

Diffusion coefficient calculation of iron in liquid lead using molecular dynamics method with new mixing rule for Lennard-Jones potential parameters

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Abstract

The diffusion coefficient data of materials are crucial for several applications, and can be calculated theoretically up to considerable accuracies. Using molecular dynamics simulation it is possible to compute this property for several conditions as temperature and pressure. The corrosion phenomena of steel types in the fast nuclear reactor can be correlated and studied based on the the diffusion process of iron atoms that dissolve into a liquid lead coolant via molecular dynamics methods using certain potential energy. A widely type of the interatomic interaction potential of materials is the Lennard-Jones potential. Regarding this potential, for a pair of different elements A and B, we can determine the potential parameter ($\sigma_{AB}, \epsilon_{AB}$) using a formula. However for a metal system as the liquid metal corrosion, the Lennard-Jones potential could be inefficiently accurate. In this study we propose a novel mixing rule to determine ($\sigma_{AB}, \epsilon_{AB}$) for better property calculation results, similar to iron diffusion coefficient. We propose a novel formula for the metal system. Using this novel formula, the molecular dynamics simulation exhibits relatively accurate results. The iron diffusion coefficient can be estimated as $D_{Fe \rightarrow Pb}(T) = 1.98847 \times 10^{-7} \exp(-37064.47/RT)$ [m²/s], with an error of apporoximately < 7.2% and > 10% for < 1073 K and $T > 1073$ K, respectively. The best calculation for $D_{Fe \rightarrow Pb}(T)$ has an error of approximately 1.55% for temperature 923 K.

Keywords: Diffusion; lennard-jones potential; liquid metals corrosion; mixing rules; molecular dynamics.

1. Introduction

Liquid lead and/or lead alloys are already known to have high potential application as coolant materials in liquid metal cooled reactors. Liquid lead has several physical and chemical advantage properties: high boiling temperature (approximately 1740 °C), low melting temperature (approximately 327 °C), and also high thermal conductivity (more than water), such that those making the liquid lead have potential applications for fast nuclear reactor designs (Zhang & Li, 2008). However, it is also well known for a long time that the structural materials (steels) used in the liquid lead cooled reactor exhibit very high corrosion when they interact with this coolant. The steel components (iron, nickel, chromium, etc) experience high dissolution within liquid lead (Kashezhev *et al.*, 2010; Zelenskii *et al.*, 2006; Zelenskii *et al.*, 2007; Zhang & Li, 2008; Zhang *et al.* 2010). Hence, with a comprehensive appropriate method of corrosion inhibition and/or finding a novel high temperature resistant material are major goals in liquid metal cooled reactor designs.

Several studies have been conducted for the aforementioned purposes by an experimental or theory/computational method. From this perspective, computational methods are very powerful and efficient approaches. In particular, the molecular dynamics (MD) method is a very good tool for studying the corrosion based on the diffusion concept. Maulana *et al.* (2008) applied the MD method to study the penetration depth of liquid lead atoms entering FeNiCr steel. In our previous studies (Arkundato *et al.*, 2010; Arkundato *et al.*, 2012; Arkundato *et al.*, 2013a; Arkundato *et al.*, 2013b; Arkundato *et al.*, 2013c; Arkundato *et al.*, 2015; Arkundato *et al.*, 2017; Arkundato *et al.*, 2019) we have used the Lennard-Jones potential to observe the corrosion of iron in lead and lead-bismuth coolant based on Lorentz-Bertholet mixing formula and obtained important results. In these studies we could present the range of oxygen concentration for the best corrosion inhibition. Sa'adah *et al.*, (2020a) adopted the Lennard-Jones potential with the Lorentz-Bertholet mixing formula to demonstrate the corrosion of iron in Pb-Mg liquid. We also applied this type of potential to investigate the corrosion of ceramics in liquid metal. Triwardani *et al.*, (2020b) also adopted the same potential and mixing rule, but by suggesting more accurate potential parameters.

In facts we actually simplified the atomic interaction of material using the Lennard-Jones potential following the Lorentz-Bertholet mixing formula for the pair interaction of two different elements. Several researchers have mentioned that the Lennard-Jones potential is not sufficient accurate in representing metals. Other potential types should be adopted to support the interaction among metallic atoms as EAM potential or others. Belashchenko (2009) adopted the EAM potential for liquid sodium. Mendeleev *et al.*,(2008), as well as other researchers, employed the EAM potential for liquid Al dan Cu.

