



Melting Curve of Cobalt using Molecular Dynamics Simulation

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ABSTRACT

Molecular dynamics simulation is used to estimate the melting point of cobalt using the embedded atomic model (EAM) potential by heat until melting, void, hysteresis and interface methods. For instance, the estimated melting temperature are 2102 K, 1944.15 K, 1731 K and 1725±25 K using these methods, respectively. Then, the melting points at different pressures are calculated. A graph depicting the variation of melting point with pressure is drawn and compared with the available simulation and experimental results. The melting point at a low-pressure range is similar to the previous diamond anvil cell experiments. Besides, using the Simon equation, we calculated the melting slope at 0 GPa pressure of 36 K/GPa for one phase and 40 K/GPa for two-phase methods.

KEYWORDS: Cobalt, melting curve, molecular dynamics simulation, Embedded Atom Method (EAM)

INTRODUCTION

Melting is one of the essential thermodynamical parameters. A variation of melting temperature of metals or alloys with pressure — a melting curve — is usually calculated using a diamond anvil cell (DAC) (Dewaele et al., 2010; Lord, Wann, et al., 2014; Lord, Wood, et al., 2014), shockwave experiments (Luo & Ahrens, 2004) and high-pressure temperature measurement method (HPTM) (Wang et al., 2020). However, setting experiments is expensive, time-consuming and challenging. Thus, a melting curve based on molecular dynamics (MD) simulation can be a good alternative. There are different ways to calculate the melting point of a system by using molecular dynamics simulation, which can be grouped into one-phase and two-phase methods (Zou et al., 2020).

Heat until melting (HUM), hysteresis and void are three one-phase methods. The easiest one is HUM, in which the solid phase is heated gradually. The melting point is estimated by looking for a sudden change in volume, density, or potential energy with

temperature. This method gives an inaccurate melting point due to the super-heating phenomenon. Super-heating is the rising of the melting point, whereas super-cooling is the lowering of the freezing point of a system. These occur because of the high heating or cooling rate, due to which a system does not get enough time to reach thermal equilibrium (Zhang et al., 2014b).

The void method creates vacancies within the supercell by deleting some atoms. The supercell is then heated gradually. The transition temperature is noted using a similar method to HUM. Vacancies lower the free energy barrier, so transition temperature decreases with the increase in vacancies (Zou et al., 2020). After a certain critical number of vacancies, the transition temperature plateaus, which is the melting temperature.

The hysteresis method is based on the classical homogeneous nucleation theory (Zou et al., 2020). In this method, a solid phase is heated gradually. The temperature after which the volume suddenly rises gives a superheating temperature (T_+). The liquid thus formed is then slowly cooled. Again, the temperature after which the volume suddenly decreases gives a super-cooling temperature (T_-). A simple empirical formula (Luo et al., 2004) shown below can be used to find the equilibrium melting temperature (T_m),

$$T_m = T_+ + T_- - \sqrt{T_+ * T_-} \quad (1)$$

Although this method is easy to follow, finding reliable T_+ and T_- requires a low heating or cooling rate i.e., substantial simulation time. The liquid state can transform into a glassy amorphous solid if the cooling rates are high. A sharp decrease in volume is not observed during cooling. Hence, no way of knowing T_- ; this method is usually difficult to implement except in the case of the simple monoatomic system (Zhang & Maginn, 2012). The two-phase/solid-liquid coexistence method overcomes this problem.

The solid-to-liquid transition takes place after the formation of a nucleus. In the two-phase method, the presence of a solid and liquid interface lowers the nucleation-free energy barrier and stops the superheating and super-cooling phenomena (Zou et al., 2020). In this method, a system with a solid-liquid interface is constructed. It is heated up to a certain temperature. If the temperature is above the melting temperature, it melts. At the same time, if the temperature is below the melting point, it solidifies. By studying the final crystal structure after heating or monitoring the density plot, movement of the interface region, or doing a common neighbor analysis, the melting temperature can be estimated to lie in an interval. The average of the two endpoints of this interval is the melting temperature.

The melting curve of different metals and alloys have been previously plotted by other researchers using molecular dynamics simulation. Zhang et al. (2014b) drew the melting curve of B2-NiAl alloy from 0 to 40 GPa by using both hysteresis and two-phase methods. Similarly, Wu et al. (2011) investigated the melting of Cu in the pressure range of 0 to 400 GPa by the solid-liquid coexistence technique. Bouchet et al. (2009) explored a variation of melting of Aluminum under pressure from 0 to 320 GPa by hysteresis and the two-phase methods.

