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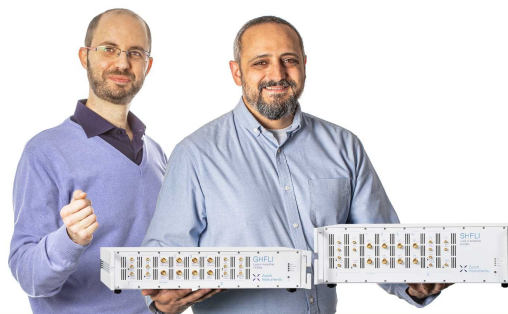
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Lennard-Jones and Morse Potential Comparison for Studying The Liquid Lead Corrosion

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Abstract. The diffusion coefficient of various materials is very important in its application in the development of science and technology, especially in the heat transfer process in the nuclear reactor. In the nuclear reactor there is a cladding which is a wrapper of uranium fuel, the cladding material will interact with molten metal (for fast reactor) at very high temperatures, causing corrosion. The corrosion can be studied based on the diffusion process of atoms of material in this high-temperature molten metal. The diffusion process can be investigated using molecular dynamics computational methods, but the accuracy of the simulation results is highly dependent on the accuracy of the interaction potential form used. In this current work, the research was conducted to see, the more suitable potential form of two simple potential types commonly used in material simulations, namely the Lennard-Jones potential and the Morse potential in describing the corrosion of iron in molten lead metal. Corrosion simulations were run using the LAMMPS molecular dynamics software. From the simulation, it seems that the Morse interaction potential is more suitable for describing the corrosion systems for liquid metal systems, especially for iron in liquid lead.

INTRODUCTION

The diffusion coefficient of various materials is very important in its application for the development of science and technology, especially in the heat transfer process in the nuclear reactor. In the fast nuclear reactor, the material used as a sleeve or cladding corrosion may occurs due to the diffusion of particles at very high temperatures due to interact with molten liquid metal coolant. Corrosion can be defined as metal damage caused by chemical reactions which generally indicate the presence of electron transfer¹. Corrosion of the cladding material is called hot corrosion, where no electron transfer or chemical reactions, and due to the solubility of solid metals. Corrosion that occurs in the cladding material in fast nuclear reactors is one of the drawbacks of using nuclear reactors. The parameter that can be used as a reference to show the process of corrosion of solid metal in liquid metal is the diffusion coefficient. It is the bigger diffusion coefficient of material, the bigger corrosion will occur.

Diffusion can be defined as the flux or flow of several ions, atoms, electrons, or molecules. The amount of flux that flows depends on the difference in concentration and temperature. The diffusion process is also closely related to the crystal structure of the material. Diffusion can also be interpreted as a phenomenon that occurs when there is a vacancy in a material due to atoms moving or jumping from one lattice to another². The ability of an atom to diffuse increases with increasing temperature, i.e. when the thermal energy gained by the atom or molecule increases. The relationship between the diffusion coefficient and temperature is shown in Equation 1.

$$D(T) = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (1)$$

where D is the diffusion coefficient (m^2/s), D_0 is the diffusion coefficient at $T = 0\text{K}$ (m^2/s), T is the temperature (K), R is the gas constant (8.32 J/mol-K), and Q is the activation energy (J/mol). The diffusion coefficient in the computer simulation is determined from the value of Mean Square Displacement (MSD) which has a correlation with Einstein's relation formulation:

$$MSD = \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle \quad (2)$$

$$D = \frac{1}{6t} MSD \quad (3)$$

The value of the diffusion coefficient can be determined and predicted using a molecular dynamics simulation method. Molecular dynamics method is a computational method used for the motion of atoms, in molecular systems or large objects such as planets. The development of molecular dynamics methods is very rapid and is widely applied to various case studies, especially for material computational research³. Molecular dynamics methods have been successfully applied in various computational materials research purposes: chemistry, physics, and biology to predict physical chemical properties⁴. The molecular dynamics method works based on the principles of classical mechanics, namely by solving Newton's law, the force acting on each atom i is shown in equation 4.

$$F_i = m_i \frac{d\vec{v}_i}{dt} \quad (4)$$

Classical mechanics states that the force is the negative of the gradient of the potential function. Particles with the number of N in a system and their interactions produce a potential between atoms of V , then the force acting on each particle is shown in Equation 5.

$$F_i = -\nabla_i V(r_1, \dots, r_N) \quad (5)$$

The force acting on a system with N number of atoms can be predicted by calculating the negative of the potential gradient resulting from the interaction between atoms⁵.