However, the Lennard-Jones potential is a simple and easy method for computing the physical properties via molecular dynamics simulation. It can be adopted as first prediction to arrive at a more general conclusion before involving more accurate investigations. In general the Lennard-Jones potential is useful in describing liquid or gaseous systems (Brodholt & Wood, 1993). Evidently, the liquid metal corrosion and its inhibition adopts the injection of oxygen gas, following diffusion process, and it is a system of solid metal-liquid-gas mixture. Hence it can

describe the corrosion of iron in liquid lead also adopting the Lennard-Jones potential with a few improvements.

At this stage, there are several mixing formulas in the scheme of the Lennard-Jones potential that have been proposed by many researchers for a number of objectives that will be discussed later. We can use these formulas in our corrosion research. However, *how accurate are these physical property calculations as diffusion coefficient?* Then this is the focus and objective of current work. We want to study the effectiveness of several available mixing rules to describe the liquid lead corrosion phenomena. First, we want to compare several available mixing rules (Lorentz-Bertholet, Halgren HGG, Waldman Hagler, etc) for the use of diffusion coefficient calculation of liquid metal system, and then attempt to develop a novel formula for mixing rule better. We compare all formulas with experimental data and determine that it is most accurate to represent the interaction of metal atoms. We expect that this novel mixing formula will be a better mixing formula to represent the interaction among atoms of metals (especially for hot corrosion in liquid molten metals) in the scheme of the Lennard-Jones potential. In this study we use the open-source Moldy molecular dynamics program for simulations (Refson, 2000), and we believed that this program can produce significant results and may be used for the general purpose of calculations. This code may be download freely from two website addresses:

(1) <http://ccl.net/cca/software/SOURCES/C/moldy/>

(2) <https://data.mendeley.com/datasets/rgnh52j3st/1>

2. Molecular dynamics method and mixing rules

The molecular dynamics simulation method is an effective method for simulating interactions among atoms/molecules of materials (solids, liquids or gases) and calculating physical properties. The simulation will be run under a certain ensemble (NPT/NVT/NVE, etc.). In fact, in the MD simulation, atoms move following the Newton's 2nd law of motion:

$$m_i \{d^2 r_i / dt^2\} = F_i \quad (1)$$

$$F_i = -\nabla \sum u_{ij}(r_{ij}) \quad (2)$$

where r is the position of atom, F is the total force experienced by an atom, $u(r)$ is the potential energy related to the force, and index i represents an atom label while index j labels other atoms, such that $i \neq j$. For the material system in MD method we usually solve the Newton equation numerically. Using the Moldy program, the Equation (1) can be solved using certain algorithm as the modified Beeman algorithm, under specific potential function of interacting atoms (Refson, 2000). One of the popular potential function $u(r)$ for representing the interaction between pair of two atoms is 12-6 form of the Lennard-Jones potential (Zhen & Davies, 1983):

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

Figure 1 describes the LJ potential and the physical meaning of its parameters σ and ϵ .

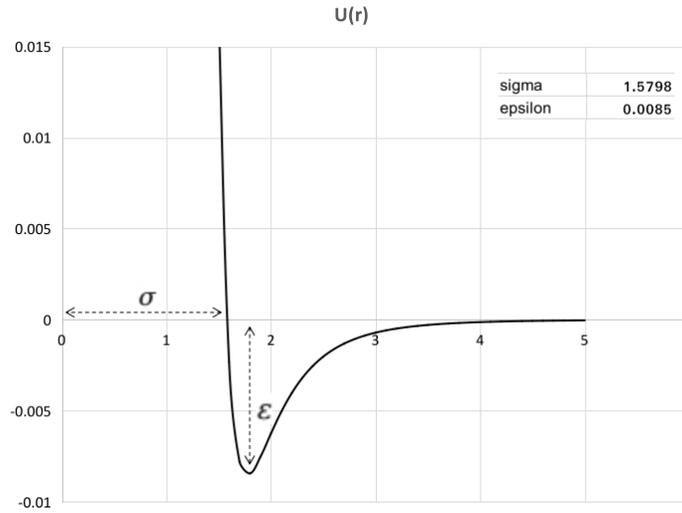


Fig. 1. Lennard-Jones potential form

This 12-6 LJ potential has two parameters, “the size parameter ” σ , and “the strength or depth parameter ” ϵ . In the MD simulation force and energy are usually evaluated only within a certain cut-off distance $r_{\text{cut-off}}$ to solve the equation of motion, for $r_{\text{cut-off}} = 2.5\sigma$.

