

# Dynamics of Mg–Zn alloy, viewing the glass melt as a one-component system

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The molten Mg–Zn alloy has been treated as a single-component system within the framework of the Ashcroft pseudopotential formalism and to evaluate the pair potential. The effective core radius was calculated using the concept of Wigner Seitz’s sphere. The longitudinal and transverse phonon frequencies were evaluated using the derived pair potential in the random phase approximation. Dynamic variables, namely, velocity autocorrelation function and power spectrum, have also been calculated, through the use of the theory of Glass and Rice in static harmonic approximation.

## 1. Introduction

Investigations of both static and dynamic properties of liquids form an important area of research both from the theoretical and experimental point of view. The so-called dynamic properties in the molten state provide the basis for deciphering the atomic structure and vibrational dynamics in terms of interatomic forces [1–3].

In the present work we have evaluated the effective interatomic potential of molten Mg<sub>50</sub>Zn<sub>50</sub> alloy using pseudopotential formalism, which has been proved to be very successful in understanding the structure and dynamics of molten metals and alloys [4–8]. We have treated the binary melt as a one-component system, analogous to a liquid metal. The effective pair potential generated is used in computing the velocity autocorrelation function and power spectrum. Further, the longitudinal and transverse phonon frequencies are estimated and then the elastic constants, using the same form of potential.

## 2. Theory

The effective pair potential is evaluated by treating the electron-ion coupling through the use of the pseudopotential concept [9] and linear screening theory. The expression for the pair potential takes into consideration both the direct electrostatic repulsion between the ions and the indirect interaction involving electron screening. The expression is as follows [10]

$$\phi(r) = \frac{(ze)^2}{r} + \frac{2(ze)^2}{\pi} \int F_N(k) \exp(-ikr) dk \quad (1)$$

The energy wave number characteristic function,  $F_N(k)$ , involves several other parameters which have been given elsewhere [11]. The binary melt Mg–Zn has been treated as a one-component metallic fluid with effective mass,  $M_{\text{eff}}$ , and effective number density,  $\rho_{\text{eff}}$

$$M_{\text{eff}} = C_1 M_1 + C_2 M_2 \quad (2)$$

$$\rho_{\text{eff}} = C_1 \rho_1 + C_2 \rho_2 \quad (3)$$

where  $C_1$  and  $C_2$  are atomic fractions of the species 1 and 2. Here 1 stands for magnesium and 2 for zinc. The effective charge is written as

$$z_{\text{eff}} = z_1 C_1 + z_2 C_2 \quad (4)$$

and the effective Fermi wave vector as

$$k_{f_{\text{eff}}} = (3\pi^2 z_{\text{eff}} \rho_{\text{eff}})^{1/3} \quad (5)$$

Thus the usual form of the ion-ion interaction potential,  $\phi(r)$ , can be conveniently rewritten in the following way

$$\phi_{\text{eff}} = \frac{(z_{\text{eff}} e)^2}{r} + \frac{2(z_{\text{eff}} e)^2}{\pi} \int dk \frac{\text{Sin } kr}{kr} \text{Cos}^2(kr_{c_{\text{eff}}}) \left[ \frac{1}{\epsilon(q)} - 1 \right] \quad (6)$$

The effective empty core radius,  $r_{c_{\text{eff}}}$  used in equation 6, is related to the Wigner–Seitz’s radius of the effective atom, and is given by [12]

$$r_{c_{\text{eff}}} = [0.51 r_{\text{alloy}} z_{\text{eff}}^{-1}] \quad (7)$$

where

$$(4/3)\pi r_{\text{alloy}}^3 = C_1(4/3)\pi r_1^3 + C_2(4/3)\pi r_2^3 \quad (8)$$

and  $r_1$  and  $r_2$  are the Wigner–Seitz’s radii of species 1 and 2 and  $C_1 + C_2 = 1$ .

In the collisionless regime [13], for times smaller than the relaxation time which is of the order of  $10^{-12}$ s, we may treat a liquid as a quasi-crystalline structure with a characteristic frequency,  $\omega_0$ . In analogy with the theory of solids, a simple model which can be considered for liquids, is that of a Brownian particle diffusing in a harmonic well of frequency  $\omega_0$ . The characteristic frequency is that frequency with which the maximum number of atoms vibrate in the well.

