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Static structure, microscopic dynamics and electronic properties of the liquid Bi–Pb alloy. An *ab initio* molecular dynamics study

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ABSTRACT

We perform an *ab initio* molecular dynamics study of the static, dynamic and electronic properties of the liquid Bi_xPb_{1-x} alloy at three concentrations, including the eutectic one, $x = 0.55$. This alloy is of particular technological interest for its possible use as coolant in fast reactors. Our predictions are in good agreement with the available experimental data. In particular, the computed total static structure factors reproduce accurately the neutron diffraction results, and the predicted adiabatic sound velocity and shear viscosity compare well with the experimental values. The partial dynamic structure factors exhibit clear side peaks indicative of propagating density fluctuations, and the longitudinal and transverse dispersion relations show several branches, which we analyze in detail. The electronic density of states show that the liquid Bi–Pb alloy is a good metal, but with strong deviations from the free-electron parabolic curve.

1. Introduction

Heavy liquid metals such as liquid lead (*l*-Pb), liquid bismuth (*l*-Bi) and the lead–bismuth eutectic (LBE) alloy were proposed as possible coolants for fission reactors as early as in the 1950s, although it was finally *l*-Na the preferred choice in the 1960s. However, the LBE alloy was used as coolant in small fission reactors developed during that period in the USSR. More recently, there has been a renewed interest in the LBE alloy as a coolant for the new generation of fast reactors as well as an accelerator-driven system for the transmutation of high-level radioactive waste (see, e.g., Refs. [1,2]). There are a number of features which make the LBE alloy an excellent candidate as coolant in fast reactors; among others, the following: (i) the LBE alloy melts at 398 K and boils at 1943 K, which implies a wide temperature range for the existence in the liquid state, (ii) the LBE is chemically inert with air and water and it has good heat transfer characteristics, and (iii) it has low moderation and low neutron absorption and activation, which is of paramount importance for a fast reactor. Consequently, given its technological importance, it is of great interest to perform a comprehensive study of the properties of the liquid Bi_xPb_{1-x} alloy at several concentrations, including the eutectic one $x = 0.55$, in order to achieve a better understanding of the behavior of this peculiar liquid–metal system. For this purpose, *ab initio* molecular dynamics (AIMD) methods, which have become widespread in recent years, are particularly useful because they provide accurate information of the properties of condensed matter systems in general and, in particular, those of liquid metals.

Recently, we have investigated the properties of *l*-Pb [3] and *l*-Bi [4] by means of AIMD simulations based on PARSEC, a real-space implementation of pseudopotentials constructed within the density functional theory (DFT) [5]. The computed results showed a good general agreement with available experimental data, thus confirming the adequacy of this technique to achieve a reliable description of the properties of heavy liquid metals. In the work described here we use the same AIMD method to investigate the static, dynamic and electronic properties of the liquid Bi_xPb_{1-x} alloy, with special attention to the eutectic composition. The study is not trivial since specific problems arise when passing from the one-component systems to binary alloys. We note that the experimental information of the dynamic properties of the liquid Bi_xPb_{1-x} alloy, including the transport coefficients, is very scarce. However, the total static structure factor has been obtained by both neutron scattering (NS) [6,7] and X-ray (XR) methods [7–9] at several concentrations and temperatures. These structural results, along with some thermodynamic measurements [8,9], suggest an hetero-coordination tendency in the system, i.e., a preference for unlike atom pairs. As it will be seen, the hetero-coordination tendency in the liquid Bi_xPb_{1-x} alloy, which has been predicted by classical molecular dynamics (CMD) simulations using a semiempirical potential based on the tight-binding method [10], is manifested in several of the properties investigated in the present paper by AIMD simulations.

In Section 2 we briefly describe the computational method used in the present work, giving the technical details which are strictly necessary. In Section 3 we present and discuss our results,

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comparing them with available experimental data. Finally, in Section 4, we summarize our main conclusions.

2. Technical details

Computational approaches based on DFT have proved to be very successful in the study of the electronic structure of matter. Among these approaches, the real-space pseudopotential techniques present several computational advantages (see, e.g., Ref. [11]). Pseudopotential theory allows one to focus on the chemically active valence electrons by replacing the strong all-electron atomic potential by a weak pseudopotential, which effectively reproduces the effects of the ionic core on the valence states. On the other hand, working in the real-space has some advantages that make such methods highly attractive for computation of the electronic structure of large and complex systems. For example, there is no "formal" basis, calculations being performed directly on a real-space grid which is independent of the ionic positions; in fact, only one parameter, the spacing of the grid, needs to be refined to control convergence. Moreover, real-space methods are semi-local, which facilitates implementation on parallel computers.

