

Molecular dynamics simulation for thermodynamic properties of Ni-Al alloy

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Abstract

Here I present a series of Molecular dynamics (MD) simulations to provide the thermodynamic data for considering the potential application of MD simulation in Calculation of Phase Diagrams (CALPHAD). We try to reproduce the thermodynamic properties for the Ni-Al alloy system, such as mixing energy for liquid at high temperature, melting temperature, latent heat, heat capacity etc. We also perform some calculations at high pressure to see the flexibility of MD simulation.

Keywords: Molecular dynamics, thermodynamics, Ni-Al

1. Introduction

Thermodynamic properties of materials are important to capture the phase transformation for the system and useful for both academic and industry community. CALPHAD stands for Calculation of Phase Diagrams is the method to build up thermodynamic modeling combined with experimental data and first-principle data[1]. Nowadays CALPHAD is becoming more and more popular to determine the thermodynamics of many different materials.

However, there are many different kinds of systems in the nature and the experimental data is always expensive or rare, so that the database of this case for CALPHAD is hard to accumulate. Then the accurate first-principle data is becoming a good way to be combined into the database, but not only the experimental data. Based on powerful densityfunctional theory (DFT) calculation, people developed the quasi-harmonic calculation combining DFT and phonon calculation to provide the finite-temperature thermodynamic data[2][3]. This kind of calculation provide accurate enough thermodynamic data and assist the CALPHAD modeling for the solid phase. Many phase diagrams are revised by this kind of method and get improved a lot.

Unfortunately, as this method is based on OK DFT calculation and phonon calculation, so it cannot be directly applied to the liquid phase. For liquid phase, there are other challenges. On the one hand, we don't have a pretty good thermodynamic model for the liquid phase. There are several thermodynamic models for liquid phase: random mixing model, associate model, quasi-chemical model, etc. However, they all have some artificial parameters and cannot capture the whole real physics of the liquid phase. On the other hand, the lack of experimental data for liquid phase is more severe than solid phase due to variant reasons. For example, the experimental determination of the properties for liquid phase is difficult, as the liquid phases are basically stable only at high temperature[4].

Molecular Dynamic (MD) simulation may provide an opportunity to deal with this challenge. MD can definitely simulate the liquid phase or even more complex phases such as glass phase. On the other hand, MD simulation is able to provide lots of thermodynamic information at some extreme conditions to supplement the thermodynamic database for CALPHAD. A typical example is at high-pressure case, which always has no available data at this kind of extreme condition. However, the high-pressure situation is actually not that rare, it should exist in many planets distributed in the universe. For example, the pressure in the Earth's inner core is about 330 to 360 GPa. Therefore, one of the key motivations for studying high pressure environment is to understand the core structure of the planet from thermodynamics which is under high-pressure and high-temperature condition here[5].

In this term project, we shall see how MD simulation provides the significant thermodynamic data by the virtual simulation and even help us to analyze the phase transition. We will select Ni-Al alloy to test our method. Ni-Al system is a kind of typical high-temperature materials[6] used in many different areas such as aerospace applications[7]. The thermodynamic modeling has been performed a lot for Ni-Al system through different methods[8][9][10][11]. However, the phase diagram produced seems still not perfect because the thermodynamic model available is hard to capture the ordering very clearly for the solid solution and liquid phase, a good attempt is presented several years ago[12]. But it's only for FCC structure due to the limitation from the model.

We will try to reproduce the thermodynamics of Ni-Al system from the CALPHAD point of view to check whether it is possible to combine MD and CALPHAD to build up the reliable thermodynamic database for the future. We especially want to observe the thermodynamics for the liquid phase, as it's always lack of enough data to do the thermodynamic modeling. We also try to do some calculations at high pressures, as it's also in a field without too much experimental data.

With these kinds of confirmation for the validate of the data, it may have the chance to assist the CALPHAD modeling for other different systems through this kind of methodology from MD simulation in the future.

2. Computational Setup

Here we take use of EAM Ni-Al potential from Mishin[13][14] to do the calculation, as EAM potentials fit for the metals very much. The cutoff radius is $r_c = 0.5954\text{nm}$, and we must select the size larger than $2r_c$. So we select the computational cell as $7 \times 7 \times 7$ for most of the calculation and $7 \times 7 \times 14$ for the melting temperature calculation. We choose the initial atomic parameter is 0.2892nm for NiAl and 0.3559nm for Ni_3Al based on the first principle calculation results from Materials Project[15]. Most of the calculation is done for NiAl . The only calculation done for Ni_3Al is for the high-pressure melting phenomenon observation.

We basically use the periodic boundary for most of the calculation as all the thermodynamic properties are bulk properties and only the free boundary for z direction to simulate the melting temperature calculation to observe the melting phenomenon.

For the long-time calculation, we generally use $\Delta t = 0.0004\text{ps}$; For the short time calculation, we use $\Delta t = 0.0002\text{ps}$ to provide more accurate results. We observe the total energy conservation with these two settings.

