Chapter 6

Phonons in Binary and Bulk Metallic Glasses

Proceedings of RTMS- 2011 (AIP CP) (in press)

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6.1 Introduction

Metallic glasses are a subject of interest for researchers as they have found wide ranging applications in the field of materials science [1]. Such solids have electronic properties normally associated with solids, but the atomic arrangement is not spatially periodic. Binary metallic glasses composed of metals; in particular transition metals provide us with physically interesting system for theoretical investigations [1]. The use of pseudopotential theory within model potential formalism allows us to calculate interatomic potentials. Based on the interatomic interaction, we can calculate the thermodynamic, mechanical and electronic transport properties of such amorphous materials [2]. Earlier, theoretical and experimental work is performed in order to understand the structure and dynamics of two and multicomponent metallic glasses [3-6]. Such study involves the measurement of collective density waves for large momentum and for a few metallic glasses; it is possible to measure the dynamical structure factors up to large momentum. These calculations are based on the realistic potential derived using pseudopotential theory. The Copper based binary and bulk metallic glasses are studied in different concentrations, experimentally as well as theoretically [7,8]. In the present chapter, we have reported the results of our theoretical study of collective dynamics of Copper based binary and bulk metallic glasses in different composition, for which no earlier theoretical data are available.

6.2 Theory

There are mainly three theoretical approaches to calculate the longitudinal and transverse phonon frequencies in glassy systems. The first and the oldest one is the approach of Hubbard and Beeby (HB) [9]. The second one is that due to Takeno and Goda (TG) [10] and the third approach is due to Bhatia and Singh (BS) [11]. All three approaches are based on the calculation of interatomic force constants using pseudopotential theory. Also, these three approaches are computationally simple and yet justifiable. According to the HB approach, liquid differs from a solid in two different ways. Firstly, the atoms in the liquid do not form a regular array and secondly the atoms moves more freely in liquid compared to a solid. According to the TG approach, which is a quasi crystalline approach, the correlation function for the displacement of atoms itself depends on the phonon frequencies. In the BS approach, there are two main assumptions. (i) The ions interact with the central pair wise
potential, which is effective between nearest neighbors only and (ii) the force on an ion due to volume dependent energy in the metallic systems could be calculated using Thomas-Fermi approximations. Recently, the BS model was improved by Shukla and Campanha [12]. From all of these approaches, we have used the HB approach in the present work to calculate the longitudinal and transverse phonon frequencies in binary and bulk metallic glassy system. This approach is simple and it has been used earlier by many researchers to compute phonon frequencies in binary systems. Also, we have extended this approach to study the phonon frequencies in ternary glass forming system. We have shown that the HB approach yields good results for phonon frequencies. We have also calculated the elastic constants namely longitudinal and transverse phonon frequencies, isothermal bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio and elastic Debye temperature. All the calculated elastic properties are found to agree well with the available experimental and other theoretical data in literature.

There are two main ingredients when calculating the phonon frequencies in glassy system using HB approach. The first is the effective interatomic pair potential and the second is the pair correlation function. The effective interatomic interaction in the present work is calculated using second order perturbation theory [13]. The effective interatomic interaction for a s-p bonded system is given by,

\[
V_{s-p}(r) = \frac{Z^2 e^2}{r} + \frac{2}{\pi} \int dq \ F(q) \ \text{exp}(-iq\cdot r)
\]  

(6.1)

Here, \( F(q) \) is energy wave number characteristic. It is given by,

\[
F(q) = -\frac{\Omega_{0,eff} q^2}{16\pi} \left|W_{B,eff}^B(q)\right|^2 \left[\frac{\epsilon_{H,eff}^B(q) - 1}{1 + (\epsilon_{H,eff}^B(q) - 1)(1 - f_{eff}(q))}\right]
\]

(6.2)

