

## Collective modes in $\text{Ca}_{70}\text{Mg}_{30}$ glass<sup>†</sup>

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**Abstract.** The self-consistent phonon scheme given by Takeno and Goda, involving multiple scattering and phonon eigen frequencies which are expressed in terms of many-body correlation functions of atoms as well as of interatomic potential in the solids, has been used to generate the collective modes in the  $\text{Ca}_{70}\text{Mg}_{30}$  glass. A model potential is proposed to describe the effective interaction in the glass. Three different forms of the local field correction functions viz. Hartree, Taylor and Ichimaru and Utsumi are used to examine relative influence of exchange and correlation effects. The phonon frequencies of the longitudinal and transverse modes are computed employing the theoretical formulation of Hubbard and Beeby. The elastic property of the glassy system is then studied using the long wavelength limits of the phonon modes. The theoretical computations reproduce much better dispersion curves (both for the longitudinal and transverse phonons) compared to earlier reports and are found to be in good agreement with the available experimental results due to neutron scattering.

**Keywords.** Metallic glass; pair correlation function; phonon frequencies; sound velocities; elastic properties.

### 1. Introduction

Metallic glasses have found wide ranging applications in the field of materials science and engineering during the last three decades. Such solids have electronic properties normally associated with metals but atomic arrangement is not spatially periodic. Binary metallic glasses made up of components of simple metals provide us with physically interesting systems for theoretical investigations. The simple structure of binary alloys lets us to use the pseudopotential theory to calculate the interatomic potentials between simple metal components to a high degree of accuracy. Based on the knowledge of interatomic interactions we can understand the thermodynamic, mechanical and electronic transport properties of amorphous materials. Such investigations involve measurements of collective density waves at larger momenta and for a few metallic glasses it is possible to measure the dynamical structure factors upto very large wave vectors (Suck *et al* 1980, 1981a, b, 1983). These calculations are based on the realistic interatomic potential derived by the pseudopotential method. The  $\text{Ca}_{70}\text{Mg}_{30}$  glass has been theoretically investigated by Hafner (1983) and Hafner and Jaswal (1988) on the basis of  $S(\mathbf{q}, \omega)$  and by Bhatia and Singh (1985) using a model approach and assuming the force among nearest neighbours as central and volume

dependent. The phonon frequencies of various binary alloys and metallic glasses have been theoretically investigated by many workers (Saxena *et al* 1988, 1990, 1991; Agarwal and Kachhava 1992, 1993a, b; Thakore *et al* 1996, 1997, 1998). Appreciating the continuous success of applicability of pseudopotential in the study of metallic glasses we thought it worthwhile to test a typical local pseudopotential. Hence in the present work we have proposed such application of a model pseudopotential. Deviating from a routine approach we have made use of three prominent screening functions to examine the relative influence of exchange and correlation effects. This has been carried out by studying collective modes and elastic properties of  $\text{Ca}_{70}\text{Mg}_{30}$  glass.

### 2. Theory

There are two main theoretical approaches to compute the phonon frequencies of alloys: One is by evaluation of force constants as was done by Bhatia and Singh (1985). The second approach is the quasi-crystalline approximation technique with interatomic pseudopotential developed by Takeno and Goda (1971). In the present study we have used the approach of Takeno and Goda (1971) because it enables us to make use of various dielectric functions in the formulation.

The fundamental ingredient which goes into the calculations of the vibrational dynamics of simple binary alloys and glasses are the effective pair potential which consists of two contributions. One is the direct interaction between

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ions given by  $(Ze^2/r)$  while the other contribution is due to the indirect interaction between ions through the electron cloud. The indirect interaction is calculated using the normalized energy wave number characteristics.

The effective pair potential for the binary system can be found in two different ways. One way of finding the effective pair potential is to use the concept of individual interactions (Saxena *et al* 1988, 1990). In this concept a binary mixture  $A_xB_{1-x}$  is thought of as a three-component fluid consisting of the bare ions of the two individual species i.e. AA, BB and mixed ions AB immersed in a uniform electron gas. Another way of finding the effective pair potential is to treat the binary alloy as an one component metallic fluid, i.e. the concept of effective atom (Saxena *et al* 1991; Agarwal and Kachhava 1992, 1993a, b). In this concept a simple binary disordered system  $A_xB_{1-x}$  can be looked upon as an assembly of the effective atoms (i.e. one component system). Interatomic interactions between these effective atoms of the alloy are then calculated in the usual way followed for a single component liquid metal instead of taking the alloy as the mixture of individual components AA, BB and AB. In the present study we have considered the metallic glass  $Ca_{70}Mg_{30}$  as a one component fluid for investigating the phonon frequencies and its elastic properties.