Meanwhile, Equation (3) will be applied for the same type of atoms generally. For a pair of different types of atoms (for example iron and lead), usually we need to define specific potential parameter. Simply, we need to determine a suitable mixing rule to mix two parameters σ and ϵ that belong to each interacting elements. In this study we check several available mixing rules and use them to calculate the diffusion coefficient of iron in liquid molten lead, compare with experimental data, and then try to develop a novel mixing rule for the best calculation.

2.1 The Mixing formula/rules

2.1.1 Lorentz-Bertholet mixing formula

The cross interactions among different elements of material system could follow the very popular Lorentz-Berthelot mixing rule (Brodholt & Wood, 1993; Al-Matar & Rockstraw, 2004; Maulana, 2008). This form uses arithmetic average for defining “collision diameter” σ_{AB} and geometric average for defining “the well depth” ϵ_{AB} :

$$\sigma_{AB} = 0.5 \times (\sigma_{AA} + \sigma_{BB}) \quad (4a)$$

$$\epsilon_{AB} = (\epsilon_{AA} \times \epsilon_{BB})^{0.5} \quad (4b)$$

2.1.2 Fender-Halsey mixing formula

Another mixing formula is Fender-Halsey (FH) (Fender & Halsey, 1962). The formula is likely:

$$\sigma_{AB} = 0.5 \times (\sigma_{AA} + \sigma_{BB}) \quad (5a)$$

$$\varepsilon_{AB} = 2 (\varepsilon_{AA} \times \varepsilon_{BB}) / (\varepsilon_{AA} + \varepsilon_{BB}) \quad (5b)$$

2.1.3 Madar-Rockstraw mixing formula

Matar and Rockstraw (2006) suggested the mixing formula as (Al-Matar & Rockstraw, 2006)

$$\sigma_{AB} = \left(\frac{0.5640\sigma_{AA}^6 + 0.9464\sigma_{AA}^3\sigma_{BB}^3 + 0.4896\sigma_{BB}^6}{2} \right)^{1/6} \quad (6a)$$

$$\varepsilon_{AB} = \left(\frac{0.0799\varepsilon_{AA} + 1.912939769(\varepsilon_{AA} \times \varepsilon_{BB})^{1/2} + 0.0071\varepsilon_{BB}}{2} \right) \left(\frac{\sigma_{AA}^3 \times \sigma_{BB}^3}{\sigma_{AB}} \right) \quad (6b)$$

2.1.4 Lee-Sandler mixing formula

Later, Lee and Sandler (Kontogeorgis & Folas, 2010) suggested the mixing formula of two different atoms as:

$$\sigma_{AB} = 0.5 \times (\sigma_{AA} + \sigma_{BB}) \quad (7a)$$

$$\varepsilon_{AB} = \left(\frac{\varepsilon_{AA}^{2/3} + \varepsilon_{BB}^{2/3}}{2} \right)^{3/2} \quad (7b)$$

2.1.5 Halgren-HHG mixing formula

The Halgren HHG mixing rule implemented a weighted average of the arithmetic-mean rule for a collision diameter as (Al-Matar & Rockstraw, 2004):

$$\sigma_{AB} = (\sigma_{AA}^3 + \sigma_{BB}^3) / (\sigma_{AA}^2 + \sigma_{BB}^2) \quad (8a)$$

$$\varepsilon_{AB} = 4(\varepsilon_{AA} \times \varepsilon_{BB}) / (\varepsilon_{AA}^{1/2} + \varepsilon_{BB}^{1/2})^2 \quad (8b)$$