In order to calculate the mixing energy for the liquid phase at some temperature, we generate several (11) different compositions FCC crystal structures including pure Ni and pure Al for this binary system by assigning the type of the atoms randomly with some ratio in the crystal generator code with some random number settings. Here we use $\Delta t = 0.0004ps$ and 600000 steps to simulate the process. After that we perform constant-temperature(2500K) constant pressure(0GPa) calculations and collect several equilibrium trajectory data to average to get the internal energy for the corresponding composition. After that we calculate the mixing energy through this kind of formula:

$$\Delta H_{mix}(X_{Al}, T) = U(X_{Al}, T) - [X_{Al}U_{Al}(T) + (1 - X_{Al})U_{Ni}(T)]$$

In order to determine the melting temperature, we construct $7 \times 7 \times 14$ computational cell and assigned the free boundary conditions only through the z directions but keep the other two directions as the periodic boundary conditions. Then change the pressure control setting to let it only control the directions with periodic boundary condition. Then we perform the constant pressure calculation with velocity distribution methods to control the temperature and observe how temperature changes. We set the initial temperature $T = 2400K$ to make sure we can see the melting clearly along the z direction. We take the long-time simulation to make sure we observe the equilibrium, which means $\Delta t = 0.0004ps$ with 1000000 steps.

Follow professor's advice and the previous papers[16][17], we try to calculate the thermodynamic properties through a series of constant pressure calculations after it reaches the equilibrium temperature.

As we know the temperature variation with pressure can be estimated from classical thermodynamics,

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{VT\alpha}{C_p}$$

we use $\Delta t = 0.0002ps$ and 400000 steps which is enough to reach the equilibrium. We select $P = -4GPa, 0GPa, 4GPa, 8GPa, 12GPa$ and variant temperature to collect the enough data for liquid and solid phase. Control the different pressure and collect the data of different volume and the different equilibrium temperature, we can get a series figure about *Energy v.s. Temperature* and *Volume v.s. Temperature*.

Based on these data, we can estimate $V, \alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P, C_p = \left(\frac{\partial H}{\partial T}\right)_P$. Then we are ready to integrate the Clapeyron equation to get the P-T diagram to estimate the high-pressure case. Besides, we have $\Delta H_m = \Delta U_m + P\Delta V_m, \Delta S_m = \frac{\Delta H_m}{T_m}$ for the melting properties.

In order to deal with the data simply and finish them in time, we just do the polynomial fitting to get the polynomial function to do the derivative analytically to get what we want thermodynamic properties. I think numerical derivative is also fine here, but I prefer to get an analytical expression. However, during the fitting process, it seems that the higher order polynomial fitting function will become ill-conditioned based on these data. So we are limited to use the second order polynomial fitting function which may not good enough. However, I don't have to much experience in this kind of behavior fitting and have no time to design some better fitting function, so I just keep using this kind of polynomial fitting function.

When we integral the Clapeyron equation, in order to simplify it due to time-limit, I just think of it's as a straight line and use the data at 0GPa, to fit for the line to get the slope to determine it.

In order to check the melting temperature range at high pressure, we do the similar constant-pressure calculations at some different pressures to observe the equilibrium temperature with time settings: $\Delta t = 0.0002ps$ and 600000 steps. We try several times to try to reach the maximum overheating temperature and get the corresponding data.

In order to observe the melting phenomena at high pressure, we set the condition like this: $P = 30GPa$, $T_{initial} = 3460K$ with velocity distribution and do the long-time($\Delta t = 0.0005ps$ and 800000 steps) simulation with constant pressure for Ni_3Al . We perform 10 times under the same condition to observe the melting process.

3. Results of the simulations

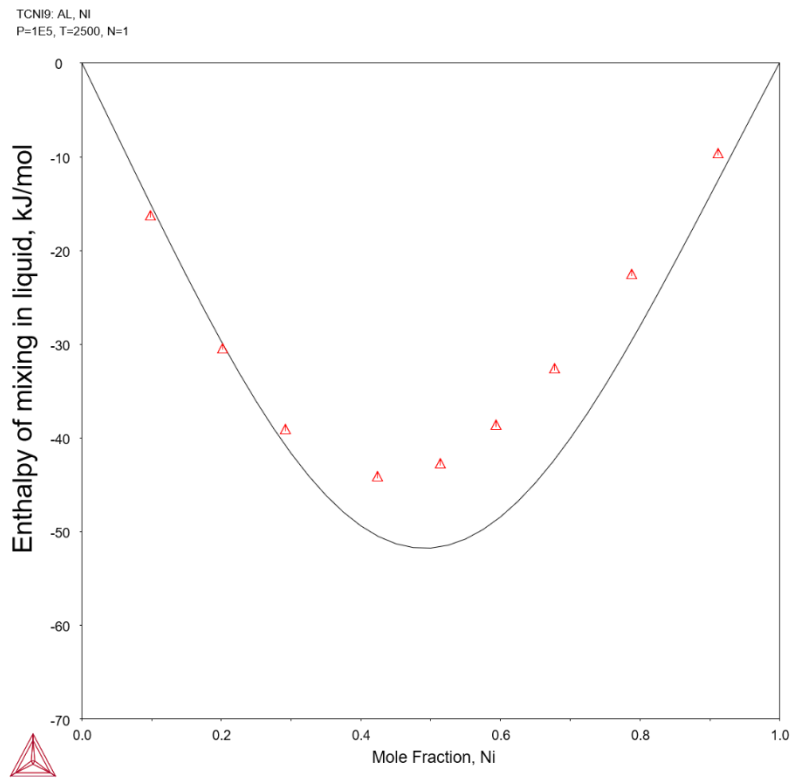


Fig. 1. The enthalpy of mixing for liquid phase at 2500K. The black line is the calculated result in commercial database: TCNI9, the red ▲ is the results calculated from MD simulation at the same condition.

