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Rigid Procedure to Calculate the Melting Point of Metal Using the Solid-Liquid Phase (Coexistence) Method

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ABSTRACT

Melting point, particularly metal, is one of the important data for many applications. For developing new materials, adequate theories for melting point are very crucial. The determination of melting point using the popular phase-change curve method is very easy but usually overestimate. In current work, we determine the melting point of a pure metal (iron) using the method of solid-liquid phase coexistence. For this goal, molecular dynamics simulation was applied to obtain data of trajectories of atoms. Simulation (LAMMPS) and data analysis (OVITO) procedures are strictly applied to obtain the accurate melting point of iron based on the obtained trajectories data. For initial structure design of simulation, we used the ATOMSK program. The melting point of iron obtained using the phase change curve (PCC) method is about 2750 K < T_{PCC} < 3250 K and using the coexistence phase (CP) method is T_{CP} = 2325 K. A more accurate calculation needs to include defects factor in the simulated material and calculation. In this research we use the Morse potential to represent all of the atomic interaction among atoms of Fe material.

1. INTRODUCTION

Complete information on materials that are workable at high temperatures is very important for many applications (Rogachev, 2019). Nuclear reactors are one of them that requires the support of high-temperature materials in order to be able to withstand very high temperature in the inner reactor core. The spacecraft must also have a protective material that is heat resistant due to the friction of the aircraft with the atmosphere during the journey, especially when the spacecraft enters the layers of the atmosphere layers. For this reason, various further studies need to be carried out to obtain superior materials with high performance. New materials need to be created to be able to support technological applications. Meanwhile, theoretical and experimental studies are also required to produce superior materials. In particular, the theory for the calculation of the material melting must be accurate.

One of the most promising ways to calculate melting point of the material is to use the molecular dynamics (MD) method. This method can be used to guess the melting point of new materials.

Theoretically, many properties of materials such as melting points can be computed using molecular dynamics (MD) simulation method. This computational method has been succesfully applied in many applications. In previous works, we have used the MD method to study the iron corrosion in

nuclear reactor (Arkundato et al., 2013a; 2013b), the relationship between temperature and density of liquid lead (Imanullah et al., 2018) and also the performance of steel FeNiCr under high temperature molten liquid lead (Arkundato et al., 2019).

In simulation, the MD method uses an input of potential energy of material. Depending on what materials will be simulated and investigated, the type of potential energy used will determine the results. (Maghfiroh et al., 2020) reported the melting point of some metals using the Lennard-Jones potential energy, based on the corrected potential parameters. To improve the accuracy of the calculation for alloy metal, (Arkundato et al., 2022) have proposed a new mixing formula for MD calculation under the Lennard-Jones potential scheme.

Related to the melting point calculation using the MD simulation, several methods may be applied i.e. 1) Phase change curve method, 2) Two phases coexistence method and 3) Z method. However, calculation of melting points by using the phase change curve, usually produces an overestimated result, compared with available experimental data. The second and third method are considered more accurate.

As we know, the molecular dynamics simulation requires data of the potential energy of interactions between the atoms constituting metal crystal. In this work, we use the Morse potential which is considered more suitable than the Lennard-Jones potential. The purpose of this research is to find out the melting point of iron metal using molecular dynamics simulation method, based on the phase coexistence method. To realize the simulation, the integration of Newton's motion equations used the LAMMPS code, to prepare metal crystals structure we use ATOMSK, OVITO and GNUPLOT softwares. All simulations were done in Linux based HPC-GPU server facility.

The melting point of matter are affected by defects (vacancies and impurities) (Matthai & Rainbow, 2017), As a preliminary study, we focused on how to apply a rigid procedure of melting point calculation using two phase method. The important thing of our current work is to use the CNA (common neighbor analysis) method to help to predict the melting point from data of simulation results.

2. METHODOLOGY

2.1 Phase Change Model

The melting point of a substance or material is the temperature at which a solid and liquid phase may coexist in equilibrium and the temperature for which matter changes from solid to liquid form. Melting point also depends on pressure, so it should be specified (Helmenstine, 2021).

