Structure and dynamics of a two-component metallic glass

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Abstract. Computations of the frequencies of longitudinal and transverse phonon modes in a two-component metallic glass ($Mg_{70}Zn_{30}$) based on the pseudopotential approach used for the calculation of interatomic pair potential have been presented. The theory employed for these calculations is a self-consistent phonon theory as developed by Takeno and Goda for amorphous solids. The computed results are compared with molecular dynamics and neutron inelastic scattering experiments. It appears that the short-wavelength collective excitations detected in this glass arise from longitudinal phonon excitations and probably not from a diffuse Umklapp scattering from transverse acoustic waves.

1. Introduction

Metallic glasses are solids which have electronic properties normally associated with metals but atomic arrangements which are not spatially periodic. Non-crystalline and amorphous are equivalent terms used to describe the atomic-scale structure of such materials. Until recently, metallic glasses which are stable at room temperature were composed of several elements, at least one of which was a transition metal. Now, however, it has become possible to make stable metallic glasses with only two components, both of which are simple metals (e.g. Mg–Zn, Ca–Mg and Ca–Al). It is obvious that such substances should prove to be easier and more convenient systems for theoretical investigation.

   Although we have sufficient understanding of the properties of collective density waves in amorphous solids, much less attention has been given to the application of collective motion in the study of dynamical structure and phonon dispersion in binary and multicomponent metallic glasses. Partial wavenumber-dependent spectral functions have been computed [1] for Ca–Mg, Mg–Zn and Ca–Zn alloys, but there are very few systematic investigations [2, 3] of dynamical concentration fluctuation in metallic glasses or glass-forming alloys.

   Because of the presence of only two components, the model structure of binary metallic glass remains relatively simple and, furthermore, using pseudopotential theory it is possible to calculate the interatomic potentials between simple metals to a high degree of accuracy.

   In the present paper, the interatomic potentials $\varphi_{Mg-Mg}(r)$, $\varphi_{Mg-Zn}(r)$ and $\varphi_{Zn-Zn}(r)$ for $Mg_{70}Zn_{30}$ have been calculated within the framework of the pseudopotential approach.

Using the potentials thus obtained the frequencies of longitudinal and transverse phonon modes are computed employing the theory of amorphous solids [4]. The computed results are compared with the molecular dynamics results and neutron inelastic scattering experiments.

2. Theory

The form of the effective ion–ion pair potential in a single-component fluid (metallic fluid), employing the empty-core model potential of Ashcroft [5] and the screening function of Hubbard and Sham [6], is given as

$$\varphi(r) = \frac{(Ze)^2}{r} + \frac{2(Ze)^2}{\pi} \int dQ \frac{\sin(Qr)}{Qr} \cos^2(Qr_c) \left(\frac{1}{\varepsilon(Q)} - 1 \right) \tag{1}$$

where Z, r_c and $\varepsilon(Q)$ are the valency, core radius and static dielectric function, respectively.

Knowing the pair potential for a single component as given in equation (1), the mean-effective-density-dependent interatomic potential in the case of a two-component metallic glass of the type $A_{1-x}B_x$ can be written as

$$\varphi_{eff}(r) = C_A^2 \varphi_{AA}(r) + 2C_A C_B \varphi_{AB}(r) + C_B^2 \varphi_{BB}(r) \tag{2}$$

where C_A and C_B are the concentration fractions of the A and B components, respectively, and are given as

$$C_A = (1 - X)V_A/[(1 - X)V_A + XV_B]$$

$$C_B = XV_B/[(1 - X)V_A + XV_B].$$

V_A and V_B are the molar volumes of the A and B components, respectively. In equation (2), $\varphi_{AA}(r)$, $\varphi_{BB}(r)$ and $\varphi_{AB}(r)$ are the partial pair potentials for A–A, B–B and A–B, respectively, in the $A_{1-x}B_x$ metallic glass. Using equation (1), one can write

