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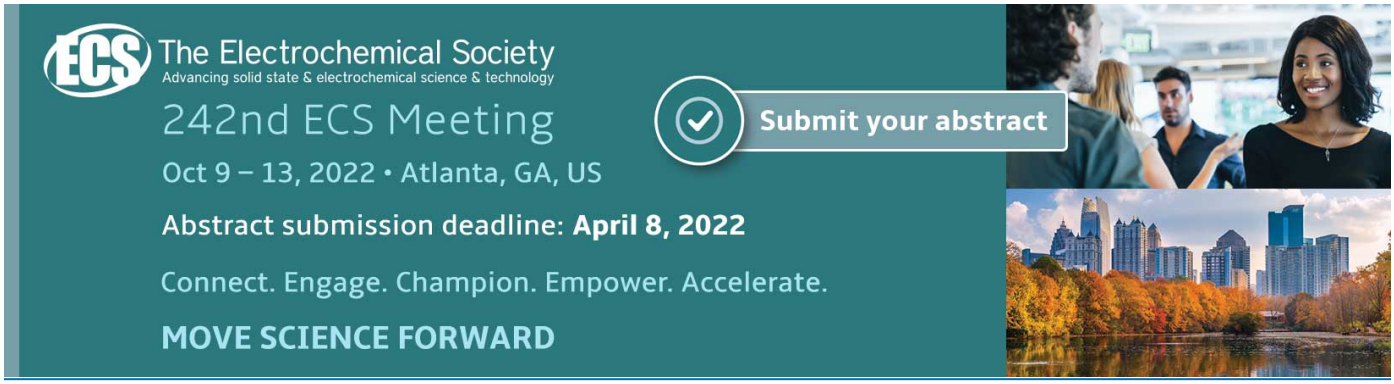

Self-diffusion coefficient of fe, pb, ni and Cr by molecular dynamics simulation using the potential morse

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Abstract. The molecular dynamics simulation using the Morse potential has been applied to calculate the value of self-diffusion coefficients $D(T)$ of some pure metals as Pb, Cr, Ni, and Fe. The simulation then was done using the MOLDY molecular dynamics program. The procedure to calculate these coefficients following several steps: first, determining the Morse potential parameters as $\mathcal{D}$, a and r_0; second, simulating the material under consideration using Moldy based on the appropriate ensemble; third, diffusion coefficient calculation using the Green-Kubo method for specific temperature; and fourth, the temperature-dependent diffusion coefficient $D(T)$ based on the Arrhenius. The simulation work has obtained the best results as following: for Pb metal the Morse potential parameter ($a = 1.4795\ \text{A}^{-1}$, $r_0 = 3.733$ Å, and $\mathcal{D} = 0.2348$ eV) with $D(T) = 9.68 \times 10^{-9} \exp\left(\frac{-3890.79}{RT}\right)$ [m^2/s] ; for Cr metal the potential parameters ($\mathcal{D} = 0.3292$ eV , $a = 1.1005\ \text{A}^{-1}$, and $r_0 = 2.2032$ Å), with $D(T) = 1.73 \times 10^{-3} \exp\left(\frac{-8725.54}{RT}\right)$ [m^2/s]; for Ni metal the Morse potential parameter ($\mathcal{D} = 0.3784$ eV , $a = 1.0649\ \text{A}^{-1}$, $r_0 = 2.085$ Å), with $D(T) = 8.5 \times 10^{-4} \exp\left(\frac{-15794.9}{RT}\right)$ [m^2/s]; and for Fe metal the potential parameter ($\mathcal{D} = 0.4174$ eV, $a = 1.5974\ \text{A}^{-1}$, $r_0 = 2.840$ Å) with $D(T) = 4.22 \times 10^{-7} \exp\left(\frac{-5878.49}{RT}\right)$ [m^2/s]. The calculated diffusion coefficients of the work have significant application as for the corrosion study of steels in nuclear reactor design.

