \frac{2}{\omega_i} \left[ \delta(\omega - \omega_i) + \delta(\omega + \omega_i) \right]
\] (11)
The numerical iteration can be done only for a finite number of time steps, which leads to a broadening of the δ-functions. The broadening is inversely proportional to the number of iterations. Apart from this known broadening and errors introduced by the numerical integration itself, the result is exact.

We summed the projected densities of states of the three Cartesian coordinates of six inner atoms (Fig. 3). The result shows the separated peak at the top of the spectrum, although it is lower than the corresponding peak in the 87 atom cluster. This very high peak in the spectrum of the 87 atom cluster might be caused by the especially high density of six membered rings in the Harvard model. Preliminary results of calculations on the 883 atom cluster which took distant dependent forces into account again showed the same general characteristics although the peaks were less pronounced as would be expected. The small peak at .25 could be identified as a strong surface mode which penetrates to the central atoms with a small amplitude.

Until recently there has been little work on phonons in metallic glasses either experimentally or theoretically. One notable exception is the work of Weaire et al.14 on the elastic properties of Bernal glasses. Preliminary results by H.A. Mook15 on the metallic glass Co₄P using a time of flight technique give a density of states with a high frequency peak and a maximum frequency close to that of h.c.p. cobalt.15 Presumably he is seeing essentially the Co density of states. The small and light P atoms are thought to fill the holes in the Bernal structure16 and give a narrow P band at higher frequencies which are yet to be investigated.

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REFERENCES


FIGURE CAPTIONS

Fig. 1. The phonon density of states for close packed crystals determined by Brillouin zone integration. The frequency scale is in units of the maximum frequency. The f.c.c. Ni spectra was computed from experimental dispersion curves. The f.c.c. and h.c.p. spectra are for a model with only nearest neighbor central force constant $\kappa$, which gives a maximum frequency of $(8 \kappa/m)^{1/2}$.

Fig. 2. Histogram of the phonon density of states of the 87 atom cluster. The cluster has free surface atoms and the spectrum is projected onto the 19 fully bonded atoms at the center. The frequency is in units of $(8 \kappa/m)^{1/2}$.

Fig. 3. The phonon density of states of the 888 atom cluster. The cluster has free surface atoms. The spectrum is projected onto six atoms at the center of the cluster. The frequency is in units of $(8 \kappa/m)^{1/2}$. The full width at half height of the resolution function is shown.
Ni (exp.)

f.c.c.

h.c.p.

DENSITY OF STATES

FREQUENCY

0.2 0.4 0.6 0.8 1.0