

Diffusion coefficient of copper, tin and copper tin alloy

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Abstract. Pseudopotential formalism is used to construct an ionic effective potential (ion-ion potential screened by electrons). Molecular Dynamics is used in conjunction with the constructed effective potential to get the atomic structure factor of the pure components copper and tin which are compared to the experimental ones.

We selected the Shaw Optimized Model Potential having proved that it adequately describes the atomic structure, we used it to calculate the velocity autocorrelation function and to deduce the self diffusion of pure metals: copper, tin and the diffusion coefficient of copper in the $\text{Sn}_{95,6\%}\text{Cu}_{4,4\%}$.

1 Introduction

The study of diffusion in liquid metals is of scientific importance as well as potential application in material science, physics and chemistry field [1 to 4]. The traditional lead-tin solders have been widely used in the industry for a long time. The lead poisoning commonly occurs following prolonged exposure to lead or lead compounds. The damage often is induced slowly, but definitely, it is now well recognized as a health threat. The solder materials containing lead are replaced by lead free solder materials in electronic products.

To study the atomic transport properties of liquid tin and copper which are depended both on the electronic and the ionic structure, we use the pseudopotential formalism to construct an ionic effective potential (ion-ion potential screened by electrons). Molecular Dynamics is used in conjunction with the constructed effective potential to get the atomic structure factor of pure copper and tin and the $\text{Sn}_{95,6\%}\text{Cu}_{4,4\%}$ alloy which is a well known lead free solder. Our methodology is to use a local pseudopotential [5], to fit the core parameter on the atomic structure of the pure metal which is a very severe criterium. For noble

metals we used the concept of effective valence [6]. Then we calculate consistently the velocity autocorrelation function and we deduce the self diffusion of pure metals: copper, tin and the diffusion coefficient of copper in the $\text{Sn}_{95,6\%}\text{Cu}_{4,4\%}$.

We used the local Optimised Model Potential (OMP) proposed by Shaw [5] and the Ichimaru-Utsumi [7] dielectric function. We use $Z=4$ as chemical valence for tin, and $Z_{\text{eff}}=1.56$ [6] for copper taken from the bibliography.

The structure calculation was performed by molecular dynamics (MD) on a 4000 particles NVT system. Our calculated pair correlation functions and structure factors are compared to the experimental ones. We first present the calculation of the ion-ion effective potential. We show that the local Shaw pseudopotential represents very good the structure of the pure metals (what is not true for all pseudopotentials). More, it is transferable to the alloy since a very good agreement is obtained for the copper-tin liquid alloy. We also discuss the coherence with the electronic transport properties such as the diffusion coefficient. Then we conclude. (Unless explicitly stated

otherwise, atomic units are used throughout: $\hbar = e = m = 1$).

2 Effective potential

The local pseudo-potential theory is clearly explained in the references [7-9]. The expression of the ion-ion effective potential $V(r)$ calculated from the pseudo-potential for alloys is given by:

$$V_{(2)}(\vec{R}_a, \vec{R}_b) = V_{\text{eff}}^{ab}(r) = \frac{Z_a Z_b}{r} \left[1 - \frac{2}{\pi} \int F_{ab}^N \frac{\sin qr}{q} dq \right]$$

Here the quantity r is the inter-ionic distance. The index a and b refer to atoms of type a and b . Z_a and Z_b are the effective valence characterizing each metals.

