



서울대학교
SEOUL NATIONAL UNIVERSITY

Application of machine learning potential to quantum diffusion of hydrogen isotopes in bcc metal: Machine Learning Path Integral Molecular Dynamics

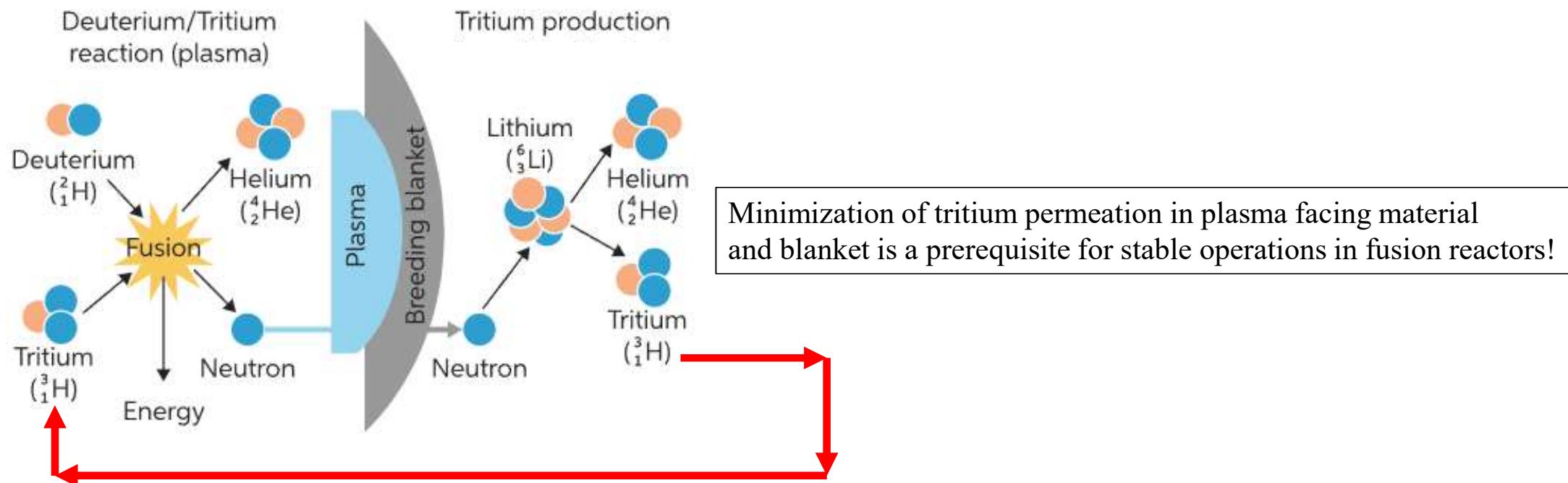
2022 Japan-Korea Tritium Workshop
Hyukjoon Kwon, Takuji Oda*

Contents

1. Introduction
2. Equation of Motion: path integral formalism
3. Force field: moment tensor potential
4. Simulation Conditions
5. Results
6. Conclusion
7. Acknowledgments
8. References

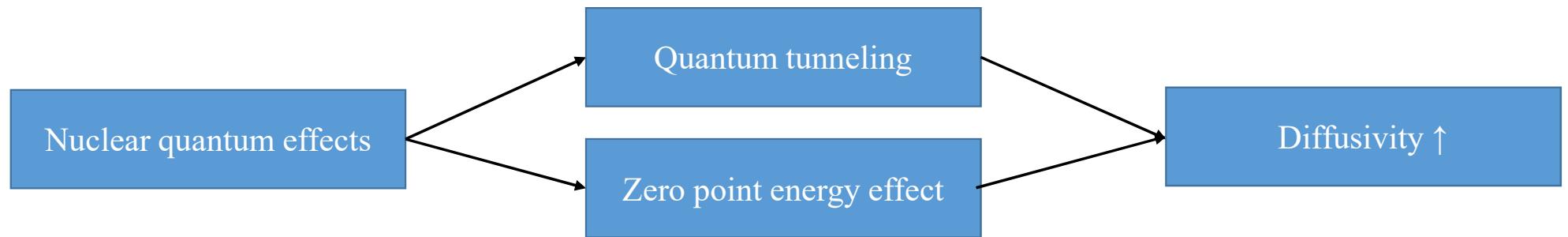
1. Introduction

- Hydrogen isotopes can enter and diffuse through metals even at room temperature.



