

The Structure of Liquid Alloys with Chemical Short Range Order

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Abstract

We present a study of the structural properties of liquid binary alloys with chemical short range order starting from the effective interatomic pair potentials. The interatomic pair potentials are derived using the second order pseudopotential theory and the static structure is obtained using the modified hypernetted chain approximation. The partial structure factors $S_{ij}(q)$ and the concentration - fluctuation structure factor $S_{cc}(q)$ are calculated to analyze the ordering tendencies in a binary alloy.

In this work, liquid Li-Mg alloy is studied as a test case. The agreement between theory and experiment is quite good. We conclude that the structural properties of liquid alloys with chemical short range order, may be studied successfully by employing analytical Pettifor-Ward pair potentials.

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1. Introduction

The main structural and thermodynamic properties of binary liquid alloys with a strongly non-ideal mixing behaviour have been of longstanding interest. Liquid alloys of alkali or alkaline-earth metals with other monovalent and polyvalent metals have been studied very thoroughly. Their thermodynamic excess functions, static structure factors are well known experimentally [1]. However, the theoretical interpretation is still at a rather empirical level and has two main problems: Firstly, the electron-ion pseudopotentials have the problem of non-transferability from pure metal to alloy case. Secondly, the

theoretical determination of $g(r)$ (or of its Fourier transform, the static structure factor $S(q)$) using a suitable statistical mechanics route is also problematic [2].

In earlier works, the proposed pseudopotentials were not successful enough for application to the calculations of thermodynamic properties of systems with chemical short range order [3]. This is mainly due to the long range Friedel oscillations in interatomic pair potentials. This prompts us to consider the application of the Pettifor-Ward (hereafter PW) analytic pair potential in the form of a tree exponentially damped oscillatory terms [4]. This form is proved successful in explaining the structure and thermodynamic properties of liquid simple metals [5,6] and binary alloys which show homocoordination [7,8].

In this work we present a study of chemical short range order (CSRO) in liquid metallic alloys, considering Li-Mg alloy as a test case. In principle, the pseudopotential can be of local or non-local character. But, the present study is based on effective interatomic pair potentials derived from local pseudopotentials using second order perturbation theory. We summarize the theoretical basis for these calculations in Section 2. The evaluation of the interatomic pair potentials are described in Section 2.1. The structure of a binary liquid alloy is calculated using the modified hypernetted chain (MHNC) theory which is described in Section 2.2. The results and conclusion are summarized in Section 3.

2. Theory

2.1. Effective Interatomic Pair Potentials

The computation of the effective interatomic potential is based on the use of second-order pseudopotential theory. The result is ($i, j = 1, 2$)

$$\Phi_{ij}(r) = \frac{z_i z_j}{r} + \Phi_{ij}^{ind}(r), \quad (1)$$

where the Fourier transform (FT) of the indirect part is given by,

$$\tilde{\Phi}_{ij}^{ind}(q) = \chi(q) \tilde{v}_i(q) \tilde{v}_j(q), \quad (2)$$

where the tilde over $v_i(q)$ denotes FT of the electron-ion pseudopotential $v_i(r)$ and $\chi(q)$ is the response function of the electron gas. The effects of exchange and correlation between the electrons are accounted for by the introduction of a local field factor $G(q)$ in the response function as,

$$\chi(q) = \frac{\chi^{(0)}(q)}{1 - \frac{4\pi}{q^2} [1 - G(q)] \chi^{(0)}(q)}, \quad (3)$$

where $\chi^{(0)}(q)$ is the response function of a non-interacting electron gas (Lindhard polarizability). We have used the local density approximation (LDA) [9] version of the local field factor using the correlation energy of Vosko, Wilk and Nussair [10]. The results

thus obtained are compared with those obtained by the use of PW analytic pair potential form,

$$\Phi(r, r_s) = \frac{z_i z_j}{r} \sum_{n=1}^3 A_n \cos(k_n r + \alpha_n) \exp(-\kappa_n r), \quad (4)$$

(for more details see Reference [11].)