The normalized energy wave number characteristic $F_{ab}^N(q)$ in reciprocal space is defined from the Fourier transform of the local electron-ion model potential:

$$F_{ab}^N(q) = \frac{1}{Z_a Z_b} \left(\frac{\Omega_0 q^2}{4\pi} \right)^2 w_a(q) w_b(q) \frac{\varepsilon(q) - 1}{\varepsilon(q) [g_{xc}(q) - 1]}$$

Where Ω_0 is the mean atomic volume. The quantity $\varepsilon(q)$ is the dielectric function, and the function $g_{xc}(q)$ is the exchange and correlation term. We use the Shaw local pseudo-potential, whose expression in real space is:

$$w_0(r) = \begin{cases} A & r < R_c \\ -\frac{Z_{\text{eff}}}{r} & r < R_c \end{cases}$$

For the local Shaw [9] Optimized Model Potential (OMP), the core radius R_c is given by the optimization condition, ($A = -Z_{\text{eff}}/R_c$). The Fourier transform $w_0(q)$ of $w_0(r)$ is expressed as:

$$\hat{w}_0(q) = \frac{1}{\Omega_0} \int e^{-i\vec{q}\vec{r}} w_0(r) d^3r$$

3 Molecular dynamics

The structure is calculated by a simulation code. This code uses the standard Verlet [10] algorithm and processes in NVT ensemble. The number of involved particles in the cubic simulation box for pure copper is equal to 4000. More, we consider periodic conditions. The side length is equal to 44.51 Å. The time step δt is equal to $2 \cdot 10^{-15}$ s and the number of iterations after thermalization is equal to 20000. The code computes the pair correlation function $g(r)$ for each configuration and gives the mean value.

$$g_{ab}(r) = \frac{dn_{ab}(r)}{4\pi r^2 \rho_b dr}$$

$$\rho_b = c_b \times \rho_a$$

with

The partial structure factors are calculated by the Faber Ziman formalism:

$$a_{ab}(q) = 1 + \frac{4\pi\rho_0}{q} \int_0^\infty r (g_{ab}(r) - 1) \sin(qr) dr$$

The total structure factor $S(q)$ is simply obtained from:

$$S_{\text{total}}(q) = \sum_a \sum_b c_a c_b \frac{f_a(q) f_b(q)}{\langle f(q) \rangle^2} a_{ab}(q)$$

4 Atomic transport properties

The same recorded atomic configurations allow us to calculate the self-diffusion constant D at a given temperature from the recorded atomic velocities $\vec{v}_{i(a)}(t)$ at time t , by integral over the velocity autocorrelation function (VAF) $Z_{ab}(t)$ defined as follows [11-13].

$$Z_{ab}(t) = \frac{1}{3} X_a X_b N (\vec{v}_a(t) - \vec{v}_b(t)) \cdot (\vec{v}_a(0) - \vec{v}_b(0))$$

Where N is the total number of particles,

$$\vec{v}_a(t) = \frac{1}{N_a} \sum_{l(a)=1}^{N_a} \vec{v}_{l(a)}(t)$$

N_a is the number of a -type particles, $\vec{v}_{l(a)}(t)$ is the velocity of the a -type particle $l(a)$. $Z_{ab}(t)$ is defined as the time correlation function of the relative velocity of the centre of mass of species a with respect to the center of species b . It is decomposed into self-contributions, $Z_{ab}^0(t)$ and distinct contribution: $Z_{ab}^d(t)$:

$$Z_{ab}(t) = (1 - \delta_{ab}) Z_{ab}^0(t) + x_a x_b Z_{ab}^d(t)$$

Where $Z_{ab}^d(t)$ is Kronecker's symbol.

$$Z_{ab}^0(t) = x_b Z_a^s(t) + x_a Z_b^s(t)$$

$Z_a^s(t)$ is the velocity autocorrelation function of a tagged a -type particle in the fluid. The time integrals of all the $Z_{ab}(t)$, $Z_{ab}^0(t)$, $Z_{ab}^d(t)$ and $Z_{ab}^s(t)$ give the associated diffusion coefficients (DC), namely D_{ab} , D_{ab}^0 , D_{ab}^d and D_{ab}^s respectively. The D_{ab}^s is the usual self diffusion coefficients.

$$D_{12} = D_{12}^0 + x_1 x_2 D_{12}^d = D_{12}^0 (1 + \gamma_{12})$$

With $D_{12}^0 = x_2 D_1^s + x_1 D_2^s$ and γ_{12} measures the deviation from an ideal mixture, it equals zero when all species are identical.