The first and second term in above expression (6.1) is due to the Coulomb interaction between ions and indirect interaction through the conduction electrons, respectively. \( \mathbf{q} \) and \( e \) are q-space wave vector and charge of electron, respectively. \( W_{B,eff}^B(q) \) is the effective bare ion-ion interaction, which in the present work is
calculated using Ashcroft empty core model potential [14]. $\varepsilon_{H}^{\text{eff}}(q)$ is the Hartree dielectric response function [15] and $f_{\text{eff}}(q)$ is the local field correction function. Five different forms of local field correction functions due to Hartree (H) [16], Taylor (T) [17], Ichimaru and Utsumi (IU) [18], Farid et al (F) [19] and Sarkar et al (S) [20] are employed in the present study to understand the influence of exchange-correlation effects on phonon frequencies and related elastic constants of glasses. The parameter of the potential is determined by procedure given in Ref. [8]. In the present work, as the glassy systems under study are composed of transition metals, we have also added the d-band correction to the pair potential. The d-band correction is given by [7],

$$V_d(r) = \frac{225}{\pi^2} Z_d \frac{r_d^6}{r^8} - \frac{28.1}{\pi} \left( \frac{12}{n_c} \right)^{1/2} Z_d \left( 1 - \frac{Z_d}{10} \right) \frac{r_d^3}{r^5}$$  \(6.3\)

As a result, the total effective pair potential is given by,

$$V_{\text{eff}}(r) = V_{\text{sp}}(r) + V_d(r)$$ \(6.4\)

In the present work, we have considered the concept of effective atoms to compute the pair potential.

The second ingredient is the pair correlation function of atoms. For a non crystalline system like glasses and liquids, pair correlation function is a measure of particle correlation in momentum space and it contains useful information about structural properties. The pair correlation function can be computed from the pair potential using the following equation [1],

$$g(r) = \exp \left( \frac{-V_{\text{eff}}(r)}{k_BT} \right) - 1$$ \(6.5\)

Here, $k_B$ is the Boltzman’s constant and $T$ is the absolute temperature. Many researchers have also reported the pair correlation function of glassy systems using inelastic X-ray scattering and inelastic neutron scattering experiments [4,6].
Once the pair potential and pair correlation functions are obtained, the longitudinal and transverse phonon frequencies using HB approach are given by [9],

\[ \omega_l^2(q) = \omega_E^2 \left[ 1 - \frac{3\sin(q\sigma)}{(q\sigma)} - \frac{6\cos(q\sigma)}{(q\sigma)^2} + \frac{6\sin(q\sigma)}{(q\sigma)^3} \right] \]

and

\[ \omega_t^2(q) = \omega_E^2 \left[ 1 + \frac{3\cos(q\sigma)}{(q\sigma)} - \frac{3\sin(q\sigma)}{(q\sigma)^3} \right] \] (6.6)

Here, \( \omega_E \) is the maximum phonon frequency and is given by following expression [9],

\[ \omega_E^2 = \frac{4\pi}{3M_{\text{eff}}\Omega_{\text{eff}}} \int_0^\infty g(r) r^2 \frac{d^2V(r)}{dr^2} dr \] (6.7)

The upper limit in the integration is decided, where the convergences in the pair correlation function is observed. \( M_{\text{eff}} \) is the effective atomic mass. The hard sphere diameter of the system is calculated from the physical argument that the product of the static pair correlation function \( g(r) \) and the second order derivative of the interatomic potential \( V(r) \) is peaked at ‘\( \sigma \)’, which is the hard sphere diameter.

Since in the long wavelength limit the phonon dispersion curves show elastic behavior, it permits us to write the longitudinal and transverse sound velocities \( v_L \) and \( v_T \), respectively) using the following expressions,

\[ \omega_l(q) \propto q \quad \text{and} \quad \omega_t(q) \propto q \]

Therefore,

\[ \omega_l(q) = v_L q \quad \text{and} \quad \omega_t(q) = v_T q \] (6.8)

The elastic properties like bulk modulus \( (B_T) \), Modulus of rigidity \( (G) \), Poisson’s ratio \( (\xi) \), Young’s modulus \( (Y) \) and Debye temperature \( (\theta_D) \) are computed
using following expressions depending on longitudinal and transverse sound
velocities ($v_l$ and $v_t$, respectively) as [21],

$$B_T = \rho \left( v_l^2 - \frac{4}{3} v_t^2 \right)$$  \hspace{1cm} (6.9)