As heat is transferred into a solid, its temperature may increase until the melting point is reached. More heat applied will be used to convert the solid into a liquid phase at a temperature. Further, when all the solid has completely melted, additional heat will raise the temperature of the liquid. In this case, the melting temperature of a solid is generally considered to be the same as the freezing point of its corresponding liquid. However, because a liquid may freeze in different crystal systems, and because impurities lower the freezing point, so the actual freezing point may not be the same as the melting point, so we are prefer using the melting point to characterize a substances (Britannica, 2021).

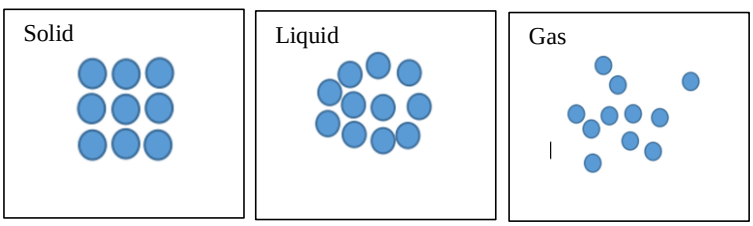


Figure 1. Three forms of a phase of substance.

We generally know the 3 types of phases of substances as Figure 1. A solid has been known having the strongest molecular bonds, while gases have the weakest molecular bonds between the molecules that make up the substance. Solid phases also have a very distinct molecular preparation where the molecules are held in place and do not move. However, they will vibrate in place as an

oscillator, and as the temperature of the solid increases the vibration of each molecule will also increase until a phase change occurs, and the solid melts into a liquid. The Morse Potential is often used to describe the vibration mode of a bound molecule in metal (Kozlov et al., 1972).

It is possible for more than one phase to exist together at the same time in the substance. For example, when a liquid and solid exist together, we called this as a saturated mixture. When a substance becomes a saturated mixture, it means that the substance has reached a step of phase change, liquid or condense. If this phase change occurs, the saturated mixture of a substance will remain at the same temperature until the phase change has been completed. During the phase change process, heat does still leave or enter the substance as energy (latent heat). Certain substance requires more latent heat to pass in or out for the phase change to be completed. We can describe the steps of phase change as Figure 2.