The most simple and straightforward way to determine the dynamic correlation in liquids, is to start from the basis of single-particle motion. Utilizing the concept of Brownian motion of particles, we can study

the theories of transport in dense fluids [14], and then compute the dynamic correlation functions. We use the time-dependent Langevin equation which shows the dependency of the transport coefficient on the wave vector and frequency, and the theory of Glass and Rice [15] in static harmonic approximation to evaluate the velocity autocorrelation function and power spectrum, in molten Mg–Zn alloy, treating the binary melt as a one-component system like a liquid metal. This has been done by introducing the concept that the motion of “effective atoms” in an alloy is analogous to the single-particle motion in liquid metals.

The differential equation they obtained is

$$\frac{d^2\psi}{dt^2} + \frac{d\psi}{dt} + \omega_0 = 0 \quad (9)$$

where  $\psi = \langle v(t)v(0) \rangle / \langle v^2 \rangle$ ,  $\langle v^2 \rangle$  being the average thermal velocity. The solution for the above equation can be written as

$$\psi(t) = \exp(-\beta_0 t/2) [\cos(\xi t) + \beta_0/\xi \sin(\xi t)] \quad (10)$$

where

$$\xi^2 = \omega_0^2 - \beta_0^2/4 \quad (11)$$

and

$$\beta_0 = (MD/k_B T) \omega_0^2 \quad (12)$$

where  $M$  and  $D$  are the effective mass and diffusion coefficient of the alloy (see Table I).

Apart from the velocity autocorrelation function which defines the microscopic motion of atoms during short times, another important dynamic parameter is the power spectrum,  $g(\omega)$ , which is actually the cosine Fourier transform of  $\psi(t)$ . It is given by [15]

$$g(\omega) = \frac{k_B T}{MD} \int dt \cos(\omega t) \psi(t) \quad (13)$$

Liquids unlike solids, do not form a regular array, the atoms being more mobile than in solids. Hubbard and Beeby [16] first considered a cold amorphous solid which is in a disordered state and finally developed a theory by generalizing in a straightforward fashion, to allow for the motion of atoms in the disordered system. They thus obtained the following expressions for the longitudinal and transverse phonon frequencies

$$\omega_L^2(k) = \omega_0^2 \left[ 1 - \frac{3 \sin k\sigma}{k\sigma} - \frac{6 \cos k\sigma}{(k\sigma)^2} + \frac{6 \sin k\sigma}{(k\sigma)^3} \right] \quad (14)$$

$$\omega_T^2(k) = \omega_0^2 \left[ 1 - \frac{3 \cos k\sigma}{(k\sigma)^2} - \frac{3 \sin k\sigma}{(k\sigma)^3} \right] \quad (15)$$

where

$$\omega_0 = \frac{4\pi\rho_{\text{eff}}}{3M} \int dr r^2 g(r) \phi''_{\text{eff}}(r) \quad (16)$$

### 3. Results and discussion

The interaction potential calculated through Equation 6 shows a hard repulsive part followed by an attractive well (see Fig. 1). The oscillations at large  $r$  are less in the sense that the amplitude dampens

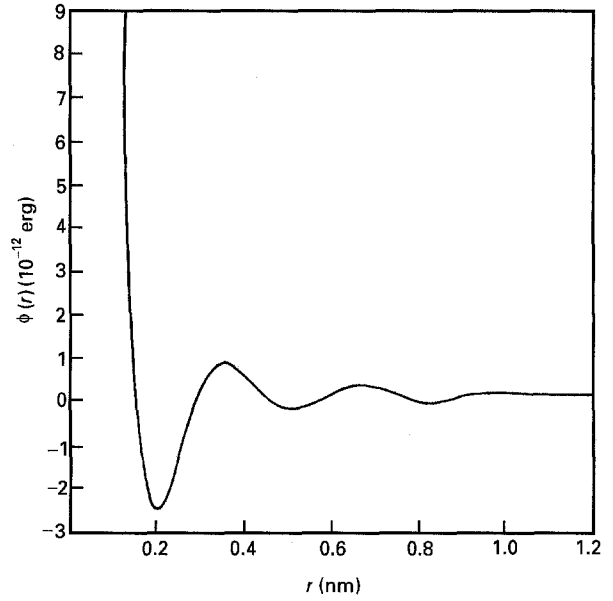


Figure 1 Effective interaction potential of Mg<sub>50</sub>Zn<sub>50</sub> melt at 926 K.

