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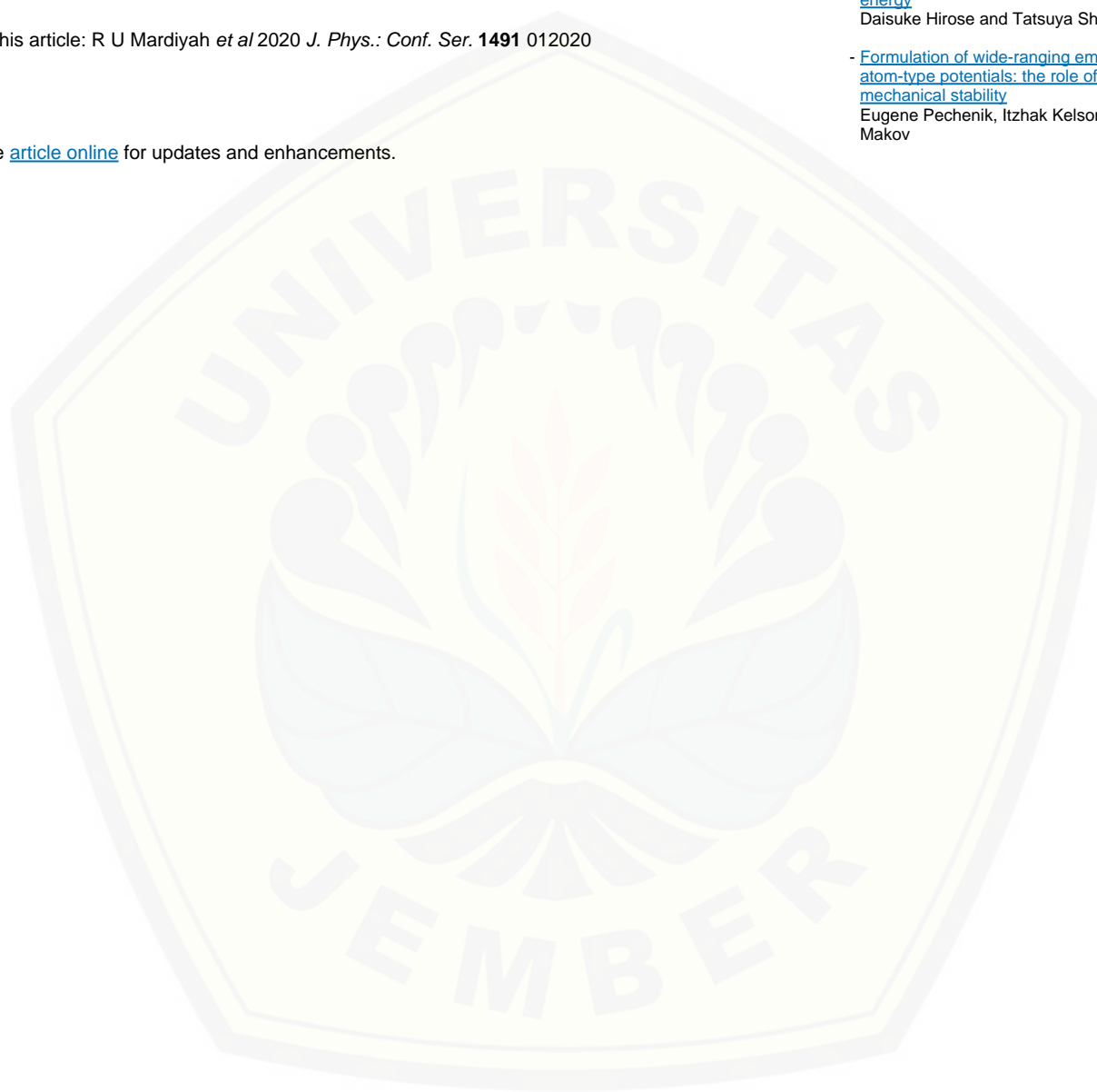
Energy Cohesive Calculation for Some Pure Metals Using the Lennard-Jones Potential in Lammps Molecular Dynamics

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Energy Cohesive Calculation for Some Pure Metals Using the Lennard-Jones Potential in Lammps Molecular Dynamics

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Abstract. It has been determined by molecular dynamics simulation method the parameter potentials (ε, σ) of the Lennard-Jones potential based on the cohesive energy value for some pure metals. The LAMMPS molecular dynamics software was used to simulate and calculate the cohesive energy of the metals. To determine the best value of (ε, σ) we verified all calculations using the available experimental data of cohesive energy of the metals. The discrepancy of cohesive energy between simulation and experimental data were limited not more than 0.1 % to get best value of the Lennard-Jones parameter potentials (ε, σ).