1. Introduction

- Computational approach on hydrogen transport requires special treatment.
- This is because the nuclear quantum effects of hydrogen are sometimes not negligible even at room temperature.



∴ Our goal is to computationally estimate hydrogen and tritium diffusivity in bcc metals (Fe, W) and reveal isotopes effects.

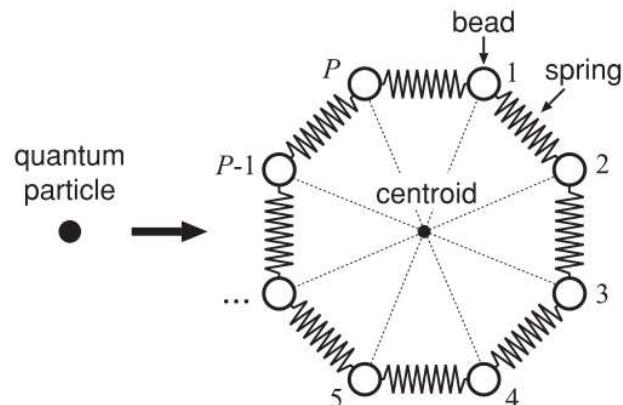
2. Equation of motion: Path Integral Formalism

➤ In classical mechanics,

$$\mathcal{H}_{classcial}(\mathbf{q}, \mathbf{p}) = \sum \left(\frac{\mathbf{p}^2}{2m_I} \right) + U(\mathbf{q}) \quad \longrightarrow \quad Z_{classical} = \int d\mathbf{q}d\mathbf{p} \exp[-\beta \mathcal{H}_{classcial}]$$

Kinetic E Potential E

➤ In path integral (PI) formalism,

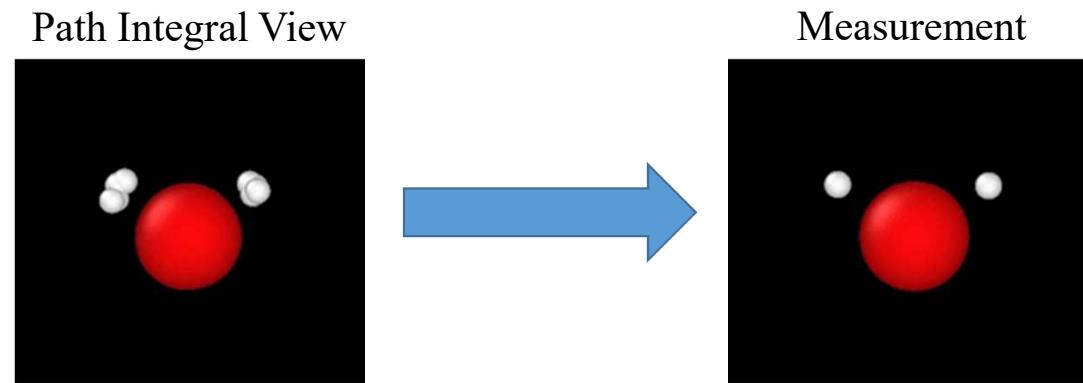


$$\mathcal{H}_{classical} + U_{spring} \rightarrow \mathcal{H}_{PI} \rightarrow Z_{PI}$$

$$\therefore (\# \text{ of beads}) \rightarrow \infty, Z_{PI} = Z_{quantum}$$

2. Equation of motion: Path Integral Molecular Dynamics (PIMD)

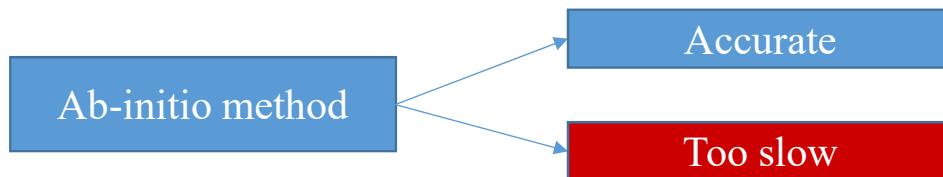
➤ Example: water molecule (H_2O) with 4 beads



∴ By describing hydrogen with PIMD, its nuclear quantum effects can be reproduced !