The effective interaction in the alloy can be written as,

$$V^{\text{eff}}(r) = \frac{(Z_{\text{eff}} e)^2}{r} + \frac{\Omega_{0 \text{ eff}}}{p^2} \int F_{\text{eff}}(q) \left[ \frac{\sin(qr)}{qr} \right] q^2 dq. \quad (1)$$

Here  $Z_{\text{eff}}$  and  $\Omega_{0 \text{ eff}}$  are the effective valence and atomic volume of the one component fluid respectively, given by

$$Z_{\text{eff}} = xZ_A + (1-x)Z_B, \quad (2)$$

and

$$\Omega_{0 \text{ eff}} = x\Omega_{0A} + (1-x)\Omega_{0B}. \quad (3)$$

The energy wave number characteristics appearing in (1) may be written as

$$F_{\text{eff}}(q) = -\frac{\Omega_{0 \text{ eff}} q^2}{16p} |W_B^{\text{eff}}(q)|^2 \times \frac{[e_H^{\text{eff}}(q) - 1]}{\{1 + [e_H^{\text{eff}}(q) - 1][1 - f_{\text{eff}}(q)]\}}. \quad (4)$$

Here  $W_B^{\text{eff}}(q)$  is the effective bare ion potential,  $e_H^{\text{eff}}(q)$  the Hartree dielectric response function and  $f_{\text{eff}}(q)$  the local field correction function to introduce the exchange and correlation effects. The local field functions due to Hartree (H) (Harrison 1966), Taylor (T) (1978) and Ichimaru and Utsumi (IU) (1981) are used in the present

study. Reasons for selecting these three screening functions is that H function is the static dielectric function and does not include exchange and correlation effects. The T function covers the overall features of the various local field correction functions proposed before 1978 and it satisfies the compressibility sum rule. The IU function possesses various interesting properties and has not been used in the study of binary alloys and metallic glasses. This function accurately reproduces the Monte Carlo results as well as those of the microscopic calculations and satisfies the self-consistency conditions in the compressibility sum rule and the short range correlations.

In the present study we have proposed the use of our model potential (Jani *et al* 1993) which is of the form (in real space)

$$W(r) = -\frac{2Ze^2}{r} + e^1 e^{-r/r_c} \cdot \frac{Ze^2}{r}; \quad r \leq r_c; \\ = -\frac{Ze^2}{r}; \quad r \leq r_c. \quad (5)$$

The bare ion form factor of this potential is

$$W_B^{\text{eff}}(q) = -\frac{8pZ^{\text{eff}}}{\Omega_0^{\text{eff}} q^2} \left[ 2 - \cos(qr_c) - \frac{e^1 q^2 r_c^2}{(1 + q^2 r_c^2)} \right. \\ \left. + \frac{qr_c}{(1 + q^2 r_c^2)} \{ \sin(qr_c) + qr_c \cos(qr_c) \} \right]. \quad (6)$$

A quantity which is equally important as the pair potential while studying a disordered system is  $g(r)$ , the pair correlation function. It provides us with the statistical description of the structure of the system under investigation. The complete information of the precise position and momentum of each particle at each instant of time is contained in this function. The function  $g(r)$  can be obtained using X-ray diffraction and neutron scattering experiments (Hujiben *et al* 1979; Nassif *et al* 1983) or computed theoretically from the effective pair potentials (Faber 1972; Agarwal and Kachhava 1993b).

The function  $g(r)$  is presently calculated using the expression (Faber 1972; Agarwal and Kachhava 1993b),

$$g(r) = \exp(-V^{\text{eff}}(r)/k_B T) - 1. \quad (7)$$

Here  $k_B$  is the Boltzmann's constant and  $T$  the temperature.