2.1.6 Smith-Kong mixing formula

Smith developed a combine rule by considering the repulsive interaction of simple molecules. His mixing rule includes the atomic distortion theory for repulsion interaction. Kong then used Smith's approach and a geometric mean relationship for the attractive interactions and applied it to the LJ mixing formula as (Schnabel *et al.*, 2009)

$$\sigma_{AB}^{SK} = \left\{ \frac{[(\varepsilon_{AA} \times \sigma_{AA}^{12})^{1/13} + (\varepsilon_{BB} \times \sigma_{BB}^{12})^{1/13}]^{13}}{2^{13} \sqrt{(\varepsilon_{AA} \times \sigma_{AA}^6) \times (\varepsilon_{BB} \times \sigma_{BB}^6)}} \right\}^{1/6} \quad (9a)$$

$$\varepsilon_{AB}^{SK} = \left\{ \frac{2^{13} \times (\varepsilon_{AA} \times \sigma_{AA}^6) \times (\varepsilon_{BB} \times \sigma_{BB}^6)}{[(\varepsilon_{AA} \times \sigma_{AA}^{12})^{1/13} + (\varepsilon_{BB} \times \sigma_{BB}^{12})^{1/13}]^{13}} \right\}^{1/6} \quad (9b)$$

2.1.7 Waldman-Hagler mixing formula

Waldman and Hagler also formulated the cross interaction term for rare gas van der waals parameters as presented below (Waldman and Hagler, 1993)

$$\sigma_{AB} = \left\{ \frac{\sigma_{AA}^6 + \sigma_{BB}^6}{2} \right\}^{1/6} \quad (10a)$$

$$\varepsilon_{AB} = \{ \varepsilon_{AA} \times \varepsilon_{BB} \}^{1/2} \left\{ \frac{\sigma_{AA}^3 \times \sigma_{BB}^3}{\sigma_{AB}^6} \right\} \quad (10b)$$

2.1.8 New mixing formula

In this work, we develop a novel mixing formula or rule by modifying the collision diameter σ_{AB} and the well depth ε_{AB} as:

$$\sigma_{AB} = \{ \sigma_{AA}^2 + \sigma_{BB}^2 \}^{1/6} \quad (11a)$$

$$\varepsilon_{AB} = \{ \varepsilon_{AA}^2 + \varepsilon_{BB}^2 \}^{1/2} \quad (11b)$$

3. Diffusion coefficient calculation

The liquid lead corrosion may be observed as an effect of high dissolution of steel components into liquid lead. In particular, for the hot corrosion as in the liquid lead corrosion, we can consider the corrosion as a diffusion process where no transfer of electrons (Manly, 1959). Subsequently, we can run MD simulation as a classical MD simulation. The most prevalent component of steel material is iron, and the steel corrosion in liquid lead may be modelled mostly as the iron corrosion in liquid lead. The diffusion coefficient that describes the diffusion of iron may be calculated by following these equations below (Kupryazhkin *et al.*, 2008):

$$\text{MSD} = \left\langle \left| \vec{R}(t) - \vec{R}(0) \right|^2 \right\rangle \quad (\text{mean square displacement}) \quad (12)$$

$$D = \text{MSD}/6t \quad (\text{diffusion coefficient}) \quad (13)$$

where t is time and $R(t)$ is related to atomic trajectory. The temperature dependence of the diffusion coefficient can be predicted by following the Arrhenius formula,

$$D(T) = D_0 \exp(-A/RT) \quad (14)$$

where T represents temperature, A is an activation energy for diffusion to be happen, and R is a universal gaseous constant. This Arrhenius form of temperature dependent diffusion coefficient is prevalent in several application fields (Abidli *et al.*, 2021).

4. Simulation procedure and calculation

The objective of this study is to find the best mixing formula that produces the diffusion coefficient of iron within liquid lead that agree with experimental data. We calculate the iron diffusion coefficient $D_{Fe \rightarrow Pb}$ for different types of mixing formulas (Equation (4 – 11)) and then compare them with available experimental data. There were two experimental results for the comparison, develop by Robertson: (1) single value of iron diffusion at temperature 750 °C and (2) temperature dependent of iron diffusion (Zhang & Li, 2008). Robertson reported that the single value of iron diffusion coefficient measurement was $D_{Fe \rightarrow Pb} = 2.80 \times 10^{-9} \text{ m}^2/\text{s}$ at 750 °C, and developing the formula of the temperature dependent diffusion coefficient of iron as:

$$D_{Fe \rightarrow Pb}(T) = 4.9 \times 10^{-7} \cdot \exp(-44100/RT) \quad [\text{m}^2/\text{s}] \quad (15)$$

Based on the Equation (15), $D_{Fe \rightarrow Pb} = 2.74 \times 10^{-9} \text{ m}^2/\text{s}$ at 750 °C. Comparing several mixing formulas, the best formula is one that produces the smallest discrepancy compared with the value, $D_{Fe \rightarrow Pb} = 2.73 \times 10^{-9} \text{ m}^2/\text{s}$.