3. Force Field: Moment Tensor Potential (MTP)

- ① PI formalism requires much more computational resources.
 - ✓ This is because sufficient number of beads are required to accurately describe nuclear quantum effects.
 - ✓ Thus, it is inevitable to give up Ab-initio quantum chemistry method to produce accurate force fields.



- ② Moment tensor potential (MTP) can be a prominent potential for path integral MD.
 - ✓ MTP is a machine learning interatomic potential.
 - ✓ MTP mimics a target force field with a set of polynomials.
 - Radial part: Chebyshev radial polynomials
 - Angular part: Tensor products of position vectors.
- ∴ With MTP, PIMD simulations become fast and accurate.

3. Force Field: Moment Tensor Potential (MTP)

- MTPs for H in bcc Fe and bcc W systems were generated from active learning.
 - ✓ The target reference force field was from density functional theory (DFT).

Comparison of MTP, DFT and experiments (**bcc Fe**)

	bcc Fe (DFT error)	Experiments
Lattice constant	2.832 Å (-0.005 %)	2.860 Å (293 K)
Elastic constant (C11)	258 GPa (-7.2 %)	240 GPa
Elastic constant (C12)	142 GPa (-4.2 %)	136 GPa
Elastic constant (C44)	96 GPa (-2.5 %)	131 GPa

Lattice constant: Basinski, Z. S. Series A, Mathematical and Physical Sciences, Volume 229, Issue 1179, pp. 459-467 (1955)
 Elastic constants: J. Appl. Phys. 100, 113530 (2006)

3. Force Field: Moment Tensor Potential (MTP)

- MTPs for H in bcc Fe and bcc W systems were generated from active learning.
 - ✓ The target reference force field was from density functional theory (DFT).

Comparison of MTP, DFT and experiments (**bcc Fe**)

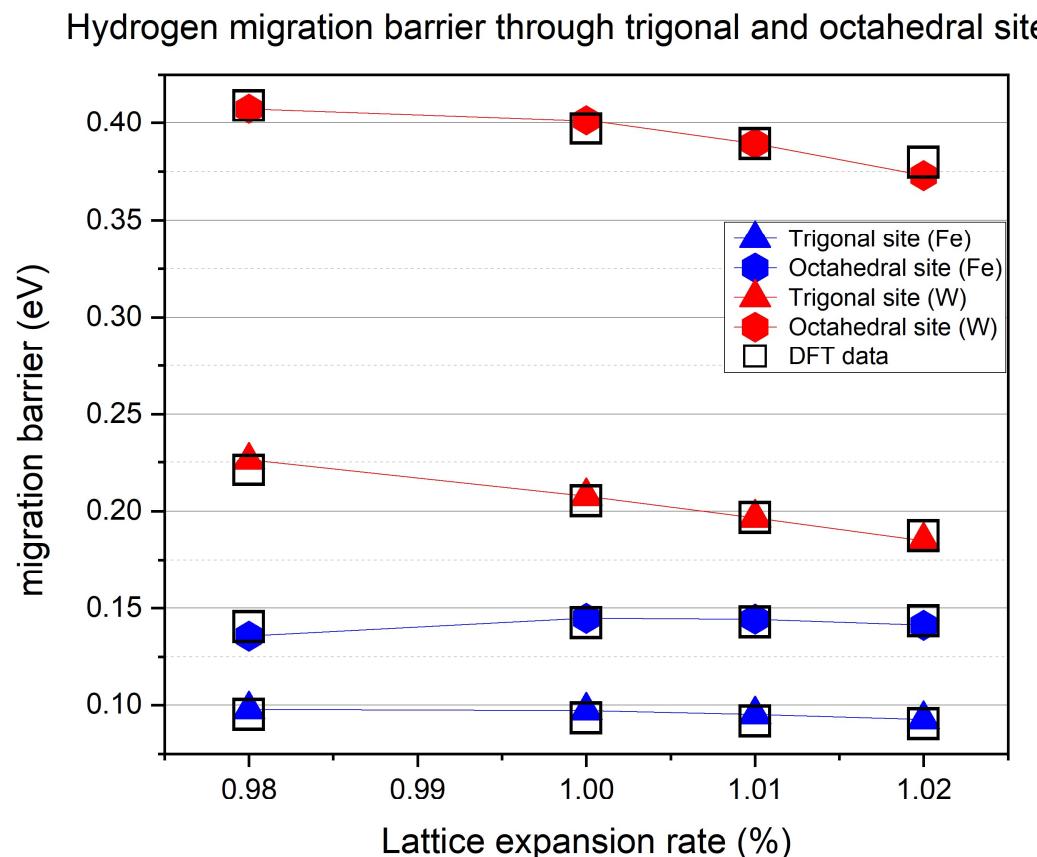
	bcc W (DFT error)	Experiments
Lattice constant	3.172 Å (+0.02 %)	3.165 Å (298 K)
Elastic constant (C11)	533 GPa (-1.8 %)	533 GPa
Elastic constant (C12)	203 GPa (-2.3 %)	205 GPa
Elastic constant (C44)	140 GPa (-2.1 %)	163 GPa