The longitudinal and transverse frequencies in terms of effective potential and pair correlation function can be computed using the secular equation following Takeno and Goda (1971) as,

$$\det | \mathbf{w}^2 \mathbf{d}(\mathbf{ab}) - D_{ab}(q) | = 0, \quad (8)$$

where  $D_{ab}(q)$  is the dynamical matrix. With the physical argument that the product of the static pair correlation function ' $g(r)$ ' and the second derivative of the inter-atomic potential  $V^{\text{eff}}(r)$  is peaked near ' $\mathbf{s}$ ', the hard sphere diameter, the expressions for the longitudinal phonon frequency  $\omega_L(q)$  and transverse phonon frequency  $\omega_T(q)$  can be written according to Hubbard and Beeby (1969) as,

$$\omega_L^2(q) = \omega_E^2 \left[ 1 - \frac{3\sin(q\mathbf{s})}{(q\mathbf{s})} - \frac{6\cos(q\mathbf{s})}{(q\mathbf{s})^2} - \frac{6\sin(q\mathbf{s})}{(q\mathbf{s})^3} \right], \quad (9)$$

$$\omega_T^2(q) = \omega_E^2 \left[ 1 + \frac{3\cos(q\mathbf{s})}{(q\mathbf{s})} - \frac{3\sin(q\mathbf{s})}{(q\mathbf{s})^3} \right], \quad (10)$$

where

$$\omega_E = \frac{4\mathbf{p} n_{\text{eff}}}{3M_{\text{eff}}} \int_0^\infty g(r) r^2 V^{\text{eff}}(r) dr, \quad (11)$$

is the maximum phonon frequency.  $M_{\text{eff}}$  is the effective atomic mass and  $n_{\text{eff}}$  the effective number density while  $V^{\text{eff}}(r)$  is the second derivative of the effective pair potential. The atomic mass and number density are given by,

$$M_{\text{eff}} = xM_A + (1-x)M_B, \quad (12)$$

$$n_{\text{eff}} = xn_A + (1-x)n_B. \quad (13)$$

$M_A$ ,  $M_B$ ,  $n_A$  and  $n_B$  represent the atomic masses and number densities of the pure A and B species which make up the glass. In the long wavelength limit the phonon dispersion curves show an elastic behaviour. In this limit

$$\omega_L \propto q \text{ and } \omega_T \propto q,$$

$$\therefore \omega_L = v_L q \text{ and } \omega_T = v_T q. \quad (14)$$

$v_L$  and  $v_T$  are the longitudinal and transverse sound velocities in the glass respectively. The isothermal bulk modulus  $B_T$ , modulus of rigidity  $G$ , Poisson's ratio  $\mathbf{s}$  and Young's modulus are found using the expressions (Hafner 1983; Hafner and Jaswal 1988; Bansal and Doremus 1989; Varshneya *et al* 1993)

$$B_T = \mathbf{r}(v_L^2 - 4/3 v_T^2), \quad (15)$$

$$G = \mathbf{r} v_T^2. \quad (16)$$

$\mathbf{r}$  is the isotropic density of the solid.

$$\mathbf{s} = \frac{1 - 2(v_T^2/v_L^2)}{2 - 2(v_T^2/v_L^2)}, \quad (17)$$

and

$$Y = 2G(\mathbf{s} + 1). \quad (18)$$

### 3. Results and discussion

The pair potentials generated for the glass  $\text{Ca}_{70}\text{Mg}_{30}$  using our model potential in combination with the Hartree, Taylor and Ichimaru–Utsumi local field correction functions are displayed in figure 1. A study of this figure shows that the general trend of the pair potentials in all the cases is same. But the position of the first minima is greatly affected by the type of screening used. The pair potentials calculated using (1) combined with the knowledge of ' $g(r)$ ', the pair correlation function, allows us to compute longitudinal and transverse phonon frequencies in a binary mixture via (9)–(11). Instead of the usual practice of using the experimental values of  $g(r)$  for studying the phonon dynamics, in the present investigation we have used the pair correlation function  $g(r)$  calculated using the effective pair potential to give the calculations a flavour of our own model potential.

Figure 2 shows the pair correlation functions for the binary alloys calculated using (7) and used in (9)–(10) for computing the phonon frequencies. Here the value of the parameter  $r_c$  (core radius) is adjusted such that the calculated values of  $g(r)$  agree with the experimental values of  $g(r)$  as close as possible.