Firstly, I present the mixing enthalpy of liquid at 2500K for $NiAl$ with 50%-50% composition in fig.1. Comparing the results with the Thermo-Calc database[18], as we don't have the experimental data at 2500K for liquid phase but can use the thermodynamic model to produce it.

Qualitatively, the behaviors are consistent to each other and produce relatively good results. The deviation between 0.4 and 0.8 mole fraction of Ni may come from the lack of the experimental liquid

data for CALPHAD modeling. If we don't have the reliable experimental liquid data, the parameters of the thermodynamic model are hard to determine and so that the database may not accurate enough.

The melting temperature is also determined by relaxing the structure with one direction of free boundary, see fig.2. After averaging the trajectory of the equilibrium, the melting temperature is determined as $T_m = 1763.1K$.

Phase	Ni	Ni ₃ Al	NiAl	Al
EAM (present)	1701	1678	1780	1042
Experiment	1728	1645	1911	933
Discrepancy (%)	1.6	1.9	6.8	11.7

This is the table in [13], which presents the melting temperature based on the simulation with the original potential. My calculated result is very close to their calculated value, 1780K for *NiAl* phase. Similarly, it looks still close to the experimental data, but of course it has relatively large deviation compared to the experimental data just like what they presented.

Based on the CALPHAD's point of view, the transition temperature should be very accurate to determine the phase diagram. Hundreds of Kelvins is definitely unacceptable for this case and may lead to terrible phase diagram shape and mislead the experimental people. This maybe the reason why we basically not use the simulation data as the phase equilibrium data such as phase boundary, phase fraction, transition temperature, to determine the phase equilibrium in CALPHAD because of their large error bar.

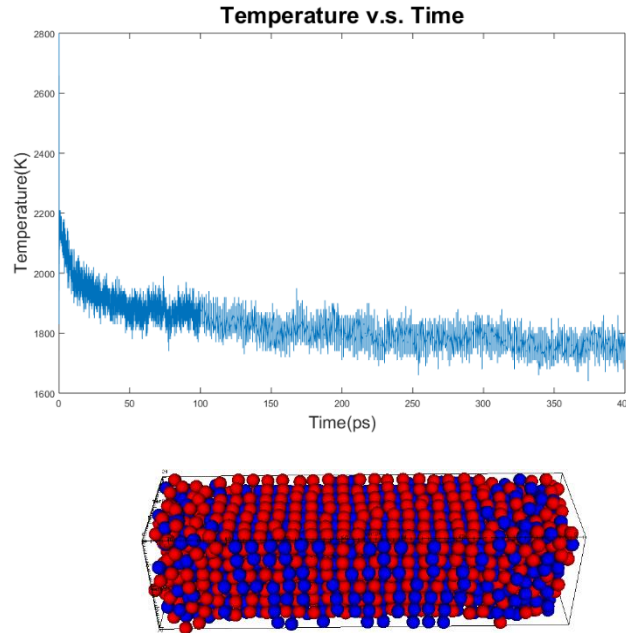
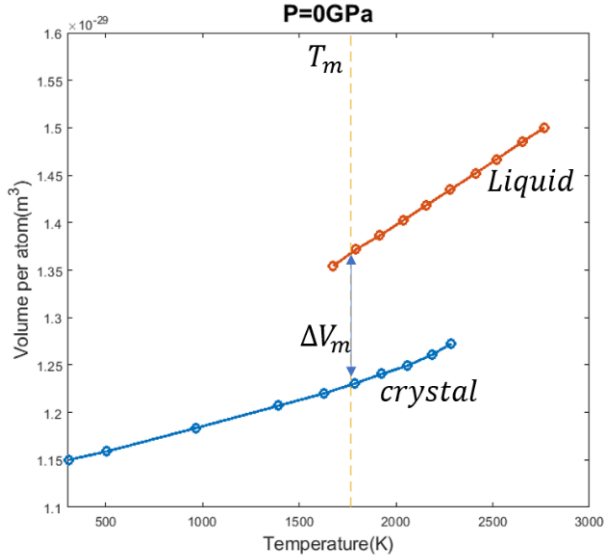


Fig. 2. Determine the melting temperature at 0 Pa through MD simulation. The bottom is the final structure, the top is how the temperature relaxed to the equilibrium. The initial temperature setting is $T = 2400K$. Average the equilibrium trajectory of the MD simulation, which I think is about 300ps-400ps, we get the $T_m = 1763.1K$.