1. Theoretical Background

The diffusion coefficient is a physical quantity that is quite important to know because of its potential applications. One useful application of molecular dynamics simulation is to calculate the self-diffusion coefficient of the material. This method becomes very important whenever the experimental data is not available for application, especially for any temperatures that we want to know. The study of the theory of diffusion coefficients is often to find an accurate method in determining the vapor pressure of solutions at high temperatures. Per definition, the diffusion is a process in which matter is transferred from one part to another as a molecular motion randomly [1]. This diffusion process is related to the diffusion coefficient D. In the electronics industry information on self-diffusion coefficients is very important for studying component resilience [2].

The diffusion coefficient is often used to check the value of reinforcement in metals or produced compounds. The process of atomic diffusion in material involves the transfer of atoms from the high concentration part to a lower concentration in the material. Arkundato has used the diffusion coefficient to study the corrosion phenomena of iron in liquid metal using Lennard-Jones potential, simulated in the Moldy program [3]. In this case, the classical Morse potential is often to be considered the better potential for metals compared with the Lennard-Jones potential.

Theoretically or computationally, to determine the self-diffusion coefficient can be done using various methods, especially molecular dynamics methods. Molecular dynamics is a simulation technique that allows atoms of the material to interact with each other to evolve over a period of time

so that all atoms of material will form a particular path called a trajectory $\boldsymbol{r}(t)$. The calculation of (self-) diffusion coefficient with the molecular dynamics computational method can be done in two ways, namely through the Einstein formula (relation) and the Green-Kubo formulation. The Green-Kubo formulation is defined through the VACF (*Velocity Autorrelation Function*) function, which is a formula for autocorrelating the speed function or can optionally calculate the total correlation speed function of the same data source. While the Einstein relation is a theory that studies the properties of atoms and molecular kinetics where the diffusion coefficient is obtained from the slope of MSD (*Mean Square Displacement*) versus time *t*.

In this work the calculation of the self-diffusion coefficient *D* used the Green-Kubo formulation, for several metal elements of alloy steel components such as Pb, Cr, Ni, and Fe. As the molecular dynamics simulation needs a potential function, we used the Morse potential that having three parameters i.e a [A^{-1}], r_0 [Å], and $\mathcal{D}$ [eV]. The problem is then to determine the most appropriate parameters that can be used in the MOLDY simulation. To support this necessary, we will use the Morse potential parameters from available references, then making some correction to these parameters by comparing the simulation results and available experimental data. After we can determine the best Morse potential parameters then we continue to calculate the temperature-dependent diffusion coefficient $D(T)$ using Arrhenius formula. Table 1 is experimental data of diffusion coefficient for Fe, Pb, Ni and Cr.

Table 1. Self-diffusion coefficient of materials from the experiment

Authors	**Element**	$\boldsymbol{T}$ **(K)**	$\boldsymbol{D}$ $(\mathbf{m^2/s})$
Winkelmann [4]	Pb	743	4.58×10^{-9}
Donald & Wendelin [5]	Fe	3000	1.74×10^{-7}
Maier *et al*. [6]	Ni	813	9.6×10^{-5}
Neumann [7]	Cr	1369	9.7×10^{-4}

According to Refson [8], the Green-Kubo Formulation is defined through the VACF function which is a formula for autocorrelating the speed function or it can also be called VTF (*Velocity Total Correlation Function*) . The self-diffusion coefficient, *D* can be obtained from the VACF integration as:

$$D = \frac{1}{3}\int_0^\infty Z(t)\,dt \qquad (1)$$

And according to Arrhenius formula. the temperature-dependent diffusion coefficient can be formulated as:

$$D(T) = D_0 \exp\left(\frac{-E}{RT}\right) \qquad (2)$$

Where D_0 is the self-diffusion coefficient at temperature T = 0 K in-unit $\mathrm{m/s^2}$, E is the activation energy in unit $\mathrm{J/mol}$, T is the temperature in unit Kelvin (K) dan R is a universal gas constant (0,082 L.atm/mol K).