After the simulation, the diffusion coefficient D can be easily determined and calculated from MSD file of Moldy MD simulation output, following Equation (12 – 14). The procedure of (corrosion) simulation follows these below steps:

- (I) Prepare the values of potential parameter ($\sigma_{AB}, \epsilon_{AB}$), for the mixing formula calculated by Equation (4 – 11).
- (II) Prepare inputs of the Moldy simulation in two files: specification and control files.
 - 1). Specification file comprises the potential parameter (σ, ϵ), number of atoms, type of atoms, coordinates of atoms in material, etc. In this simulation, the material system under study (FePb) was designed with 22815 Fe atoms in the form of bcc solid crystals and 11189 Pb atoms in the form of liquid state. We place the iron bcc crystal at the center of the liquid lead material.

Potential parameters for interaction among atoms following the Lennard-Jones potential (Equation (3)) is given by Table 1, including for different types of the mixing formula (Equation (4 - 11)). In Table 1., we adopt data of potential parameters from Zhen & Davies (1983) for the interaction of same type of atoms Fe-Fe and Pb-Pb. The potential parameter of Fe-Fe is $\sigma_{AA} = 2.3193 \text{ \AA}$ and $\epsilon_{AA} = 0.4007 \text{ eV}$, and for Pb-Pb is $\sigma_{AA} = 3.1888 \text{ \AA}$ and $\epsilon_{AA} = 0.191 \text{ eV}$.

Table 1. List of Fe-Pb potential parameters for different mixing formulas

Potential parameters	Lorentz-Bertholet	Fender Halsey	Madar-Rockstraw	Lee-Sandler	Halgren-HHG	Smith-Kong	Waldman-Hagler	New formula
Equation	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
$\sigma_{AB} (\text{\AA}) \square$	2.7541	2.7541	2.8104	2.7541	2.8880	1.1289	2.9070	1.5798
$\epsilon_{AB} (\text{eV}) \square$	0.3503	0.3248	0.2928	0.3687	0.3371	0.3207	0.2348	0.5705

2) The control file demonstrates how the simulation will be run. This includes temperature T (1023K), pressure P (0 Mpa), integration step $nsteps$ (100000), timestep (0.0001 ps), ensemble NPT (Andersen constant pressure, Nose Hoover Thermostat), equilibration condition *begin-average* (at step 50000), $r_{\text{cut-off}} = 8.125 \text{ \AA}$.

(III) Running simulation

To run the simulation using the command line as: `$moldy control_name output_name`

There are two kind of simulations here,

- (1) The first simulation is to compute the diffusion coefficient calculation (D) for all of the mixing formulas at temperature 1023 K or 750 °C,
- (2) The second simulation will be run at temperatures 623 K, 723 K, 823 K, 923 K, 1023 K, 1123 K, 1223 K, 1323 K. This step will be run after the best mixing formula can be found after comparison of the mixing formulas. This step determines the temperature dependent diffusion coefficient $D(T)$ based on the Arrhenius formula.

(IV) Calculation of diffusion coefficient D , Equation (13). The diffusion coefficient of Fe into Pb can be computed by extracting the output of simulation using Moldy's utility command line (as in manual):

`$msd -r save_file -d dump_file -t x-xx -m x-xx -o output_name`

(V) Comparison of the obtained diffusion coefficients with available experimental data using the data as reported by Zhang & Li (2008) which was explained before. The choice of simulating the phenomena at a temperature of 750 °C because of following the temperature of experimental data.

