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Molecular Dynamics Study of Self-Diffusion in Zr

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Motivation and Outline

Diffusivity in the vacancy or interstitial mechanism of self-diffusion:

$$D = a^2 f \gamma v x_e^d e^{-G_m^d / kT} = a^2 f \gamma v x_e^d e^{S_m^d / T} e^{-E_m^d / kT}$$

where

$$x_e^d = e^{-G_f^d / kT} = e^{S_f^d / T} e^{-E_f^d / kT}$$

➤ All input parameters can be determined from $T=0$ *ab initio* calculations.

- ❑ Do these parameters depend on temperature?
- ❑ What can we do if a phase is unstable (not metastable) at $T=0$?

Outline:

- ❑ Semi-empirical potential for Zr
- ❑ Temperature dependence of the point defect formation energies
- ❑ Effective diffusivity from MD simulation
- ❑ Equilibrium point defect concentration
- ❑ Calculation of diffusivity and comparison with experiment
- ❑ Summary

Embedded Atom Method (EAM) Potential

Potential energy:

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \varphi(r_{ij}) + \sum_{i=1}^N F(\rho_i)$$

where φ is the pair potential contribution to the cohesive energy and F represents the energy to embed an atom in a background charge density, ρ_i :

$$\rho_i = \sum_{\substack{j=1 \\ j \neq i}}^N \psi(r_{ij})$$

where ψ is the contribution from neighboring atom j .

- All EAM functions are fitted to material properties taken either from experiment or *ab initio* calculations.
 - Different problems may require using different semi-empirical potentials.
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Development of EAM Potential for Pure Zr¹

Motivation: semi-empirical potentials for simulation of Cu-Zr amorphous alloys.

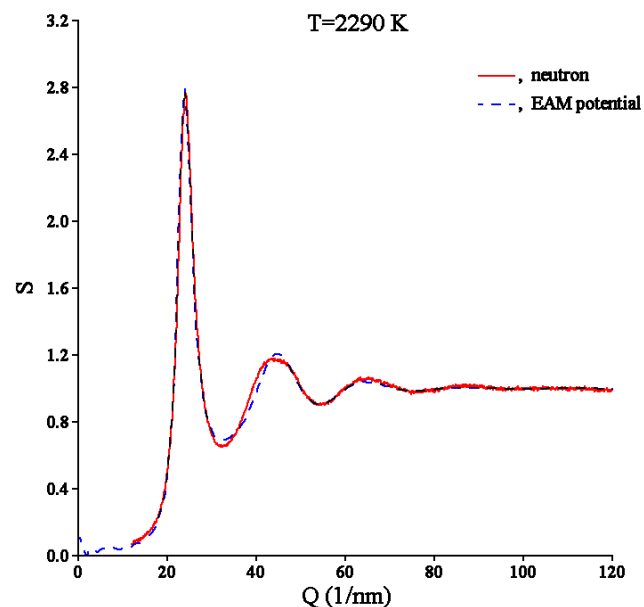
Main focus: phase transformations and liquid structure.

$T_{\alpha \rightarrow \beta}$ can be determined from:

$$\int_{T_{\alpha \rightarrow \beta}}^{T_m^\beta} \frac{\Delta H^{\alpha \rightarrow \beta}}{T^2} dT + \int_{T_m^\beta}^{T_m^\alpha} \frac{\Delta H_m^\alpha}{T^2} dT = 0$$

$T_{\alpha \rightarrow \beta}$ can be fitted by the choice of T_m^α .

Liquid structure can be fitted via the BGB equation².



Property	Target value	EAM potential
a (hcp, T=0) (Å)	3.232	3.220
c (hcp, T=0) (Å)	5.182	5.215
E_{coh} (hcp, T=0) (eV/atom)	-6.32	-6.47
C_{11} (hcp, T=0) (GPa)	155	165
C_{12} (hcp, T=0) (GPa)	67	65
C_{44} (hcp, T=0) (GPa)	36	48
C_{13} (hcp, T=0) (GPa)	65	63
C_{33} (hcp, T=0) (GPa)	172	180
$\Delta E_{\text{hcp} \rightarrow \text{bcc}}$ (T=0) (eV/atom)	0.071	0.052
$\Delta E_{\text{hcp} \rightarrow \text{fcc}}$ (T=0) (eV/atom)	0.032	0.030
$T_{\text{hcp} \rightarrow \text{bcc}}$ (K)	1136	1233
$\Delta H_{\text{hcp} \rightarrow \text{bcc}}$ (eV/atom)	0.040	0.039
$\Delta V_{\text{hcp} \rightarrow \text{bcc}}$ (%)	-0.4	-0.8
T_m (K)	2128	2109
ΔH_m (eV/atom)	0.151	0.179
ΔV_m (%)	3.9	2.6

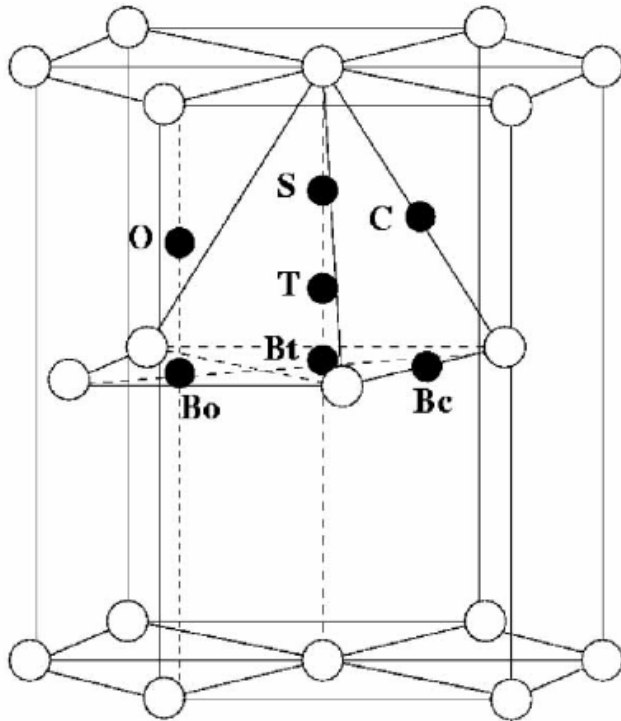
- The potential correctly describes the phase transformations in Zr.
- The potential correctly describes the liquid structure.

¹ M.I. Mendeleev and G.J. Ackland, Phil. Mag. Letters **87**, 349-359 (2007).

² M.I. Mendeleev and D.J. Srolovitz, Phys. Rev. B, **66**, 014205 (2002).