2.2. The Liquid State Theory

There is no exact theory of the liquid state. All existing theories necessarily involve some approximation. The central problem of liquid state physics is the determination of the pair correlation function $g(r)$ (or of its Fourier transform, the static structure factor $S(q)$) using the methods of classical statistical mechanics. Two main approaches are usually employed: one involves computer simulation, such as the Monte Carlo (MC), and molecular dynamics (MD) methods. The alternative approach is semi-analytic and may be divided in two classes. One is based on thermodynamic perturbation theory relative to some reference system. The other approach is based on integro-differential equations, relating the pair potential $\Phi(r)$ and the pair correlation function $g(r)$ for a simple liquid. The starting point of most integral equation theories is a Ornstein-Zernike equation (O-Z), which for a homogeneous binary system can be written as

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^2 \rho_k \int h_{ik}(|\vec{r} - \vec{r}'|) c_{kj}(\vec{r}') d^3 \vec{r}'. \quad (5)$$

The O-Z equation decomposes the total correlation function $h_{ij}(r) = g_{ij}(r) - 1$ into the direct correlation function $c_{ij}(r)$, where ρ_k denote the partial ionic number densities. O-Z equation is supplemented by the exact closure relation

$$c_{ij}(r) = h_{ij}(r) - \ln\{g_{ij}(r) \exp[\beta\Phi_{ij}(r) + B_{ij}(r)]\}, \quad (6)$$

where $\Phi_{ij}(r)$ is the interatomic pair potential, $\beta = (k_B T)^{-1}$ is the inverse temperature and $B_{ij}(r)$ denote the bridge function, for which some approximation must be made. In our calculations of structure we use the modified hypernetted chain (MHNC) theory, where the bridge functions are constructed by solving the Percus-Yevick (PY) equation for a reference system interacting with the repulsive part of the given effective interatomic pair potentials; this is known as the MHNC-REP approximation [12].

For binary alloys a complete description of the distribution of interatomic distances requires three structure factors instead of one in the case of a simple liquid. The classical partial structure factors $S_{ij}(q)$, ($i, j = 1, 2$) [13] are related to the number concentration structure factors $S_{\alpha\beta}(q)$, ($\alpha, \beta = N, C$), which have been proposed by Bhatia and Thornton [14]. Direct information on short range order is offered by $S_{\alpha\beta}(q)$. Each of the three $S_{\alpha\beta}(q)$ and vice versa. Important relations also exist between $S_{\alpha\beta}(0)$, which is the long wavelength limit of this structure factor and $S_{ij}(0)$. Its concentration dependence has been shown to be related to the bonding type and to the occurrence in the melt of

chemical equilibria. Some information about the composition fluctuations in liquid alloys can be obtained from the value of $S_{CC}(0)$. There is an important relation between the concentration-concentration structure factors $S_{CC}(q)$ and the experimentally measured total static structure factor $S(q)$, namely $S(q) = S_{CC}(q)/c_1c_2$, where c_1 and c_2 are concentrations of 1 and 2 species.

3. Results and Conclusion

The theoretical basis described in the preceding section was applied to study the structure of liquid Li-Mg alloys. The phase diagram of Li-Mg shows that Li and Mg are completely miscible in liquid state and even show some heterocoordination. Ruppertsberg et.al., [15] have studied both the thermodynamic properties and structure of liquid Li-Mg alloys at several compositions and temperatures. Experimental results, at temperatures $T = 675\text{K}$ and 875K , and Mg concentration $c_{Mg} = 0.3$, the latter corresponding to the zero alloy, shows some preference for heterocoordination. Hafner et.al. [16] have studied for Li-Mg alloys at $T=940\text{K}$. Their theoretical results predict a weak tendency towards heterocoordination. We have used the same experimental densities of Li-Mg alloys measured experimentally.

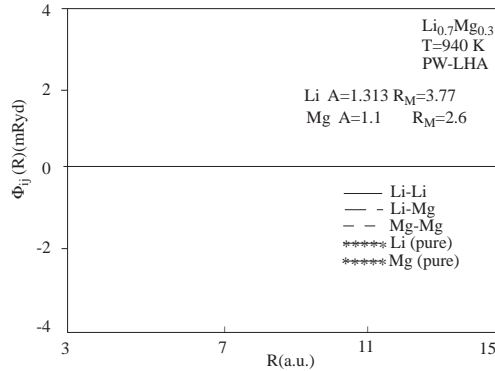


Figure 1. Effective interatomic pair potentials $\Phi_{ij}(R)$, which are obtained by the PW analytic pair potential form using LHA pseudopotential for $\text{Li}_{0.7}\text{Mg}_{0.3}$ liquid alloy, calculated at $T=940\text{K}$.

