



# Diffusion properties of liquid lithium–lead alloys from atomistic simulation



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## ABSTRACT

Liquid Li and Li–Pb alloy are the most potential candidate materials for the blanket of thermonuclear fusion reactor. In the present paper, the diffusion behaviors of liquid Li, Pb and Li–Pb alloys are studied by molecular dynamics simulations with a modified analytical embedded atom method potential. The obtained diffusion coefficients of liquid Li and Pb are in good agreement with the experimental results. For liquid Li–Pb alloys, the mutual diffusion coefficient increases monotonously with increasing Li content, while the diffusion coefficients of components do not increase until the concentration of Li is more than 50%.

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## 1. Introduction

As promising candidate materials for the blanket in fusion reactor, liquid Li–Pb alloys have obvious advantage in safety performance, chemical stability and neutron multiplication ability [1]. So it is very important to study the diffusion properties of liquid Li and Li–Pb alloys for the design and development of blanket. There are a few experimental reports on liquid Li self-diffusion coefficients (SDC), but these studies were performed at a narrow temperature range due to the high risk of measurement of liquid Li [2–4]. And the diffusion behaviors of liquid Pb were investigated in several experiments [5–8]. Molecular dynamics (MD) simulation has been proved to be a powerful approach to the simulation of liquid metals. The diffusion characteristics of liquid Li and Pb were obtained by a series of simulations [9–14].

However, the research about liquid Li–Pb alloys was scarce, especially for their diffusive behaviors. Jauch and Schulz [15] studied experimentally some basic properties of Li–Pb alloys, such as the thermal expansion coefficient, thermal conductivity, and viscosity coefficient. The mutual diffusion coefficients ( $D_M$ ) of some liquid Sn alloys have been obtained by simulation [16,17]; however, to our best known, there is no experimental study on the mutual diffusion behaviors of liquid Li–Pb alloys, and there is no related simulation study because of the lack of interatomic potential for them. In this work, a new type of modified analytic embedded atom method (MAEAM) potential is developed to predict the diffusion properties, which is of important significance to enrich

the thermodynamic database of liquid Li–Pb alloys and promote their engineering application.

## 2. Computational method

### 2.1. MAEAM potential

The embedded atom method (EAM) was first proposed by Baskes and Daw based on density function theory [18]. Within the framework of EAM, an analytical embedded-atom method was developed by Johnson [19]. To modify the deviations from spherically symmetric distribution and the linear superposition of atomic electron density, a modified term is introduced into the potential expression and the pair potential function is reconstructed in the MAEAM [20]. The MAEAM potential has been successfully applied to study the dynamic load, thermodynamic properties and atomic self-diffusion on surface [20–23]. The function form of modified term is somewhat arbitrary, and the validation can be checked through comparison of the results with experimental measurements and first principle calculations. For the situation of Li and Pb, this mathematical form for modified term is more suitable for describing liquid state than other forms. According to our former practices [20–22], the system energy is empirically written as

$$E = \sum_i^N E_i \quad (1)$$

where  $N$  is the atomic number of the system, and the  $E_i$  is the total energy of atomic  $i$ , which is the sum of embedded energy  $F(\rho_i)$ , pair-

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wise interaction  $\Phi(r_{ij})$  and a modified energy  $M(P_i)$ , and the formula is given by

$$E_i = F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \Phi(r_{ij}) + M(P_i). \quad (2)$$

The embedded energy is

$$F(\rho_i) = -F_0[1 - n \ln(\rho_i/\rho_e)](\rho_i/\rho_e)^n, \quad (3)$$

where  $\rho_i$  is the total electron density at the site of atom  $i$ , and it is expressed as

$$\rho_i = \sum_{j \neq i} f_e \left( \frac{r_1}{r_{ij}} \right)^\beta \left( \frac{r_{ce} - r_{ij}}{r_{ce} - r_1} \right)^2. \quad (4)$$

Here  $r_{ce}$  is the cutoff distance of electron density function, and is expressed by

$$r_{ce} = r_5 + (r_6 - r_5)/2, \quad (5)$$

where  $r_i$  ( $i = 1, 2, 3, \dots$ ) denote the  $i$ -th nearest neighbor distance at equilibrium state. The pairwise interaction term  $\Phi(r_{ij})$  is a function of the distance  $r_{ij}$  between atom  $i$  and  $j$ , which is written as

$$\Phi(r) = k_1 \left[ 1 + k_2 \ln \left( \frac{r}{r_1} \right) + k_3 \left( \frac{r}{r_1} \right) \right] \left[ \left( \frac{r_1}{r} \right)^{u_1} + k_4 \left( \frac{r_1}{r} \right)^{u_2} \right] \left( 1 - \frac{r}{r_c} \right)^2. \quad (6)$$

The cutoff distance  $r_c$  of pairwise interaction is

$$r_c = r_4 + k_c(r_5 - r_4), \quad (7)$$

which means that the pairwise interaction is ignored when  $r > r_c$ . The energy modified term  $M(P_i)$  is expressed as

$$M(P_i) = -\alpha P_i P_e / (P_i + P_e)^2, \quad (8)$$

where

$$P_i = \sum_{j \neq i} g_e \left( \frac{r_1}{r_{ij}} \right)^\gamma \left( \frac{r_{ce} - r_{ij}}{r_{ce} - r_1} \right)^2. \quad (9)$$

All the potential parameters  $F_0$ ,  $n$ ,  $\rho_e$ ,  $f_e$ ,  $\beta$ ,  $k_i$  ( $i = 1, 2, 3, 4$ ),  $u_1$ ,  $u_2$ ,  $k_c$ ,  $\alpha$ ,  $P_e$ ,  $g_e$  and  $\gamma$  are obtained by fitting the cohesive energy ( $E_c$ ), lattice parameter ( $a$ ), elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ) and formation energy of defects ( $E_{1v}$ ), these experimental and calculated values are listed in Table 1 [24–27]. The potential parameters of Li and Pb are listed in Table 2.