The molecular dynamics simulation requires a potential function that describes the interactions between the atoms of the material. One of the factors that determine the accuracy of the calculation of physical quantities is that the potential form used must be precise. This simulation was carried out with two potential interactions, namely the Lennard-Jones potential and the Morse potential. The Lennard-Jones potential describes the interaction between two neutral atoms or molecules that attract each other at a distance and repel each other at a close distance. Lennard-Jones potential parameters include (σ) and (ϵ) obtained based on fitting experimental data⁶. In general, the Lennard-Jones potential is shown in equation 6⁷.

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

TABLE 1. Potential Parameters for Lennard-Jones Interaksi Interaction

Pair Interaction	ϵ (eV) ⁸	σ (Å) ⁸
Fe-Fe	0.400	2.319
Pb-Pb	0.191	3.189

Morse potential is a model of interaction between atoms for potential energy derived from diatomic molecules. Morse potential describes a diatomic system that relates potential energy and distance in a diatomic system and the relationship between atomic or molecular bonds with the distance⁹. The Morse potential explicitly includes bond breaking effects, such as the presence of bound conditions, making it the best approximation for the vibrational structure of a QHO (Quantum Harmonic Oscillator). Morse potential can be used to model interactions between atoms, although it is very simple but is not used in modern spectroscopy¹⁰. Morse potential can be determined by Equation 7.

$$U(r_{ij}) = \mathcal{D} [e^{-2a(r_{ij}-r_0)} - 2e^{-a(r_{ij}-r_0)}] \quad (7)$$

where r is the distance between atoms, \mathcal{D} is the energy of molecular dissociation or bond breaking, and a is the length parameter (curvature potential at the origin)¹¹.

TABLE 2. Morse Potential Parameters

Metal	$a = \text{\AA}^{-1}$	$r_0 = \text{\AA}^{12}$	\mathcal{D} (eV) ¹²
Pb	1.1836	3.733	0.2348
Fe	1.3885	2.845	0.4174

In this current work, the simulations were carried out using the LAMMPS program and visualization using OVITO. LAMMPS is a program that contains a set of classical molecular dynamics codes, which can model the

behavior of up to a million particles, in liquid, solid or gaseous states. In general, the LAMMPS program integrates Newton's equations of motion for a collection of atoms, molecules, or macroscopic atoms that interact with each other at near or far distances with various boundary conditions¹³.

OVITO is a program that can be used for visualization and scientific analysis of atomistic data simulation results¹⁴. The OVITO program uses the C++ language and is classified as an open source program that is used as a support program in analyzing data from molecular dynamics simulations, such as LAMMPS.

This simulation was conducted to determine the most suitable form of interaction potential used in describing the corrosion of iron in molten lead metal. The interaction potential used is the Lennard-Jones potential and the Morse potential. The two types of potential are simple potentials commonly used in material simulation. The simulation system is modeled by placing iron in molten lead metal. The diffusion coefficient was calculated by the two interaction potentials at a temperature of 1023K using the Einstein relation formulation.