As already indicated in Section 2, the evaluation of the interatomic pair potential requires, the electron-ion pseudopotential. In this work two different model pseudopotentials, the local Heine-Abarenkov pseudopotential (LHA) and Ashcroft Empty-Core pseudopotential (EC) are studied. The model radius R_M for LHA model potential are from Ref. [17]. The other LHA model potential parameter A for Mg is 1.1, which is fitted by adjusting the height of the first peak of the static structure factor $S(q)$, and for Li the A value that is used is the same value used for Li-Na alloys given in Ref. [8]. In the case of EC model potential, the adjustable parameter r_c is fitted by adjusting the height of

the first peak of the static structure factor $S(q)$, and found to be 1.46a.u. and 1.53a.u. for Li and Mg, respectively.

The interatomic pair potentials derived from LHA model potential using PW analytic pair potential form are shown in Figure 1. The results, obtained by using EC model potential are given in Figure 2 for purposes of comparison.

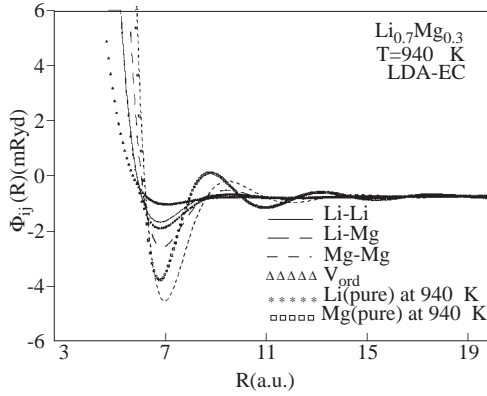


Figure 2. Effective interatomic pair potentials $\Phi_{ij}(R)$ for the $\text{Li}_{0.7}\text{Mg}_{0.3}$ liquid alloy, calculated at $T=940\text{K}$ derived from EC pseudopotential using LDA.

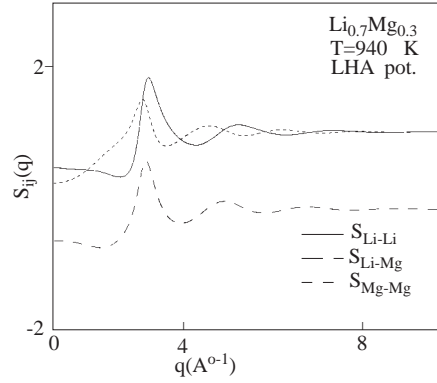


Figure 3. The partial static structure factors $S_{ij}(q)$ calculated for the $\text{Li}_{0.7}\text{Mg}_{0.3}$ liquid alloy at $T=940\text{K}$ using LHA potential.

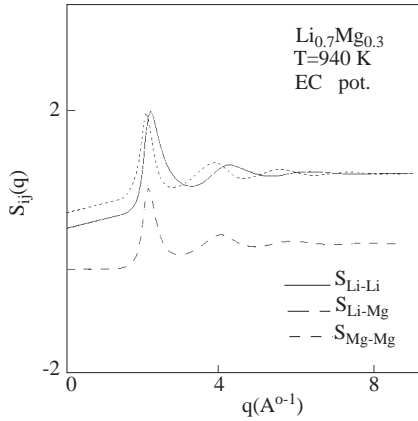


Figure 4. The partial static structure factors $S_{ij}(q)$ calculated for the $\text{Li}_{0.7}\text{Mg}_{0.3}$ liquid alloy at $T=940\text{K}$ using EC potential.

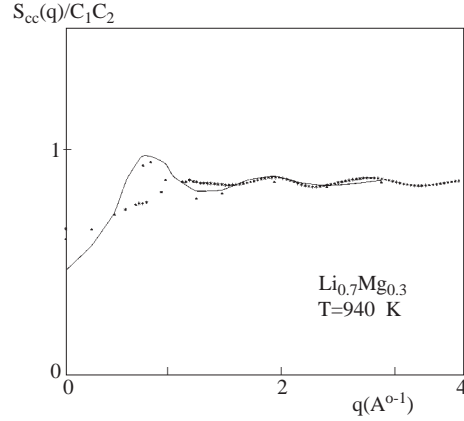


Figure 5. Total static structure factors. Solid line: experimental data for Li-Mg [15], stars: EC potential results, solid triangles: LHA potential results.

We have used two different approaches to calculate $S_{ij}(q)$, which differ in the form of the local-field correction $G(q)$ used. The PW results using LHA are shown in Fig. 3. The LDA results using EC are shown in Fig. 4.

These partial static structure factors are then used to calculate $S_{cc}(q)/c_1c_2$. The results are shown in Fig. 5. As may easily be seen from the figure, the LHA-PW results are in better agreement with the experiment. The LHA-PW approach will be tested better if it is applied to those alloys that show stronger chemical short range order.

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