Study of Phase Transition in Pure Zirconium using Monte Carlo Simulation

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Abstract

NPT Monte Carlo simulation is implemented to study the transition temperature of pure zirconium HPC to BCC phase transformation at hight temperature and low pressure.Burgers transformation is used to minimize crystal shearing effect that inhibits solid-solid phase transformation. The pair correlation function and the structure factor are calculated at room temperature for a transformation from random intial configuration to HCP lattice when calculating c/a value is nontrivial. We calculate free energy to locate the transition temperature. This is compared to the experimental value and the molecular dynamics simulation of 1233 K[2].

1 Introduction

We are interested in phase diagram of Zirconium-based systems. The phase diagram is a road map to alloy design and development. Zirconium based alloy is useful in many mission-critical applications for example: using it as cladding material for nuclear fuse and reactor and thermal barrier coating for turbine blades. The reliable phase-equilibrium data at high temperature of such systems is difficult to obtained using conventional experimental techniques. In the present work we will use Metropolis Monte Carlo method to investigate the phase boundary of solid-solid Hexagonal Closed Packed (HCP) phase to Body Centered Cubic (BCC) phase transition for pure zirconium metal. Specifically in this paper we will use the isothermal-isobaric

Monte Carlo simulation to study the HCP(α phase) to BCC(β phase) transition at high temperature. The area of interest is near the y-axis in the T-P phase diagram as shown in fig.1. This paper has four sections. In the next section, the theory and basic building blocks of our simulation are discussed. In section III, we will discuss about our results. Finally in section IV, we will summarize our findings.

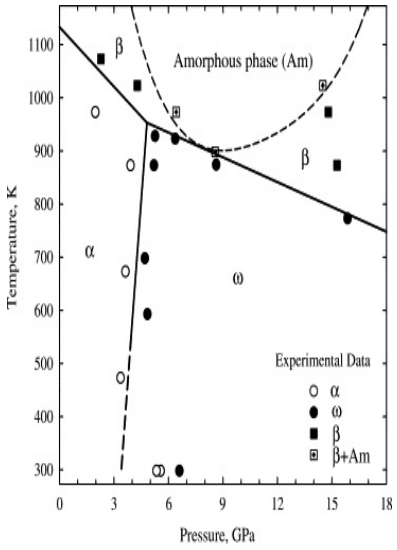


Figure 1: The phase diagram of pure zirconium metal in pressure-temperature plane. The area in the phase diagram explored in this paper is the low pressure-high temperature α to β phase transformation.[1]

2 Theory

There are some theoretical concepts we need to discuss before we can start on the simulation. These are potential, The algorithm for doing isothermal-isobaric Monte Carlo moves(NPT Monte Carlo), and free energy calculation. In the next subsection, a brief description of the potential used is given.

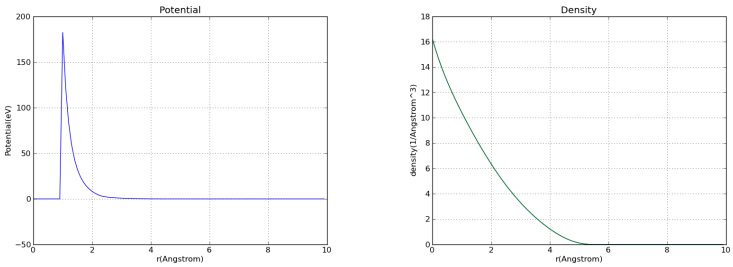
2.1 Embedded Atom Potential

Since there are delocalized electrons in metal, the usual pair potential is an inadequate description. Finding an appropriate potential for metal is

nontrivial. In this project, we apply the potential used in molecular dynamics to calculate the potential for our Monte Carlo moves. The most general empirical potential used is the embedded atom model potential. The insight for constructing EAM potential can be gained by consider the pudding model for metal. Each atom has two types of potential energy. The first one is due to the pair potential between atoms. the second one is the force exerted on the atomic nucleus due to the averaged configuration of the electron cloud. The second term is parameterized by a pairwise function: the density function. The total energy in EAM is:

$$U_{tot} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V(r_{ij}) + \sum_{i=1}^{N} F(\rho_i)[2]$$

where the idices i and j idicates each of the end atoms, $V(r)$ is a pairwise potential, $F(\rho)$ is the embedding energy function and $\rho_i = \sum_j \phi(r_{ij})$ where $\phi(r)$ is the density function. Determining the form of the potential is a complex nonlinear optimization problem, which will not be elaborated here. On the other hand we will examine the plots of the potential and state its important features that we need to consider in our simulation. The complete expression of the EAM potential used can be found in ref... Fig.2 illustrates



(a) Pair Potential (b) Density Function

Figure 2: Potential and Density Function plot for the specific EAM potential that is used. The electron density is short range, only the electron density less than 5Åis considered

the plot of the potential and the desity function. It is important to note that the pairwise potential used has a hardcore condition. Any monte carlo move that gives rise to an interatomic distance less than 1 Åis not allowed.