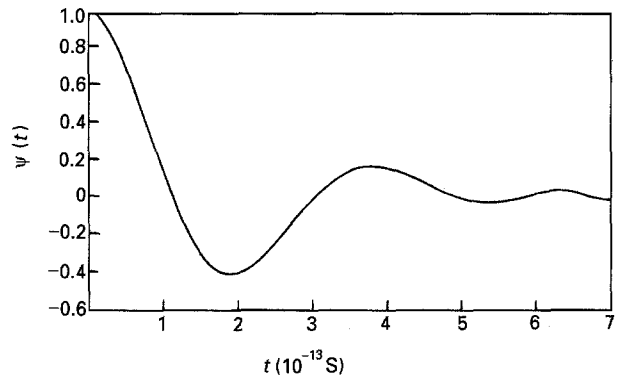


Figure 2 Velocity autocorrelation function  $\psi(t)$  versus  $t$  curve.

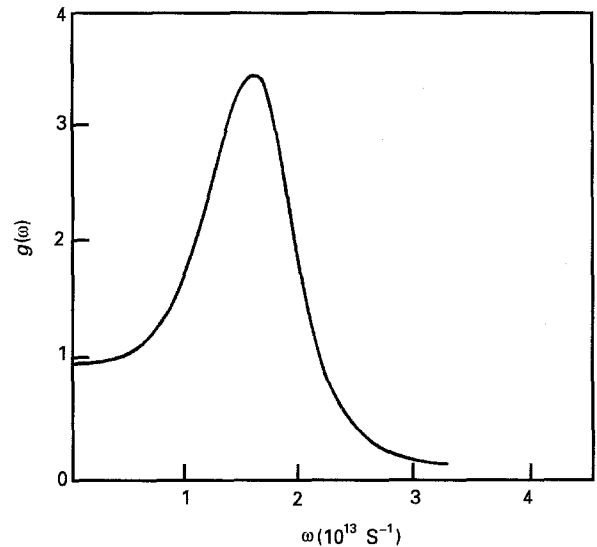


Figure 3 Power spectrum  $g(\omega)$  versus  $\omega$  curve.

quickly because the coulomb repulsive potential dominates over the oscillations due to ion–electron–ion interactions.

The velocity autocorrelation function,  $\psi(t)$ , for molten Mg–Zn alloy as computed, shows rapid initial

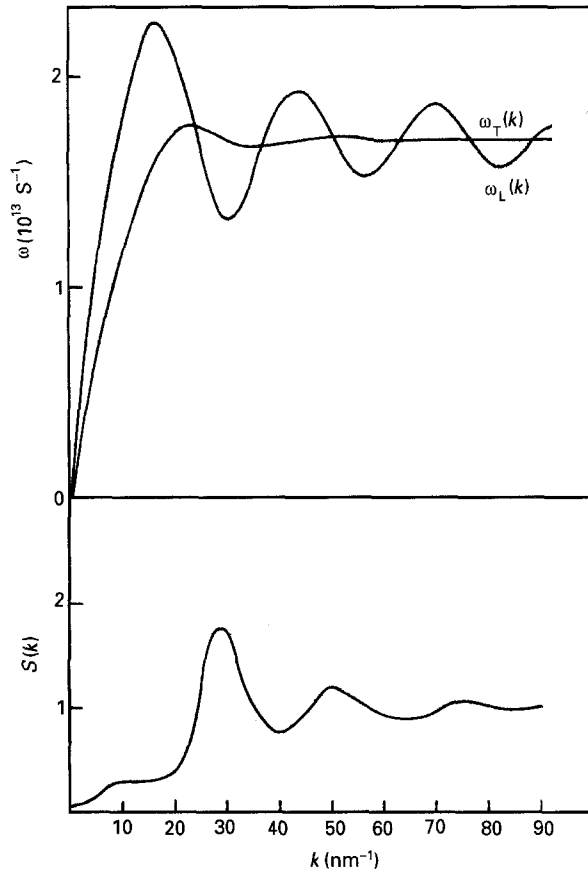


Figure 4 Longitudinal and transverse phonon dispersion curve and structure factor  $S(k)$  versus  $k$  curve.