Co is a grey, ductile, brittle and magnetic trace metal. It is an essential transition metal with a wide range of applications in making batteries, high-temperature and corrosion-resistant superalloys, magnetic alloys, catalysts and as a binder for carbide materials (Roberts & Gunn, 2014). It is also one of the main components of iron alloy present inside the earth's core. Therefore, Co's high temperature and pressure behaviour can shed light on earth's core's properties. It can also help make its high-temperature applications more reliable. Molecular dynamics simulations can be a quick and

inexpensive alternative to experiments to investigate the melting behavior of Co at the atomic level. It can provide insights into the underlying mechanisms that govern its melting.

This paper aims to provide the details of estimating a system's melting point using molecular dynamics simulation. In this study, we evaluated the melting point of Co using HUM, void, hysteresis and two-phase methods. We also traced a variation of the melting point of Co by hysteresis and two-phase methods and compared it with the available experimental and simulation data.

RESEARCH METHODS

Potential

We used the embedded atom method (EAM) potential (Daw & Baskes, 1984) to model the interaction between the Co atoms in which the total potential energy (U) is given by,

$$E = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) \quad (2)$$

where $F_i(\rho_i)$ is the energy required to embed atom i at the site with electron density (ρ_i), r_{ij} is the distance between atoms i and j , and ϕ_{ij} is the inter-atomic pair interaction. The host electron density at position i is calculated by

$$\rho_i = \sum_{j \neq i} \rho_j(r_{ij}) \quad (3)$$

where ρ_j is the contribution to the electron density of atoms j .

In this study, we used Co's EAM potential constructed by Zhou et al. (2004).

Molecular Dynamics Simulation

We performed all the calculations in LAMMPS (Thompson et al., 2022) molecular dynamics simulation package. The periodic boundary condition is used in all directions. A velocity Verlet algorithm is used for integrating Newton's equation of motion with a time-step of 1 femtosecond. Temperature and pressure are maintained using the Noose Hoover barostat and thermostat (Hoover, 1985) with a time constant of 1000 and 100 femtoseconds, respectively.

For one phase—HUM, void and hysteresis—methods, we considered a supercell of $8 \times 8 \times 8$ of Co face-centered cubic (FCC) structure containing 2048 atoms. The supercell is heated or cooled at an interval of 100 K in the NPT ensemble. To get a more accurate result, near superheating (T_+) and super-cooling (T_-) temperatures, the interval is decreased to 50 K. A total of 300000 steps are used for each interval. The system is equilibrated for 250000 steps, and the data of the remaining 50000 steps are stored for calculating statistical averages. A single data point is obtained for each interval. In the HUM method, the melting point is the temperature at which there is a sudden spike in volume vs temperature graph. In the void method, different percentages of atoms of the supercell are deleted to create different void sizes. The melting temperature is noted for each void size. It decreases with the increase in the removal of supercell atoms. After a certain threshold number of atoms are deleted, the melting temperature plateaus. This temperature at the plateau region is considered the actual melting temperature. For the hysteresis method, superheating (T_+) and super-cooling (T_-) temperatures are obtained by plotting a graph, as shown in Figure 1. The melting point is estimated by using the formula given in equation (1).

A $6 \times 6 \times 14$ orthorhombic supercell of Co is considered with 2016 atoms for the two-phase method. One half of the simulation cell is fixed while the other half is heated

to 6000 K and 0 GPa pressure in NPT to melt it completely. Due to periodic boundary conditions, a system with two solid/liquid interfaces is formed, which is heated at different temperatures. A simulation of 150000 steps is carried out. The system is equilibrated for 100000 steps and data from the remaining 50000 steps are collected for later analysis. The system either solidifies or melts based on whether this temperature is lower or higher than the melting point. The melting point lies between the temperatures at which the system either solidifies or melts. Numerically, it is estimated by taking the average of the nearest two temperatures at which the considered two-phase system solidifies or melts.

Melting and crystallization are monitored by visually inspecting the system, doing common neighbour analysis (CNA) using Ovito (Stukowski, 2010) software, or plotting radial distribution graphs. The CNA algorithm studies the local 3D crystal structure. It counts the common closet neighbours around a reference pair of atoms and groups them accordingly into FCC, HCP, BCC, or other crystal structures (Tsuzuki et al., 2007). Finally, by varying the pressure, we traced the melting curve.