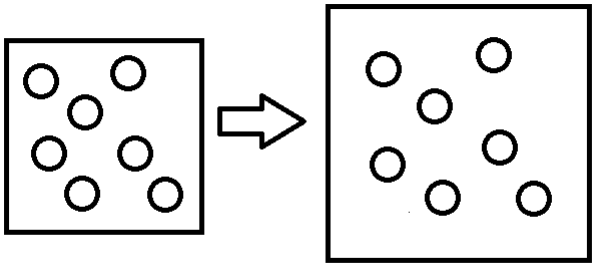


Figure 3: This figure shows the rescaling of the the simulation box after a volume-change.

2.2 NPT Monte Carlo

The NPT MC is applied in this project as a remedy of the shearing problem in solid. This ensemble and the Burgers transformation, which will be introduced in the next section, are proven to effectively solve this problem for HCP to BCC phase transition. The isothermal-isobaric ensemble corresponds to constant T,P, N, specified as inputs of the simulation. This can be thought as having the simulation coupled to the heat and volume bath. The basic idea of NPT is similar to that of the Metropolis MC except for the addition of the volume scaling moves. The sketch of the algorithm is:

- Volume Scaling Move
  1. Pick a random change in volume uniformly from ΔV in range of $[-\delta V_{max}, \delta V_{max}]$ then make $V \leftarrow V + \Delta V$
  2. Scale the entire simulation box uniformly along each axis.
  3. Scale the positions of particles uniformly
  4. Recalculate the total potential energy
  5. Accept with P^{acc}

- Random Particle displacement Move
  1. Pick a particle randomly then update the position by sampling from a gaussian distribution
  2. Update the energy
  3. Accept with P^{acc}

The re-scaling procedure is in such a way that the dimensionless(normalized) coordinates remain the same. The normalization is done as

$$(S_{x,1}, S_{y,1}, ..., S_{z,N}) = (\frac{x_1}{L}, \frac{y_1}{L}, ..., \frac{z_N}{L})$$

where L is the width of the simulation box. This procedure is illustrated in fig.3.
The frequency of the moves is an important consideration to ensure the markovian nature of the simulation. 1. Pick a random number from a uniform distribution $[0, 1]$
2. if $r < 1/(N + 1)$, do a volume scaling move. Otherwise, do the update position move. This way will allow us to attempt on average of 1 volume scaling move for every N attempted displacement moves. Note that to ensure the Markovian nature this is drawn from a uniform probability. The final ingredient is the acceptance probability(P^{acc}). From the detailed balance equation

$$\frac{P^{acc}_{old\to new}}{P^{acc}_{new\to old}} = \frac{T_{new\to old}p_{new}}{T_{old\to new}p_{old}}, \tag{1}$$

we have to compute the probability of the move(p_m) and the transition probability(T). p_m can be calculated in a similar manner as the Metropolis MC., however now the exponent is the Gibbs free energy. p_m can be written as

$$p_m = \frac{e^{-\beta U-\beta PV}}{\Lambda_T^{3N} N!} \times \frac{dr^N dV}{Z}$$

where Λ_T is the thermal wavelength and Z is the partition function. The transition probability for the displacement move cancels out as in the Metropolis MC. The transition probability for the volume scaling move can be separated in to two parts: the probability to pick V_2 given V_1 is given by

$$\alpha(V_1 \to V_2) = \frac{1}{2\delta V_{max}}$$

The secon part of the transition probability is the probability to pick r^N_{new} given r^N_{old}. This is given as

$$\frac{T_{new\to old}}{T_{old\to new}} = \left(\frac{V_{new}}{V_{old}}\right)^N$$

From all the ingredients, the acceptance probability can be derived using eq.1 to be

$$P^{acc}_{old\to new} = min\{1, e^{Nln\left(\frac{V_{new}}{V_{old}}\right)-\beta\Delta U-\beta P\Delta V}\} \tag{2}$$