The Morse potential is a suitable potential in the case of diatomic molecules discovered by Phillip M. Morse in 1929:

$$\varphi(r_{ij}) = \mathcal{D}\left[e^{-2a(r_{ij}-r_0)} - 2e^{-a(r_{ij}-r_0)}\right] \qquad (3)$$

where r is the distance between atoms, $\mathcal{D}$ is the molecular associated energy (Release of bonds) and a is a length parameter which is a potential curvature at the origin [8]. Table 2. is a Morse potential parameter for some metals.

Table 2. Potential parameters of Morse

Metal	$\alpha = A^{-1}$	$r_0 =$ Å	$\mathcal{D}$ **(eV)**
Pb	1,1836	3,733	0,2348
Ag	1,3690	3,115	0,3323
Ni	1,4199	2,780	0,4205
Cu	1,3588	2,866	0,3429
Al	1,1646	3,253	0,2703
Ca	0,80535	4,569	0,1623
Sr	0,73776	4,988	0,1513
Mo	1,5079	2,976	0,8032
W	1,4116	3,032	0,9906
Cr	1,5721	2,754	0,4414
Fe	1,3885	2,845	0,4174
Ba	0,65698	5,373	0,1416
K	0,49767	6,369	0,05424
Na	0,58993	5,336	0,06334
Cs	0,41569	7,557	0,04485
Rb	0,42981	7,207	0,04644

Source: (Girifalco and Weizer) [10]

In this work, the MD simulation was realized using the MOLDY program. This program was chosen because it is relatively very accurate and is still used in actual research and can be formed for many types of materials from liquid, solids or gases [8].

One of the important applications of the diffusion coefficient is as in the nuclear reactor power plant design. The liquid lead cooled fast nuclear reactor, using the liquid lead to move the heat from the reactor core to the turbine system. However, the liquid lead caused very high corrosion for steels used in the reactor. This hot corrosion can be studied and seen as the diffusion process. In the diffusion process we need to compute the diffusion coefficient. The corrosion because of the high dissolution of steel components (Fe, Ni, Cr, etc) flowing into the liquid lead [11-14]. In our previous work we have calculated the diffusion coefficients of Fe in the liquid lead with molecular dynamics simulations. But we used the Lennard-Jones Potential [15-18]. The Lennard-Jones potential is very simple and may not accurate for metal. The Morse potential is better for the metal system, as our goal in this current work.

2. Method

The calculation of the diffusion coefficient and simulations following this procedure:

(1) determining the best Morse potential parameters as $\mathcal{D}$, a and r_0 of element. For the first simulation we use parameters as in Table 2.

(2) simulating the material under consideration, based on an appropriate ensemble and control parameters.

(3) diffusion coefficient calculation using the Green-Kubo method. Compare the calculated diffusion value with available experimental data (Table 1) the setting up the parameters a [A^{-1}], r_0 [Å], and $\mathcal{D}$ [eV] till the discrepancy of simulation dan experimental value is under tolerance < 5.00 %. Discrepancy *d* can be computed by:

$$d = \left| \frac{D_T^{sim} - D_T^{exp}}{D_T^{exp}} \right| \times 100\% \qquad (4)$$

(4) calculation of the temperature-dependent diffusion coefficient $D(T)$ based on the Arrhenius for the best parameter of a [A^{-1}], r_0 [Å], and $\mathcal{D}$ [eV] of the element in point (3).

D_T^{sim} is the self-diffusion coefficient from simulation result, D_T^{exp} is the experimental self-diffusion coefficient from existing reference (Table 1).

3.Results and Discussions

3.1 Parameters and Diffusion of Lead Pb

For Pb Metal, the potential parameter of Morse potential was verified and corrected at temperature 743 K. Using potential parameter in Table 2 for Pb, then the self-diffusion coefficient by simulation was $D_T = 7.113 \times 10^{-8}$ m^2/s. This shows the discrepancy d = 1453% compared with the experimental value in Table 1, so that it needs to be corrected. By small changing of old parameter then-new parameter $a = 1.4795$ A^{-1}, $r_0 = 3.733$ Å, and value $\mathcal{D} = 0.2348$ eV have produced the self-diffusion coefficient of lead Pb i.e $D_T = 4.38 \times 10^{-9}$ m^2/s with discrepancy d of 4%. Then that new parameter of Morse potential will be used to predict the temperature-dependent self-diffusion coefficient using the Arrhenius model. The temperature of simulations for this calculation is in the range of 500 - 2000 K. Figure 1 is a plot of ln D vs 1/T for several temperatures to determine the coefficients D_0 and E of Equation (4) for lead Pb.