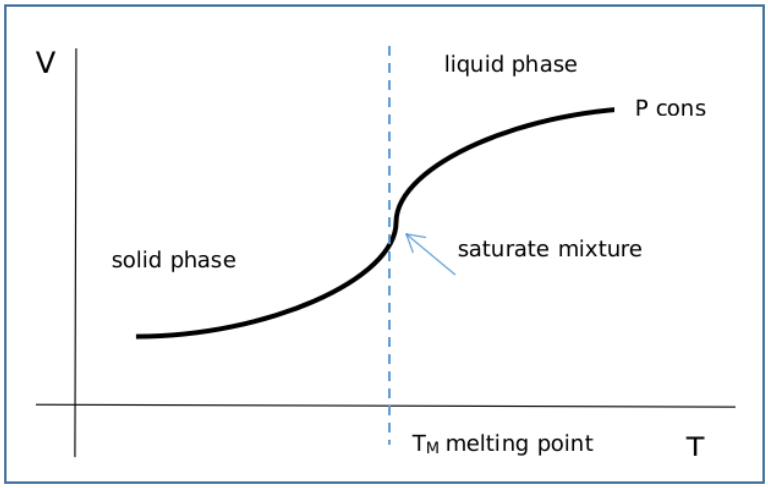


Figure 2. Diagram (curve) of phase change of a substance

2.2 Two-Phase (Coexistence) Method

Another method to estimate the melting point of a substance using molecular dynamics is a common and simple approach called the two–phase simulation technique. The main idea of this method and technique is the direct simulation of coexistence of the two phases, liquid and solid, at a given temperature and pressure (NPT ensemble). The simulation box is divided into two halves cell, one is filled with atoms arranged in a solid structure and the other with atoms from a liquid simulation of the same system, but both should be at the same density. We can design this using NVT ensemble. If we perform NPT molecular dynamics simulation on this composite solid-liquid system for sufficiently long times, we can find step-by-step the melting point T_M at the chosen pressure: if the applied temperature in NPT simulation is lower than T_M, the solid phase will start to grow, finally filling the whole simulation cell (the liquid half freezes). If the applied temperature is higher than T_M, the liquid phase fills the cell instead (the solid half melts). We may need many NPT simulations with different temperature till we found the melting point. We explain the procedure in the following discussion (Davis, 2008).

2.3 Molecular Dynamics Method

The Morse potential is a convenient interatomic interaction model for the potential energy of a diatomic molecule substance. It is a better approximation for a vibrational structure of a molecule than the quantum harmonic oscillator because it explicitly includes the effects of bond breaking, such as the existence of unbound states. The Morse potential can also be used to model other interactions such as the interaction between an atom and a surface. The popular mathematical form of the Morse potential is given by,

$$V(r) = D_e\left(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\right) \qquad (1)$$

This potential is simple and easy to use for application because it contains only three potential parameters D_e (depth of potential), a and r_e. In this research we investigate the iron metal (Fe) that has

potential parameters as Girifalco reported that are D_e = 0.4147 eV, a = 1.3885 (Å^{-1}) and r_e = 2.845 Å (Girifalco and Weizer, 1959).

In the (classical) molecular dynamics simulation, actually we solve Newton second equation of motion $\boldsymbol{F} = m\boldsymbol{a}$, based on the certain potential energy function. In this case we use Morse potential $V(r)$ that related to the force via $F = -\mathrm{d}V/\mathrm{d}r$ to support the atomic interaction among atoms of iron. During simulation at certain T (temperature), P (pressure) and V (volume) all atoms will be conditioned to move following the Newton equation (1). The solution of the equation is the trajectory of all atoms that from here we can compute all needed physical variable as the melting point T_M. All these needs are facilitated by the LAMMPS program (Thompson et al., 2022).

2.4 Simulation Procedure

Determination of the melting point of iron using the solid-liquid two-phase coexistence method is carried out by observing the micro-structure of the constituent atoms of the iron, before and after simulation at a certain temperature. Simulations were performed in ensemble NPT. We can check the micro-structure of iron by looking at the bcc structure of iron based on the CNA value with OVITO code. If we define T_{melt} is the melting point and the given simulated is T_{sim}. Then we can determine the melting point of material as the following rule:

1. If $T_{sim} < T_{melt}$, then after NPT simulation we will see the solidification process in which the percentage of bcc crystal of iron will increases, T_{sim} is not T_{melt}
2. If $T_{sim} > T_{melt}$, then after NPT simulation we will see the melting process in which the percentage of bcc crystal of iron will decreases, T_{sim} is also not T_{melt}
3. When $T_{sim} = T_{melt}$, then after NPT simulation we will see the percentage of bcc crystal of iron will relatively unchanged, $T_{sim} = T_{melt.}$

The thing to note in the application of the two-phase coexistence method is that we must carefully look at the snapshot of the microstructure after the simulation. The rigid procedure of simulation to measure the melting point of material is as following steps:

1. Create Fe 16x16x16 BCC crystal supercell using the ATOMSK code (Hirel, 2015). To ascertain the material to be simulated, check with OVITO code to see the geometry of the system, Radial Distribution Function (RDF) and Common Neighbor Analysis (CNA) value. Make sure the extension of the generated file by ATOMSK is lmp (LAMMPS version). The **Fe_supercell.lmp** will be used as an input of LAMMPS molecular dynamics code.
2. Do LAMMPS simulation to this **Fe_supercell.lmp** at room temperature to check the lattice constant of Fe. This should be the best lattice constant for your Morse potential in LAMMPS simulation.
3. Do the NPT ensemble LAMMPS simulation using **Fe_supercell.lmp** from T = 300 K to T = 5000 K to determine the Melting Point (MP) by applying the phase-change curve (PCC) method. Let's say the melting point is T_{PCC-MP}. This is to be able to estimate the interval of the melting temperature of the material, namely the upper limit and the lower limit of the temperature of the melting area. We will use this area of melting temperature as a reference in step No. 6 later.
4. Do the NVT ensemble LAMMPS simulation using **Fe_supercell.lmp** at T = 4000 K to get Fe liquid with same density of **Fe_supercell.** Save the dump file as **Fe_liquid.lmp**
5. Modify the **Fe_liquid.lmp** (at T = 4000 K) and **Fe_supercell.lmp** (before simulation) to create the solid-liquid coexistence material system. Let's say we call **Fe-solid-liquid.lmp**.
6. Do several NPT simulations for certain temperature (we call T_{sim} which we set from step No.1). After simulation check whether the CNA value of bcc iron in the **Fe-solid-liquid.lmp** is changed or not. THE CNA value can be computed by OVITO code. If the CNA value of bcc crystal is similar between **Fe_supercell.lmp** and **Fe-solid-liquid.lmp** then we have gotten our melting point that is $T_{sim} = T_{melt.}$ (Stukowski, 2010).
7. Repeat No. 6 for several NVT simulation with different T till you get your $T_{CP-MP.}$ What can be seen during the simulation is, if the input T is less than the T melting point sought then the liquid Fe part will solidify so that the CNA BCC number increases, and if the input T is higher than the melting

point sought then the solid Fe again will melt. The easiest reference is to look for the *T* input, so after simulation the CNA value before and after the simulation remain unchanged, which means that is where the melting point is sought.

3. RESULTS AND DISCUSSION

3.1 Lattice Constant

Before we set-up the Fe supercell for simulation, it is important to check whether the lattice constant of the iron is suitable for our Morse potential parameter of iron. We can do LAMMPS simulation for this purpose. We got the lattice constant is 2.86404 Å as we concluded from Figure 3. We use this value for creating supercell with ATOMSK later.

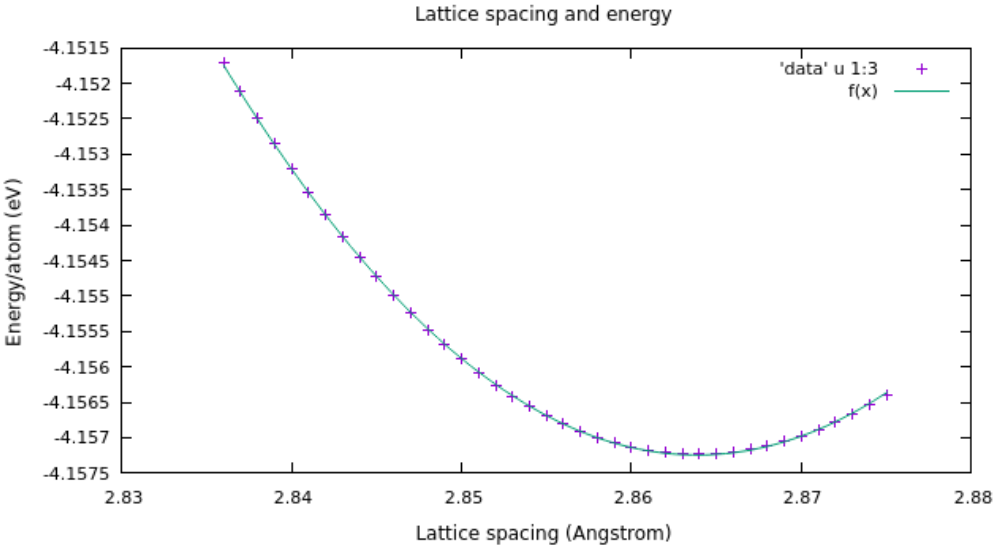


Figure 3. Curve lattice constant versus energy/atom.