2.3 Free Energy Calculation

Free energy is computed here to find the stable phase at different (Temperature, Pressure) coordinates. For system interacts with continuous potential $U(\mathbf{r}^N)$, the free energy can be calculated using the method of potential switching. We write an effective potential energy depends on a railing parameter λ. The potential is modified to be

$$\tilde{U}(\mathbf{r}) = U(\mathbf{r}_0) + (1-\lambda)[U(\mathbf{r}) - U(\mathbf{r}_0)] + \lambda \sum_i^N \alpha_i (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \tag{3}$$

where σ_i are spring constants at i-th lattice site. When $\lambda = 1$, the potential reduces to the perfect Einstein lattice case that we use as our reference state since its free energy can be computed analytically:

$$F_{Ein} = U(\mathbf{r}_0^N) - \frac{3}{2\beta} \sum_{i=1}^N ln(\pi \alpha_i \beta) \tag{4}$$

The free energy then can be calculated from a reference configuration which is the Einstein lattice. We integrate λ with respect to the reference state to the EAM potential. This is good because the expection value of $\frac{\partial U}{\partial \lambda}$ can be sampled from our Monte Carlo ensemble.

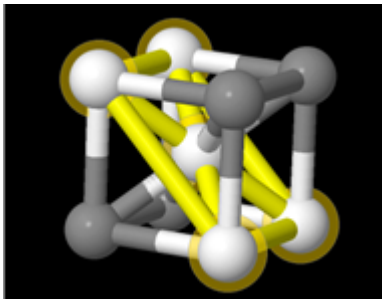
$$F = F_{EIN} + \int_{\lambda=1}^{\lambda=0} d\lambda \langle \frac{\partial U(\lambda)}{\partial \lambda} \rangle \tag{5}$$

From eq.3 and eq.5, free energy can be written as

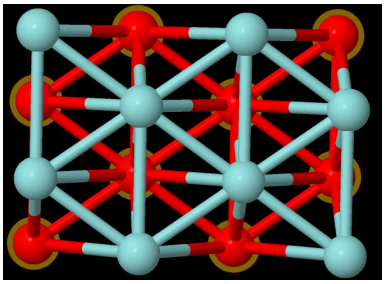
$$F = F_{EIN} + \int_{\lambda=1}^{\lambda=0} d\lambda \sum_{i=1}^N \alpha_i (\mathbf{r}_i - \mathbf{r}_{0,i})^2 - [U(\mathbf{r}) - U(\mathbf{r}_0)] \rangle [4] \tag{6}$$

2.4 Burgers Transformation

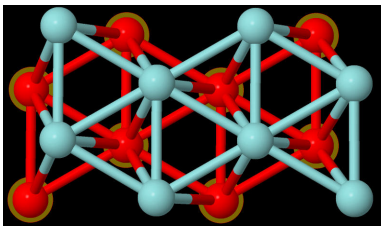
The accepted pathway for BCC-HCP transformation is called the Burgers mechanism originally proposed for Zirconium[5]. It can be divided into three phases. In the first stage, the (110)BCC planes undergo shear to transform into the HCP basal (0001) plane(fig.4(b) and fig.4(c). Secondly, the shifting of the atoms in the (110) plane leads to an FCC type of structure. Lastly, alternate planes shift in the in the [110]BCC direction, completing the transformation.



(a) This figure shows the 110 plane of BCC on the unit lattice



(b) The illustration of the 110 plane of BCC



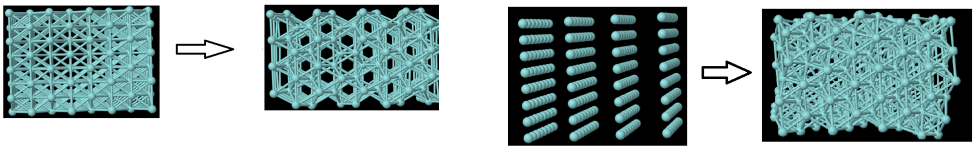
(c) The illustration of the 0001 plane of HCP

Figure 4: This figure illustrates the steps of the Burgers transformation

3 Results and Discussion

Metropolis Monte Carlo simulations were carried out under NPT ensemble using Zr EAM potential for different combinations of temperature and starting configuration. The initial setup consisted of a cuboidal box having 256 atoms. The 3 box lengths were allowed to change independently, keeping the overall shape cuboidal. The pressure was kept constant at one atmosphere. To verify the potential, we perform some simulation runs and calculate some observables to compare to molecular dynamics calculation and experimental results. The expected value from experiments is a=3.232 and the molecular dynamics result is a=3.232[2]. When starting from an initial BCC configuration at room temperature, as shown in the fig.5(a), the super cell equilibrates to a perfect HCP lattice via the Burgers transform pathway within 1 million Monte Carlo steps. The lattice parameter and c/a ratio have been reproduced within reasonable accuracy of experimental values.