$$\varphi_{AA}(r) = \frac{(Z_A e)^2}{r} + \frac{2(Z_A e)^2}{\pi} \int dQ \frac{\sin(Qr)}{Qr} \cos^2(Qr_c^A) \left(\frac{1}{\varepsilon_{AA}(Q)} - 1 \right) \tag{3}$$

where

$$\varepsilon_{AA}(Q) = 1 - [(4\pi e^2/Q^2)\chi_A(Q)]/[1 + (4\pi e^2/Q^2)\chi_A(Q)G_A(Q)]$$

in which $\chi_A(Q)$ takes into account the coulombic interaction between the electrons and is expressed as

$$\chi_A(Q) = -(mK_F^A/\pi^2\hbar^2)\{\tfrac{1}{2} + [(4K_F^{A2} - Q^2)/8K_F^A Q] \ln|(2K_F^A + Q)/(2K_F^A - Q)|\}.$$

Here, $G_A(Q)$, called the local field function, including the exchange and correlation energies among the electrons, is written in the form $G_A(Q) = Q^2/[2(Q^2 + \nu K_F^{A2})]$ with $\nu = 2/(1 + 0.153/\pi K_F^A)$. The expression for the partial pair potential $\varphi_{BB}(r)$ between

B types of atom is similarly written by simply replacing the subscripts A and superscripts A by B in equation (3). Furthermore, $\varphi_{AB}(r)$ is expressed as

$$\varphi_{AB}(r) = \frac{(Z_{AB}e)^2}{r} + \frac{2(Z_{AB}e)^2}{\pi} \int dQ \frac{\sin(Qr)}{Qr} \cos^2(Qr_c^{AB}) \left(\frac{1}{\varepsilon_{AB}(Q)} - 1\right). \tag{4}$$

The value of r_c^{AB} is obtained in terms of r_c^A and r_c^B using the relation

$$r_c^{AB} = (r_c^A + r_c^B)/2.$$

Furthermore, the Fermi wavenumber K_F for the A–B component is determined using the following expression from the free-electron theory:

$$K_F^{AB} = (3\pi^2 Z^{AB} \rho^{AB})^{1/3}$$

where Z^{AB} is the mean valency of the metallic glass and ρ^{AB} is the mean number density of A–B pairs in the metallic glass $A_{1-x}B_x$. Quite often, simple extrapolation of the number of valence electrons from the values for the pure component can give K_F for A–B pairs but these values lead to the totally inconsistent results of the experimentally observed temperature coefficient of resistivity. Moreover, it should be remembered that, while $S(Q)$ can be experimentally determined for an amorphous material, at present there is no simple way to determine K_F directly. The effective pair potential obtained above has been used to study the dynamical structure and hence the properties of a binary metallic glass. The phonon eigenfrequencies are physically more meaningful quantities with which we study the anharmonicity of the glass under consideration. The expression for the longitudinal and transverse phonon eigenfrequencies for the virtual atoms contain many-body correlation functions and are given as

$$\omega_l^2(Q) = \frac{4\pi\rho^{eff}}{M} \int_0^\infty dr \, g_{eff}(r) \left[r\varphi'_{eff}(r) \left(1 - \frac{\sin(Qr)}{Qr}\right) + [r^2 \varphi''_{eff}(r) - r\varphi'_{eff}(r)] \right.$$

$$\left. \times \left(\tfrac{1}{3} - \frac{\sin(Qr)}{Qr} - \frac{2\cos(Qr)}{(Qr)^2} + \frac{2\sin(Qr)}{(Qr)^3}\right) \right] \tag{5}$$

and

$$\omega_t^2(Q) = \frac{4\pi\rho^{eff}}{M} \int_0^\infty dr \, g_{eff}(r) \left[r\varphi'_{eff}(r) \left(1 - \frac{\sin(Qr)}{Qr}\right) \right.$$

$$\left. + [r^2 \varphi''_{eff}(r) - r\varphi'_{eff}(r)] \left(\tfrac{1}{3} + \frac{\cos(Qr)}{(Qr)^2} - \frac{\sin(Qr)}{(Qr)^3}\right) \right] \tag{6}$$

where M is the effective mass of the atom and ρ^{eff} is the effective number density of the glass.