RESULTS AND DISCUSSION

One-Phase Method

Figure 1

Variation of Volume with Temperature for Hysteresis Method at $P = 0$ GPa

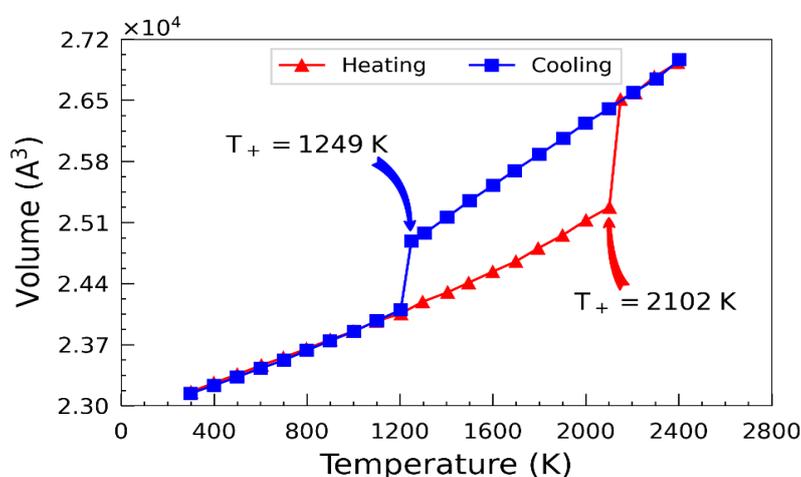
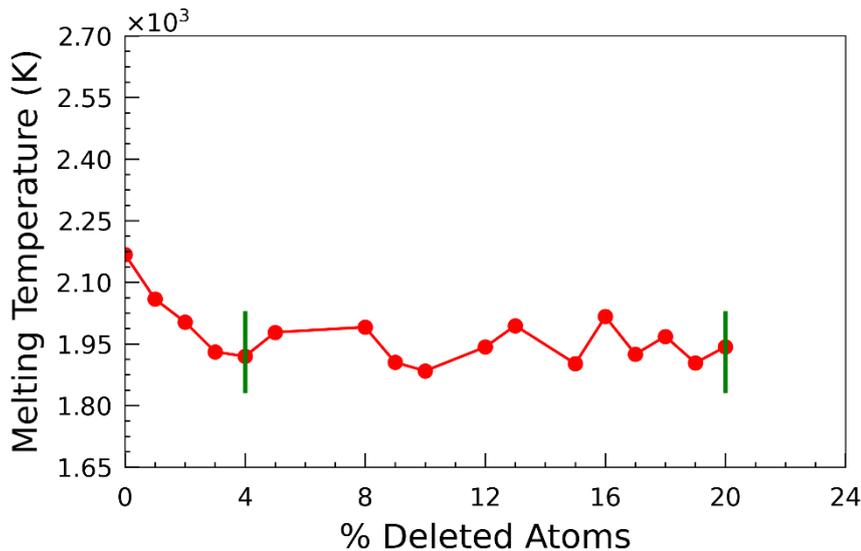


Figure 1 shows the variation of volume with the temperature at zero pressure. The lower trace is the HUM method. We can see a sudden change in volume at the temperature of 2102 K, which signifies the phase transition of Co from the solid to the liquid state. This temperature is the estimated melting temperature of Co by the HUM method, which is way higher than the experimental value of 1768 K (Fernández Guillermet, 1987). When the crystal is cooled, the volume starts to decrease. However, the sudden volume change is observed not at 2102 K but at 1249 K. It is due to the hysteresis effect that occurs during the cooling of heated crystal structures.

Figure 2

Melting Temperature as a Function of the Percentage of Deleted Atoms of Supercell



A graph showing melting temperature as a function of the percentage of deleted atoms is shown in Figure 2. We can observe that the melting point of Co at first quickly decreases with the rise in the percentage of deleted supercell atoms. When more than 4% of atoms are deleted, the melting point plateaus. The average of this region —denoted by two green lines in Figure 2— gives the estimated melting point of 1944.15 K.

The sudden change in volume at 2102 K and 1249 K temperatures are superheating (T+) and super-cooling (T-) temperatures, respectively. Plugging these values in the empirical formula of the hysteresis method, we calculated the melting point of Co to be 1731 K, which is very close to the experimental value.

Therefore, we can conclude among the one-phase methods, estimating the melting point using the hysteresis method is more accurate than the HUM or void methods.