In order to get the thermodynamic property at the melting temperature, we plot the volume and internal energy figure with temperature in fig.3.

(a)



(b)

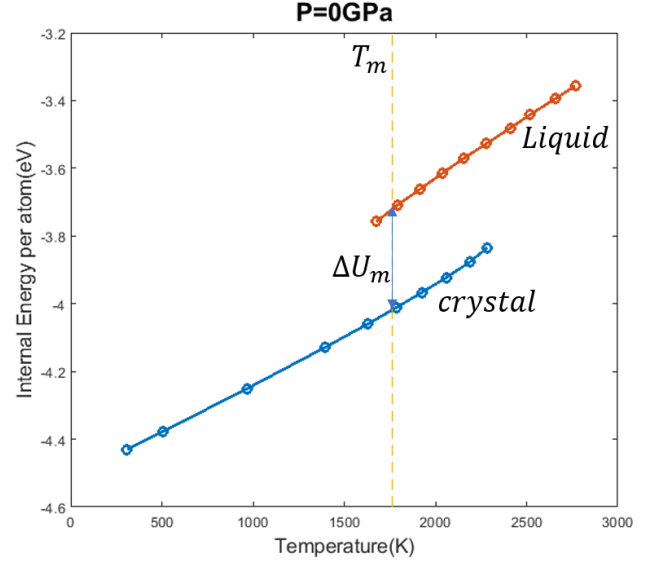


Fig. 3. (a) is for volume v.s. temperature, (b) is for internal energy v.s. temperature from the MD simulation. The crystal and the liquid phases are both plotted.

With the melting temperature determined from the previous results,

$$T_m = 1763.1K$$

Based on these figures, we calculate some results:

$$\Delta H_m(P = 0GPa) = \Delta U_m = 0.297eV$$

$$\Delta V_m = 1.384 \times 10^{-30}m^3$$

$$\Delta S_m = 1.687 \times 10^{-4}eV/K$$

All these results are for per atom.

As time is limited, I only compare the latent heat for this kind of calculation. Based on Thermo-Calc's database[18], the latent heat is about $\Delta H_m = -21680J/mol$. Based on our calculation, I transfer the same unit, then the result is $\Delta H_m(MD) = -28607J/mol$.

There are many reasons can lead to this relatively large deviation. First of all, the melting temperature in CALPHAD database is not the same as the one in our MD simulations. This will lead to some deviation when we compare the latent heat. Another reason is the liquid model in CALPHAD database is always not that accurate, so it's also possible that the deviation is coming from the database.

We also try to compare the internal energy v.s. temperature with experiments in fig.4. Based on the data we found, they are consistent with each other pretty well, so we should believe at least the internal energy is very reliable based on the MD simulation.

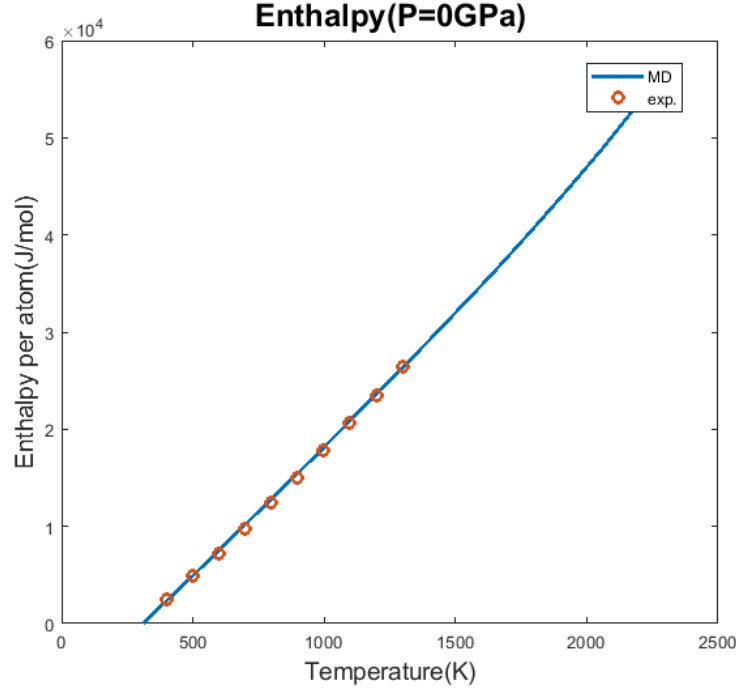
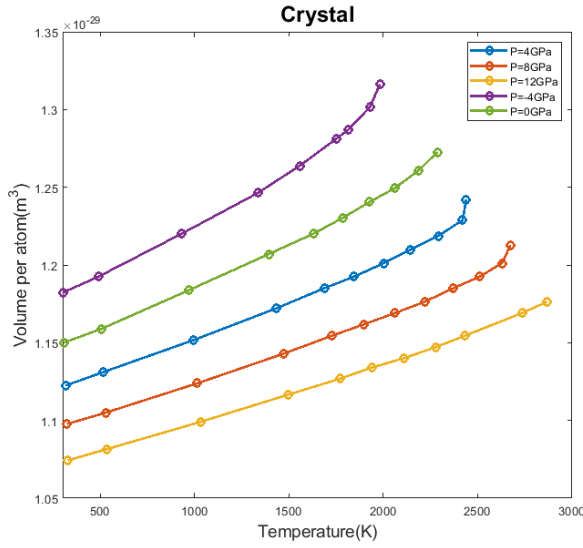