3. Results and discussion

Partial pair potentials calculated for Mg–Mg, Zn–Zn and Mg–Zn components are employed using equation (2) in the computation of the effective pair potential for $Mg_{70}Zn_{30}$ glass. The partial pair potentials and effective pair potential of the glass are
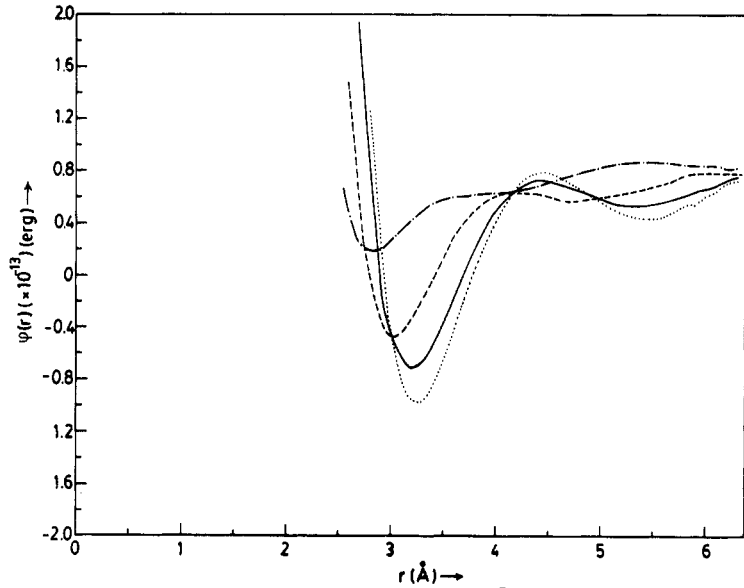
Figure 1. Pair potentials for metallic glass $Mg_{70}Zn_{30}$: . . . . , $\varphi_{Mg-Mg}(r)$; $- \cdot -$, $\varphi_{Zn-Zn}(r)$; $---$, $\varphi_{Mg-Zn}(r)$; ———, $\varphi_{eff}(r)$.

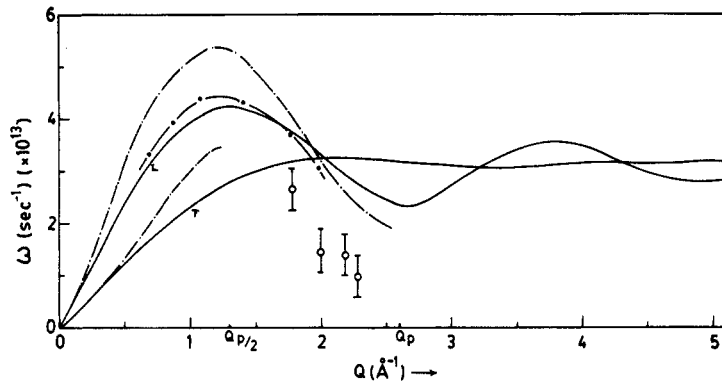**Figure 2.** The longitudinal and transverse phonon dispersion relations for metallic glass $Mg_{70}Zn_{30}$ (———), compared with the experimental data from Suck *et al* [10] (neutron inelastic scattering) ($\bar{\underline{\Phi}}$), the model calculation of Tomanek [9] ($- \cdot -$) and the molecular dynamics of von Heimendahl [8] ($---$).

