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Structure factors and phonon dispersion in liquid $Li_{0.61}Na_{0.39}$ alloy

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Abstract. The phonon spectra for liquid Li and Na have been computed through the phenomenological model of Bhatia and Singh for disordered systems like liquids and glasses and the obtained results have been compared with the available data obtained by inelastic neutron scattering (INS) and inelastic X-ray scattering (IXS) experiments. The effective pair potentials and their space derivatives are important ingredients in the computation of the dispersion curves. The pair potentials are obtained using the pseudo-potential theory. The empty core model proposed by Ashcroft is widely used for pseudo-potential calculations for alkali metals. But, it is thought to be unsuitable for Li because of its simple 1s electronic structure. However, it can be used with an additional term known as Born–Mayer (BM) core term. The influence of the BM core term on the phonon dispersion is discussed. The same pseudo-potential formalism has been employed to obtain the dispersion relation in liquid $Li_{0.61}Na_{0.39}$ alloy. Apart from the phonon spectra, the Ashcroft–Langreth structure factors in the alloy are derived in the Percus–Yevick approximation.

Keywords. Dispersion curves; zero alloy; Born–Mayer core.

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1. Introduction

Collective excitations in fluids have been studied experimentally, theoretically and by computer simulations for almost four decades [1–4]. Lot of effort has been put to the study of the dynamical properties of liquid metals [5] both theoretically and experimentally. The investigation of collective modes in liquid alloys has, comparatively received less attention. Interest in the collective excitations in liquid binary systems was generated by the pioneering work of Jacucci and McDonald [6] carried out in $Na_{0.5}K_{0.5}$ liquid alloy. After that, several other experimental [7,8] and theoretical studies [9–11], including molecular dynamics (MD) simulations [12–14] have been performed. In this work, we present a theoretical study on the structural features of liquid $Li_{0.61}Na_{0.39}$ alloy, which exhibits typical phase separation tendency. This binary liquid alloy at this particular composition, i.e. $Li_{0.61}Na_{0.39}$ is called

'zero alloy'. This composition has the particular advantage that, due to the negative scattering length of ^{7}Li, coherent scattering is only from concentration fluctuations $S_{cc}(Q,\omega)$, i.e. $S(Q) = S_{cc}(Q)/C_{\mathrm{Li}}C_{\mathrm{Na}}$; and the coefficient for scattering from number density fluctuations, $S_{\mathrm{NN}}(Q,\omega)$ is zero. Small angle X-ray scattering [15] and neutron diffraction studies [16] have examined the structure factor of this alloy. The measured total dynamical structure factor, $S(Q,\omega)$, in the explored (Q,ω) region decreased monotonically as a function of ω, and side peaks, which would have indicated collective modes, were absent. Recently, dynamical properties of liquid Li–Na alloy at 'zero alloy' composition by orbital-free *ab initio* molecular dynamics (OF-AIMD) [17] and memory function formalism [18] have revealed the existence of propagating sound modes.

Stimulated by the recently reported collective excitations by MD simulation, which is not exhibited by the Li–Na alloy at 'zero alloy' composition, we present in this paper, the computed dispersion relations using effective pair potentials derived by pseudo-potential method incorporated in phenomenological theory of phonons in disordered systems proposed by Bhatia and Singh [19]. Our results agree both qualitatively and quantitatively well with those obtained from IXS experiments for liquid Na and also qualitatively fairly well with the IXS results and neutron data in the case of liquid lithium. The computed phonon spectra for liquid $\mathrm{Li}_{0.61}\mathrm{Na}_{0.39}$, 'zero alloy', are in fair agreement with both the MD simulation results, one obtained using memory function formalism and the other recently reported data through OF-AIMD method.

2. Theory

The pair potential in pseudo-potential formalism is expressed as

$$V(r) = Z^2/r\left(1 - \frac{2}{\pi}\int F_{\mathrm{N}}(q)\frac{\sin(qr)}{q}\,\mathrm{d}q\right), \tag{1}$$

where the symbols have their usual meaning. In the present case, the pair potential given by eq. (1) includes an additional Born–Mayer core term $A\mathrm{e}^{-\alpha r}$. Then, the direct interaction between the ions will be given by the term

$$Ze^2/r + A\mathrm{e}^{-ar}, \tag{2}$$

where $A = a[1 + 2Z/n]\exp(2\alpha R_{\mathrm{BM}})$ with $\alpha = 1.533$ a.u. and $a = 2.296$ a.u. for all metals.

The theory of Bhatia and Singh for phonon dispersion in disordered systems assumes that (i) the ions interact with a central pair-wise potential $V(r)$, which is effective between nearest neighbour only and (ii) the force on an ion could be calculated using Thomas Fermi method. Under these assumptions, the expressions for the longitudinal and transverse phonon frequencies are

$$\rho\omega_{\mathrm{L}}^2 = \frac{2n_c}{a^2}(\beta I_0 + \delta I_2) + \frac{\kappa_e\kappa_{\mathrm{TF}}^2[G(qr_s)]^2}{q^2 + \kappa_{\mathrm{TF}}^2\tilde{g}(q)}, \tag{3}$$

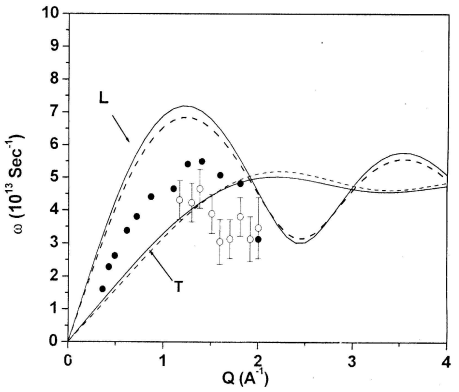

Figure 1. Phonon dispersion curves for liquid Li. - - - Present results with BM core, —— present results without BM core, • INS results [21], ○ IXS results [22].

