# Study of Phase Transition in Pure Zirconium using Monte Carlo Simulation

Abhinav Jain
Wathid Assawasunthonnet

@Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

# Outline

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- Why Interesting?

## 2. Theory

- NPT Monte Carlo Move
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- free energy calculation

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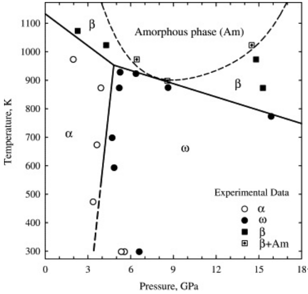
- Results Presentation
- Summary and Discussion

# Introduction



[1]

- Goal:To study the phase transition of Zirconium from Hexagonal closed-packed(HCP) into the Body Centered Cubic(BCC)
- The transition temperature has been calculated using other methods but never been done with Monte Carlo simulation.
- We are hoping that by computing the free energy we can avoid the transition barrier problem.

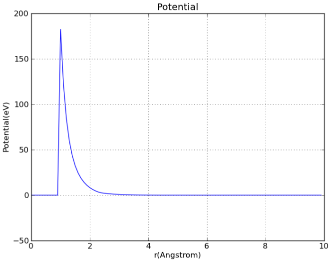
[1] Jianzhong, Z.*et al.*,JPChS **66**, 1213-1219(2005)

# Model

- Embedded Atom Model Potential

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

where $\rho_i = \sum_j \phi(r_{ij})$



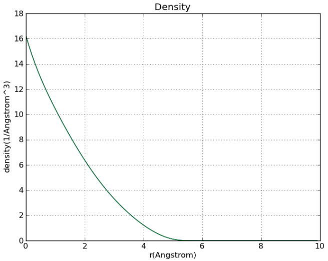



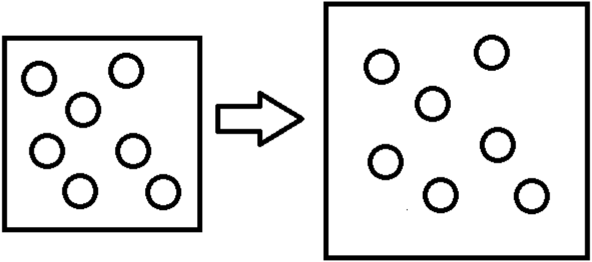

Figure : Potential and Density Function

*M. I. Mendelev and G. J. Ackland, PML Vol.* ***87****, No.5, 349-359 (2007)*

# NPT Monte Carlo

- Volume Scaling Move

  1. Pick a random change in volume uniformly from $\Delta V$ 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 $P^{acc}$



# NPT Monte Carlo

- 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 $P^{acc}$
- Frequency of the Moves
  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.
- Check the Virial Pressure

$$< P > = < \frac{Nk_B T}{V} - \frac{1}{3V} \sum_{i<j} F(r_{ij}) r_{ij} >$$

*A. J. Schultz and D. A. Kofke, PRE* ***84****, 046712 (2011)*

# Acceptance Criterion

- The detailed balance

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

- Computing the $p_m$ and T

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

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

- Acceptance Probability

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

# Free Energy Calculation

The potential is modified to be

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

The free energy then can be calculated from a reference configuration which is the Einstein lattice.

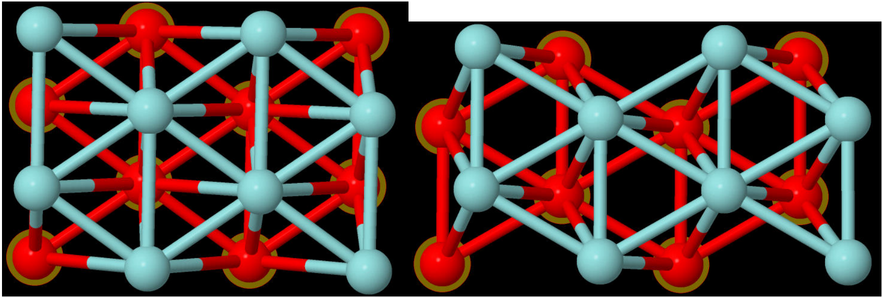
$$F = F_{EIN} + \int_{\lambda=1}^{\lambda=0} \langle \frac{\partial U(\lambda)}{\partial \lambda} \rangle$$

$$F_{EIN} = U(\mathbf{r}_0) - \frac{3}{2\beta} \sum_i^N ln(\frac{\pi}{\alpha_i \beta})$$

*Frenkel and Smit., Understanding Molecular Simulation(2002)*

# Setting up the Runs

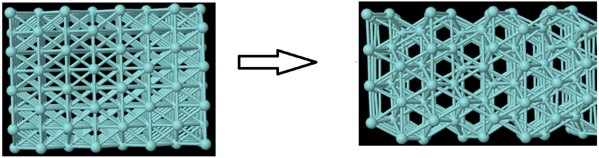
- Burgers Transformation Pathway



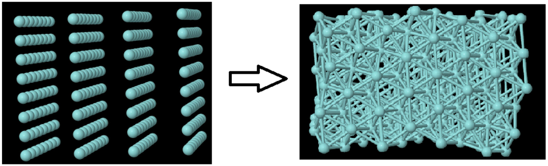
*W. G. Burgers, Physika, i, 561 (1934)*

# Result1

- BCC to HCP at 300 K.



- Random to HCP at 300 K.



# Result2: Lattice Constant Results

- Potential Verification

Table : 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 |

Table : 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 |

# Result3: Free Energy

- The free energy for HCP and BCC configurations at T=1200, P=1 atm

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

- The free energy for HCP and BCC configurations at T=1300, P=1 atm

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

- Expected $T_{transition} = 1233K$.

*M. I. Mendelev and G. J. Ackland, PML Vol.* ***87****, No.5, 349-359 (2007)*

# Summary and Discussion

- An attempt was made to validate zirconium EAM potential using NPT Monte Carlo simulation
- HCP relaxed phase obtained from initial BCC structure as well as random initial structure
- Free energy calculation shows that the transition temperature should lie between 1200 K and 1300 K.
- Burgers transformation is used to ensure that cuboid periodic boundary condition is suitable for both BCC and HCP.

# Thank you