5. Results and discussions

5.1 Diffusion coefficient of iron in liquid lead

The iron diffusion coefficients calculation for different mixing formulas can be summarized as presented in Table 2. The corrosion of iron was regarded as diffusion of iron atoms flowing into the liquid lead coolant. The higher the diffusion coefficient of iron ($D_{Fe \rightarrow Pb}$), more corrosion of iron in liquid lead. The corrosion was evaluated at temperature 1023 K (or 750 °C). The diffusion coefficient was measured in m^2/s . To justify which mixing rule is better than others, we compared the diffusion coefficient from simulation results with $D_{Fe \rightarrow Pb} = 2.73 \times 10^{-9} [m^2/s]$ of available experimental data (Zhang & Li, 2008). From our calculation, the diffusion coefficient of iron in liquid lead can be presented as in Table 2.

Table 2. Comparison D of different mixing formulas and experiment $D_{Fe \rightarrow Pb} = 2.73 \times 10^{-9} [m^2/s]$.

No.	Mixing rule/formula	$D_{Fe \rightarrow Pb} [m^2/s]$ (simulation)	% discrepancy (simulation and experiment)
1	Lorentz-Bertholet (LB)	1.295×10^{-9}	52.56%
2	Fender-Halsey (FH)	1.306×10^{-9}	52.16%
3	Madar-Rockstraw (MR)	1.308×10^{-9}	52.09%
4	Lee-Sandler (LS)	1.311×10^{-9}	51.98%
5	Halgren-HHG (HHG)	1.312×10^{-9}	51.94%
6	Smith-Kong (SK)	1.313×10^{-9}	51.90%
7	Waldman-Hagler (WH)	1.289×10^{-9}	52.78%
8	New formula (NF)	2.719×10^{-9}	0.40%

W.M. Robertson stated that this formula will be valid for calculation of diffusion coefficient of iron in liquid lead for the temperature 500 °C to 750 °C (Zhang & Li, 2008). From Table 2, it can be observed that all mixing formulas No.1 to No.7 have the discrepancy of approximately 52%. However, using the new mixing formula (NF), the discrepancy between simulation and experiment is only about 0.40%. Hence, our mixing formula has shown better result for treating the different type of atom Fe and Pb, especially for studying corrosions of this metal systems that is iron in liquid lead.

The diffusion process should be a temperature dependent process. We need to know how the new formula above can also consistently be used to calculate the diffusion coefficient of iron at various temperatures. From single temperature we got very good result, the error is only approximately 0.40%.

5.2 Temperature dependent diffusion coefficient of iron in liquid lead

Is there any certain temperature area that shows a mismatch between the simulation results and the experimental results? Now we discuss about the temperature dependent diffusion coefficient $D(T)$ or rather is $D_{Fe \rightarrow Pb}(T)$ for iron in liquid lead. To determine this physical variable, we will use the Arrhenius equation model to determine the relationship between D diffusion coefficient and T temperature as Equation (14), or rather is

$$D_{Fe \rightarrow Pb}(T) = D_0 \exp(-A/RT) \quad (16)$$

To determine the parameter D_0 and A (an activation energy such that the diffusion process can occur), we need to obtain a linear graph between $\ln D$ and $1/T$:

$$\ln D_{Fe \rightarrow Pb}(T) = (-A/R)(1/T) + \ln D_0 \quad (17)$$

The data of this graph were collected from simulations for eight temperatures to produce the diffusion coefficients of iron in liquid lead as in Table 3. All of the simulations using our new formula of potential parameter as in equation (11).

Table 3. The plot graph between $\ln D_{Fe \rightarrow Pb}(T)$ and $1/T$ for iron diffusion coefficient

No.	T [K]	$D_{Fe \rightarrow Pb}$ [m ² /s]	$1/T$	$\ln D_{Fe \rightarrow Pb}(T)$
1	623	$2.3456795783 \times 10^{-10}$	0.001605	-22.17328
2	723	$3.9752703205 \times 10^{-10}$	0.001383	-21.64576
3	823	$8.4197082436 \times 10^{-10}$	0.001215	-20.89528
4	923	$4.9522904843 \times 10^{-10}$	0.001083	-21.42600
5	1023	$2.78602483974 \times 10^{-9}$	0.000978	-19.69865
6	1123	$4.47737065256 \times 10^{-9}$	0.000890	-19.22423
7	1223	$6.68402505385 \times 10^{-9}$	0.000818	-18.82355
8	1323	$8.89067945514 \times 10^{-9}$	0.000756	-18.53826

The plot of $\ln D_{Fe \rightarrow Pb}(T)$ and $1/T$ for iron diffusion coefficient based on the above Table 3 can be observed as following Figure 2.