In this work, we adopted a real-space pseudopotential approach to study the liquid alloy Bi_xPb_{1-x}. Specifically, we performed AIMD simulations using the PARSEC code [5]. In this method, the Kohn–Sham equations are solved self-consistently on a rectangular three-dimensional real-space grid within a supercell geometry [12]. The core electrons of the Bi (Pb) atoms were represented by norm-conserving pseudopotentials generated for the reference configurations $[Xe](4f^{14}5d^{10})6s^2 6p^3 6d^0 5f^0$ ($[Xe](4f^{14}5d^{10})6s^2 6p^2 6d^0 5f^0$) using the Troullier–Martins prescription [13], with a radial cutoff of 3.0 a.u. (3.2 a.u.), for the *s*, *p*, *d*, and *f* channels. The potentials were made separable by the procedure of Kleinman and Bylander [14], with the *p* potential chosen to be the local component. The partial-core correction for nonlinear exchange correlation was included. The local density functional of Ceperley and Alder [15] was used as parameterized by Perdew and Zunger [16], and the single Γ-point was employed in sampling the Brillouin zone. A spacing of 0.64 a.u. was used for constructing the real-space grid.

Calculations were performed at the three thermodynamic states shown in Table 1. One hundred and sixty atoms were placed at random in a cubic supercell with dimensions chosen so as to obtain the experimental number density corresponding to each state [6]. The cell was coupled to a virtual heat bath via the Langevin equation of motion [17] and was heated to far above the target temperature in order to eradicate any memory of its initial configuration; the temperature was then set to the required temperature, the system allowed to stabilize, and gradually decoupled from the virtual heat bath; and finally an AIMD simulation run was performed over 10,000 time steps (50 ps of simulated time), ion dynamics being generated using the Beeman algorithm [18] with Hellmann–Feynman forces [19]. Only data from this latter simulation run were used in calculating the static, dynamic and electronic properties reported below.

Table 1
Thermodynamic data of the liquid Bi_xPb_{1-x} alloy used as imput in the present AIMD study. The values of the total ionic number density, ρ, were taken from Ref. [6].

$x = x_{Bi}$	ρ (Å^{-3})	T (K)
0.30	0.03077	540
0.55	0.03025	450
0.80	0.02958	540

3. Results

3.1. Structural properties

Fig. 1 shows the calculated partial pair-distribution functions $g_{ij}(r)$ of the liquid Bi_xPb_{1-x} alloy at the three concentrations considered in this work. They undergo appreciable changes as the Bi concentration is varied, although the positions of the maxima in $g_{BiBi}(r)$ and $g_{PbPb}(r)$ are almost independent of concentration due to the fact that the Bi and Pb atoms have similar atomic radii. The changes in $g_{BiBi}(r)$ are less marked than those in $g_{BiPb}(r)$ and $g_{PbPb}(r)$. With increasing the Bi concentration, the height of the main peak of both $g_{PbPb}(r)$ and $g_{BiPb}(r)$ decreases, whereas that of $g_{BiBi}(r)$ slightly increases. For all concentrations, $g_{BiBi}(r)$ has a shoulder at the right hand side of its main peak, which is located at ≈5 Å. A similar feature has been found in the pair-distribution function $g(r)$ of pure *l*-Bi near melting, which was connected with the division of the first coordination shell of a Bi atom in the crystal into two subshells [4].

From the knowledge of $g_{ij}(r)$, the distribution of nearest neighbors (NNs) can readily be obtained. If n_{ij} denote the number of *j*-type particles around an *i*-type particle within a sphere of radius R_{ij}, then

$$n_{ij} = 4\pi\rho x_j \int_0^{R_{ij}} r^2 g_{ij}(r) dr, \qquad (1)$$

where x_j is the concentration of the *j*-type particles and R_{ij} can be identified with the position of the first minimum of the corresponding radial distribution function $G_{ij}(r) = 4\pi r^2\, g_{ij}(r)$ [20]. The calculated n_{ij} are given in Table 2. For all states, the average number of NNs around a Pb atom increases (from 9.6 to 11.04) with Pb concentration towards the corresponding value of pure Pb (around 12) [3]. In a similar way, the number of NNs around a Bi atom decreases (from 9.5 to 7.7) with increasing Bi concentration towards the corresponding value for pure Bi (around 8) [4].

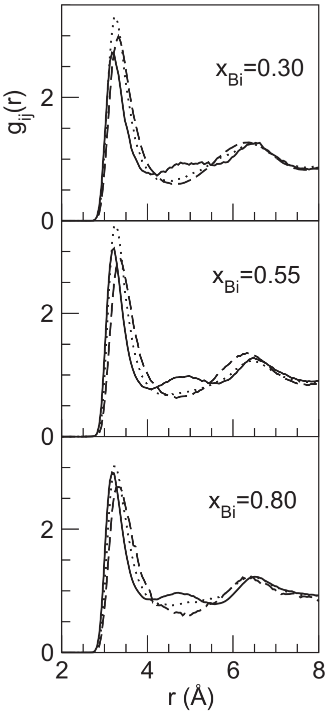

Fig. 1. Partial pair-distribution functions $g_{ij}(r)$ of the liquid Bi–Pb alloy at the three concentrations considered. Full, dashed and dotted lines correspond to $g_{BiBi}(r)$, $g_{PbPb}(r)$ and $g_{BiPb}(r)$, respectively.