It is evident from figure 2 that the present yielding of the pair correlation functions are in very good agreement

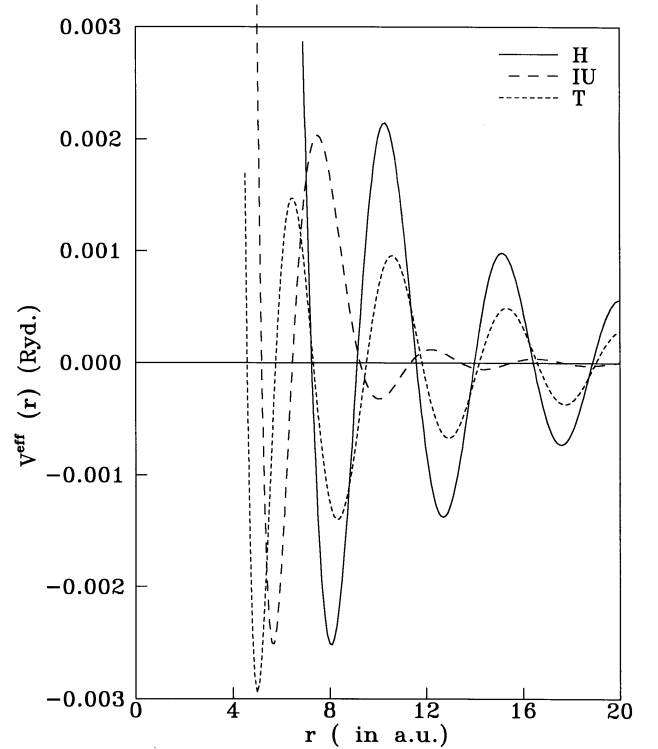
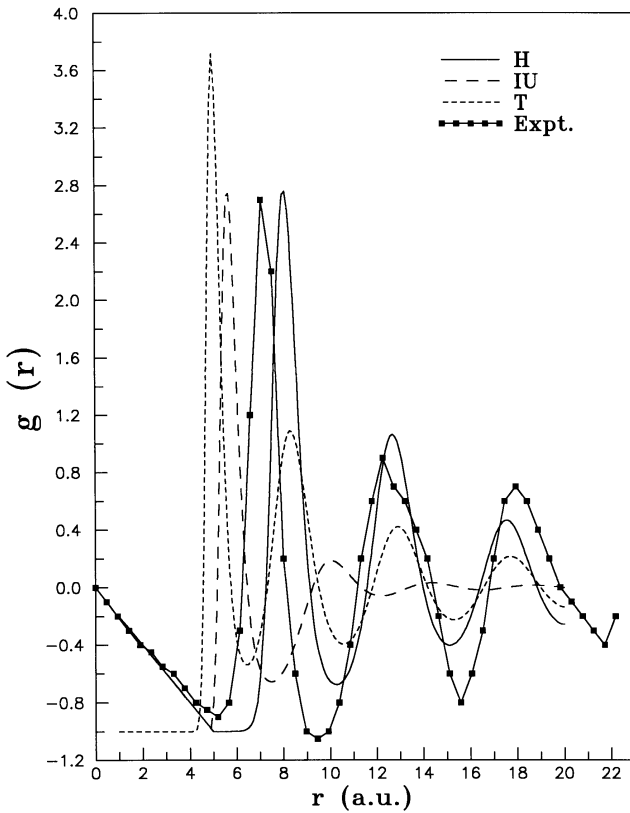


Figure 1. Pair potentials for the  $\text{Ca}_{70}\text{Mg}_{30}$  glass.