MATERIALS AND METHOD

Materials

Iron is a metal that is relatively diverse in its use. The structure of iron can be divided into two types, namely BCC (Body Centered Cubic) and FCC (Face Centered Cubic) with a lattice constant $a = 2.861\text{\AA}$. The difference in the crystal structure of iron is influenced by temperature condition. At 1184K, the crystal structure of iron is BCC. Meanwhile, when the iron is above that temperature, namely $1184\text{K} < \text{iron} < 1665\text{K}$, the iron crystal structure is in the form of FCC. When the iron increases in temperature $> 1665\text{K}$, the iron will return to the BCC phase. The BCC phase can be maintained until the iron reaches its melting point¹⁵. Iron has a melting point at 1811K and a boiling point at 3134K¹⁶.

Lead is a chemical element in group IVA in periodic table which has an atomic number of 82 with an atomic mass of 207.20 g/cm³ and a density of 11.34 g/cm³. Lead is composed of an FCC crystal structure with a melting point of 327 °C and a boiling point of 1740 °C¹⁷. At a temperature of 500-600 °C lead can evaporate and form oxygen in the air in the form of lead oxide (PbO). Lead is one of the dangerous heavy metals because it has carcinogenic properties, can cause mutations, decompose in the long term, and its toxicity does not change¹⁸.

Computational Method

This research begins with creating a simulation system. The simulation system is modeled in the form of a simulation box measuring 66.20Å x 66.20Å x 66.20Å. The simulation system consists of molten iron (Fe) and lead (Pb). In the simulation box, iron metal (Fe) is placed in the middle of molten lead (Pb). The number of iron atoms is 1331 atoms and the liquid metal is composed of 5698 Pb atoms.

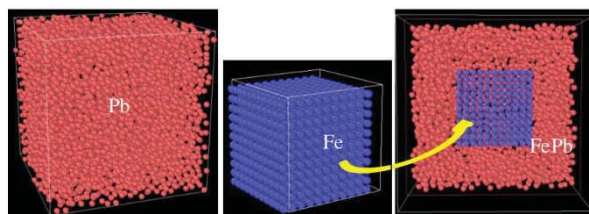


FIGURE 1. Ferrous metal in molten lead

Next step, is creating the input script for running LAMMPS simulation that prepared in a file (<https://www.lammps.org/>). The input file contains "Lammps command line" to compute the physical quantities, in this case are the diffusion coefficient (D_T), as well as some data that affect the state of the simulation system such as metal crystal shape, crystal constant, atomic number, atomic weight, potential shape and parameters, number of simulation steps, temperature T(K) simulation, and pressure P(atm) simulation.

```

# ----- Initialize Simulation -----
clear
units metal
dimension 3
boundary p p p
atom_style atomic
atom_modify map array

# ----- Create Atoms -----
read_data FePbbaru
mass 1 207.2 ##Pb
mass 2 55.845 ##Fe

# ----- Define Interatomic Potential -----
group timbal type 1
group besi type 2

pair_style morse 12.9
pair_coeff 1 1 0.2348 1.1836 3.733 10.9
pair_coeff 2 2 0.4174 1.3885 2.845 10.9
pair_coeff 1 2 0.0490 1.2861 5.3102 12.9

min_style sd
minimize 1.0e-12 1.0e-25 5000 10000

timestep 0.001

thermo 1000
thermo_style custom step temp vol press pe etotal

velocity all create 1075 2231234 dist uniform mom yes rot yes
run 0
velocity all scale 1075

velocity all create 1023 41254 dist uniform mom yes rot yes
fix mynpt all npt temp 1023.0 1023.0 10.0 iso 0.0 0.0 1000.0
run 220000
unfix mynpt

velocity all create 1075 2231234 dist uniform mom yes rot yes
run 0
velocity all scale 1075

dump mydump all custom 1000 all.dump type x y z

fix mynvt all nvt temp 1023 1023 100

compute 2 besi msd com yes
compute 3 besi vacf
compute 4 besi temp
fix 5 besi ave/time 1 1 1 c_4 c_2[4] c_3[4] file besi.msd

run 50000
undump mydump

```

In our simulation, one of the results is MSD data file, is used to get the value of the diffusion coefficient (D_T). The MSD output data will be represented in the form of a graph of the MSD value against the timestep used to obtain the diffusion coefficient (D_T). To determine the slope of the MSD graph against the timestep, it is done using the gnuplot software. The commands line to determine the slope of gnuplot from terminal OS linux are typing¹⁹:

```
f(x)=a*x+b
fit f(x) './out.msdf' u 1:3 via a,b
plot './out.msdf' , f(x)
```

In the first column of out.msdf file should be in time domain. Fitting results will be automatically saved in the fit.log file. The slope is converted to m^2/s , then the diffusion coefficient (D_T) can be determined. Diffusion coefficient from simulation results then were compared with the available diffusion coefficient experimental data.