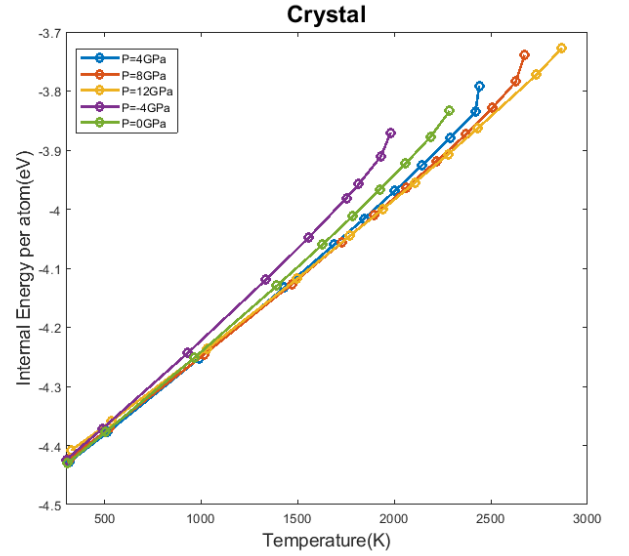
Fig. 4. The comparison between experimental data[19] and present MD simulation about the enthalpy for the temperature dependence.

In order to get the thermal expansion and heat capacity, we plot the volume v.s. temperature and internal energy v.s. temperature with different pressure for crystal and liquid in fig.5. Then we can take use of $\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P$, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ to calculate the thermodynamic property for the specific pressure.

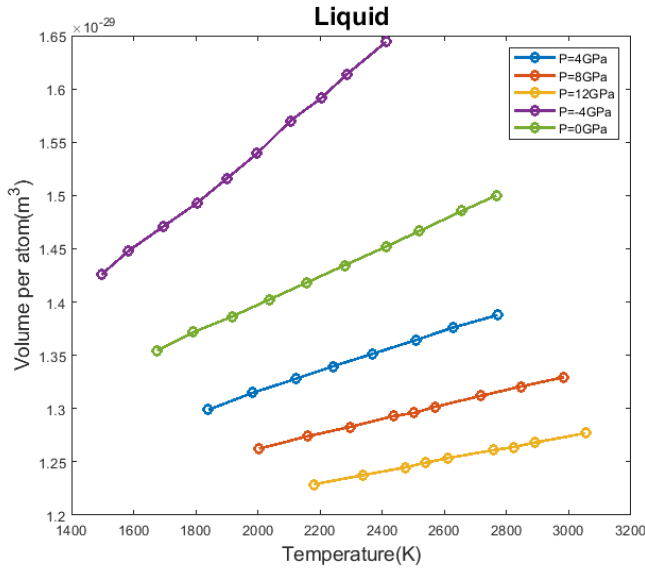
(a)



(b)



(c)



(d)

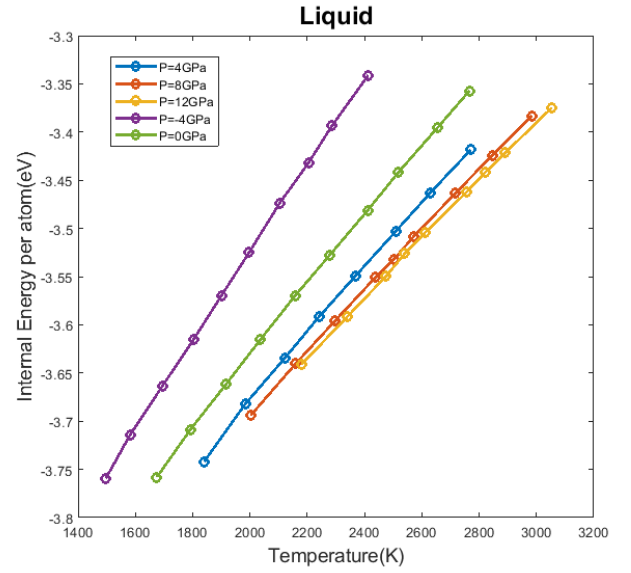


Fig. 5. volume v.s. temperature and internal energy v.s. temperature with different pressure for crystal and liquid from present MD simulation.

Due to the limited time, I just calculate the thermal expansion and the heat capacity at 0GPa and to compare with the experimental data in fig.6.

In order to do the first derivative calculation, we fit the data to the polynomial function to get the analytical expression and do the analytical first derivative calculation to plot the results.