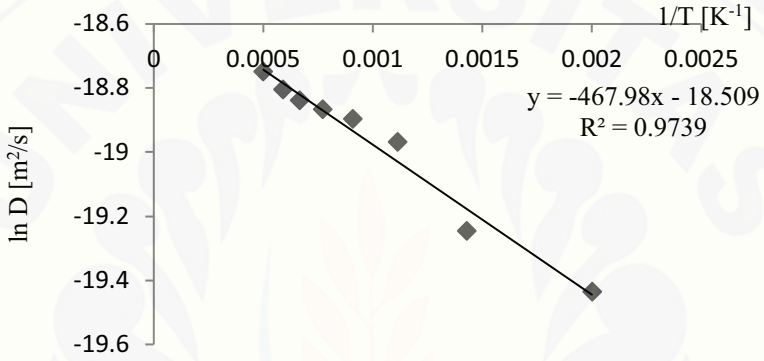

Figure 1. Graph of ln D vs 1/T for Pb

The line equation of the graph in Figure 1 is $y = -467.98x - 18.509$. Then we can obtain the coefficient D_0 and E and writing the temperature-dependent of the diffusion coefficient in the form of $D(T) = 9.68 \times 10^{-9} \exp\left(\frac{-3890.79}{RT}\right)$. Figure 2 is the plot of this formula:

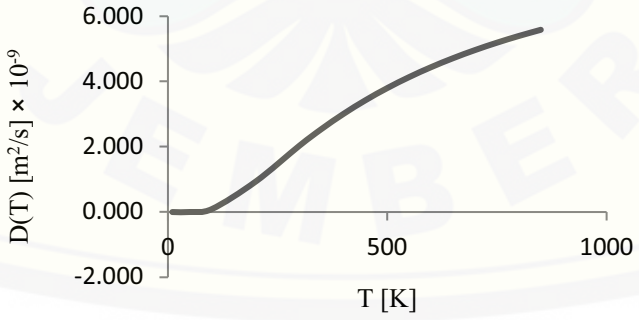

Figure 2. The plot of D(T) of lead Pb for several T

3.2 Parameters and Diffusion of Chromium

For Cr Chromium we evaluated at a temperature of 1369K as in Table 1. As explained in the case of Pb before, then for Chromium we got:

Before correction. We obtain from the simulation that the diffusion coefficient is $D_T = 1.04973 \times 10^{-6}$ m^2/s . The potential parameters used in this simulation using old parameters as in Table 2. The discrepancy of D_T between simulation and experiment is d = 99.89%.

After correction. After we make the correction using new Morse potential we get $D_T = 9.41 \times 10^{-4}$ m^2/s,

The new parameters are $\mathcal{D}$ = 0.3292 eV, $a = 1.1005$ A^{-1}, and $r_0 = 2.2032$ Å . The discrepancy of D_T is only = 2.99%

The temperature-dependent diffusion coefficient was calculated at temperature 500 to 700 K as in Figure 3.

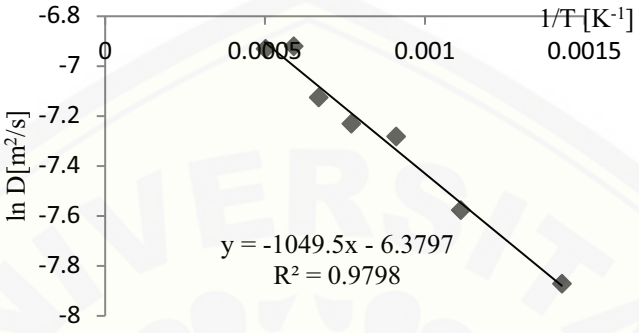

Figure 3. Graph of ln D vs 1/T for Cr

The line equation of the graph is $y = -1049.5x - 6{,}3797$. Then we can write $D(T) = 1.73 \times 10^{-3} \exp\left(\frac{-8725.54}{RT}\right)$. Figure 4 is the plot of *D*(*T*).