$\rho$ is the isotropic density.

$$\xi = \frac{v_l^2 - 2(v_t^2)}{2(v_l^2 - v_t^2)},$$  \hspace{1cm} (6.10)

$$G = \rho v_l^2$$  \hspace{1cm} (6.11)

$$Y = 2G(\xi + 1)$$  \hspace{1cm} (6.12)

and

$$\theta_D = \frac{h}{k_B} \left[ \left( \frac{9 \rho}{4 \pi} \right)^{1/3} \left( \frac{1}{v_l^3} + \frac{2}{v_t^3} \right)^{1/3} \right]$$  \hspace{1cm} (6.13)

,where, $h$ is Planck’s constant and $k_B$ is Boltzman constant.

| Table 6.1. Input parameters used in the calculations [22]. |
|---|---|---|---|---|
| Properties | Cu$_{50}$Zr$_{50}$ | Cu$_{65}$Zr$_{35}$ | Cu$_{33.3}$Zr$_{66.7}$ | Cu$_{60}$Ti$_{20}$Zr$_{20}$ |
| $Z_s$ | 2.5 | 2.05 | 3.001 | 1.5 |
| $Z_d$ | 6 | 7.05 | 4.8333 | 6.7 |
| $r_c^{eff}$ (au) | 0.909 | 1.145 | 0.822743 | 1.295 |
| $\Omega_{0,eff}^{(au)3}$ | 118.188 | 106.544 | 131.2331 | 102.827 |
| $M_{eff}$ (amu) | 77.38 | 73.228 | 81.9958 | 65.948 |
| $T$ (K) | 300 | 300 | 300 | 300 |
| $\rho$ (gm/cm$^3$) | 7.334 | 7.699 | 7.313 | 7.185 |
6.3 Results

1) \(\text{Cu}_{50}\text{Zr}_{50}\)

The form factors are computed using five different forms of local field correction functions, which are further used to compute pair potential for the non-crystalline \(\text{Cu}_{50}\text{Zr}_{50}\) binary glass in the framework of second order perturbation theory. The calculated pair potential for the alloy is shown in Figure 6.1. The first minimum in the pair potential occurs nearly at same interatomic spacing. However, the magnitude of potential energy at first neighbor (covered by ellipse in figure 1) is greatly affected by type of screening used. The results of pair potential obtained using T, IU and F and S functions are very near to each other.

Figure 6.2 shows the pair correlation function computed using the presently computed pair potential along with the experimental values [4]. Overall good agreement is observed. Using the pair potential and the experimental pair correlation function \(g(r)\) [4], we have computed the longitudinal and transverse phonon frequencies. The longitudinal and transverse phonon frequencies for binary \(\text{Cu}_{50}\text{Zr}_{50}\) alloy are shown in Figures 6.3 and Figure 6.4, respectively. It is seen from the results of phonon frequencies that the nature of phonon frequencies is not much affected by different screening functions used, but both the longitudinal and transverse frequencies computed using T, IU, F and S functions show deviation with respect to static H screening function. It can also be observed that the oscillations are prominent in the longitudinal mode as compared to transverse mode which indicates that the collective excitations at larger wave vector transfer due to the dispersion of longitudinal excitation only. On the other hand the transverse modes undergo larger thermal modulation due to the anharmonicity of the vibrations in the glass. The first minimum in the longitudinal branch of the dispersion curve falls at a value \(q = 2.8 \text{ Å}^{-1}\), near which the static structure factor shows its principal peak [4]. In the long wavelength limit the dispersion curves are linear and confirming characteristics of elastic waves.