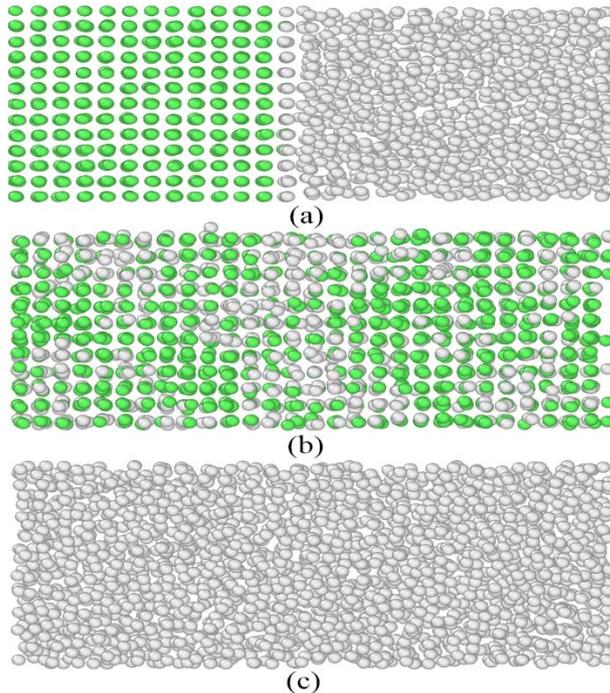
Two-Phase/ Interface Method

A solid-interface system at different temperatures is shown in Figure 3. The periodic arrangement of atoms in Figure 3(b) and left side of Figure 3(a) denotes solid Co. The irregular distribution of atoms in Figure 3(c) and right side of Figure 3(a) is a melted Co crystal structure.

We ran the CNA algorithm provided by Ovito software to study the change in the local crystalline structure of Co during heating. The CNA snapshots of the crystal structures of Co initial structure, at 1700 K and 1750 K are shown in Figure 3. The initial structure's (Figure 3(a) left side is crystalline, while the right side is amorphous. When the system is heated, the percentage of the FCC structure decreases (Figure 3(b)). It completely vanishes at 1750 K (Figure 3(c)), indicating a complete melt of the considered Co structure.

Figure 3

Co Two-Phase Structure at 0 GPa, (a) Initial Configuration, (b) at 1700 K & (c) at 1750 K

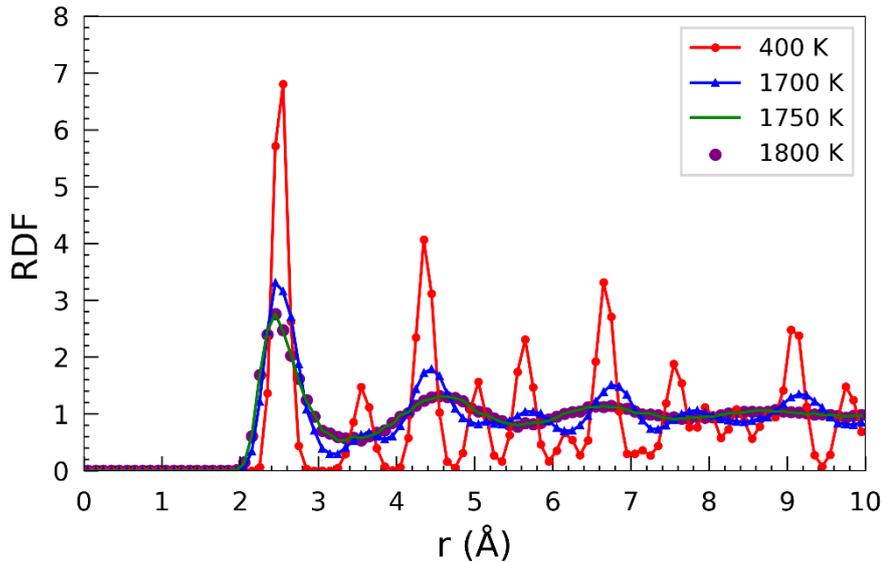


Note: Color shows local crystal structure obtained via CNA function of Ovito —green atoms are in FCC, and grey atoms are in unknown crystal structure configuration.

We further analyzed the structure of Co by plotting a radial distribution function (RDF). An RDF shows the probability of finding an atom at a distance from a reference atom. The nature of the RDF of a system can be used to determine whether it is in the solid or liquid phase. An RDF of a solid phase has a well-defined periodic peak. When the system is heated, the lattice atoms start to vibrate, decreasing the height of the periodic peaks in the RDF of the solid phase. After the temperature reaches the melting point, a prominent peak at the beginning, which converges to unity at a large distance is observed in the RDF. This nature of RDF signifies the complete transition from a solid to a liquid phase. The RDF of both phases is zero at a short distance due to the strong repulsive force between the atoms.