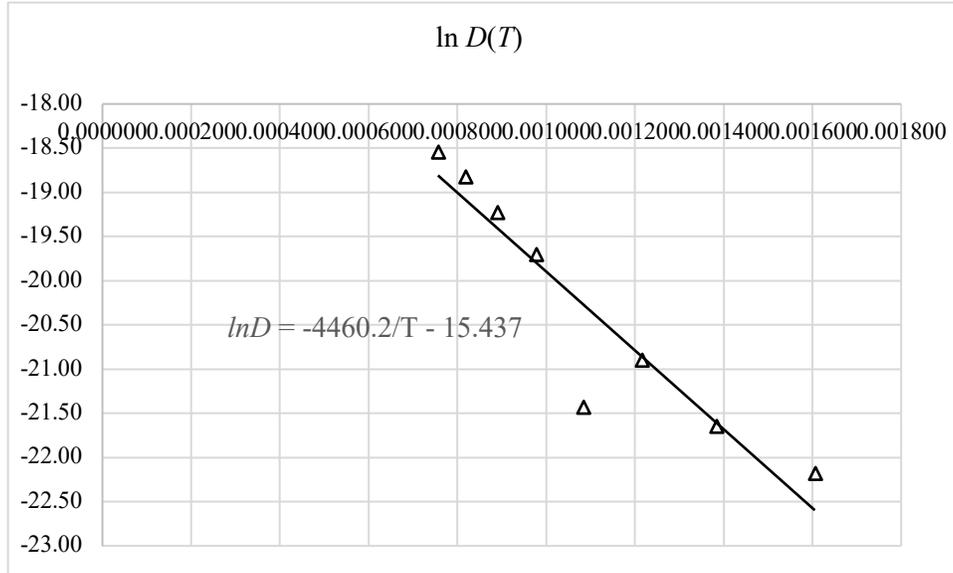


Fig. 2. Plot of $\ln D_{Fe \rightarrow Pb}(T)$ and $1/T$ for iron diffusion coefficient

From Figure 2 we can determine that $D_0 = 1.98847 \times 10^{-7} \text{ m}^2/\text{s}$ and also activation energy $A = 37064.47279 \text{ kJ/mol}$. Based on these values, the temperature dependent diffusion coefficient of iron in liquid lead can be written as

$$D_{Fe \rightarrow Pb}(T) = 1.98847 \times 10^{-7} \exp(-37064.47/RT) \quad [\text{m}^2/\text{s}] \quad (18)$$

This result, Equation (18), can be compared with Robertson experimental result (equation (15)) as in Figure 3 below.