The interdiffusion coefficient is given:

$$D_{\text{int}} = \theta D_{12} = \theta (1 + \gamma_{12}) D_{12}^0$$

Where $\theta = x_1 x_2 / S_{cc}(q \rightarrow 0)$ For a nearly ideal mixture

$$\theta \approx 0, \gamma_{12} = 0 \text{ And therefore } D_{\text{int}} = D_{12}^0$$

$S_{cc}(q)$ are the partial Bhatia-Thornton concentration-concentration structure factors.

5 Results and discussion

For both metals the density is calculated using Lucas [14] compilation of density as a function of temperature under the form: $d = a - b(T - T_M)$, where T_M is the melting temperature of the metal. These parameters are given in Table 1.

Table 1. Density parameters [14] of the two heavy metals used for our calculations.

Element	copper	tin
T_M (°C)	1084,5	232
Density value a ($g \cdot cm^{-3}$)	7,937	6.986
Density value b ($g \cdot cm^{-3} \cdot K^{-1}$)	7,325	6.38

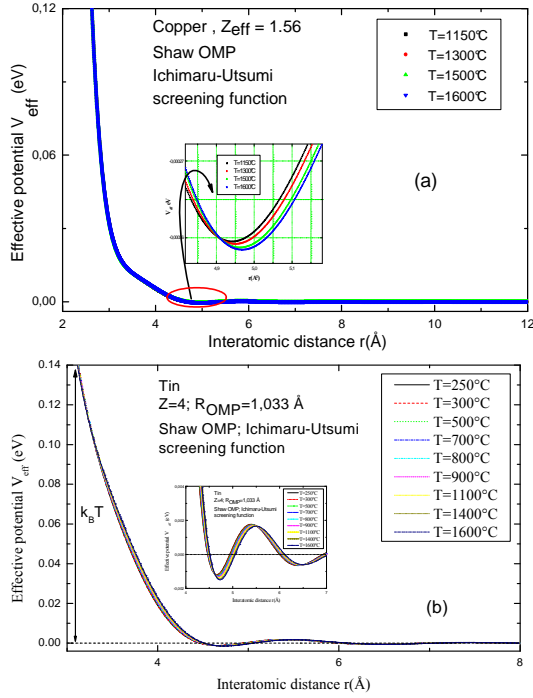


Fig. 1: Ion-ion effective potential for: (a) Copper: $Z = 1.56$, (b) tin: $Z = 4$.

The effective potentials for liquid copper and tin are calculated, from the OMP local pseudo-potential, with respectively core radius values equal to $1,57\text{\AA}$ and $1,032\text{\AA}$. For alloys, we work with the same parameters than for pure metals. (see Figure 1).

We then calculate by DM the pair correlation functions which are displayed together with the Waseda's experimental ones. The structure factor is obtained by Fourier transformation. Our calculated curves are compared to experimental ones (copper: figure 2, tin: figure 3). The results are of Waseda [15], Eder (Square) [16], Alemany (Apriangle) [17]