Presently calculated bulk modulus \((B_T)\), modulus of rigidity \((G)\), Poisson’s ratio \((\xi)\), Young’s modulus \((Y)\), Debye Temperature \((\theta_D)\) and sound velocities are shown in Table 6.2. The presently calculated elastic constants of \(\text{Cu}_{50}\text{Zr}_{50}\) glass using H function are higher in magnitude as compared to calculated values using T, IU, F and S functions. Elastic constants (except isothermal bulk modulus) calculated using
other four screening function namely T, IU, F and S are very close to experimental data [23]. The experimental data of longitudinal and transverse sound velocity of Cu$_{50}$Zr$_{50}$ glass are not available. So, we have calculated these values from the known values of other elastic constants and shown them in Table 6.1. Calculated longitudinal sound velocity shows high deviation from experimental data than the transverse sound velocity. It is also to observe that the isothermal bulk modulus calculated in the present work is underestimated largely when compared to experimental and other theoretical results. The possible reason behind the underestimation of isothermal bulk modulus can be the theoretical approach used, namely the HB approach. Earlier, Pratap et al [7] have studied the vibrational dynamics and related properties of Cu$_{57}$Zr$_{43}$ glass using HB and Takeno-Goda (TG) [10] approaches. In their work also, the calculated isothermal bulk modulus using HB approach was largely underestimated as compared to that calculated using TG approach and other data. So, possible reason behind the underestimation of isothermal bulk modulus lies in the HB formulation. In the long wavelength limit, the ratio of longitudinal $v_l$ to the transverse $v_t$ sound velocity is found to be 1.73. As a result, the Poisson’s ratio, which is calculated solely in terms of $v_l$ and $v_t$, comes out to be a constant 0.25. Since, the presently calculated Poisson’s ratio is underestimated, bulk modulus is also underestimated. So, we believe that improvement of HB approach in long wavelength limit may yield better results of bulk modulus of Cu$_{50}$Zr$_{50}$ glass.

Finally, we conclude here that the PDC generated from HB approach reproduces satisfactorily general characteristics of dispersion curves. The present computation does not include any kind of fitting with experimental data. This also confirms the applicability of the model potential in the aforesaid properties and supports the present approach.
Figure 6.1 Effective pair potential in Cu\textsubscript{50}Zr\textsubscript{50} metallic glass.

Figure 6.2 Pair correlation function (full line) of Cu\textsubscript{50}Zr\textsubscript{50} glass along with experimental results (symbols) [4].
Figure 6.3 Longitudinal phonon frequencies in Cu$_{50}$Zr$_{50}$ glass.

Figure 6.4 Transverse phonon frequencies in Cu$_{50}$Zr$_{50}$ glass.
Table 6.2. Calculated elastic properties of Cu\textsubscript{50}Zr\textsubscript{50} metallic glass.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H</th>
<th>T</th>
<th>IU</th>
<th>F</th>
<th>S</th>
<th>Exp. [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_l$ ($10^5$ cm/sec)</td>
<td>4.2021</td>
<td>3.6920</td>
<td>3.6940</td>
<td>3.6951</td>
<td>3.8016</td>
<td>4.301</td>
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<tr>
<td>$v_t$ ($10^5$ cm/sec)</td>
<td>2.4261</td>
<td>2.130</td>
<td>2.1327</td>
<td>2.1333</td>
<td>2.1948</td>
<td>2.066</td>
</tr>
<tr>
<td>$B_T$ (GPa)</td>
<td>71.95</td>
<td>55.54</td>
<td>55.60</td>
<td>55.63</td>
<td>58.89</td>
<td>101.2</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>43.17</td>
<td>33.32</td>
<td>33.36</td>
<td>33.38</td>
<td>35.33</td>
<td>31.3</td>
</tr>
<tr>
<td>$Y$ (GPa)</td>
<td>107.9</td>
<td>83.31</td>
<td>83.40</td>
<td>83.45</td>
<td>88.33</td>
<td>84.0</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>$\theta_D$(K)</td>
<td>308.887</td>
<td>271.387</td>
<td>271.537</td>
<td>271.613</td>
<td>279.445</td>
<td>317*</td>
</tr>
</tbody>
</table>

* Data averaged over pure crystalline Cu and Zr [24].