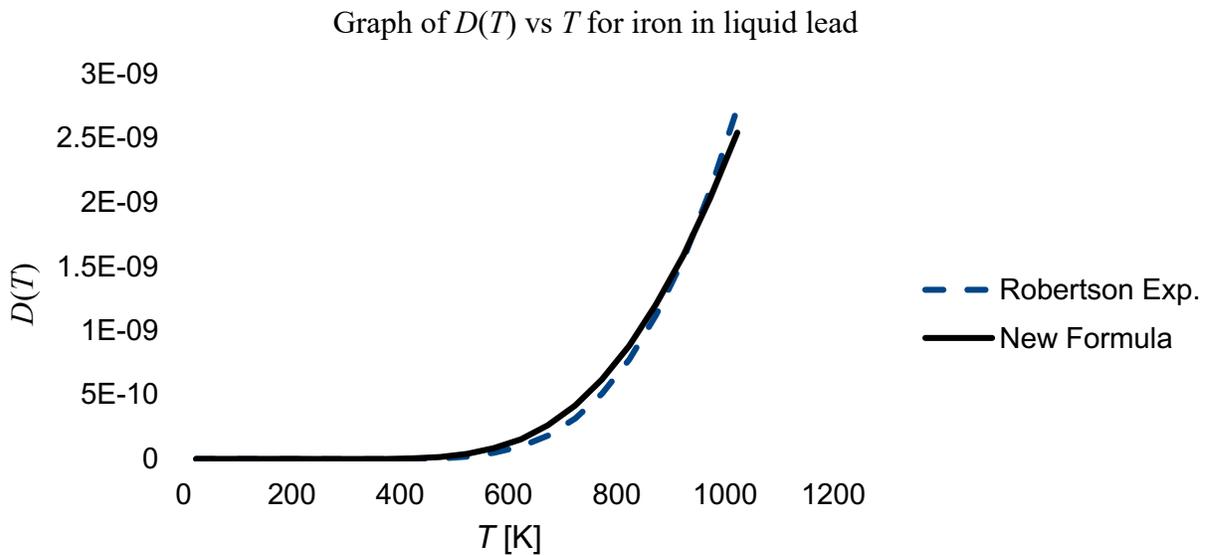


Fig. 3. Plot of equation (15) and (18)

Now we can discuss more details about the simulation result. Lets us to compare for some points at higher temperatures (873 K to 1423 K). Table 4 shows the comparison between Robertson curve (Equation (15)) and our calculation using new formula (equation (18)).

Table 4. Comparison between experiment and simulation results of $D(T)$

T [K]	Robertson Curve	New Formula	% discrepancy
873	1.12247×10^{-9}	1.20137×10^{-9}	7.03%
923	1.56022×10^{-9}	1.58443×10^{-9}	1.55%
973	2.09653×10^{-9}	2.03103×10^{-9}	3.12%
1023	2.73699×10^{-9}	2.54108×10^{-9}	7.16%
1073	3.48543×10^{-9}	3.11353×10^{-9}	10.67%
1123	4.3440×10^{-9}	3.74654×10^{-9}	13.75%
1173	5.31338×10^{-9}	4.43767×10^{-9}	16.48%
1223	6.39292×10^{-9}	5.18403×10^{-9}	18.91%
1273	7.58084×10^{-9}	5.98242×10^{-9}	21.08%

From Table 4, we can obtain important points: that is the New Formula will relatively match with experimental result for temperature interval of 873 K to 1023 K, with discrepancy not more than 7.2% and has a very good agreement at a temperature of approximately 923 K with discrepancy is about only 1.55%. At a temperature more than 1023 K, the discrepancy will increase to value about 21% at temperature 1273 K. Based on this simulation results it seems that we can state that the New Formula can be used to describe, explain and predict the properties and phenomena of liquid lead (and alloy) metal, for example for studying the liquid lead corrosion. The novel formula may applied accurately at temperature not more then 1023 K if we limit our calculation error not more then 7.2%, compared to experimental result. At least, the important thing is the Lennard-Jones potential remains a good approximation to study a metal system, especially for preliminary prediction, with a modified potential parameters, as we suggested in our current work.

6. Conclusions

Based on the molecular dynamics simulation using the Lennard-Jones potential with the novel mixing formula to compute the cross-term of potential parameters, the diffusion coefficient calculation of iron in liquid lead has shown a significant improvement of accuracy in comparison with the experimental value. In this study, for liquid metal system as in the corrosion liquid metal phenomena, using the novel mixing rule for calculating the cross-term of Lennard-Jones potential parameter ($\sigma_{AB}, \epsilon_{AB}$), we have the following accurate results:

1. novel mixing rules:

$$\text{sigma parameter } \sigma_{AB} = \{\sigma_{AA}^2 + \sigma_{BB}^2\}^{1/6} [\text{\AA}]$$

$$\text{epsilon parameter } \epsilon_{AB} = \{\epsilon_{AA}^2 + \epsilon_{BB}^2\}^{1/2} [\text{eV}],$$

2. diffusion coefficient:

$$D_{Fe \rightarrow Pb}(T) = 1.98847 \times 10^{-7} \exp(-37064.47/RT) \quad [\text{m}^2/\text{s}],$$

3. calculation error of $D_{Fe \rightarrow Pb}(T)$:

< 7.2% and > 10% for $T < 1073$ K and $T > 1073$ K, respectively, with the best prediction of $D_{Fe \rightarrow Pb}(T)$ for the error of approximately 1.55% at the temperature 923 K.

In this study, we have applied our novel mixing formula just for liquid metal system including only two types of atom (Fe and Pb). We haven't implemented to other materials, yet. It is important to verify this new formula for other materials and phenomena for the next study. However, at least, for liquid lead corrosion, as our simulation results we believe this novel formula can be adopted to study the corrosion phenomena in liquid metals better.

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