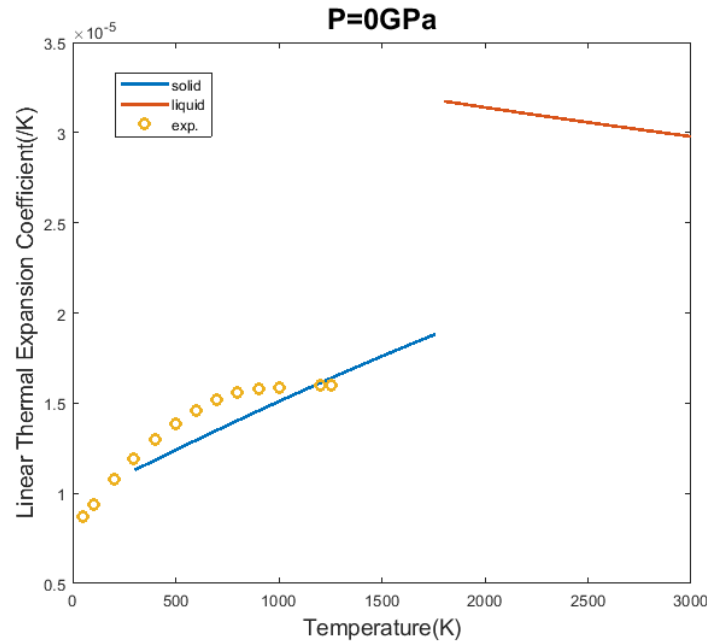


Fig. 6. Thermal expansion coefficient v.s. temperature at 0GPa from MD simulation, note we transfer the volume thermal expansion to the linear thermal expansion to compare with the experimental data in [20].

Because of the fitting issue, the final analytical expression seems like a straight line, which shows the results is numerically close to each other actually but may lose some features due to the fitting process.

The calculated heat capacity seems that it has the same issue for the fitting function which lead to only the linear dependence of the heat capacity, see fig.7. However, after comparing with the experimental data, I found it fits for the experimental data very well but only has a small deviation for each temperature. I am not very sure but it may come from the electron contribution for the heat capacity which MD simulation can not cover. For the liquid part, I think it's an unexpected result but I don't find the experimental data to compare. Basically, the experimental data for the thermodynamic property of the liquid phase.

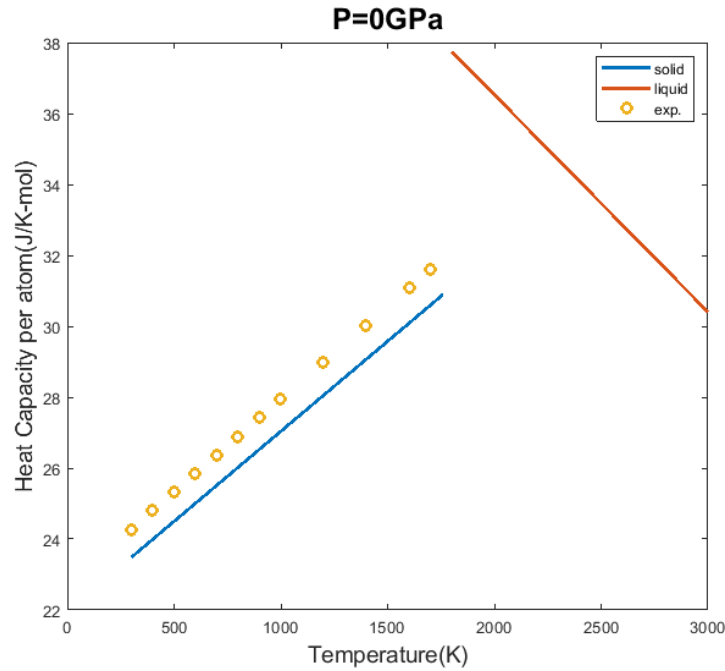


Fig. 7. The temperature dependence of the heat capacity from MD simulation at 0GPa. The experimental data is taken from [21].

Intuitively, the heat capacity of the liquid phase seems that It shouldn't decrease. However, we observe it in our MD simulation. It may come from the computational problem. It is also possible that the potential may not accurate enough to describe the liquid phase. It may also come from the issue caused by the not well-chosen fitting function.

Actually, in Thermal-Calc database, the heat capacity of the liquid phase is always reaching to a constant when it is higher than the melting temperature. That maybe one kind of artifact in thermodynamic modeling, as the present liquid model in CALPHAD database can't capture too much physics.

However, I noticed the heat capacity does decrease in some system. Some previous literature provide some theoretical and experimental results on this kind of liquid thermodynamic problems [22][23][24]. Some of the results are provided in the fig. 8. We can observe the decreasing of the heat capacity with the increasing temperature for liquid will happen in some system. Unfortunately, we don't have too much data for other metals with high melting temperature. Different metals may have very different behaviors.

Actually, up to I known, there is only clear theory for solid heat capacity which is based on the phonon, quantization for the atomic vibration based on Einstein model and Debye model. But for liquid, phonon is seen to be damped. Recent years, a new kind of quasiparticle, *anakeon* is proposed by Bellissard and

Egami to identify the topological degrees of freedom, representing the unpredictable sudden change in the local configuration of atoms due to the local stress and the thermal motion[25][26]. This may provide a potential explanation for the liquid heat capacity.