3.2 Fe Supercell

Molecular dynamics method needs many atoms to get more accurate calculation. We can build this supercell with ATOMSK code. For our goal we use the following command:

$atomsk --create bcc 2.86404 Fe -duplicate 16 16 16 Fe_supercell.xsf

3.3 Fe_supercell.lmp

Because we use LAMMPS molecular dynamics code, then we need to change to lammps data format (lmp). We can use ATOMSK or OVITO to correct this format from xsf to lmp format. This Fe_supercell.lmp is our input of read_data command line in LAMMPS (Figure 4).

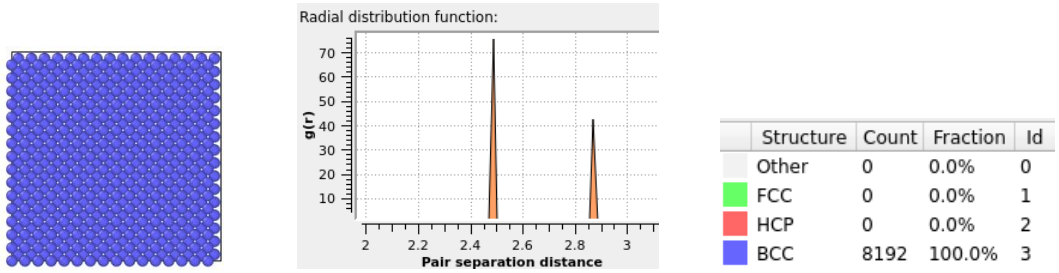


Figure 4. Structure of supercell (left), RDF (middle) and CNA value of Fe_supercell (right)

3.4 NPT Simulation in Phase-Change Method

NPT simulation is actually to know the melting point with phase-change curve method as we explained before. Using our input of Fe_supercell.lmp we can do NPT simulation from T = 300 K to 5000 K. From Figure 5 we can see the complete liquid phase in above temperature 3000 K based on the heating curve. From the simulation via heating curve, the area of melting of iron metal is between T = 2750 K and 3250 K. Thus, the phase change curve method overestimated the melting temperature in which the experiment T *is* 1811 K (https://www.periodic-table.org/Iron-melting-point/).

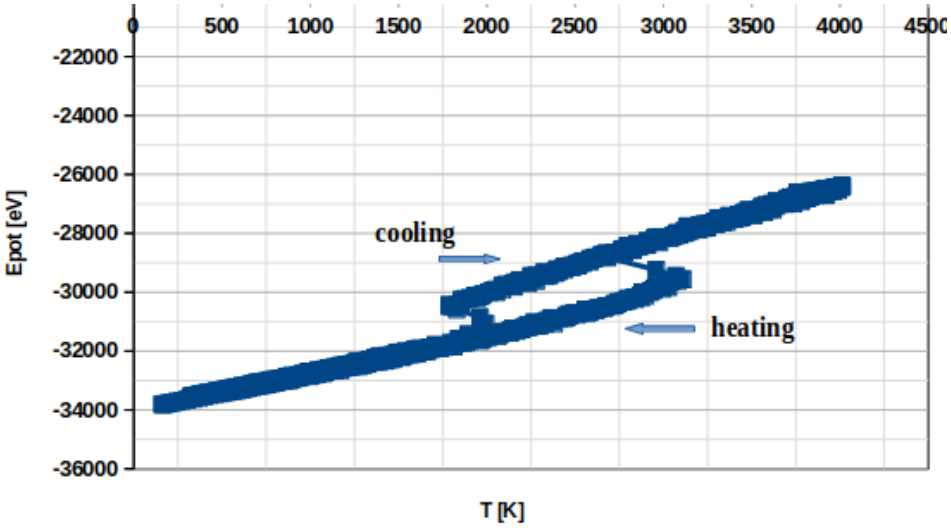


Figure 5. The phase change curve of iron. The melting point is about T = 2750K - 3250 K via heating curve.