decay, obeying the boundary condition that  $Lt_{t \rightarrow 0} \psi(t) = 1$ . It then attains a negative minimum and ultimately approaches zero in an oscillatory manner (see Fig. 2). The oscillations in the long-range part account for the collective nature of forces by the surrounding atoms. The cosine Fourier transform of the velocity autocorrelation function gives the power spectrum curve,  $g(\omega)$ , when plotted against  $\omega$ . The importance of this curve is that the maximum value of  $\omega$ , at which  $g(\omega)$  has its peak (Fig. 3), corresponds to the characteristic frequency  $\omega_0$ , with which maximum number of atoms vibrate in the well (see Table I).

The motion of effective atoms are then studied through the collective excitations by computing the longitudinal and transverse phonon frequencies using the theory of Hubbard and Beeby [16]. The dispersion curves so obtained reproduce all the characteristic features, as expected (Fig. 4).

In the low wave-vector region, both the dispersion curves are linear and have the characteristics of elastic waves. Quite significantly the minima in the longitudinal dispersion curve almost coincides with the principal peak position of the structure factor curve, as

predicted by Bhatia and Singh [17] and Takeno and Goda [13] (see Fig. 4). Theoreticians and experimentalists are of the opinion that the minimum arises from a process analogous to the unklapp scattering in crystalline solids and the sharp first maxima in  $S(k)$  acts like a smeared reciprocal lattice vector. The oscillations are predominant in the longitudinal phonon modes as compared to the transverse ones, showing that the collective excitations in the large  $k$  region are due to longitudinal phonons only.

The elastic constants  $C_{11}$  and  $C_{44}$  can be evaluated from the slope of the phonon dispersion curves and compared with those obtained from Schofield's equation [18] which can be written as

$$C_{11} = \rho_{\text{eff}} k_B T \left( 3 + \frac{2I_1}{5} + \frac{I_2}{5} \right) \quad (17)$$

$$C_{44} = \rho_{\text{eff}} k_B T \left( 1 + \frac{4I_1}{15} + \frac{I_2}{15} \right) \quad (18)$$

where

$$I_1 = \frac{\rho_{\text{eff}}}{2k_B T} \int g(r) r \phi'(r) dr \quad (19)$$

$$I_2 = \frac{\rho_{\text{eff}}}{2k_B T} \int g(r) r^2 \phi''(r) dr \quad (20)$$

Knowing  $C_{11}$  and  $C_{44}$ ,  $C_{12}$  can be calculated using Cauchy's relation

$$C_{11} = C_{12} + 2C_{44} \quad (21)$$

The values of the elastic constants obtained show good agreement with each other (Table II).

The isothermal compressibility,  $\beta_T$ , can be obtained from  $C_{11}$  using the following expression

$$C_{11} = \gamma / \beta_T \quad (22)$$

where  $\gamma$  is the specific heat ratio, which is assumed to be unity.  $\beta_T$  can also be calculated from the long-wave limit structure factor  $S(0)$  using the equation

$$S(0) = \rho k_B T \beta_T \quad (23)$$

Further we know that

$$1/\beta_T = \rho_w (v_L^2 - 4v_T^2/3) \quad (24)$$

where  $\rho_w$  is the weight density. The calculated value of  $\beta_T$  using this equation comes out to be 7.89. All the  $\beta_T$  values obtained through different equations are

TABLE II Values of elastic constants

Elastic constant ( $10^{11}$ dyn $\text{cm}^{-2}$ )	Elastic constant ( $10^{11}$ dyn $\text{cm}^{-2}$ )	
	From $\omega(k)$ versus $k$ curve	From $I_1$ and $I_2$ integrals
$C_{11}$	1.39	1.35
$C_{44}$	0.54	0.60

TABLE I Parameters obtained from present calculation, temperature 926 K.