2) Cu\textsubscript{65}Zr\textsubscript{35}

The effective pair potential for this glassy system is calculated using second order perturbation theory, including d-band correction. The calculated pair potential for the alloy is shown in Figure 6.5. The first minimum in the pair potential computed using all five local field correction functions occurs nearly at same interatomic spacing. However, the magnitude of potential energy at first neighbor is greatly affected by type of screening used. The results of pair potential obtained using T, IU and F and S functions are very near to each other. Pair potential computed using H function shows maximum potential energy as compared to other screening functions. Figure 6.6 shows the presently computed pair correlation function along with the experimental results [4]. Slight deviation occurs in the position of first peak in g(r).

Using the pair potential and the experimental pair correlation function reported in Ref. [4], we have computed the longitudinal and transverse phonon frequencies. The longitudinal and transverse phonon frequencies for binary Cu\textsubscript{65}Zr\textsubscript{35} glass are shown in Figures 6.7 and 6.8, respectively. It is seen from the results of phonon frequencies that H function generates results, higher in magnitude as compared to those computed using other four screening functions. Other four screening functions generate the results of phonon frequencies, which are near to each other. The first minimum in the longitudinal branch of the dispersion curve falls at a value $q \approx 2.8$ Å\textsuperscript{-1}.
near which the static structure factor shows its principal peak [4]. The position of first deep in longitudinal phonon frequencies corresponds to diffuse umklapp scattering process. It can also be observed that the oscillations in the longitudinal mode are responsible for momentum transfer at larger wave vector. In the long wavelength limit the dispersion curves are linear and confirming characteristics of elastic waves.

Presently calculated bulk modulus ($B_T$), modulus of rigidity ($G$), Poisson’s ratio ($\xi$), Young’s modulus ($Y$), Debye Temperature ($\theta_D$) and sound velocities are shown in Table 6.3. For this composition of Cu-Zr system, no experimental data of elastic constants are available in literature. As a result, we have averaged the elastic constants of pure Cu and Zr and the averaged values are shown in Table 6.3 along with the presently calculated values. Overall, a good agreement is observed. It is again observed in the present case that bulk modulus is underestimated. The presently calculated values of elastic constants using T, IU, F and S functions show good agreement with the averaged values. The elastic constants calculated using H function is overestimated. Thus, it is observed that proper local field correction function is necessary in order to estimate the elastic properties of metallic glasses like Cu-Zr.

![Figure 6.5](image)

**Figure 6.5** Effective pair potential in Cu$_{65}$Zr$_{35}$ metallic glass.
Figure 6.6 Pair correlation function of Cu$_{65}$Zr$_{35}$ glass along with experimental results (symbols) [4].

Figure 6.7 Longitudinal phonon frequencies in Cu$_{65}$Zr$_{35}$ glass.
Figure 6.8 Transverse phonon frequencies in Cu\textsubscript{65}Zr\textsubscript{35} glass.

Table 6.3. Calculated elastic properties of Cu\textsubscript{65}Zr\textsubscript{35} metallic glass.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H</th>
<th>T</th>
<th>IU</th>
<th>F</th>
<th>S</th>
<th>Others [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_i$ ($10^5$ cm/sec)</td>
<td>4.3795</td>
<td>3.9826</td>
<td>3.9397</td>
<td>3.9249</td>
<td>4.04</td>
<td>---</td>
</tr>
<tr>
<td>$v_t$ ($10^5$ cm/sec)</td>
<td>2.5285</td>
<td>2.2993</td>
<td>2.2745</td>
<td>2.266</td>
<td>2.333</td>
<td>---</td>
</tr>
<tr>
<td>$B_T$ (GPa)</td>
<td>76.56</td>
<td>67.84</td>
<td>61.96</td>
<td>61.49</td>
<td>65.21</td>
<td>122.885</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>45.94</td>
<td>40.71</td>
<td>37.17</td>
<td>36.89</td>
<td>39.13</td>
<td>42.75</td>
</tr>
<tr>
<td>$Y$ (GPa)</td>
<td>114.8</td>
<td>101.8</td>
<td>92.93</td>
<td>92.24</td>
<td>97.82</td>
<td>108.3</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>$\theta_D$ (K)</td>
<td>338.125</td>
<td>303.047</td>
<td>304.166</td>
<td>303.022</td>
<td>312.056</td>
<td>---</td>
</tr>
</tbody>
</table>