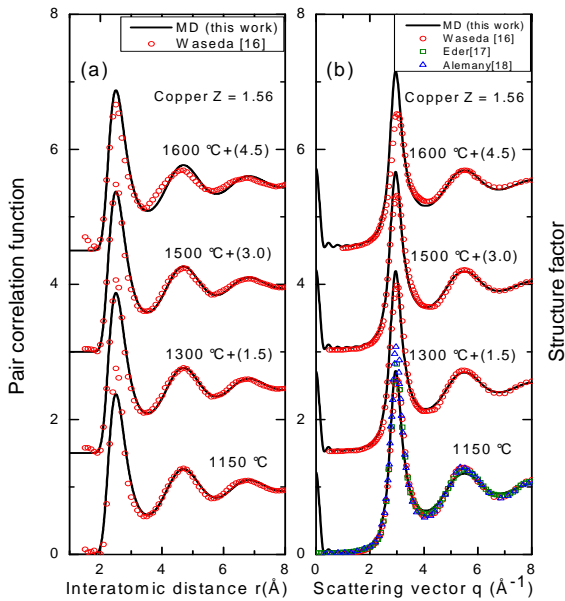


Fig. 2: Experimental Waseda (circle) [15], Eder (Square) [16], Alemany (Apriangle) [17] and computed (full line): (a) pair correlation functions, (b): structure factor for copper.

Our results for the pair correlation are in good agreement with experimental ones. The agreement is better on the structure factor. The choice of the effective valence for copper improves structure factor calculations.

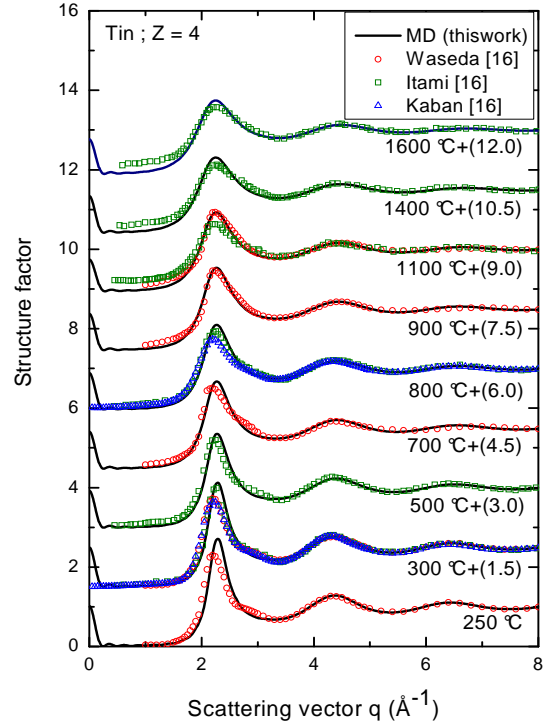


Fig. 3: Structure factor. Experimental Waseda (circle) [15], Itami (Square) [18], Kaban (Apriangle) [19] and computed (full line).

The velocity autocorrelation function calculated for each metal are presented in figure 4.

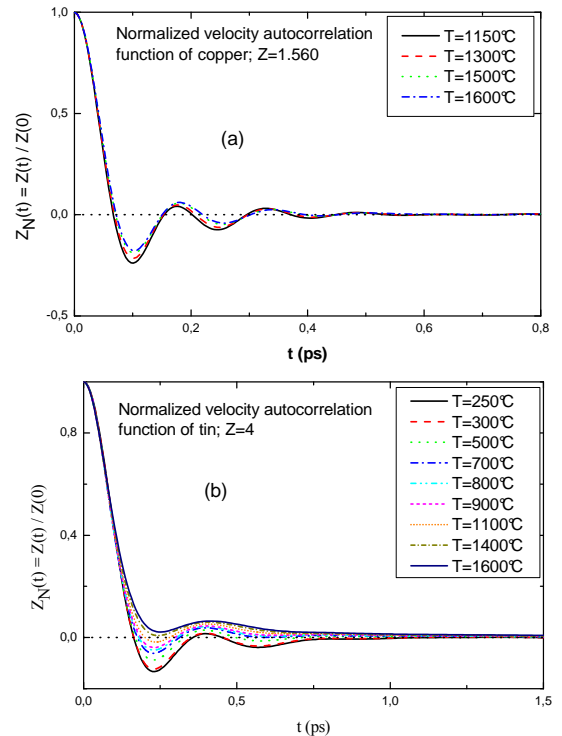


Fig. 4: Normalized velocity autocorrelation function for copper (a), Tin (b) as function of temperature.