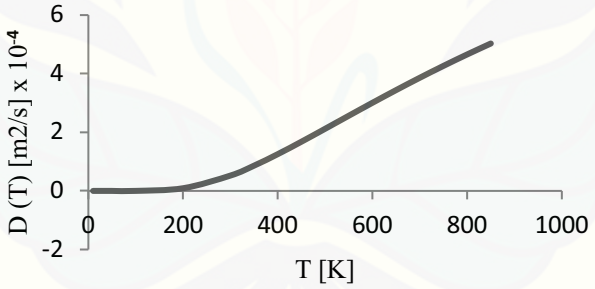

Figure 4. The plot of D(T) of chromium Cr for several *T*

3.3 Parameters and Diffusion of Nickel Ni

For Nickel we evaluated at a temperature of 813 K as in Table 1. As explained in two cases before, then for Nickel we got:

Before correction: We obtain from the simulation that the diffusion coefficient is: $D_T = 4.403 \times 10^{-7}\mathrm{m}^2/\mathrm{s}$, using the old parameter as in Table 2. The discrepancy of D_T is 99.54% between simulation results and experimental results.

After correction: We need to make correction of morse parameter to get new parameters as $\mathcal{D}$ = 0.3784 eV, $a = 1.0649$ A^{-1}, $r_0 = 2.085$ Å . We get the diffusion coefficient $D_T = 9.47 \times 10^{-5}\mathrm{m}^2/\mathrm{s}$. The discrepancy is d = 1.35%.

The temperature-dependent diffusion coefficient was calculated by using Figure 5.

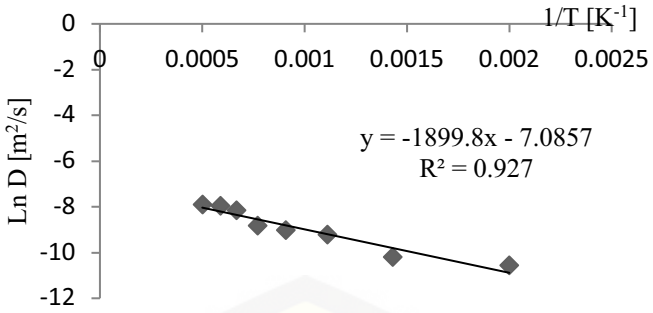

Figure 5. Graph of ln D vs 1/T for Ni

The line equation of the graph Figure 5 is y = -1899.8x – 7.0857. From this equation can be analyzed using the Arrhenius equation by looking for values D_0 and E , that the temperature-dependent diffusion coefficient $D(T) = 8.5 \times 10^{-4} \exp\left(\frac{-15794.9}{RT}\right)$. Figure 6 shows the plot of this formula for several temperatures.

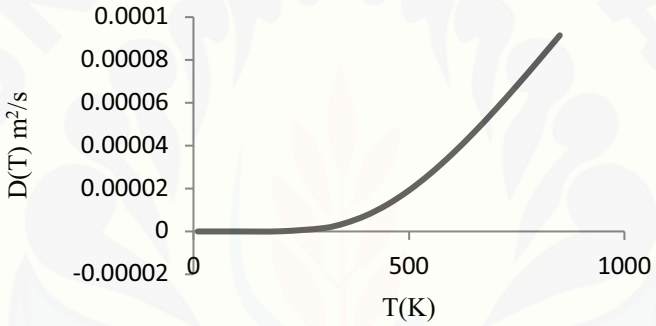

Figure 6. The plot of D(T) of nickel Ni for several T

3.4 Parameters and Diffusion of Iron Fe

For Iron Fe simulation we evaluated at a temperature of 3000K as in Table 1. The result is below. *Before correction:* Using old parameter of Morse potential as in Table 2, the diffusion coefficient is $D_T = 7.07 \times 10^{-5}$ m^2/s, The discrepancy between experiment and simulation is $d = 356.07\%$. *After correction:* Making correction to Morse potential that is $\mathcal{D} = 0.4174$ eV, $a = 1.5974$ A^{-1}, $r_0 = 2.840$ Å then the diffusion coefficient is $D_T = 1.72 \times 10^{-7}$ m^2/s . The discrepancy is $d = 1.15\%$. The temperature-dependent diffusion coefficient was calculated by using Figure 7.