Lattice constant: phys. stat. sol. 8, 2253 (1963)

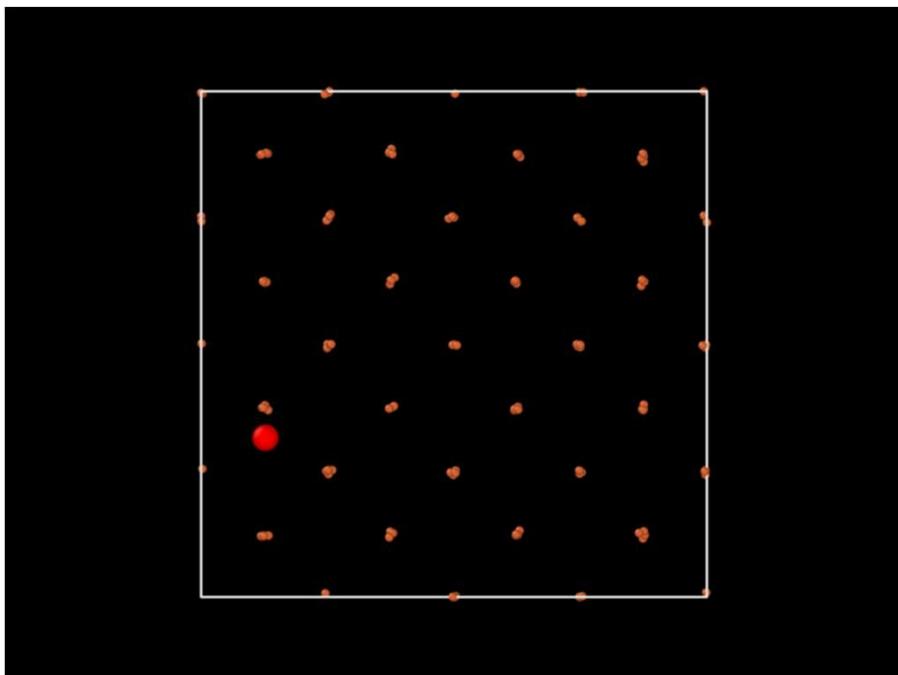
Elastic constants: : F. H. Featherston and J. R. Neighbours, Phys. Rev. 130, 1324 (1963)

3. Force Field: Moment Tensor Potential (MTP)

- MTPs for H in bcc Fe and bcc W systems were generated from active learning.
 - ✓ The target reference force field was from density functional theory (DFT).