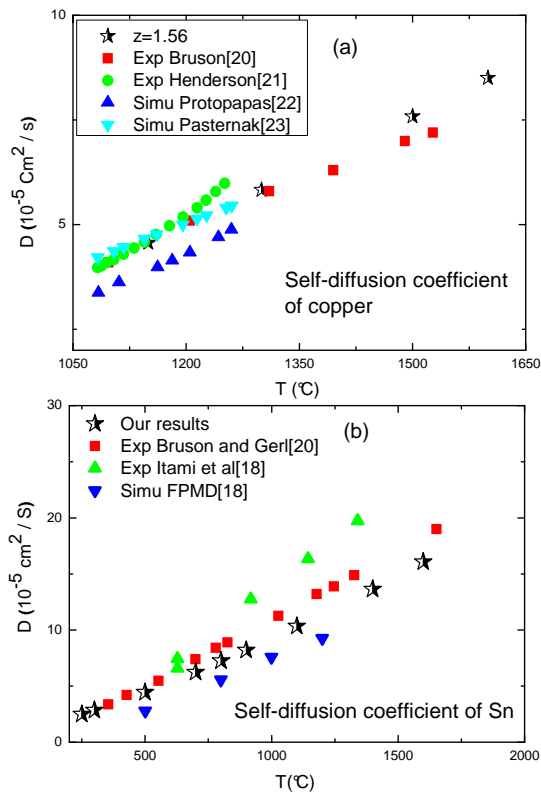


Fig.5: self diffusion coefficient as function of temperature. (a): Experimental Bruson(square)[20], Henderson (circle)[21], Protopapas(uptriangle) [22], Pasternak(downtriangle) [23].(b): Experimental Bruson(square) [20], Itami(circle) [18], FPMD(uptriangle)[18] . The computed are in (Star).

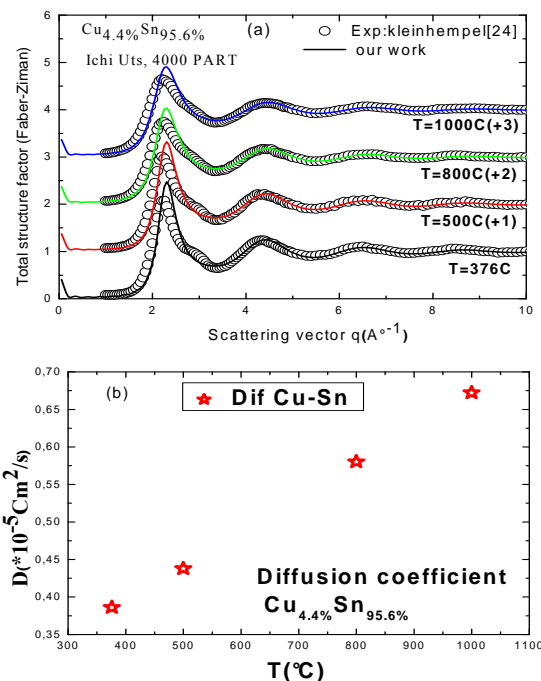


Fig.6 : (a) Experimental Kleinhempel(circle) [24], and computed (full line) total structure factor for Sn_{95.4%}Cu_{4.4%}. (b) interdiffusion in Sn_{95.4%}Cu_{4.4%} as a function of temperature.

The self diffusion results are presented in figure 5. Our results are in good agreement with measurements and theory calculations. The results for Sn_{95.4%}Cu_{4.4%} alloy are presented in figure 6.

6 Conclusion

With Shaw local potential we are able to describe the structure factor and to calculate the self diffusion of Tin and copper pure metals. The interdiffusion coefficient in Sn_{95.4%}Cu_{4.4%} alloy is in good agreement with experimental measurement. The choice of Shaw potential is promising for the study of diffusion in liquid metals since associated with MD it provides realistic values of the self diffusion coefficient.

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