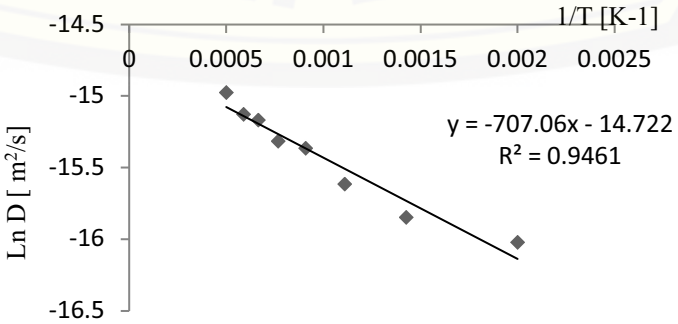

Figure 7. Graph of ln D vs 1/T for iron

We got line equation y = -707.06x – 14.722 wherefrom this equation we can get $D(T) = 4.22 \times 10^{-7} \exp\left(\frac{-5878.49}{RT}\right)$. Figure 8 shows the plot of this formula at several temperatures.

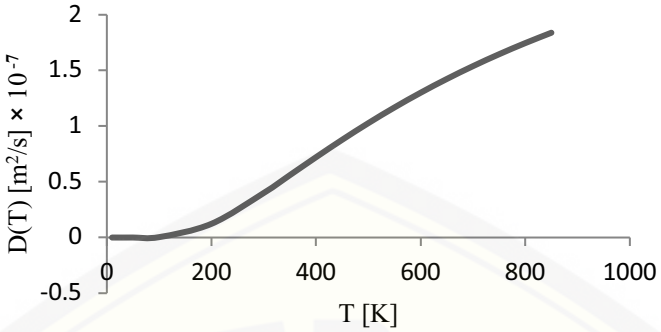

Figure 8. The plot of $D(T)$ of Fe for several temperatures

4. Conclusion

The Morse potential has been used to determine the diffusion coefficient of some metals as Pb, Ni, Cr and Fe. The used method for self-diffusion calculation is Green-Kubo using molecular dynamics simulation data. The Arrhenius formula was used to plot the temperature-dependent diffusion coefficient. All simulation data created and verified using the Moldy program. The best parameter of Morse potential can be written as below:Lead Pb

4.1 Morse potential parameter:

$$\mathcal{D} = 0.2348 \text{ eV},\ a = 1.4795 \text{ A}^{-1},\ r_0 = 3.733 \text{ Å},\ D(T) = 9.68 \times 10^{-9} \exp\left(\frac{-3890.79}{RT}\right).$$

4.2 Chromium Cr

Morse potential parameter:

$$\mathcal{D} = 0.3292 \text{ eV},\ a = 1.1005 \text{ A}^{-1},\ r_0 = 2.2032 \text{ Å}),\ D(T) = 1.73 \times 10^{-3} \exp\left(\frac{-8725.54}{RT}\right).$$

4.3 Nickel Ni

Morse potential parameter:

$$\mathcal{D} = 0.3784 \text{ eV},\ a = 1.0649 \text{ A}^{-1},\ \ r_0 = 2.085 \text{ Å}),\ D(T) = 8.5 \times 10^{-4} \exp\left(\frac{-15794.9}{RT}\right),$$

4.4 Iron Fe

Morse potential parameter

$$\mathcal{D} = 0.4174 \text{ eV},\ a = 1.5974 \text{ A}^{-1},\ \ r_0 = 2.840 \text{ Å}),\ \ D(T) = 4.22 \times 10^{-7} \exp\left(\frac{-5878.49}{RT}\right)$$

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