Melting point simulation with the phase change curve method is very easy to do with once NPT simulation as Figure 5 above. Although the result is overestimated, it can be used as the initial guess of the melting point of the material. We can use this as a guess input of NVT simulation in two phase method. We can compare the melting point results of two methods, i.e. the phase change curve method and the solid-liquid two-phase coexistence method.

3.5 Fe_liquid.lmp

Because we need to calculate the melting point using the two-phase coexistence method, we need to have the solid phase of Fe and the liquid phase of Fe. By doing the NVT simulation at T = 4000 K (as shown in Figure 5) we have this liquid phase of iron. By NVT simulation the density of the Fe system for solid and liquid is similar. Figure 6 is our liquid phase of iron. We can check the CNA value by OVITO code, all part of iron is almost in the liquid state.

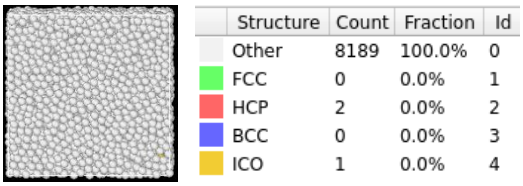
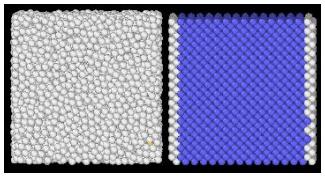


Figure 6. Liquid phase of iron at T = 4000 K.

3.6 Fe_solid-liquid.lmp

The most work of our preparation of simulation system is solid-liquid phase. We need to set-up this before doing melting simulation. We can combine solid phase and liquid phase manually (using spreadsheet program) or by using OVITO combine data sets facility. Figure 7 is our solid-liquid system.

We can see that our two phases system before simulation is approximately half solid and half liquid system. This is for NVT solid-liquid simulation system.

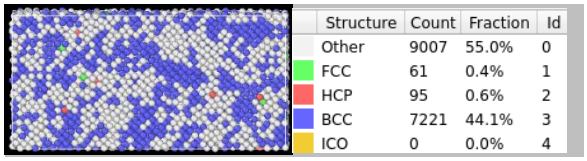


Structure	Count	Fraction	Id
Other	9206	56.2%	0
FCC	0	0.0%	1
HCP	1	0.0%	2
BCC	7176	43.8%	3

Figure 7. The solid-liquid system. Approximately half solid-half liquid system.

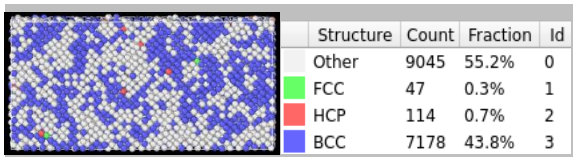
3.7 NPT Simulation in Solid-Liquid Coexistence Method

The results of the simulation of the coexistence of the two phases solid-liquid can be presented in Figure 8. We start checking the NPT simulation at T = 2300 K as Figure 8a. At temperature T = 2300 K, the BCC CNA is 44.1%. Compared with Figure 7 the CNA Fe increased from 43.8% to 44.1%. This means that the liquid part changed to solid part, which is solidification process of liquid state. This means the temperature of simulation T_{sim} is below the melting point T_{melt}.



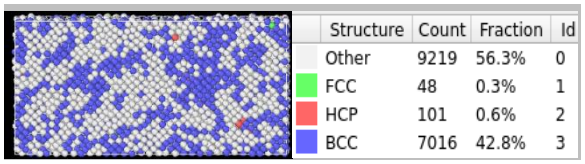
Structure	Count	Fraction	Id
Other	9007	55.0%	0
FCC	61	0.4%	1
HCP	95	0.6%	2
BCC	7221	44.1%	3
ICO	0	0.0%	4

(a) T = 2300K



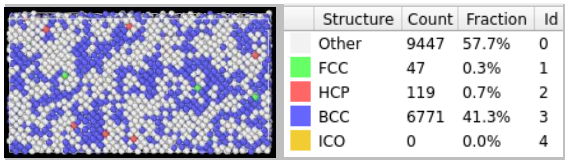
Structure	Count	Fraction	Id
Other	9045	55.2%	0
FCC	47	0.3%	1
HCP	114	0.7%	2
BCC	7178	43.8%	3