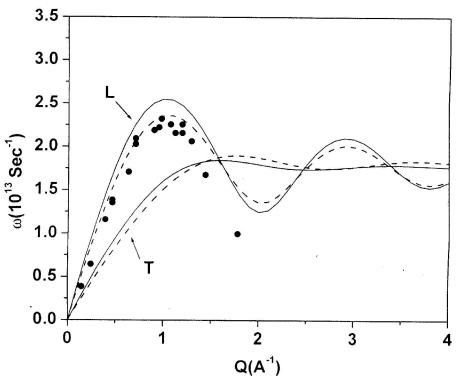

Figure 2. Phonon dispersion in liquid Na. - - - Present results with BM core, —— present results without BM core, • IXS results [22].

$$\rho\omega_{\mathrm{L}}^2 = \frac{2n_c}{a^2}\left[\beta I_0 + \frac{1}{2}\delta(I_0 - I_2)\right]. \tag{4}$$

The details of the above two expressions can be seen in ref. [19].

3. Results and discussion

The phonon eigenfrequencies have been computed using eqs (3) and (4) incorporating the derivatives of the pair potential defined by eq. (1), both considering Born–Mayer core expressed by eq. (2) and also without it. Out of the longitudinal and transverse phonon modes defined by eqs (3) and (4) shown in figure 1, the longitudinal phonon modes of liquid lithium agree fairly well with both inelastic x-ray scattering results [20] from $0.4A^{-1} \geq Q \leq 2.0A^{-1}$ and with the INS data [21] from $1A^{-1} \geq Q \leq 2.0A^{-1}$. The longitudinal phonon branch of the computed curve shown in figure 2 for liquid sodium is in excellent agreement with the experimental inelastic X-ray data of Pilgrim *et al* [22].

The two branches of the dispersion relation obtained in figure 3 for the liquid $Li_{0.61}Na_{0.39}$ are in fair match with the MD simulation results obtained both using the memory function formalism [18] and the more recently reported one, namely OF-AIMD simulation [17]. The Ashcroft–Langreth [23] partial structure factors for the $Li_{0.61}Na_{0.39}$ alloy are shown in figure 4.

As a concluding remark, we can say that the phonon dispersion obtained in the present work for $Li_{0.61}Na_{0.39}$ liquid alloy shows well-defined collective modes analogous to those found in other binary fluids. Our findings are in line with the recently reported MD simulations [21,22]. However, the longitudinal branch of the dispersion curve obtained from MD simulation lies above the present computed results. This deviation may be attributed to the difference of temperature in two cases. The present computational work has been carried out at 590 K, whereas the dynamical

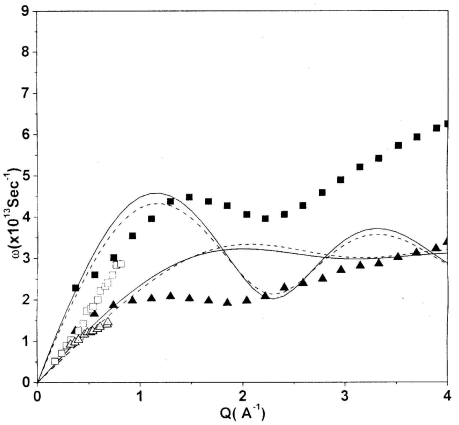

Figure 3. Phonon dispersion in liquid $Li_{0.61}Na_{0.39}$ alloy. - - - Present results with BM core, —— present results without BM core, ■ longitudinal branch from MD simulation using memory function, ▲ transverse branch from memory function, □ longitudinal branch from OF-AIMD simulation, Δ transverse branch from OF-AIMD simulation.

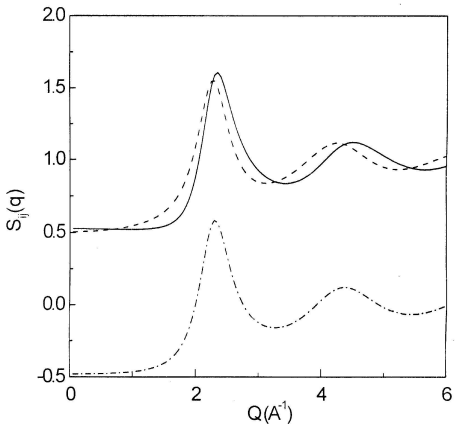

Figure 4. Ashcroft–Langreth partial structure factors. - - - Na–Na, —— Li–Li, - · - · - Li–Na.

properties of $Li_{0.61}Na_{0.39}$ alloy have been studied through MD simulations [18] at 725 K. This behaviour shows that the life-time of the phonon becomes shorter with increasing temperature. For the longitudinal mode, the peak position shifts to the high energy side at large wave numbers. Similar variation in longitudinal phonon frequency with temperature has been observed in liquid $Zr_{67}Ni_{33}$ alloys [24]. Further, the effective pair potentials used in MD simulations have been derived by neutral pseudo-atom (NPA) method. In the present computation, on the other hand, empty core model (ECM) pseudo-potentials have been utilized.

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