Point Defect Formation Energies at T=0

Schematics of the various interstitial configurations in hcp Zr¹:



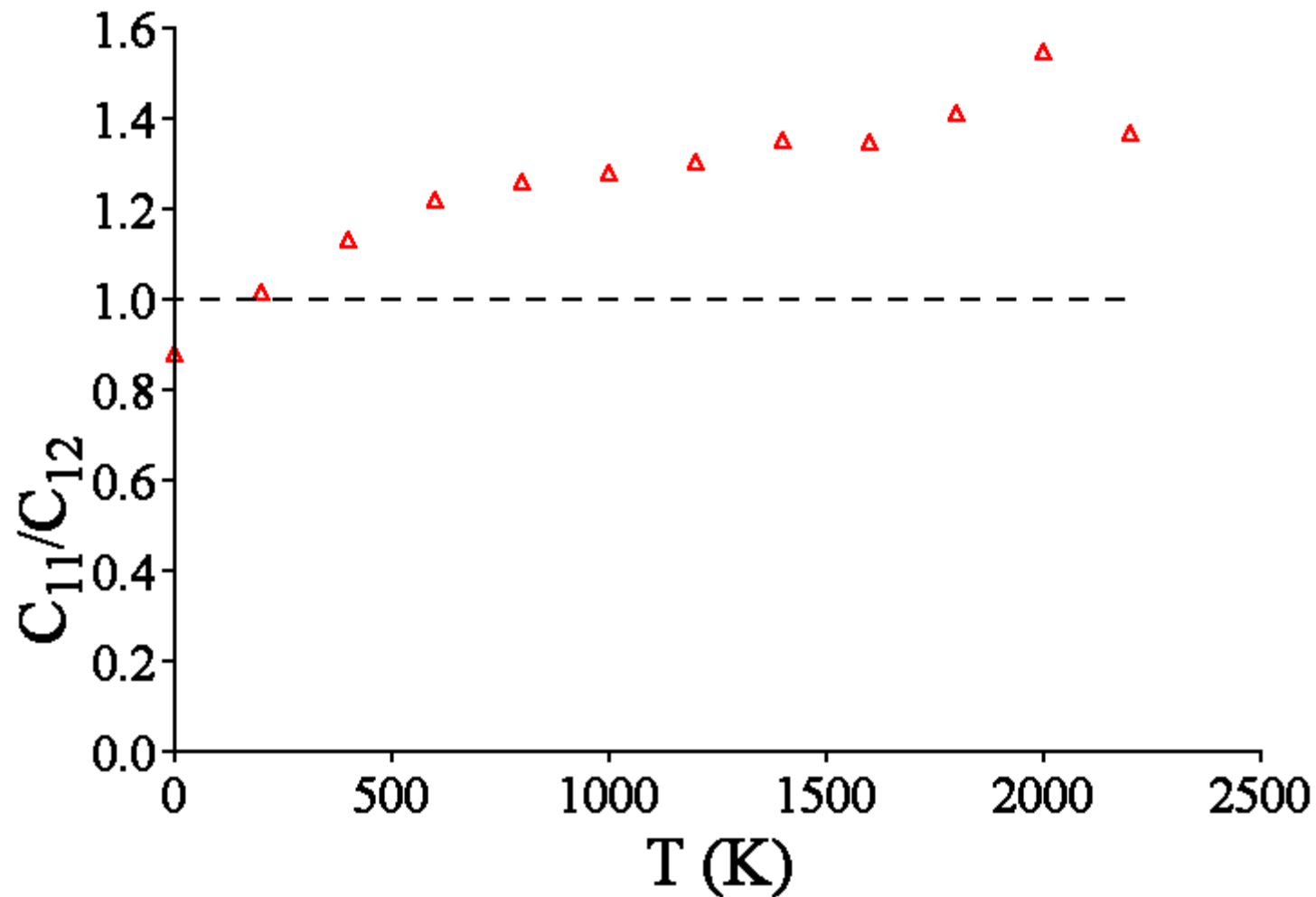
Point defects in hcp Zr:

Point defect	Target value ¹	EAM potential
vacancy	1.86	2.27
O	2.84	3.51
Bo	2.88	2.87
Bc	2.95	3.35
C	3.08	3.38
S	3.01	3.42
Bt	4.03	3.66

- The potential predicts reasonable point defect formation energies for hcp Zr.
- No data are available for point defect formation energies for bcc Zr.

¹ C. Domain and A. Legris, Phil. Mag. 85, 569-575 (2005).

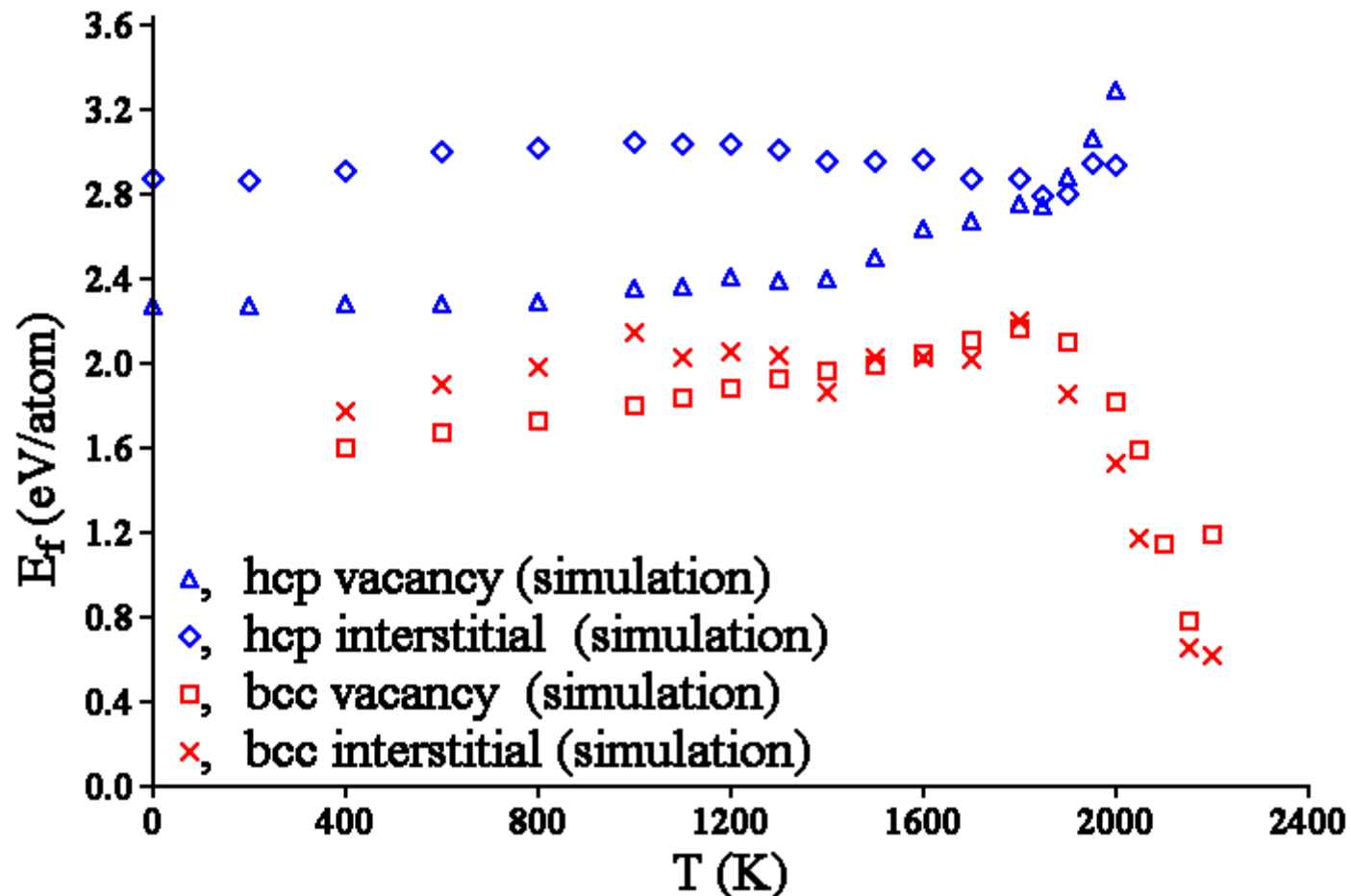
Stability of bcc Zr



- bcc Zr is mechanically unstable at $T=0$.
- bcc Zr is mechanically stable when $T > 200$ K.