For Li–Pb alloy system, the pairwise interaction between Li and Pb atoms is described as

$$\Phi_{ab}(r_{ij}) = \frac{u}{2} \left[ \Phi_{aa} \left( r_{ij} \frac{r_a}{c_{r1}} \right) + \Phi_{bb} \left( r_{ij} \frac{r_b}{c_{r1}} \right) \right], \quad (10)$$

where  $\Phi_{aa}(r)$  and  $\Phi_{bb}(r)$  are the pair potential of metallic Li and Pb, respectively.  $u$ ,  $r_a$ ,  $r_b$  and  $c_{r1}$  are adjustable parameters, which were obtained by fitting the corresponding properties of alloy and their values are also listed in Table 2.

**Table 2**  
MAEAM potential parameters of Li, Pb and Li–Pb alloys.

Parameters	Li	Pb	Li–Pb
$F_0$ (eV)	0.9121	1.6025	
$n$	0.249	0.7469	
$\rho_e$ (eV/Å <sup>3</sup> )	11.7493	12.676	
$f_e$ (eV/Å <sup>3</sup> )	1.2234	0.6407	
$\beta$	2.88	5.54	
$k_1$ (eV)	0.5417	9.1755	
$k_2$	6.5782	1.6726	
$k_3$	−2.7961	−1.1424	
$k_4$	−0.6104	−0.818	
$u_1$	−2	2	
$u_2$	2	4	
$k_c$	0.25	0.1	
$\alpha$ (eV)	$5.5561 \times 10^{-5}$	$9.7909 \times 10^{-3}$	
$P_e$ (eV/Å <sup>3</sup> )	8.8262	12.656	
$g_e$ (eV/Å <sup>3</sup> )	$4.806 \times 10^{-8}$	$4.85 \times 10^{-4}$	
$\gamma$	11.85	5.61	
$u$			2.7
$r_a$ (Å)			4.3
$r_b$ (Å)			3.6
$c_{r1}$ (Å)			2.667

## 2.2. The simulation models

For the liquid Li, Pb and Li–Pb systems used here, the initial simulation cells are constructed based on their perfect crystal lattices. The initial configuration is  $20a_0 \times 20a_0 \times 20a_0$  ( $a_0 = 3.483$  Å) body-centered cubic lattices for the metallic Li, which contains 16,000 atoms. For liquid Pb, the initial structure is  $14a_0 \times 14a_0 \times 14a_0$  ( $a_0 = 4.895$  Å) face-centered cubic lattice and the system contains 10,976 atoms. The initial configuration for liquid Li–Pb alloy is the same as Li. The periodic boundary conditions are applied in  $x$ ,  $y$  and  $z$  directions. All the MD simulations are performed with a time step of 2.0 fs, and the temperature of systems is controlled by Nose–Hoover thermostat. The liquid configurations of all samples are obtained by heating initial crystalline models up to melting temperatures by constant-pressure MD simulation. The simulation data are collected from equilibrium states under constant-volume MD simulation.

## 2.3. MSD and mutual diffusion

The most frequently used method to determine diffusion properties from molecular dynamics simulation is by the mean of the Einstein relationship [10,13,28], Which is written in the form

$$D = \lim_{t \rightarrow \infty} \frac{1}{6Nt} \left\langle \sum_{i=1}^N |r_i(t) - r_i(0)|^2 \right\rangle \quad (11)$$

where  $D$  is SDC, the angle brackets denote average atomic mean square displacement ( $MSD$ ),  $N$  is the number of particles,  $r_i(t)$  and  $r_i(0)$  are the final position and initial position of particle  $i$  over the time interval  $t$ , respectively. In this work, the simulation time for the  $MSD$  is 1 ns (500,000 steps) from equilibrium states under

**Table 1**  
Experimental values of Li and Pb parameters used in the fitting and the corresponding values calculated using in MAEAM potential.

Parameters	$a$ (Å) [24]	$E_c$ (eV) [24]	$E_{1v}$ (eV)	$C_{11}$ (GPa) [27]	$C_{12}$ (GPa) [27]	$C_{44}$ (GPa) [27]
Li (Expts.)	3.5092	−1.63	0.57 [25]	14.8	12.5	10.8
Li (Cal.)	3.483	−1.63	0.56	14.8	12.5	11.2
Pb (Expts.)	4.9095	−2.03	0.50 [26]	55.5	45.4	19.4
Pb (Cal.)	4.8951	−2.03	0.46	58	45	17

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