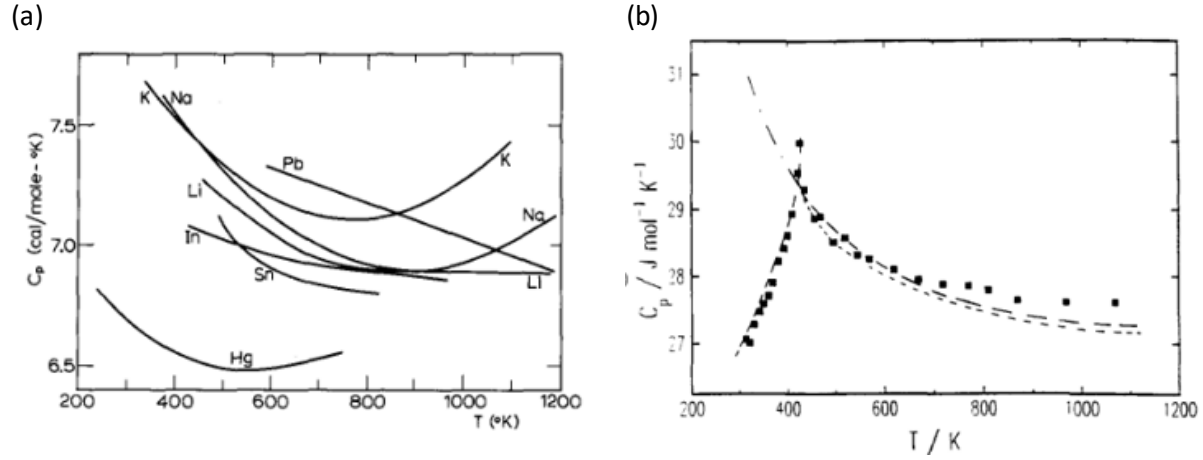


Fig. 8. The heat capacity for liquid metals at constant pressure. (a) is from [22] and (b) is from [23] for indium.

Based on the whole data in 0GPa, we can integrate the Clapeyron equation to get the P-T relation to estimate the high-pressure thermodynamics. Due to the limit of the time, I will think of the P-T relation as the linear relation to provide a first approximation. The slope of the straight is calculated only based on the data at 0GPa, so the estimation is very rough, see fig.9.

The data point provided is from several high-pressure melting simulations performed to try to reach the maximal overheating temperature, it seems the rough estimation here still good enough for fitting the maximal overheating line.

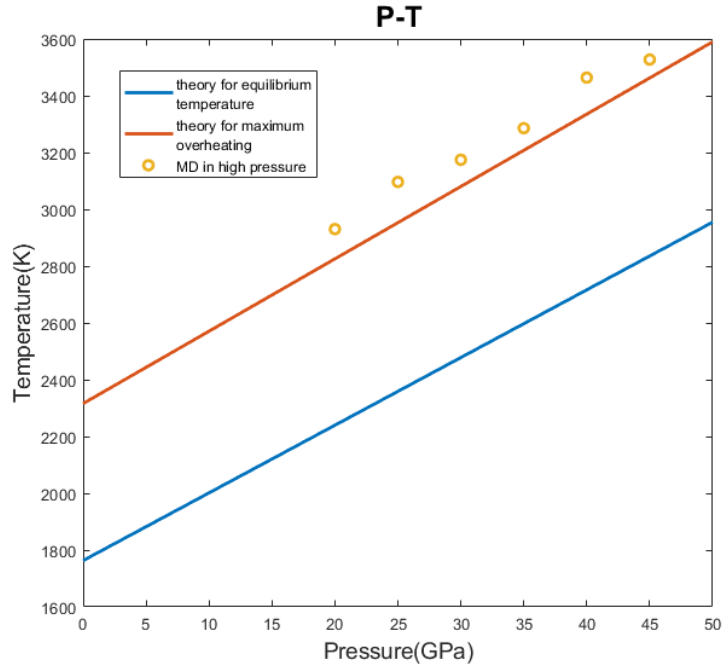


Fig. 9. The P-T diagram calculated only based on data at 0GPa and fit it for the linear function. Although the estimation is rough, it seems that it fits for the MD simulation data relatively well.

The better similar results can be seen in fig. 10. We can see the temperature range between the equilibrium T_m and maximum overheating is always increasing with the increasing of the pressure. So I guess in the high-pressure case, it will have larger range of temperature to operate between the maximum overheating and equilibrium T_m to observe the melting phenomena.

I choose Ni_3Al , 30GPa and $T = 3460K$ to observe the melting process. Then I observed the uncertainty of the nucleation/melting under this condition. This means the melting process seems a stochastic phenomenon which can't always have the exactly same process under totally the same initial condition.