Figure 4 below shows the graph of RDF of Co at 0 GPa pressure and different temperatures. Repeating pronounced peaks at 400 K implies the solid structure of Co. At 1700 K, the height of all the peaks has decreased, whereas some have disappeared altogether. The shortening of the peaks is the telltale sign of an increase in long-range disorder, suggesting the system has begun to melt. At 1750 K and 1800 K, the RDF traces have nicely overlapped. Except for the first peak, the RDF has nearly smoothed out and has begun to approach unity. The Co crystal structure has completely transitioned into the liquid phase. Now, the system has short-range order but long-range disorder, indicating a complete melt. Therefore, after analyzing RDF at different temperatures, we can also estimate that the melting temperature lies between 1700 K and 1750 K, i.e., 1725 ± 25 K at 0 GPa pressure.

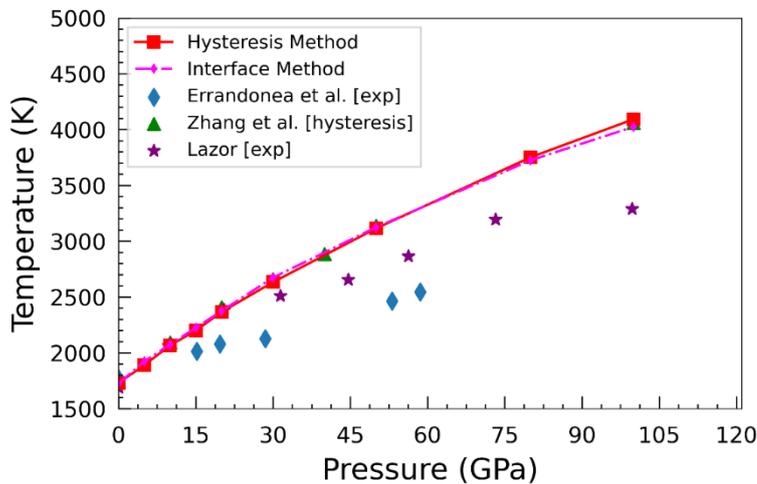
Figure 4
The Radial Distribution Function of Co at Different Temperatures and 0 Gpa Pressure



Melting Curve

A variation of melting point with temperature constitutes the melting curve. Using barostat to maintain pressure at different values, we calculated a variation of melting point with pressure. The melting curve of Co up to 100 GPa by hysteresis and two-phase methods, along with different available experimental and simulation results, is shown in Figure 5.

Figure 5
Melting Curves of Co Using Different Methods



We can observe that the melting point of Co evaluated from both experiments and simulation monotonically increases with pressure. The melting curve we got from the hysteresis and interface methods overlaps. Besides, they agree with the trace by the hysteresis method by Zhang et al. (2014a). The melting curve we got from the simulation for Co is quite similar to the DAC experiment result by Lazar (1994). However, it

diverges from the beginning compared with Errandonea and his coworker's DAC result (Errandonea et al., 2001). A significant discrepancy can be observed between our and these two experiments' results in the high-pressure range. The slope of the curve is steeper in our case. As observed in the figure, the results from these two experiments do not reasonably match each other in all the considered pressures.

Fitting the melting curve of both hysteresis and interface methods by Simon equation (Simon & Glatzel, 1929), we got,

$$\begin{aligned} T_{m\text{-hysteresis}} &= 1731 * \left(1 + \frac{P}{26.456}\right)^{0.552} \\ T_{m\text{-interface}} &= 1725 * \left(1 + \frac{P}{20.899}\right)^{0.485} \end{aligned} \quad (4)$$

From the above two equations, the slope of melting curves (dT_m/dP) can be found. The calculated dT_m/dP at 0 GPa pressure of the melting curve of one phase is 36 K/GPa and 40 K/GPa for the interface method. These initial melting slopes are almost equal to 33 K/GPa Wang et al. (2020) obtained from the HPTM experiment of Co melting.

CONCLUSION

Using molecular dynamics simulation, we estimated the melting temperature of Co using one-phase methods—HUM (2102 K), void (1944.15 K), hysteresis (1731 K)—and two methods (1725±25 K) at zero pressure. The HUM method significantly overshoots the experimental melting temperature due to the superheating phenomenon. The empirical equation of the hysteresis and two interface methods give a much better-melting temperature. Melting curves obtained via hysteresis and two-phase methods overlap and are similar with experiments in the low-pressure range only. A significant discrepancy is observed in the high-pressure range. Fitting the melting curve with the Simon function, we got an initial slope of 36 K/GPa and 40 K/GPa for the hysteresis and interface methods, respectively.

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