shown in figure 1. $\varphi_{eff}(r)$ lies in between $\varphi_{Mg-Mg}(r)$ and $\varphi_{Zn-Zn}(r)$ and shows oscillations of the repulsive potential in the larger-r region. In the large-r region, it seems that, in this glass, coulombic repulsion dominates over the oscillations due to ion–electron–ion interactions and hence the calculated pair potential converges, for $r \to \infty$, towards a finite value instead of zero. The phonon eigenfrequencies for longitudinal and transverse phonon modes are calculated using equations (5) and (6) and are shown in figure 2. The effective pair correlation function $g_{eff}(r)$ is taken from the molecular dynamics plus

potential energy mapping results of Hafner and Jaswal [7]. The molecular dynamics results of von Heimendahl [8], the results of the model calculation of Tomanek [9] and the neutron inelastic scattering experiment results of Suck *et al* [10] are also shown in the figure. It can be noted from figure 2 that oscillations are dominant in the longitudinal phonon mode, whereas the transverse phonon mode does not show an oscillation of large amplitude beyond the first maximum of the longitudinal mode; this maximum lies at $Q = Q_p/2$ where Q_p is the wavevector transfer at which the structure factor of $Mg_{70}Zn_{30}$ shows its first peak. In the high-wavevector-transfer region, damping of phonons dominates the transverse mode, indicating the fluid characteristics of the glass because of the softening of the structure of the glass. It is also observed from the longitudinal phonon mode that the spectral response is not sharp at larger Q-values. The results beyond about $1.5 \, \text{Å}^{-1}$ are almost meaningless as the spectral response measured by neutron inelastic scattering is broad and approaches the density of states at large Q.

In the long-wavelength limit, however, the frequencies of the longitudinal and transverse modes are proportional to the wavevectors and obey the relationships

$$\omega_l = C_l Q \qquad \omega_t = C_t Q$$

where C_l and C_t are the longitudinal and transverse velocities of sound in this glass. The values of C_l and C_t as calculated from the elastic part of the phonon dispersion curves, i.e. $C_l = 4.7 \times 10^5 \, \text{cm s}^{-1}$ and $C_t = 2.6 \times 10^5 \, \text{cm s}^{-1}$, are closer to those obtained through the Brillouin scattering experimental value [11], namely $C_l = 4.3 \times 10^5 \, \text{cm s}^{-1}$ and $C_t = 2.3 \times 10^5 \, \text{cm s}^{-1}$, than to the values obtained through von Heimendahl's dispersion relation, where $C_l = 5.1 \times 10^5 \, \text{cm s}^{-1}$ and $C_t = 2.5 \times 10^5 \, \text{cm s}^{-1}$. Furthermore, using these values of the longitudinal and transverse velocities of sound, the Debye temperature Θ_D has been calculated in $Mg_{70}Zn_{30}$ glass following Hafner [1]. This Θ_D value of 305.21 K is in excellent agreement with the value ($\Theta_D = 307.93$ K) computed using the Grimvall [12] formula for the Debye temperature of an alloy:

$$1/\Theta_D^2 = p_A/\Theta_{D_A}^2 + p_B/\Theta_{D_B}^2$$

where p_A and p_B are the atomic concentrations (in fact just the probabilities that the site is occupied) and Θ_{D_A} and Θ_{D_B} are the Debye temperatures [13] of the pure components of the metals in the alloy. Also, the isothermal bulk modulus B_T of an isotropic solid is given by $B_T = \rho(C_l^2 - \frac{4}{3}C_t^2)$, where ρ is the density of the isotropic solid. For amorphous $Mg_{70}Zn_{30}$, we get $B_T = 3.559 \times 10^{11} \, \text{dyn cm}^{-2}$. This is only 0.8% lower than the B_T value averaged over the crystalline metals; $B_T = 3.58 \times 10^{11} \, \text{dyn cm}^{-2}$ (the theoretical bulk moduli for the pure metals are $B_T = 3.4 \times 10^{11} \, \text{dyn cm}^{-2}$ for Mg and $B_T = 4.0 \times 10^{11}$ dyn cm^{-2} for Zn). This value of B_T for Zn has been calculated from the experimental data on isothermal compressibility [14]. Both results suggest that the longitudinal elastic modes are somewhat softer in the glassy phase.