Diffusion coefficient ( $10^{-5}$ $\text{cm}^2 \text{s}^{-1}$ )		Characteristic frequency, $\omega_0$ ( $10^{13}$ $\text{s}^{-1}$ )		
From theor. calc. [20]	From present calc.	From diff. coeff.	From $g(\omega)$ versus $\omega$	From present calc.
5.45	5.46	1.71	1.65	1.68

TABLE III Values for isothermal compressibility

Isothermal compressibility ( $10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ )			
From $C_{11}$ value obtained from $I_1$ and $I_2$ integrals	From theor. calc. [20]	From long-wave limit $S(O)$	From Eq. 24
7.12	7.17	7.68	7.89

TABLE IV Values for Debye temperature

Debye temperature (K)		
From mean value of pure species	From Eq. 25	From Eq. 26
270.0	270.22	267.78

shown in Table III. They show satisfactory interconsistency.

Further, from the low-frequency values of velocity  $v_L(0)$  and  $v_T(0)$  obtained from phonon frequencies, we can evaluate  $\theta_D$ , the Debye temperature through the following equation [17]

$$\theta_D = \frac{h 2\pi 9}{k_B 4\pi} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{1/3} \quad (25)$$

which comes out to be 270.22 K.  $\theta_D$  values for magnesium and zinc are 290 and 250 K, respectively [19]. The mean value is thus 270 K which is quite close to the value obtained through Equation 25.  $\theta_D$  can also be calculated from the following relation

$$\frac{1}{\theta_D^2} = \frac{p_1}{\theta_{D1}^2} + \frac{p_2}{\theta_D^2} \quad (26)$$

where  $\theta_{D1}$  and  $\theta_{D2}$  are the Debye temperatures of the pure species and  $p_1$  and  $p_2$  are their respective atomic fractions. The value comes out to be 267.78 K. All the calculated values thus show good agreement with each other (see Table IV).

#### 4. Conclusion

It is observed that the calculated effective interaction potential using the pseudopotential formalism with the "effective atom" concept gives a satisfactory description of dynamic, elastic and thermal properties of  $\text{Mg}_{50}\text{Zn}_{50}$  melt, at 926 K.

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#### References

1. J. HAFNER, "Amorphous Solid and Liquid State" (Plenum Press, New York, 1985).
2. Y. WASEDA, "The Structure of Non-crystalline Materials: Liquids and Amorphous Solids", (Mc Graw-Hill, New York, 1980).
3. J. HAFNER, "Glassy Metals I, Topics in Applied Physics", Vol. 64 (Springer, Berlin, 1981).
4. J. HAFNER, *Phys. Rev. A* **16** (1976) 351.
5. *Idem*, *J. Phys. F* **6** (1976) 1243.
6. N. S. SAXENA, M. RANI, A. PRATAP, PRABHU RAM and M. P. SAXENA, *Phys. Rev. B* **38** (1988) 8093.
7. M. RANI, A. PRATAP and N. S. SAXENA, *Phys. Status Solidi (b)* **149** (1988) 93.
8. R. V. GOPALA RAO and U. BANDYOPADHYAY, *Ind. J. Pure Appl. Phys.* **30** (1992) 53.
9. N. W. ASHCROFT, *Phys. Lett.* **23** (1966) 48.
10. M. SHIMOJI and T. ITAMI, "Atomic Transport in Liquid Metals", (Trans Tech, Aedermannsdorf, Switzerland, 1986).
11. K. C. JAIN, N. GUPTA and N. S. SAXENA, *Phys. Status Solidi (b)* **162** (1990) 395.
12. J. HAFNER and V. HEINE, *J. Phys. F* **13** (1983) 2479.
13. S. TAKENO and M. GODA, *Progr. Theor. Phys.* **45** (1971) 331.
14. S. A. RICE and P. GRAY, "The Statistical Mechanics of Simple Liquids" (Interscience, New York, 1965).
15. L. GLASS and S. A. RICE, *Phys. Rev. B* **176** (1968) 239.
16. J. HUBBARD and J. L. BEEBY, *J. Phys. C* **2** (1969) 556.
17. A. B. BHATIA and R. N. SINGH, *Phys. Rev. B* **31** (1985) 4751.
18. P. SCHOFIELD, *Proc. R. Phys. Soc.* **88** (1966) 149.
19. MOLWYN HUGHES, "Physical Chemistry" (Pergamon Press, London, 1961).
20. R. V. GOPALA RAO and U. BANDYOPADHYAY, *J. Phys. Condensed Matter*. **C1** (1990) 3879.

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