Point Defect Formation Energy

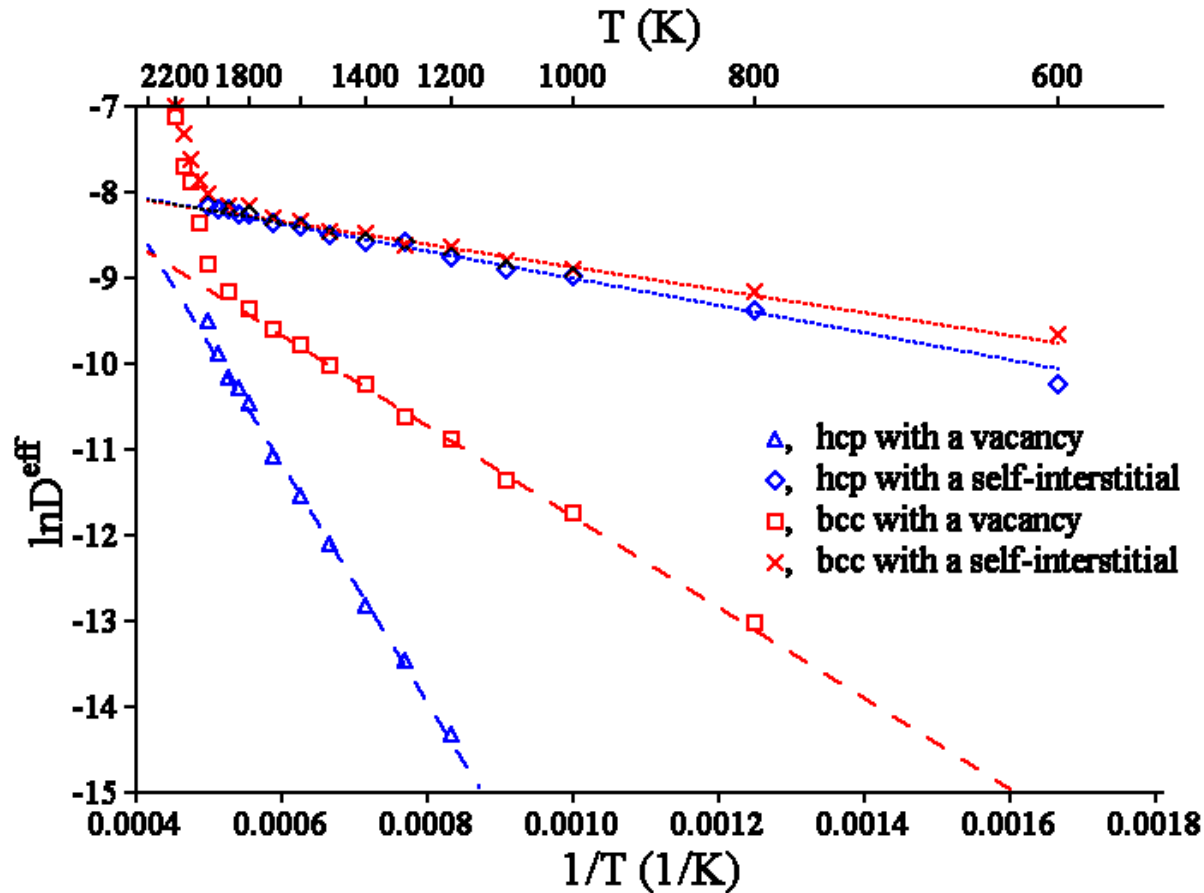
- ✓ Models contain ~2,000 atoms.
- ✓ All energies are averaged over 2,900,000 MD steps.



- Point defect formation energies depend on temperature.
- The data for bcc at high temperature have no physical sense.

Effective Diffusivity

- ✓ The same simulation as in previous slide.
- ✓ Effective diffusivity: $D^{\text{eff}} = D^{\text{sim}} / X^d$, where D^{sim} is determined from MSD.



- An Arrhenius dependence is observed at low temperatures.
- The interstitial migration energy is much smaller than the vacancy migration energy.
- The data for bcc at high temperature have no physical sense.

Activation Energy for Diffusion

Phase	Defect	E_f (eV/atom) at T=1200 K	E_m (eV/atom)	$E_f + E_m$ (eV/atom)	E_D (experiment) (eV/atom)
hcp	vacancy	2.41	1.20	3.61	3.17 ¹
	interstitial	3.04	0.14	3.18	
bcc	vacancy	1.88	0.46	2.34	2.04 ²
	interstitial	2.05	0.11	2.16	

- **The simulation data are in excellent agreement with experiment.**
- **The activation energy for diffusion in both hcp and bcc Zr is smaller in the interstitial mechanism.**

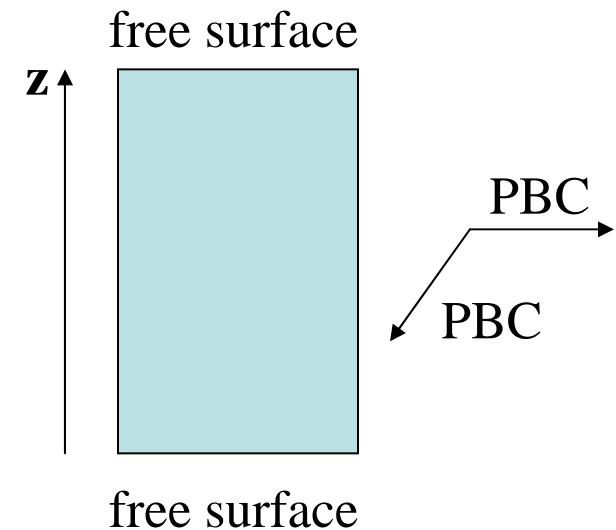
¹G.M. Hood, et. al., Defect and Diffusion Forum 143-147, 49-54 (1997).

²T.S. Lundy, et. al., in Diffusion in body-centered cubic metals (Metals Park, American Society for Metals 1965).

Equilibrium Point Defect Concentration

- ❑ The equilibrium point defect concentration can be determined from MD simulation with free surfaces.
- ❑ If model has periodic boundary conditions (PBC) in all directions, then only vacancy – interstitial pairs can form. Their concentration is related to the equilibrium vacancy and interstitial concentration as follows:

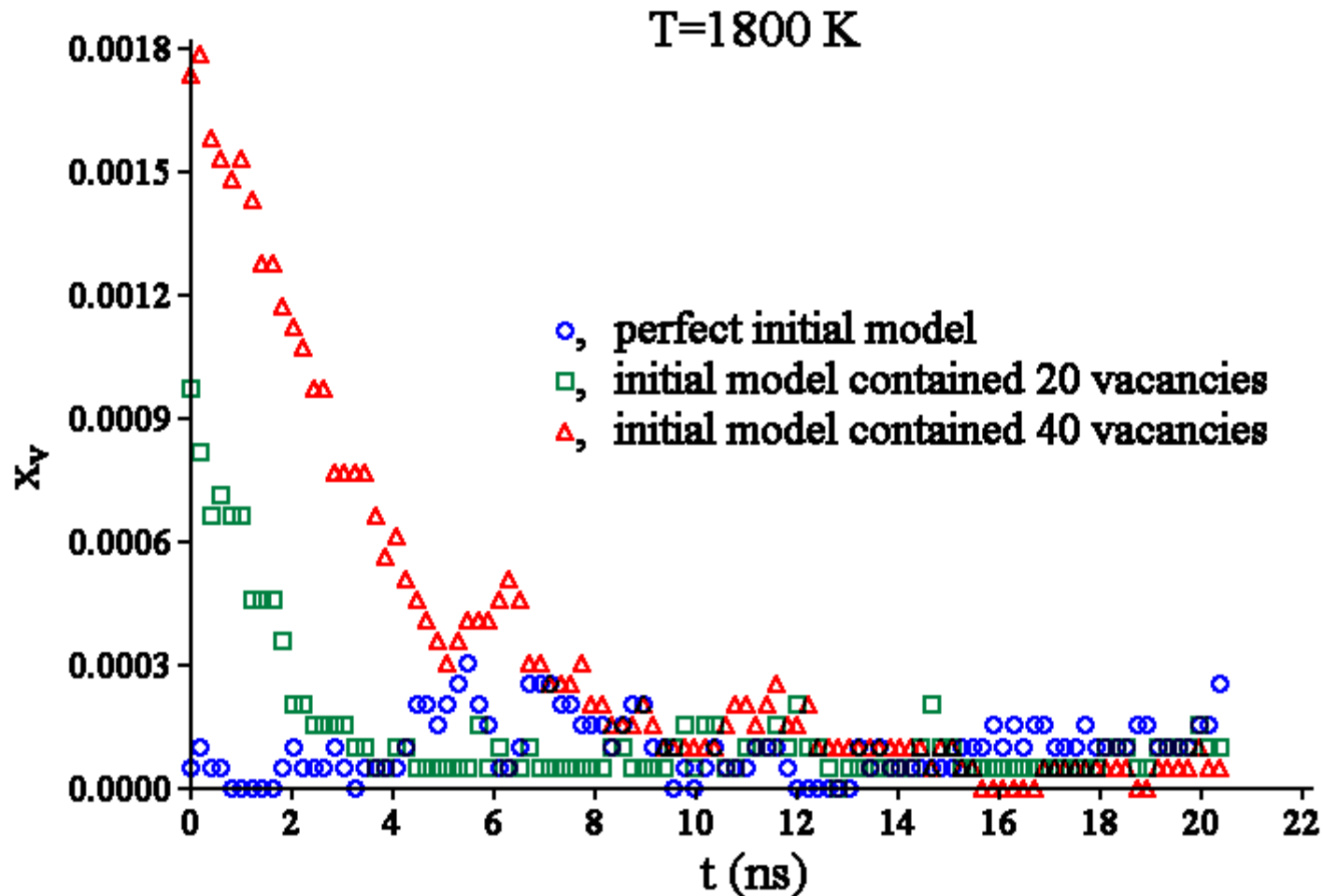
$$x_e^p = \sqrt{x_e^v x_e^i}$$



- ❑ In order to obtain the equilibrium point defect concentration large models (at least 20,000 atoms) should be used and MD should be run long enough for point defect to diffuse into bulk.

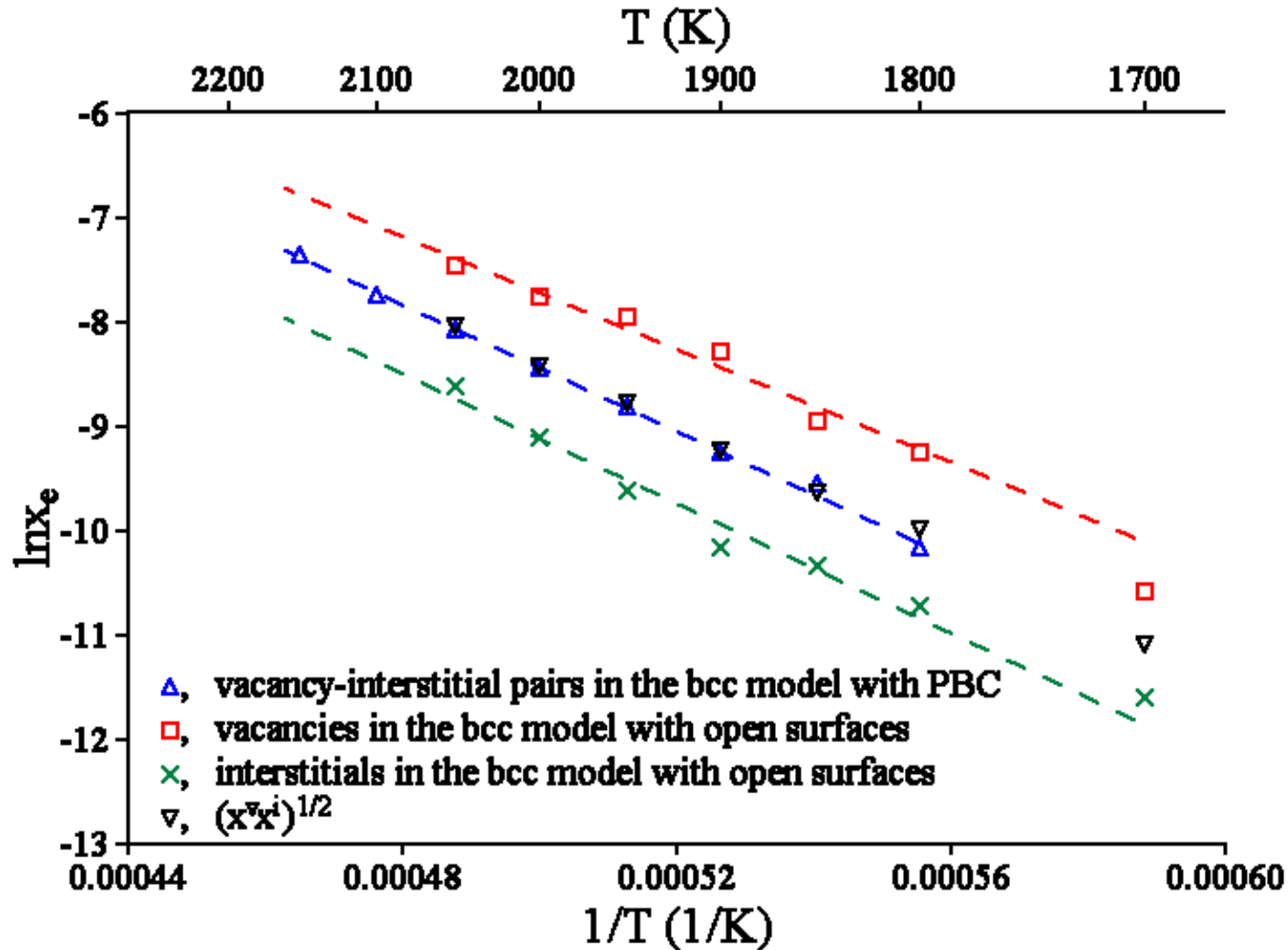
Vacancy Concentration in bcc Zr

Simulation scheme with free surfaces:



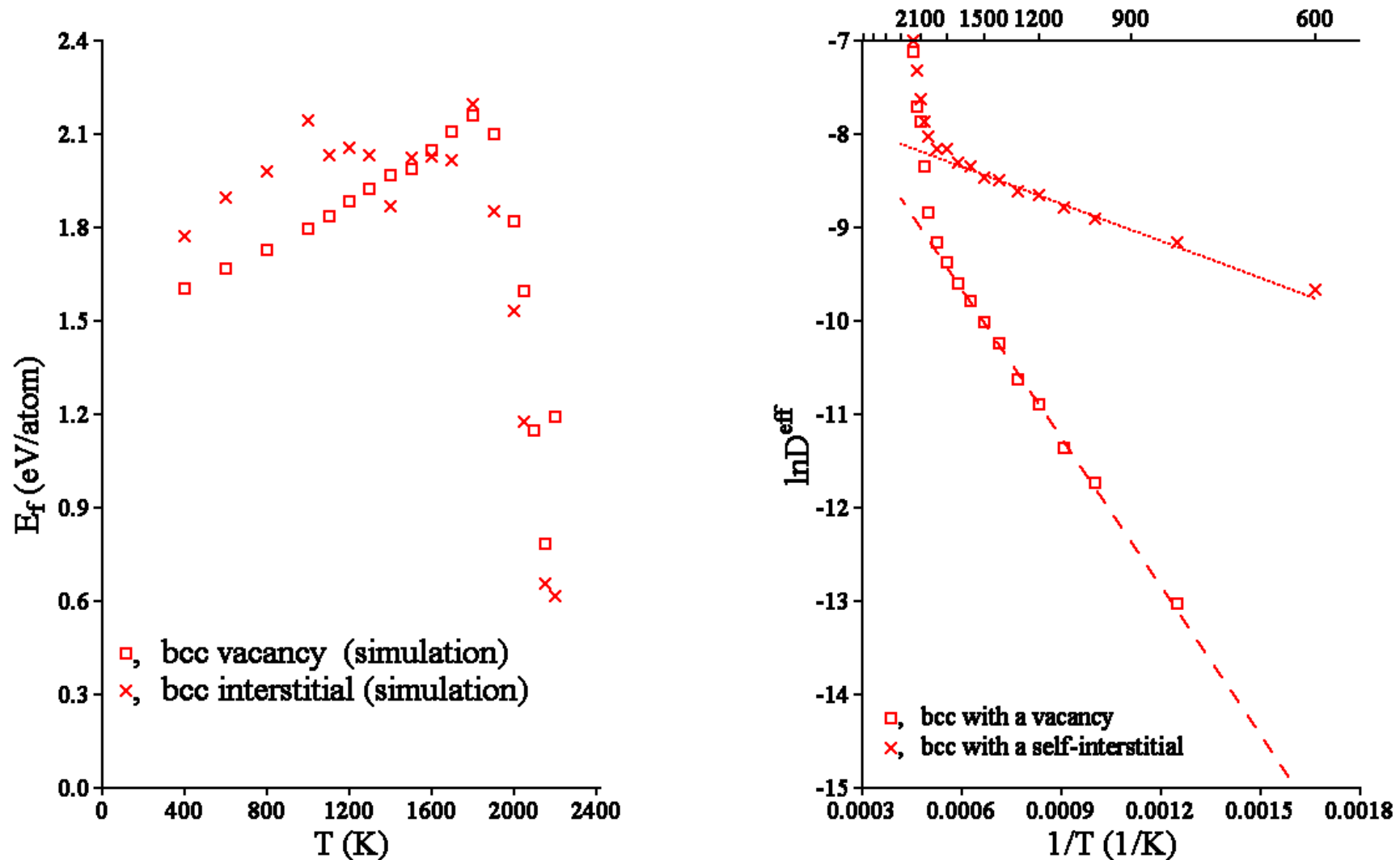
➤ The simulation time is sufficient to reach the equilibrium.

Point Defect Concentration in bcc Zr



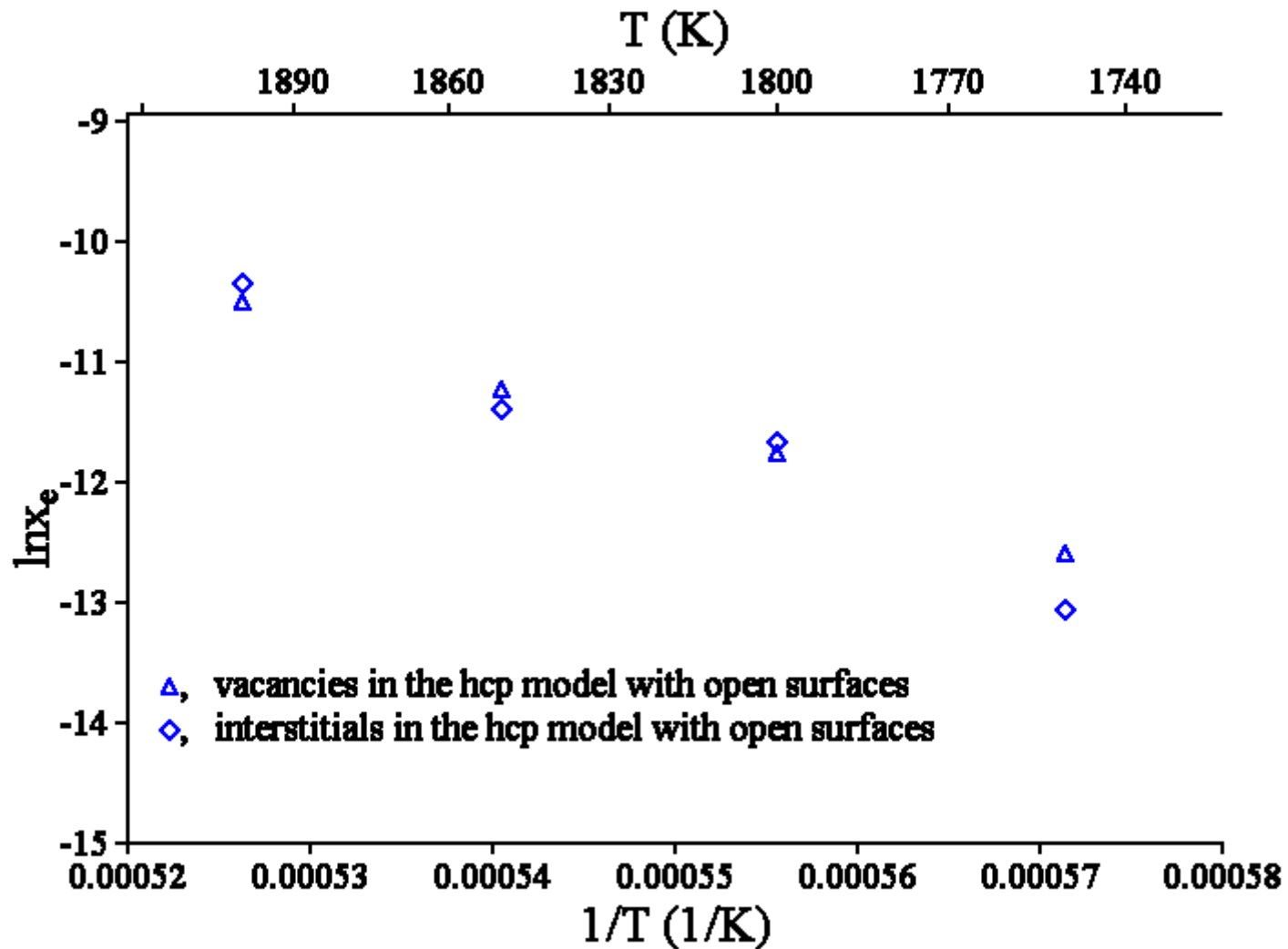
- The good agreement between the data of simulations with free surfaces and PBC in all directions proves that the simulation time was sufficient to reach the equilibrium.
- The equilibrium vacancy concentration is larger than the equilibrium interstitial concentration.