Recently Suck *et al* [10] have measured the dispersion of short-wavelength collective density fluctuations in this metallic glass ($Mg_{70}Zn_{30}$) for momentum transfer near the first maximum of the static structure factor ($Q_p = 2.61 \, \text{Å}^{-1}$) using inelastic neutron scattering. From the calculated dynamical structure factors, the dispersion of longitudinal excitations could be determined for wavevectors ranging from 0.3 to 2.4 Å^{-1}.

Transverse excitations are sufficiently well defined only for momentum transfer up to $1.2 \, \text{Å}^{-1}$ in von Heimendahl's dispersion relations. However, in the present work, the transverse phonon frequencies have been computed up to higher Q-values. The computed transverse branch neither shows oscillations at higher Q nor provides any

minimum and is monotonic. As the neutron couples directly only to the longitudinal modes, the observed collective excitations in amorphous solids have to be compared with the predicted dispersion for longitudinal modes. Both theory and experiment yield a decreasing dispersion curve with increasing momentum transfer in the region between $Q_p/2$ and Q_p (Q_p is the wavevector of the first peak in the static structure factor). The observed frequencies are a factor of about two less than the calculated dispersion. The dispersion curves obtained from the model calculation of Tomanek [9], also displayed in figure 2, lie below von Heimendahl's dispersion results of longitudinal excitations and are close to the results obtained from the present computations but are much higher than the experimental results. The quantitative difference between the present calculation and the experimental situation, in spite of good qualitative agreement, can be attributed to

(i) the sampling conditions of the experiments,
(ii) the short supply of data in the long-wavelength region and
(iii) the low effectiveness of the dielectric screening function used for the calculation of the effective pair potential.

Thus it could be concluded that the self-consistent phonon theory of Takeno and Goda [4], used in the calculations of the longitudinal and transverse phonon frequencies, in amorphous solids can explain the qualitative behaviour of the dispersion law for propagating collective excitations in $Mg_{70}Zn_{30}$ glass. It appears from the present analysis that in glass also, like liquid metals, the short-wavelength collective excitations arise from the longitudinal phonon modes and therefore could be compared with the results of the inelastic scattering of slow neutrons.

Acknowledgments

References

[1] Hafner J 1983 *Phys. Rev.* B **27** 678
[2] Suck J B, Rudin H, Güntherödt H J and Beck H 1981 *J. Phys. F: Met. Phys.* **11** 1375; 1983 *Phys. Rev. Lett.* **50** 49
[3] Suck J B, Rudin H, Güntherödt H J, Tomanek D, Beck H, Morkel C and Gläser W 1980 *J. Physique Coll.* **41** C8 175
[4] Takeno S and Goda M 1971 *Prog. Theor. Phys.* **45** 331
[5] Ashcroft N W 1966 *Phys. Lett.* **23** 48
[6] Hubbard J 1957 *Proc. R. Soc.* A **234** 336
    Sham L J 1965 *Proc. R. Soc.* A **283** 33
[7] Hafner J and Jaswal S S 1988 *Phil. Mag.* A **58** 61
[8] von Heimendahl L 1979 *J. Phys. F: Met. Phys.* **9** 161
[9] Tomanek D 1979 *Diplomarbeit* Universität Basel
[10] Suck J B, Rudin H, Güntherödt H J and Beck H 1980 *J. Phys. C: Solid State Phys.* **13** L1045
[11] Grimsditch M and Güntherödt H J 1988 private communication
[12] Grimvall G 1986 *Thermophysical Properties of Materials* (Amsterdam: North-Holland)
[13] Ashcroft N W and Stroud D 1977 *Solid State Physics* vol 33, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic) p 52
[14] Shimoji M 1977 *Liquid Metals* (London: Academic) p 26