1. Introduction

Many things need to be considered in designing materials using computational methods, such as how to calculate physical quantities and relevant parameters to be used in functions or quantities in simulation input. One parameter that needs to be considered is the parameter of interaction potential among atoms in materials. Some potential interactions that are often used for atomic interaction are the Morse, Buckingham, Gupta, Lennard-Jones and other potentials. It is often researchers using the Lennard-Jones to predict the properties of materials. The Lennard-Jones potential can be used to realize the interactions between pairs of neutral atoms and molecules in the material system [1].

The parameter values of the interaction potential among atoms are formulated in functions or potential equations and their values can be obtained in theory (quantum) calculations but can also be done by verifying the value of potential interaction parameters through (classical) simulation and then fitting to experimental data. The potential parameter of Lennard-Jones can be written mathematically in the form of equations (1).

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

$$(1)$$

where:
$U(r)$ = Lennard-Jones potential (eV)
σ = collision parameter(Å)
ε = atomic binding energy (eV)

R =   distance between atoms (Å)

The parameter of potential ε and σ is an illustration of the strength of the interaction and the radius rejects between the nuclei. Based on equation (1), the first term shows the distance parameter in the form of R^{-12} and the second term in the form of R^{-6}. If the value of $R^{-12} = \sigma$, it can be said that the distance between atoms is very close so that a repulsive force occurs. And if the value of the second term is the value of $R^{-6} > \sigma$, there will be an attractive force [2]. In general, the graph of Lennard-Jones potential can be seen as in Figure 1.
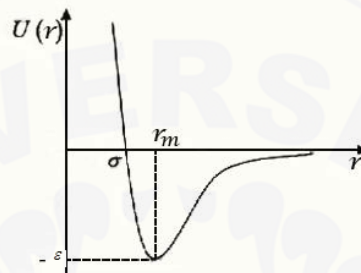
Figure 1. Potential Lennard-Jones [2]

Physical properties of a material can be predicted through simulation by observing motion of substance atoms in molecular dynamics simulation [3]. One of the calculated physical quantities is cohesive energy. Cohesive energy is the energy required by solids to separate solids into separate entities (free atoms) [4]. Cohesive energy (ΔE) for crystals can be written mathematically in equation (2) [5]. To calculate cohesive energy associated with molecules in slow gas can be calculated by equation (3).

$$\Delta E = -(E_g + E_i)$$

(2)

$$\Delta E = 2N\varepsilon \left[(P_{ij})(\tfrac{\sigma}{R})^{12} - \left((P_{ij})(\tfrac{\sigma}{R})^6 \right) \right]$$

(3)

where:
ΔE =   Cohesive energy (eV/atom)
E_g =   Kinetic energy with relative mass (eV)
E_g =   Ionization energy (eV)
N =   Number of atoms of material
σ =   Lennard-Jones potential parameter of atomic bond length (Å)
ε =   Lennard-Jones potential parameter of energy depth (eV)
R =   Separation distance between atoms (Å)
It is known that cohesive energy for gas is slow for a material with an FCC crystal structure, the value of P_{ij}^{-12} = 12.13188, P_{ij}^{-6} = 14.45392. Whereas material with BCC structure for value P_{ij}^{-12} = 9.1142, and P_{ij}^{-6} = 12.2533.

The molecular dynamics simulation has been developed in many codes. One of very popular code is the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) as in https://lammps.sandia.gov [6]. This code uses the verlet integration to solve the equation of motion of atoms of material. In this study we use the lennard-Jones (LJ) potential to describe the interaction of atoms of material (metals). To be able to observe the physical and mechanical properties of metals

under the LJ potential in Lammps simulation, we need to verify the value of the potential parameter of Lennard Jones firstly. The Lennard-Jones potentials have parameters ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) and this need to be corrected to be able to describe the interaction of atomic metal accurately using LAMMPS under verlet algorithm. To verify these values, we can use any numbers basically, then we do simulation to calculate the properties and then compare it with available experimental data. Then we make some small correction to ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) parameters for getting smallest error/discrepancy between experiment and calculation. In this study we want to know the best value of potential parameter ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) of LJ potential for pure metals by evaluating the cohesive energy of the material. To do this we will use some values of ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) of metals from available data as in Table 1, column 4 and 5 as initial input of simulation. Whenever we have obtained the best ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$), then in principle, we can use these to compute other properties of material. It is the goal of this research to find these value ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$).