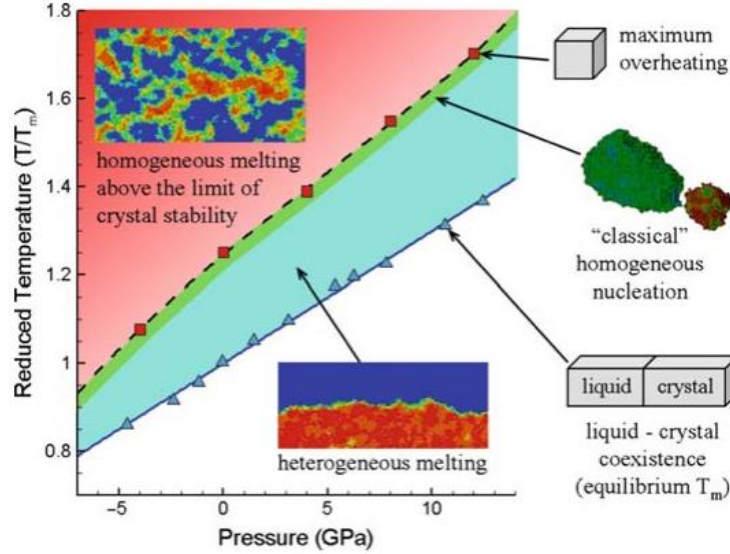


Fig. 10. This demonstrates the range of different melting v.s. the Pressure and the different mechanism of melting [27].

Here is the table about some data for the 10 tests I done.

test	1	2	3(solid)	4	5	6	7	8	9	10
Waiting time to melt (ps)	~65	~100	>400	~140	~50	~145	~120	~60	~85	~40
final temperature(K)	2255.4	2282.9	2786.0	2286.0	2289.6	2276.1	2286.3	2298.3	2288.6	2285.1
Final potential E(eV)	-5511.6	-5514.6	-5594.2	-5515.2	-5516.4	-5513.7	-5515.9	-5517.6	-5517.0	-5515.5

We can see the final temperatures and final potentials for each test which melts are all close to each other. This indicates they finally come to the same state with the unavoidable fluctuation. However, the waiting time to melt is very different between them which means the process are not identical to each other. The test 3 is even not melted during the whole simulation time, see fig.11.

The average of the waiting time is 89.44ps and the sample standard deviation is 39.01ps which means the test 3 with larger than 400ps waiting time is very rare that it is out of the 3σ range. I think there might be two reasons to explain it. On the one hand, it's just a small probability event that the melting will finally happen with much more waiting time to melt. On the other hand, the configuration shown in fig.11. may represent some metastable state which sits in a local minimum in the potential energy but very hard to relax to the global minimum due to the kinetic reasons for the limitation.

Actually, the micro-mechanism of melting/nucleation based on rigorous stochastic analysis or statistical mechanics is still incomplete. People try to take use of the Fokker-Planck equation to describe the nucleation process with the stochastic feature recently[28][29]. But the limitation is Fokker-Planck equation is that it's based on the Markovian property but nucleation may not[30]. A recent paper [31] proposed a new model with non-Markovian property to compare with classical nucleation theory but it's still just a new potential direction for the future study.

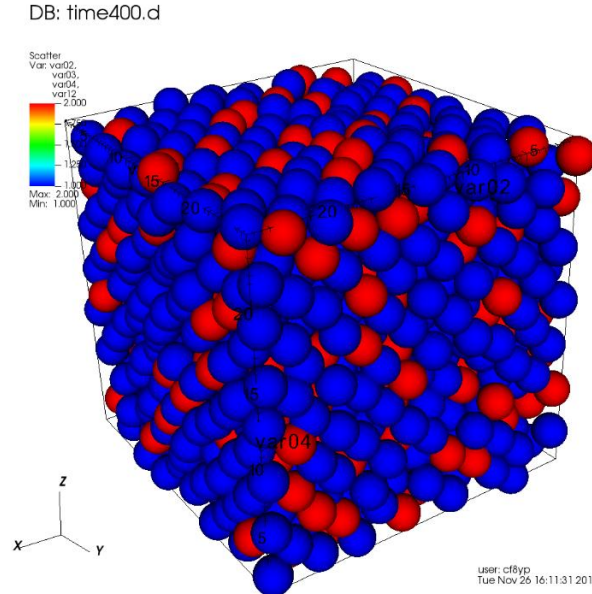


Fig. 11. The final configuration of test 3, which is not melted with the same condition. The structure is disordered but still kept the crystal structure. It is more like a disordered phase but not a liquid phase. It maybe considered as it comes to a kinetic path to a local minimum (disordered solid phase) but hard to come to the global minimum (liquid phase).

4. Conclusions

In summary, based on our calculation we can conclude:

- MD simulation does provide relatively accurate thermodynamic data to study phase transformation under variant conditions.
- However, it still has some deviations due to many different reasons.
- The temperature dependence of the heat capacity of the liquid is simulated and implies different features for crystal and liquid for this thermodynamic property.
- Melting/nucleation/phase transformation may need to be seen as a stochastic phenomenon.

For the future direction, it may be interesting to take use of Ab initio Molecular Dynamics to do the calculation to replace the traditional potential functions. Some similar attempts have been done, see also [32].

Because of the flexibility of the MD simulation, it should be possible to take use of MD simulation to produce thermodynamic data for the CALPHAD database for severe conditions such as liquid phase at high-temperature and the high-pressure state.

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