However, it takes longer to equilibrate at lower temperatures 100K, possibly due to slow dynamics. In order to confirm that the HCP phase is not



(a) The system transforms from BCC to HCP structure

(b) The system transforms from some random starting lattice to HCP

Figure 5: Our simulation shows that for T=300K and P=1 atmosphere, any lattice structure transforms to HCP lattice as expected from experiments

Table 1: Lattice values for BCC-HCP

Temperature(K)	a(Å)	c/a
100	3.240126±0.000112	1.716752±0.000086
200	3.242465±0.000163	1.718308±0.000123
300	3.243776±0.000191	1.605709 ±0.000125
400	3.245310±0.000211	1.605012 ±0.000138

being stabilized by the PBC alone, simulations were also started with arbitrary initial configuration(fig.5(b). The system equilibrates to a stable HCP phase in 1 million MC steps, albeit with a few stacking faults, and may eventually transform to perfect HCP if allowed to simulate for longer. Since this transformation was not in the (110)BCC plane, the lattice parameter and c/a ratio could not be sampled directly from the box width and length. Hence, pair distribution function was plotted to quantify the structure(fig.6(a)). The peak observed at 3.25 Åcorresponds to the nearest neighbour distance and is reasonably close to the experimental value, but also shows that system needs to equilibrate further. Another set of simulations were also carried out starting directly from the HCP phase at room temperature, with modified lattice constants.

It was observed that the system quickly equilibrated to the perfect HCP phase, reproducing the lattice constants, thus validating the potential. An attempt was also made to locate the HCP-BCC transition temperature but could not be determined using simulations alone. Neither phase undergoes

Table 2: Lattice values for HCP-HCP

Temperature(K)	a(Å)	c/a
100	3.241199±0.000070	1.607152±0.000046
200	3.242909±0.000101	1.606097 ±0.000065
300	3.246139±0.000386	1.604255 ±0.000247
400	3.247921±0.000434	1.602724 ±0.000284

Table 3: Free energy for HCP and BCC phase at 1200K.

Structure	Free Energy(eV)
HCP	-1084.5497116±23.159035337208316
BCC	-976.697421736±28.07292821723887

any transformation when close to the transition temperature, even in 2 million MC steps. This may be due to several reasons, such as hysteresis, a high transition barrier and artificial stability due to PBCs. Hence, free energy calculations were performed.

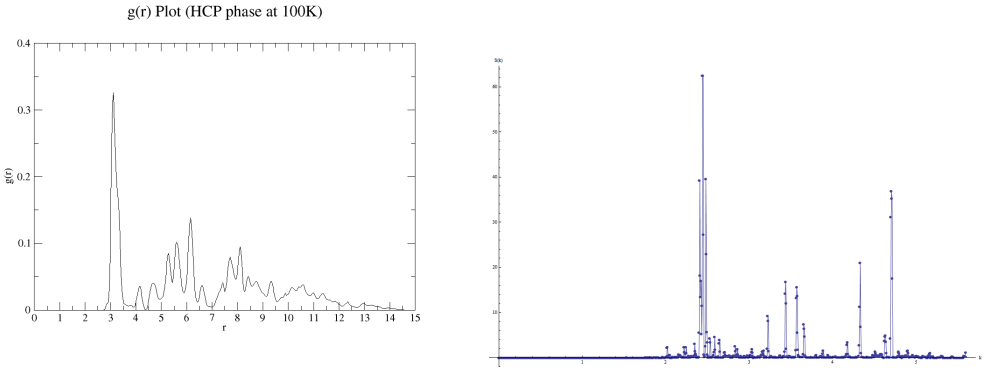
Molecular dynamics simulation reported a transition at 1233K[2]. This was confirmed by free energy results as being between 1200K-1300K. The HCP phase is more stable at 1200K while the BCC phase is more stable at 1300. However, an accurate estimate of the transition temperature could not be obtained and additional work is needed here.

4 summary

An attempt was made to validate zirconium EAM potential using NPT Monte Carlo simulation.Burgers transformation is used to ensure that cuboid periodic boundary condition is suitable for both BCC and HCP. HCP relaxed phase obtained from initial BCC structure as well as random initial structure. The pair correlation function and the structure factor are calculated at room temperature for a transformation from random intial configuration to HCP lattice when calculating c/a value is nontrivial. We found that the Free energy calculation shows that the transition temperature should lie between

Table 4: Free Energy for HCP and BCC phase at 1300K.

Structure	Free Energy(eV)
HCP	-963.295073649±28.736128637559702
BCC	-1024.00599112±26.653711893629307



(a) Pair Correlation Function of HCP phase (b) Structure factor plot for HCP phase

Figure 6: Pair correlation function and structure factor computed from the Monte Carlo simulation starting from a random initial configuration

1200 K. and 1300 K. This agrees very well with the experimental value and the molecular dynamics simulation of 1233 K[2].

References

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