What is the state of the art of this current work? The data of the ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) parameter is relatively limited that can be found from some sources, for example from internet. These parameters are very important to calculate for any properties of material. So the results of current work should be important for may applications. In our previous work we don't make some verification for the Lennard-Jones parameters yet [7-11].

2. Method

2.1 Procedure of calculation

The procedures of simulation to find the best LJ potential parameters is described as following:

1. Determine the initial guest of ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) as in column 4 & 5 Table 1.
2. Lammps simulation uses that initial ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) for cohesive energy calculation
3. Comparison the cohesive energy by simulation and by experiment: compute the discrepancy between two values simulation and experiment.
4. Make some correction to ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) by (+/-) if there is big discrepancy.
5. Redo Lammps simulation for the next new values ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$)
6. Redo comparison as step 3
7. Stop if the discrepancy is enough small ≤ 0.1 %

2.2 Procedure of simulation using LAMMPS

The installation of Lammps code in our computer is very easy. Under Linux Ubuntu OS this installation can be done by type in terminal:

$sudo apt-get install lammps (enter)

After installation, the use of lammps for simulation can be done by creating the input script in one file. Then we can start the simulation by type CLI command:

$lmp_daily <"input file name"

2.3 How to make correction for ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$)

Correction to ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) can be done by adding or subtracting with a small number from the initial ($\boldsymbol{\varepsilon}$, $\boldsymbol{\sigma}$) until the cohesive energy value obtained from the simulation approaches or equals the experimental cohesive energy value. We can do this step by step, after getting the best value of $\boldsymbol{\varepsilon}$ (the cohesive energy is close to the experiment), then, continue with the value $\boldsymbol{\sigma}$. In the same way as getting the best $\boldsymbol{\varepsilon}$ value, the value of $\boldsymbol{\sigma}$ is changed by adding or subtracting the value $\boldsymbol{\sigma}$ with a fixed value of $\boldsymbol{\varepsilon}$, using the best value $\boldsymbol{\varepsilon}$ simulation results (not using the $\boldsymbol{\varepsilon}$ value of the reference). This verification process of the ε and σ values is repeated until the % discrepancy ≤ 0.1 % is obtained for certain materials. The discrepancy of two measurements can be computed vy:

$$|\text{discrepancy}| = \frac{E_{simulation} - E_{experiment}}{E_{exsperiment}} X\ 100\% \qquad (4)$$

where:

$E_{simulation}$ = value of cohesive energy from simulation results (eV/atom)

$E_{experiment}$ = cohesive energy value from reference (experiment) (eV/atom)

By obtaining a small value of the discrepancy, showing the cohesive energy value of the simulation results close to or equal to the experimental cohesive energy value.

3. Results and Discussion

3.1 Script of input file

The simulation of cohesive energy in LAMMPS simulation can be described as following:

```
# ---------- Initializing Simulation --------------------------------
clear
units metal
dimension 3
boundary p p p
atom_style atomic
atom_modify map array
# ---------- Creating Atoms --------------------
lattice          xx xxx
region           box block 0 1 0 1 0 1 units lattice
create_box       1 box
lattice          xxx xxx orient x 1 0 0 orient y 0 1 0 orient z 0 0 1
create_atoms 1 box
replicate 1 1 1
mass 1 xxx
# ---------- Defining the Interatomic Potential ---------------------
pair_style lj/cut 3.0
pair_coeff 1 1 xxx xxx
neighbor 2.0 bin
neigh_modify delay 10 check yes
# ---------- Defining Settings ------------------------------------
compute eng all pe/atom
compute eatoms all reduce sum c_eng
# ---------- Runing Minimization ------------------------------------
reset_timestep 0
fix 1 all box/relax iso 0.0 vmax 0.001
thermo 10
thermo_style custom step pe lx ly lz press pxx pyy pzz c_eatoms
min_style cg
minimize 1e-25 1e-25 5000 10000
variable natoms equal "count(all)"
variable teng equal "c_eatoms"
variable length equal "lx"
variable ecoh equal "v_teng/v_natoms"
print "The total energy (eV) = ${teng};"
print "The number of atoms = ${natoms};"
```

```
print "The lattice constant (Angstoms) = ${length};"
print "The cohesive energy (eV) = ${ecoh};"
print "Simulations completed!"
```

3.2 Verify Lennard-Jones Potential Parameters

Table 1 is the summary of simulation results and calculation. The column 4 and 5 are the initial input of (ε, σ) and column 8 and 9 are the best value of (ε, σ) after some correction. It is from the Table 1, we can see that the discrepancy of cohesive energy before (column 6) and after (colum 10) correction of (ε, σ) is not more than 0.1% error, compare with the experimental data (column 3). The comparative results obtained are shown in Table 1.