Then using this best potential, a simulation is continuously carried out to determine the temperature-dependent diffusion coefficient $D(T)$. Simulations were carried out with various temperatures to plot a graph of the relationship between $1/T$ and $\ln D$. This graph was made to determine parameters D_0 and Q in the Arrhenius form of $D(T)$.

RESULTS AND DISCUSSIONS

In this research we compare two potential interactions, Lennard-Jones and Morse type, for computing the diffusion coefficient of iron (Fe) in molten lead (Pb). The MSD output of simulation were analyzed using the gnuplot. The diffusion coefficient of iron in liquid lead, $D(T)$, was calculated based on the Lennard-Jones and Morse interaction potentials, then both results were compared to available experimental data. The experimental diffusion coefficient was obtained from work of W. M. Robertson¹, where $D_{exp}(1023K) = 2.8 \times 10^{-9} m^2/s$.

TABLE 3. Diffusion coefficient of iron in molten lead at $T = 1023K$

Potential Type	Simulation
Morse	$D_{morse} = 2.806 \times 10^{-10} (m^2/s)$
Lennard-Jones	$D_{LJ} = 2.093 \times 10^{-11} (m^2/s)$

Based on the results obtained in Table 3 the diffusion coefficient predicted by the Morse potential is greater than the Lennard-Jones potential. A large diffusion coefficient indicates greater corrosion of iron. However, this research focuses on finding a suitable or appropriate potential with reference to the diffusion coefficient of the experimental results. It can be seen from Table 3 that D_{Morse} is much closer to D_{exp} compared to D_{LJ} . So, the diffusion coefficient calculation for liquid metal corrosion phenomena seems more accurate using the Morse Potential.

Furthermore, then the simulation were continuously carried out with Morse interaction potential to determine the temperature dependent of diffusion coefficient. Figure 2 shows the graph of $\ln D$ vs. $1/T$.

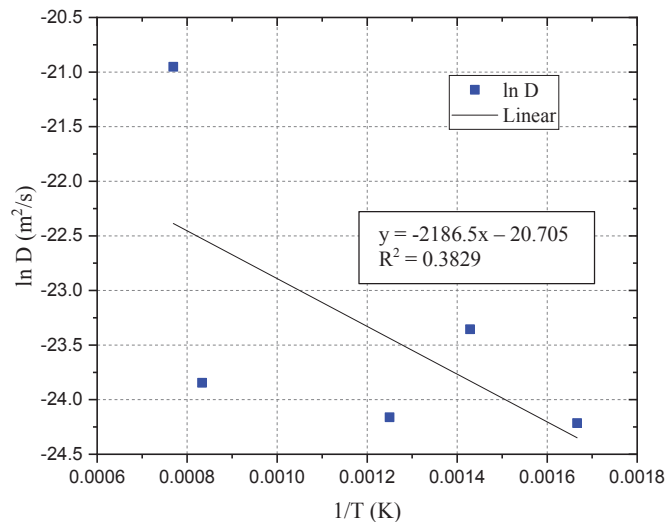


FIGURE 2. Graph of $\ln D$ vs. $1/T$

It is from Figure 3 we can take a conclusion that from simulation we have:

$$D(T) = 1.01843 \times 10^{-9} \exp(-2186.53/T) \text{ m}^2/\text{s} \quad (8)$$

We can state the $D(T)$ experimental results from previous studies by W. M. Robertson is

$$D(T) = 4.9 \times 10^{-7} \exp[(-44100 \pm 6300)/RT] \text{ m}^2/\text{s} \quad (9)$$

Further we can plot Equation (8) as in Figure 3.