3) Cu\textsubscript{33.3}Zr\textsubscript{66.7}

Recently, Nakashaima et al [6] have reported the static and dynamic structure factor of Cu-Zr\textsubscript{2} metallic glass using high resolution inelastic X-ray scattering. They have also reported the longitudinal and transverse phonon frequencies in this system,
experimentally. In the present work, we have calculated the pair potential for this binary system using second order perturbation theory. Ashcroft empty core model [14] is used to calculate the form factors. Figure 6.9 shows the presently calculated pair potential of CuZr$_2$ glassy system. The pair potential shows all broad features of interatomic interaction at low as well as high r values. Further, the experimental structure factor is Fourier transformed to obtain the pair correlation function. The pair correlation function obtained in this way is used along with the presently calculated pair potential to compute the longitudinal and transverse phonon frequencies in metallic glasses. Figure 6.10 shows the presently computed pair correlation function along with the experimental results. The position of first peak in the pair correlation function is related to the first neighbor distance, which in the presently computed pair correlation function is obtained near to experimental results. Figures 6.11 and 6.12 show the presently calculated phonon frequencies of longitudinal and transverse branch along with the corresponding experimental results, respectively. It is observed that the presently calculated phonon frequencies of longitudinal branch using S function are found to agree well with the experimental results. Further, the presently calculated phonon frequencies are found to be in phase with the experimental frequencies. The first deep in the phonon frequencies coincide with the experimental value. Thus, overall good agreement is observed. Similarly, in case of transverse frequencies, the calculated phonon frequencies show good agreement at low q values. In the present study, it is also observed that the phonon frequencies calculated using S function is large in magnitude as compared to that calculated using all other local field correction functions. Table 6.4 shows the presently calculated elastic constants along with the averaged values of elastic constants. A good agreement is observed between the presently calculated values of elastic constants using T, IU, F and S functions and the averaged values. The H function gives the higher values of elastic constants as compared to the averaged values.
Figure 6.9. Effective pair potential of Cu-Zr$_2$ system.

Figure 6.10. Pair correlation function of Cu-Zr$_2$ glass (full line) along with experimental results (symbols) [6].
Figure 6.11 Longitudinal phonon frequencies in Cu-Zr$_2$ metallic glass.

Figure 6.12 Transverse phonon frequencies in Cu-Zr$_2$ metallic glass.
Table 6.4. Calculated elastic properties of Cu$_{33.3}$Zr$_{66.7}$ metallic glass.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H</th>
<th>T</th>
<th>IU</th>
<th>F</th>
<th>S</th>
<th>Others [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_L$ ($10^5$ cm/sec)</td>
<td>3.444</td>
<td>2.909</td>
<td>2.8921</td>
<td>2.893</td>
<td>5.140</td>
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<tr>
<td>$v_L$ ($10^5$ cm/sec)</td>
<td>1.988</td>
<td>1.679</td>
<td>1.6697</td>
<td>1.670</td>
<td>2.9676</td>
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</tr>
<tr>
<td>$B_T$ (GPa)</td>
<td>46.13</td>
<td>32.91</td>
<td>32.52</td>
<td>32.56</td>
<td>102.7</td>
<td>107.237</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>27.68</td>
<td>19.74</td>
<td>19.51</td>
<td>19.54</td>
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<td>37.95</td>
</tr>
<tr>
<td>$Y$ (GPa)</td>
<td>69.2</td>
<td>49.36</td>
<td>48.79</td>
<td>48.84</td>
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<td>88.46</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>$\theta_D$ (K)</td>
<td>244.509</td>
<td>206.506</td>
<td>205.297</td>
<td>205.413</td>
<td>364.872</td>
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</tr>
</tbody>
</table>

4) Cu$_{60}$Ti$_{20}$Zr$_{20}$

Here, the empty core Ashcroft’s potential [14] is used along with various local field correction functions [16-20] to compute pair potential for the glass forming ternary Cu-Ti-Zr system. The calculated pair potential for the alloy is shown in Figure 6.13. The study reveals the general trend of the pair potentials in all the cases suggesting that the position of the first minima is greatly affected by the type of screening used. Further, from the computed pair potential, we have also computed the pair correlation function of this ternary system and the computed values are shown in Figure 6.14 along with the experimental results [25]. Using the computed pair potential and the pair correlation function $g(r)$ reported by Han et al [25], we have estimated the longitudinal and transverse phonon frequencies for binary alloys. The longitudinal and transverse phonon frequencies for ternary glass forming alloy are shown in Figures 6.15 and 6.16, respectively.