Table 1. Comparison of Values ε, σ and E_c between Simulation, Experiment and New After Correction
(For initial guest/value of ε, σ, use data from: [12,13]

Atom	Crystal	Initial Value					Correction			
		$E_{exper.}$	ε(eV)	σ(Å)	$E_{simul.}$	Discrepancy (%)	ε(eV)$_{new}$	σ(Å)$_{new}$	E_{new}	Discrepancy (%)
Fe	FCC	4.28	**0,4007**	**2,3193**	10.82	152.88	0.1584	**2.3193**	**4.279**	0.03
Pb	FCC	2.03	**0,1910**	**3,1888**	1.46	27.99	0.2650	**3.1890**	**2.032**	0.07
Ni	FCC	4.44	**0,3729**	**2,2808**	95.35	2047.58	0.0174	**2.2805**	**4.451**	0.03
Al	FCC	3.39	**0,5072**	**2,5736**	39.56	1066.92	0.0435	**2.5735**	**3.391**	0.02
Cu	FCC	3.49	**0,5203**	**2,2972**	146.93	4109.97	0.0124	**2.2966**	**3.489**	0.03
Mo	BCC	6.82	**1,1119**	**2,4892**	50.23	636.49	0.1510	**2.4892**	**6.821**	0.02
Cr	BCC	4.10	**0,6732**	**2,2813**	172.67	4111.37	0.0160	**2.2811**	**4.122**	0.03
Va	BCC	5.31	**0.4983**	**2.4391**	315.10	5834.09	0.0084	**2.4390**	**5.309**	0.02
Nb	BCC	7.57	**0.7159**	**2.6819**	103.87	1272.11	0.0522	**2.6818**	**7.570**	0.01
Ta	BCC	8.10	**0.7332**	**2.6819**	103.38	1213.32	0.0558	**2.6820**	**8.100**	0.00
W	BCC	8.90	**0.9719**	**2.5618**	70.51	692.19	0.1227	**2.5619**	**8.910**	0.07
Br	HCP	5.81	**= Al**	**= Al**	39.56	580.87	0.0745	**2.5736**	**5.811**	0.01
Ti	HCP	4.85	**0.5681**	**2.6841**	83.41	1619.84	0.0330	**2.6843**	**4.850**	0.01
Co	HCP	4.39	**0.5158**	**2.2840**	131.57	2897.07	0.0172	**2.2805**	**4.390**	0.00
P	FCC	3.43	**= N**	**= N**	1.52	55.56	0.0191	**3.6564**	**3.430**	0.01
Se	HCP	2.46	**= S**	**= S**	5.72	132.62	0.1601	**3.1888**	**2.460**	0.01
Si	FCC	4.63	**= Br**	**= Br**	5.81	25.5	0.0594	**2.5735**	**4.630**	0.00
S	FCC	2.85	**= Pb**	**= Pb**	1.46	48.71	0.3724	**3.1888**	**2.850**	0.01
Mn	BCC	2.92	**= Fe**	**= Fe**	129.06	4319.88	0.0091	**2.3187**	**2.921**	0.02
Zr	HCP	6.25	**0.7385**	**2.9318**	366.98	5771.67	0.0126	**2.9314**	**6.249**	0.00

Table 1 shows that the results of calculating the cohesive energy of materials (column 6) using the initial Lennard-Jones potential parameters (column 4 and 5) results obtained are very far from the experimental cohesive energy values (column 3). So that verification of the potential parameter values of Lennard-Jones is done so that the cohesive energy calculations obtained can be closer or equal to the results of existing experiments. For some unknown or non-reference elements regarding the magnitude of the Lennard-Jones potential parameter, an approach is taken by looking at other elements closest to these elements from the periodic table. This is done by looking at the atomic number of the closest element but the value (ε, σ) of the reference is known. The best value of (ε, σ) obtained after correction are in column 8 and 9. There are several elements that get parameter values that are larger than the initial reference, and there are several elements whose parameter values are

smaller than the parameter values based on references, and some elements whose parameter values do not change from the initial parameter values based on references.

4. Conclusion

It has been computed the cohesive energy for some metals. The calculation of cohesive energy was done by Lammps molecular dynamics simulation based on the Lennard-Jones potential. The interaction among atoms in simulated material is the Lennard-Jones potential where the best potential parameters (ε, σ) in this work was determined by comparising the simulation result and experimental data of cohesive energy. The discrepancy of simulation and experimental was determined not more than 0.1 % error. The best value of (ε, σ) of some metals as described in Table 1 column 8 and 9.

Acknowledgments

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