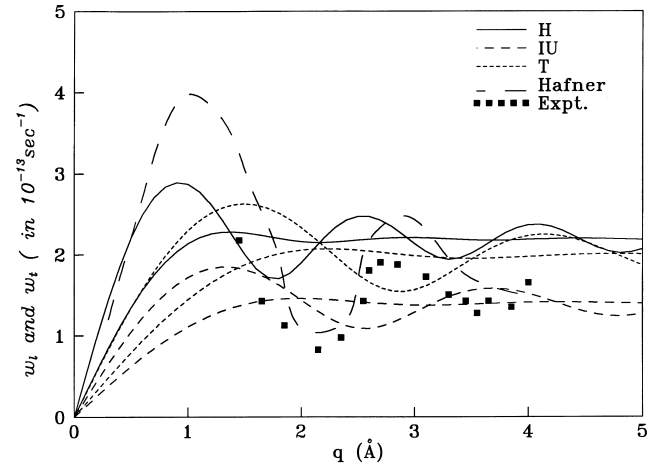
with the experimental values. The position of the first peak is important for the pair correlation function (Faber 1972). In the case of  $\text{Ca}_{70}\text{Mg}_{30}$  when compared to experimental curves it is found that the height of the first peak is almost same. The theoretically computed  $g(r)$  using the IU and H screening function lie on either side of the experimental  $g(r)$  while that for the T function has a higher peak at a lower  $r$  value. The  $w \rightarrow q$  relations for the  $\text{Ca}_{70}\text{Mg}_{30}$  are shown in figure 3 both for the longitudinal and transverse phonons along with the available experimental data as well as the theoretical results reported by Hafner (1983). It can be seen from the figure that the height of the peaks and also the position of the first peaks in the longitudinal branches is appreciably



**Figure 2.** Pair correlation function for  $\text{Ca}_{70}\text{Mg}_{30}$  glass. Experimental points are taken from Hafner and Jaswal (1988).

influenced by different screening functions. However here it is observed that the positions of first peaks obtained with the help of IU and T screening functions are close to each other but their heights are differing from each other substantially. It is also evident that the modes due to H screening function are suppressed positively due to the inclusion of exchange and correlation effects and the corresponding theoretical results are found more closer to the experimental data. Also the oscillations in the longitudinal branch is more prominent compared to the transverse branch which suggests the existence of the collective excitations at larger momentum transfer due to the longitudinal phonons only. The transverse phonons undergo large thermal modulation compared to the longitudinal phonon because of the anharmonicity of the atomic vibrations. The position of the first minima in the longitudinal branch is  $q \approx 2 \text{ \AA}^{-1}$  close to where the static structure factor shows its first peak.

Compared to the results reported by Hafner (1983) which overestimates the experimental results, the present results agree quite satisfactorily with the experimental values. In the  $\text{Ca}_{70}\text{Mg}_{30}$  glass the results due to the Taylor screening function gives the best agreement while the results due to the Hartree screening function overestimates the experimental results but are better than those of



**Figure 3.** Phonon dispersion curves for  $\text{Ca}_{70}\text{Mg}_{30}$  glass. Experimental points are taken from Suck *et al* (1980).

**Table 1.** Elastic properties of the  $\text{Ca}_{70}\text{Mg}_{30}$  glass.

	Present results			Hafner (1983)	Saxena <i>et al</i> (1991)
	H	T	IU		
$v_L$ ( $10^5$ cm/sec)	10.437	10.349	6.8217	4.67	5.66
$v_T$ ( $10^5$ cm/sec)	6.0260	5.9753	3.9385	2.34	3.55
$B_T$ ( $10^{11}$ dyne/cm <sup>2</sup> )	10.405	10.230	4.4454	2.4945	1.796
$G$ ( $10^{11}$ dyne/cm <sup>2</sup> )	6.2439	6.1393	2.6672	0.9414	1.4863
$S$	0.2499	0.2499	0.2500	0.33	0.17
$Y$ ( $10^{11}$ dyne/cm <sup>2</sup> )	15.608	15.347	6.668	2.5088	3.4951

Hafner. Table 1 gives the presently calculated numerical values of the bulk modulus, modulus of rigidity, Poisson's ratio and Young's modulus along with other available findings. Here surprisingly we have noticed that the results obtained by H and T screening functions are extremely close to each other while IU screening function gives consistently lower values than these results but close to other such theoretical results (Hafner 1983; Saxena *et al* 1991). We may remark here that the possible reason for this could be lying in the formulation of IU screening function. This indicates that in studying the elastic properties, specific features of IU screening function described in the theory part of the present paper should be taken into account while employing other screening functions and it becomes a matter of further investigation. As the phonon frequencies reported by Hafner (1983) and Saxena *et al* (1991) overestimates the neutron scattering results, the comparison of their data with the presently calculated values is not that meaningful. The  $\text{Ca}_{70}\text{Mg}_{30}$  glass is one of the metallic glasses having important engineering applications in the field of materials science. Therefore it can be concluded that, as the phonon dynamics and the elastic properties of this glass have not been investigated theoretically using the IU screening function previously, the values reported here form a very important set of data for this glass.

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