It is seen from the results of phonon frequencies that the nature of peak positions are not much affected by different screening functions but both the longitudinal and transverse frequencies show deviation for IU function with respect to static H screening function. It is obvious from the figures that the oscillations are prominent in the longitudinal mode as compared to transverse mode which indicates that the collective excitations at larger wave vector transfer due to the dispersion of longitudinal excitation. On the other hand the transverse modes undergo larger
thermal modulation due to the anharmonicity of the vibrations in the alloy. It can also be seen that the first minimum in the longitudinal branch of the dispersion curve falls at a value \( q \approx 2.8 \text{ Å}^{-1} \). In the long wavelength limit the dispersion curves are linear and confirming the characteristics of elastic waves. The PDC for transverse phonons attain maxima at a higher \( q \) value than the longitudinal phonon curve.

Presently calculated bulk modulus (\( B_T \)), modulus of rigidity (\( G \)), Poisson’s ratio (\( \xi \)), Young’s modulus (\( Y \)) and Debye temperature (\( \theta_D \)) of binary alloy are shown in Table 5. Due to unavailability of data of elastic constants of ternary glass forming alloy Cu_{60}Ti_{20}Zr_{20} alloy, we have averaged the elastic constants of pure crystalline Cu, Ti and Zr at room temperature [taken from Ref. [24]] and shown them along with the calculated data. It is to be observed from Table 6.5, that all elastic constants except isothermal bulk modulus calculated using IU function show good agreement with the averaged values. In our previous study of collective excitation in binary Cu_{50}Zr_{50} glass also, isothermal bulk modulus was underestimated. Similarly, earlier Pratap et al [7] have also reported the collective modes and elastic constants of Cu_{57}Zr_{43} glass using HB approach and TG approach. In their study also, isothermal bulk modulus, calculated using HB approach was underestimated. Thus, we believe that possible reason behind the underestimated isothermal bulk modulus lies in the HB formulation. Since the unavailability of experimental or other theoretical results of collective excitations in Cu_{60}Ti_{20}Zr_{20} alloy, we are unable to compare the longitudinal and transverse phonon frequencies of these alloys. But the present findings are significant when comparison is done with the results of elastic constants, and is found in line and supports the formulation of screening and pseudopotential used in the present investigations. Also, presently calculated data serve as guideline for further research in this direction. The present study clearly reveals the role of exchange and correlation effects in such studies.
Figure 6.13 Effective pair potential in Cu-Ti-Zr metallic glass.

Figure 6.14. Pair correlation function of Cu-Ti-Zr glass along with experimental results [25].
Figure 6.15 Longitudinal phonon frequencies in Cu-Ti-Zr glass.

Figure 6.16 Transverse phonon frequencies in Cu-Ti-Zr glass.
Table 6.5. Calculated elastic properties of Cu$_{60}$Ti$_{20}$Zr$_{20}$ metallic glass.

<table>
<thead>
<tr>
<th>Properties</th>
<th>H</th>
<th>T</th>
<th>IU</th>
<th>F</th>
<th>S</th>
<th>Others [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_\parallel$ ($10^5$ cm/sec)</td>
<td>4.3707</td>
<td>4.365</td>
<td>4.3505</td>
<td>4.351</td>
<td>4.352</td>
<td>---</td>
</tr>
<tr>
<td>$\nu_\perp$ ($10^5$ cm/sec)</td>
<td>2.5234</td>
<td>2.520</td>
<td>2.5117</td>
<td>2.512</td>
<td>2.513</td>
<td>---</td>
</tr>
<tr>
<td>$B_T$ (GPa)</td>
<td>81.71</td>
<td>76.06</td>
<td>75.55</td>
<td>75.6</td>
<td>75.62</td>
<td>124.38</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>49.02</td>
<td>45.63</td>
<td>45.33</td>
<td>45.36</td>
<td>45.375</td>
<td>44.2</td>
</tr>
<tr>
<td>$Y$ (GPa)</td>
<td>122.6</td>
<td>114.1</td>
<td>113.3</td>
<td>113.4</td>
<td>113.56</td>
<td>114.8</td>
</tr>
<tr>
<td>$\xi$</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.336</td>
</tr>
<tr>
<td>$\theta_D$ (K)</td>
<td>332.574</td>
<td>337.004</td>
<td>335.882</td>
<td>335.995</td>
<td>335.998</td>
<td>---</td>
</tr>
</tbody>
</table>
6.4 Conclusions