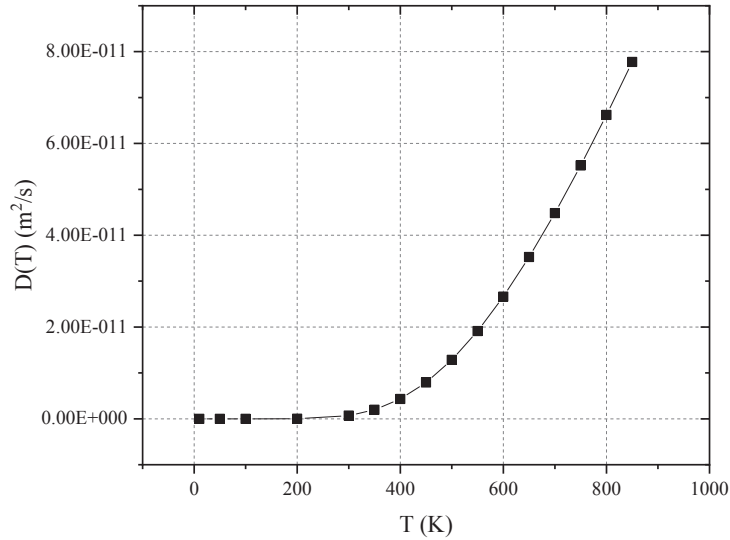


FIGURE 3. The temperature-dependent diffusion coefficients $D(T)$ of iron in liquid lead

Next, Figure 4 is the graph of $D(T)$ from simulation prediction and experimental data. From the graph we see that the Morse potential is quite good in describing the phenomenon of iron corrosion in molten lead metal based on the graph pattern which is quite similar across temperatures. We can take conclusion that the Morse potential seems more suitable to describe the corrosion phenomena than the Lennard-Jones phenomena.

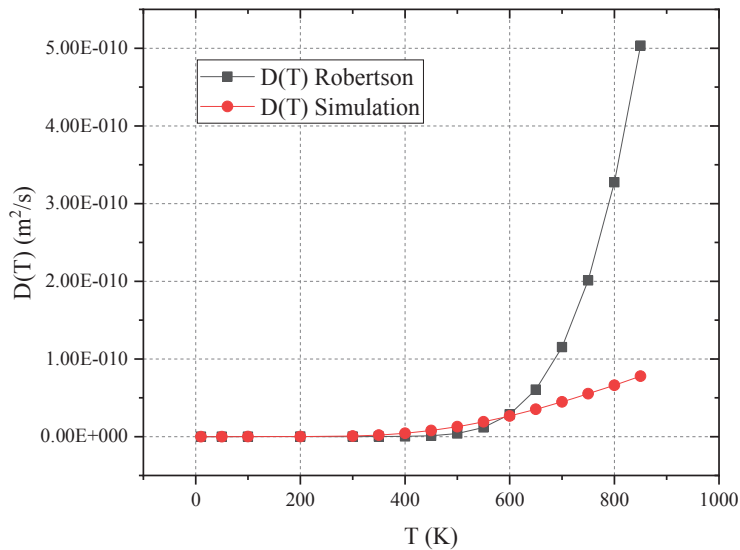


FIGURE 4. Comparison of the $D(T)$ from Robertson and $D(T)$ from Simulation

CONCLUSION

The diffusion coefficient calculation for liquid metal corrosion phenomena using Morse potential is predicted more suitable than the Lennard-Jones potential. The diffusion coefficient as a function of temperature, $D(T)$, obtained from the simulation is $D(T) = 1.01843 \times 10^{-9} \exp(-2186.53/T) \text{ m}^2/\text{s}$. This result need to be checked for bigger system of FePb using more atoms of material, to get more accurate of the result.

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