High Temperature Simulation Data



- Formation of the vacancy – interstitial pairs explains the weird high temperature MD data.

Point Defect Concentration in hcp Zr



- The equilibrium vacancy and interstitial concentrations in hcp Zr are almost the same.

Point Defect Concentration at Low Temperatures

- MD simulation provides reliable data on the point defect formation energy at low temperatures.
- MD simulation provides reliable data on the point defect concentration at high temperatures.

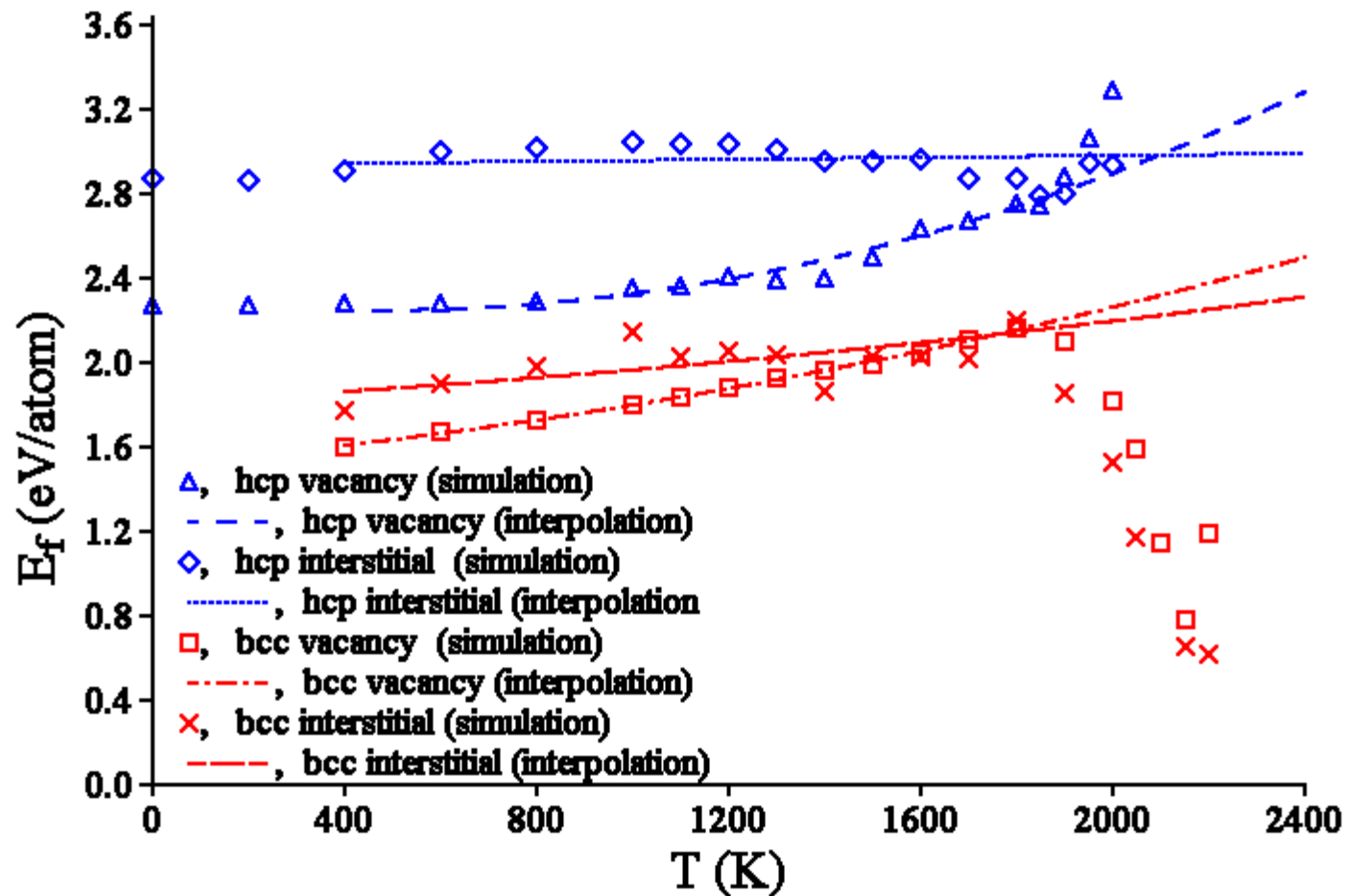
Interpolation formulas:

$$G_f = -kT \ln x_e$$
$$G_f = g_1 + g_2 T + g_3 T \ln T + g_4 T^2$$
$$E_f = g_1 - g_3 T - g_4 T^2$$
$$S_f = -g_2 - g_3 - g_3 \ln T - 2g_4 T$$