In the present chapter 6, we have computed collective modes and related elastic constants of four copper based metallic glasses using model potential formalism in conjunction with the approach of Hubbard and Beeby. Following point emerge out from the present work.

1) The pair potential is computed using second order perturbation theory. In all cases the computed pair potential is greatly affected by type of screening function used. The position and magnitude of pair potential at its first minimum is affected most.

2) From the computed pair potential, we have also computed pair correlation function for all metallic glasses, which show good agreement with the available experimental results.

3) Further, using HB approach, we have also computed phonon frequencies of longitudinal and transverse branches. The computed frequencies show all broad features of collective excitation in non crystalline materials. The computed frequencies also show its dependence on type of screening function used. The computed phonon frequencies in case of Cu-Zr\textsubscript{2} glass, agree well with the experimental findings. In particular, the phonon frequencies computed using S function agrees well with the experimental findings. The trend is exactly reproduced; however, there is little deviation as compared to experimental results. The first deep in the longitudinal branch corresponds to umklapp scattering surface. The first minimum in the longitudinal branch occurs at q value, near which the static structure factor show its principal peak. At larger momentum, phonons from longitudinal branch are found responsible for momentum transfer. On the other hand, phonons of transverse branch undergo large thermal modulation due to anharmonicity. Further, the first peak in transverse branch occurs at higher q value compared to longitudinal branch.

4) We have also calculated elastic constants from the long wavelength limit of phonon frequencies. The computed elastic constants using H functions are higher in magnitude as compared to those computed using all other local field
correction functions. In case of Cu\textsubscript{50}Zr\textsubscript{50} glass, the elastic properties computed using T, IU, F and S functions agree well with the recent experimental findings. On the other hand, H function overestimates all elastic constants, except isothermal bulk modulus. The percentage deviation of presently calculated isothermal bulk modulus is 28.903 %, 45.119 %, 45.059 %, 45.03 % and 41.808 using H, T, IU, F and S functions, respectively. The percentage deviation of presently computed value of rigidity modulus using H, T, IU, F and S functions are 37.923 %, 6.454 %, 6.581 %, 6.645 % and 12.87 %, respectively. in case of Young’s modulus, the deviation is 28.45 %, 0.821 %, 0.714 %, 0.655 % and 5.15 %, respectively using H, T, IU, F and S functions. The computed value of Poisson’s ratio shows 28.57 % deviation for all screening functions. Same trend is observed in case of all glasses, studied here. Poisson’s ratio and isothermal bulk modulus are underestimated in all cases. The possible reason behind such underestimated values lies in the HB formulation.

5) Further, it is observed in all three Cu-Zr binary glasses that as Cu concentration increases (Zr concentration decreases) values of all elastic constants increases. This observation indicates that Cu rich Cu-Zr binary systems may serve well in industries and aerospace applications, due to their higher elasticity.

6) Finally, we conclude that the model potential formalism is used here without any fitting procedure to compute phonon frequencies and elastic constants of four copper based metallic glasses. The computed phonon frequencies and elastic constants are found consistent with the experimental findings, confirming the present approach in determining collective dynamics of copper based metallic glasses.
6.5 References

15. N.W. Ashcroft and N.D. Mermin, Solid State Physics
22. C. Kittel, Introduction to Solid State Physics, Wiley India (1989)
24. www.webelements.com