(b) T = 2325K



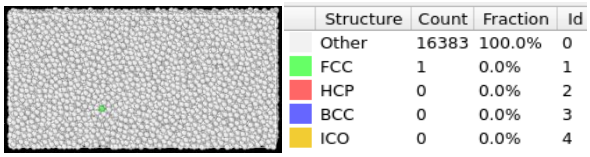
Structure	Count	Fraction	Id
Other	9219	56.3%	0
FCC	48	0.3%	1
HCP	101	0.6%	2
BCC	7016	42.8%	3

(c) T = 2330 K



Structure	Count	Fraction	Id
Other	9447	57.7%	0
FCC	47	0.3%	1
HCP	119	0.7%	2
BCC	6771	41.3%	3
ICO	0	0.0%	4

(d) T = 2350 K



Structure	Count	Fraction	Id
Other	16383	100.0%	0
FCC	1	0.0%	1
HCP	0	0.0%	2
BCC	0	0.0%	3
ICO	0	0.0%	4

(e) T = 5000 K

Figure 8. Snapshots of simulation at various temperatures and related CAN.

Now we see the final results of our work. At temperature T = 2325 K the BCC CNA is 43.8%. Compared with Figure 7, the CNA of BCC Fe in Figure 8b is similar. This means the temperature of simulation can be suspected as the melting point of iron, i.e. $T_{sim} = T_{melt} = T_{CP\text{-}MP}$. Raising the temperature to T = 2330 K shows the CNA of BCC Fe gets lower to 42.8% (Figure 8c). This means the solid part is going into liquid part. This is not the melting point. Increasing the temperature to T = 2350 K makes the CNA of BCC Fe gets lower to 41.3% (Figure 8d). This means the solid part is going into liquid part. This is also not the melting point. Finally, increasing the temperature above T = 4000 K make the CNA value get lowest 0% (Figure 8e). This means all of the solid part going to liquid part. This is exactly not the melting point.

We summarize the results in Table 1. It is clear that the melting point that we try to find is at about T = 2325 K. Compared with the melting point from phase change method i.e. 2750 K < T < 3250 K (via heating curve), our two-phases coexistence method is rather straightforward. Also, the experimental data of the melting point of iron is about T = 1811 K. So, our work is better and more

accurate than the phase change curve method. This method should be applicable for other materials. Our result T = 2325 K is still higher than experimental data T = 1811 K, however it is known that defects in material will affect to decrease the melting point of pure substances (March, 1992). So, in the future work, we need to include this defect.

Table 1. Data for searching of melting point.

***T* Simulation**	**Before Simulation**	**After Simulation**	
		Number of Fe BCC	**CNA**
One Phase			
10 K	Solid Fe BCC	8192 (solid)	100% (Fe BCC)
4000 K (NVT)	Solid Fe BCC	8189 (liquid)	~ 100% (other)
Two Phases			
10 K	Solid BCC-Liquid	7176(solid)- 9206	43.8% (BCC) - 56.2% (other)
2300 K (NVT)	Solid BCC-Liquid	7221(solid)- 9007	44.1% (BCC) - 55.0% (other)
2325 K (NVT)	Solid BCC-Liquid	7178(solid)- 9045	43.8% (BCC) - 55.2% (other)
2350 K (NVT)	Solid BCC-Liquid	6771(solid)- 9447	41.3% (BCC) - 57.7% (other)
5000 K (NVT)	Solid BCC-Liquid	16383 (liquid)	100 % liquid

4. CONCLUSION

The melting point of ferrous metal based on the two-phase coexistence method is better than that calculated using the substance phase change curve method. The melting point from the two-phase coexistence method is T = 2325 K, while the value from the substance phase change curve method is 2750 K - 3250 K. Therefore, it possible to obtain better results using the two-phase coexistence method by implementing rigid simulation step-by-step procedures.

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