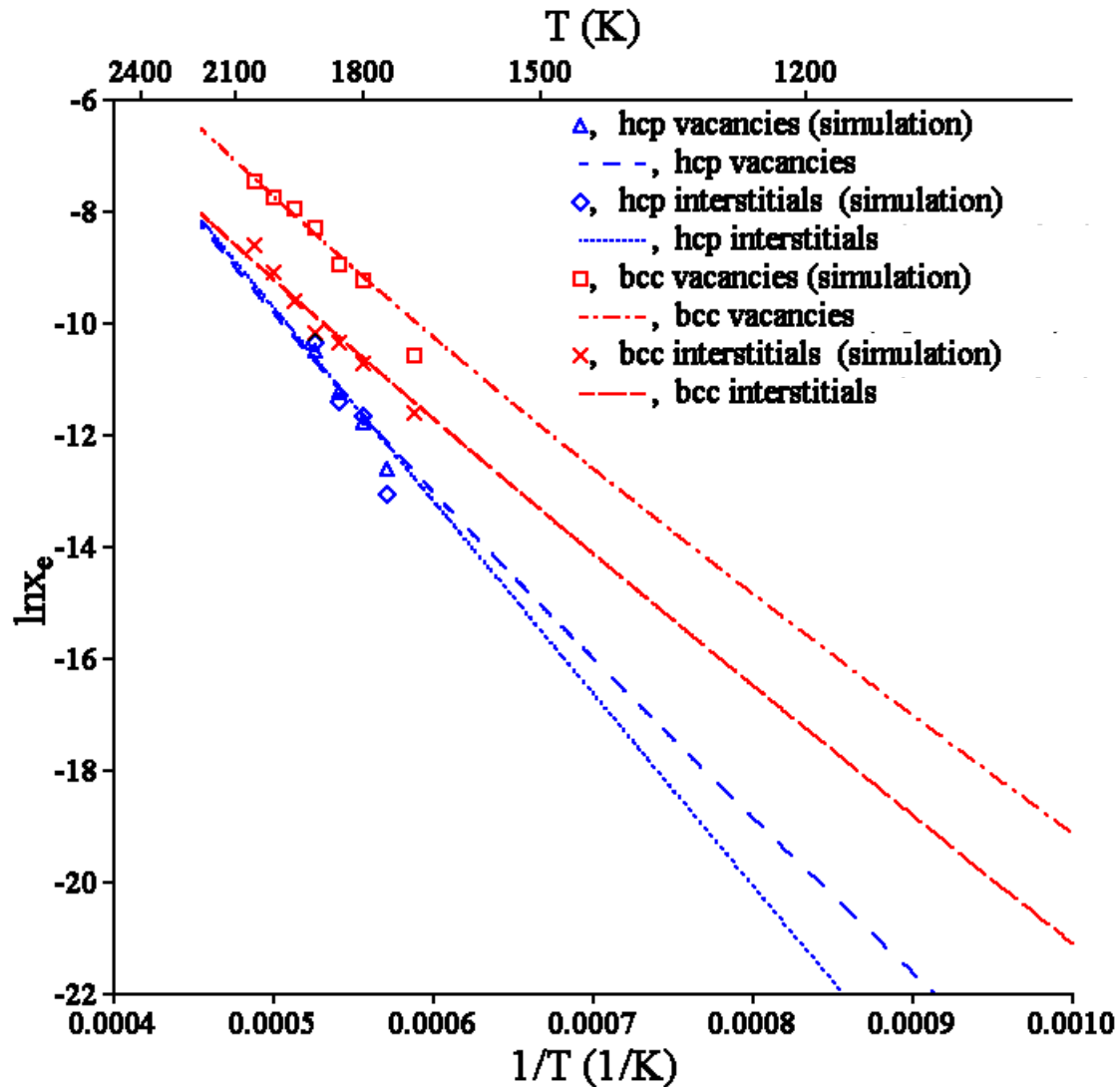
The diffusivity can be calculated via

$$D = x_e D_{\text{eff}}$$

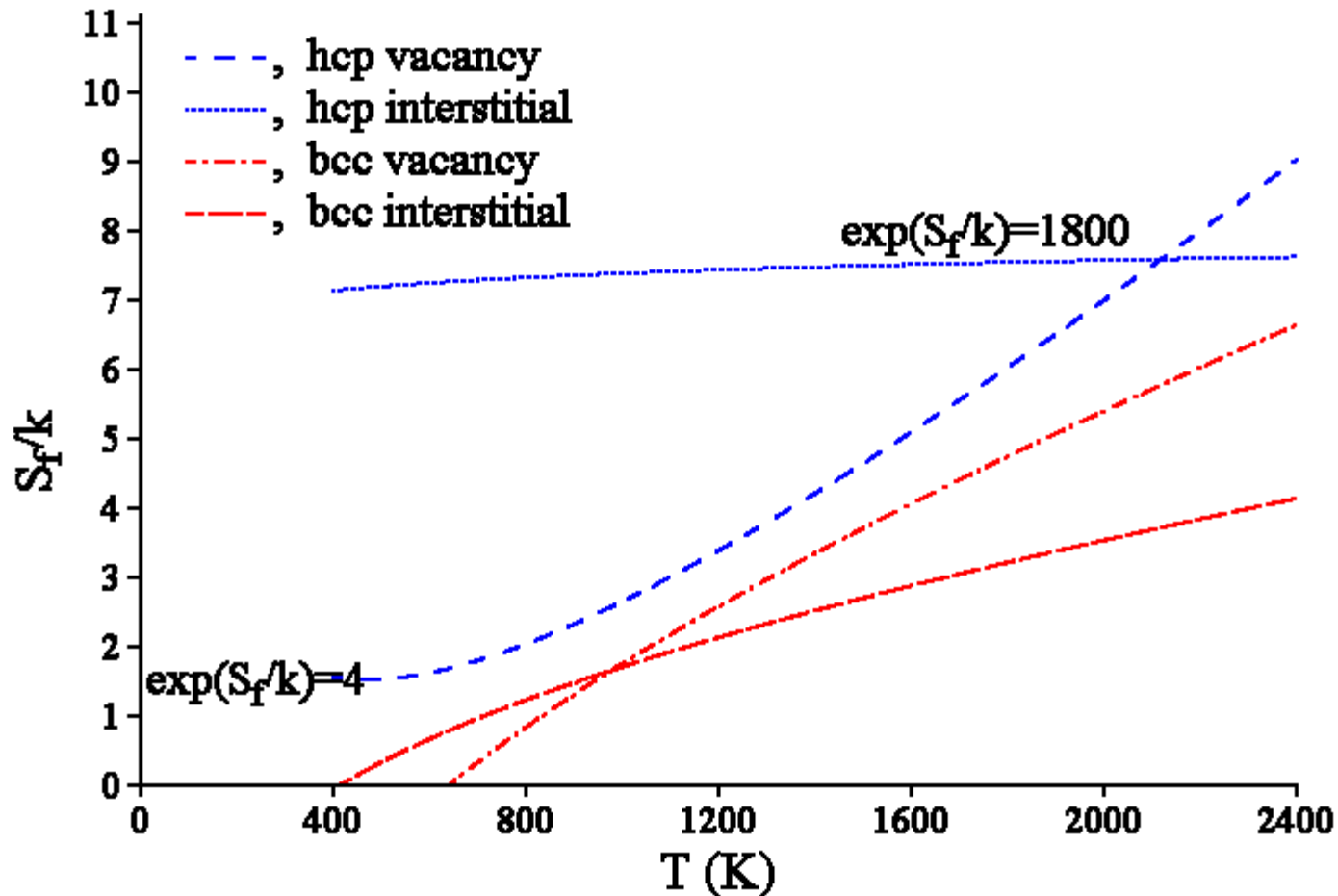
Point Defect Formation Energy



Point Defect Concentrations

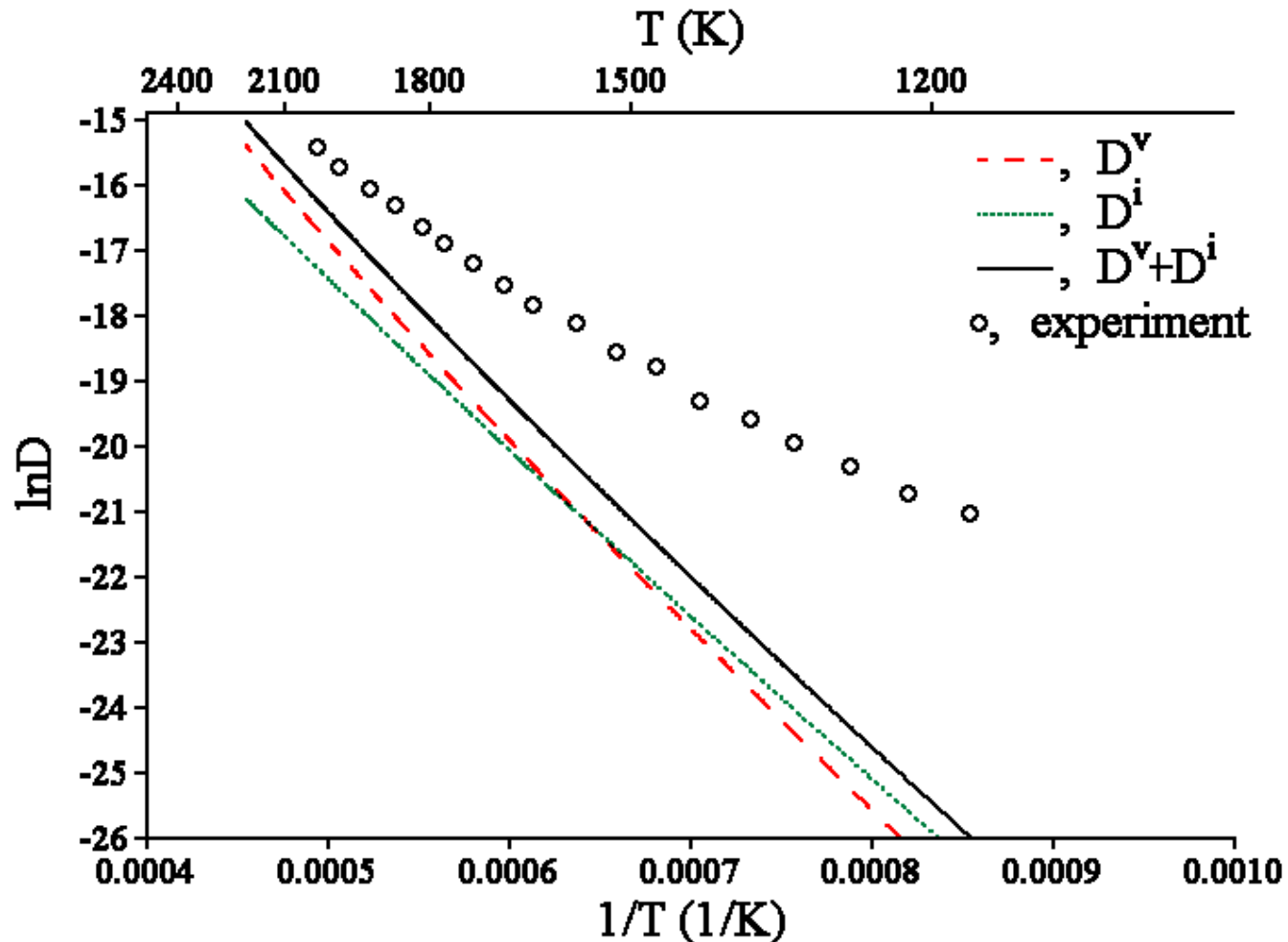


Point Defect Formation Entropy



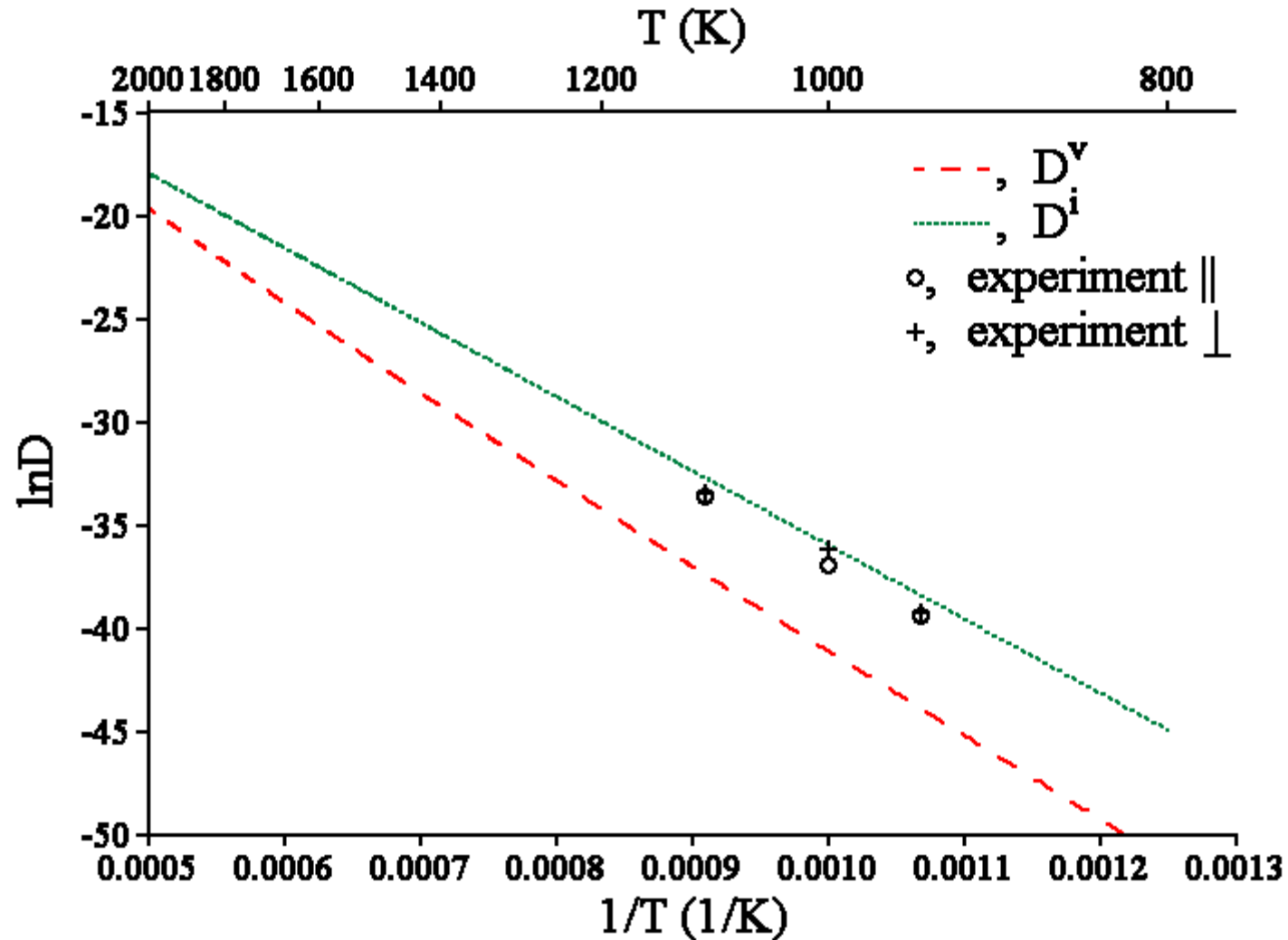
- The interstitial formation entropy is much larger than the vacancy formation entropy in hcp Zr.
- The interstitial and vacancy formation entropies are about the same in bcc Zr.
- The point defect formation entropy can dramatically modify the diffusivity.

Self-Diffusion in bcc Zr



- The simulation provides reasonable agreement with experiment only at high temperatures.
- Both vacancy and interstitial mechanism contribute to self-diffusion.

Self-Diffusion in hcp Zr



- The simulation provides excellent agreement with experiment.
- Self-diffusion proceeds via the interstitial mechanism.

Summary

- The point defect properties and diffusivity are obtained from MD simulation without use of harmonic approximation.
- Point defect formation energy and entropy depend on temperature.
- The simulation data can be summarized as follows:

Phase	Formation energy	Formation entropy	Point defect concentration	Migration energy	Diffusion mechanism
hcp	$E_f^v < E_f^i$	$S_f^v < S_f^i$	$x_f^v \approx x_f^i$	$E_m^v > E_m^i$	interstitial
bcc	$E_f^v \leq E_f^i$	$S_f^v \approx S_f^i$	$x_f^v > x_f^i$	$E_m^v > E_m^i$	interstitial & vacancy