4. Simulation Conditions



Centroid visualization in 001 direction

Simulation Conditions

One hydrogen in $4 \times 4 \times 4$ bcc periodic cells

Canonical ensemble

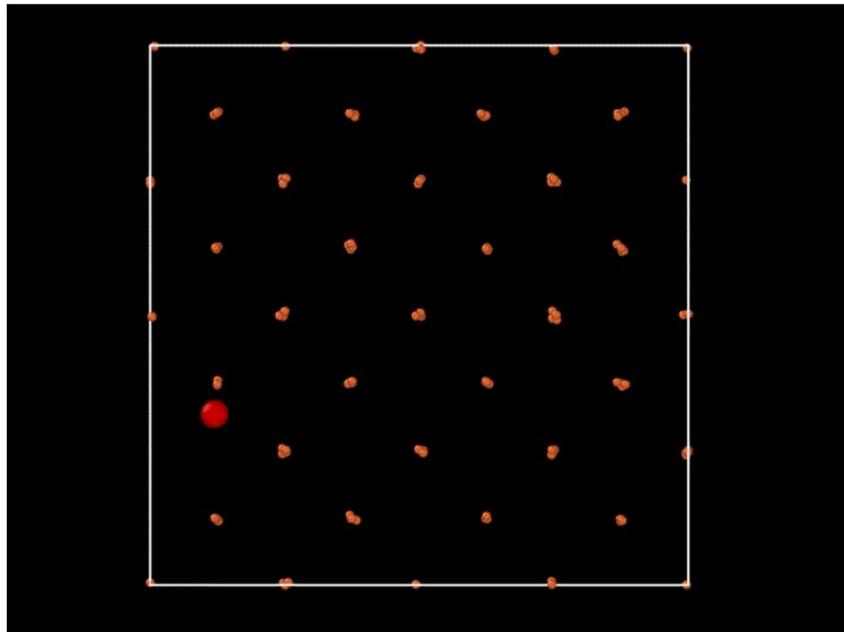
30 ns of production time

Ring-polymer molecular dynamics (RPMD)

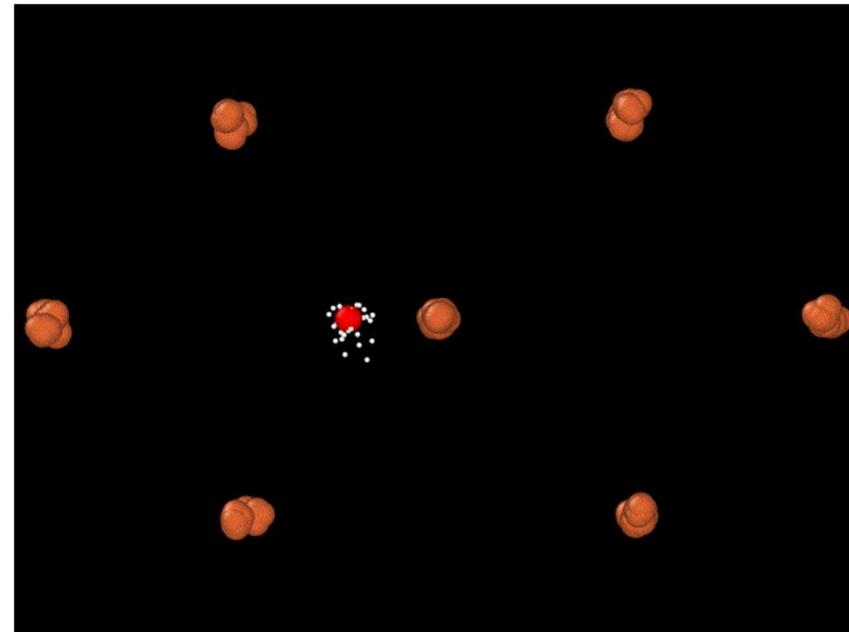
4. Simulation Conditions

Animation of H diffusion in bcc Fe at 200 K

12



classical molecular dynamics (classical MD)



Ring-polymer molecular dynamics (RPMD)

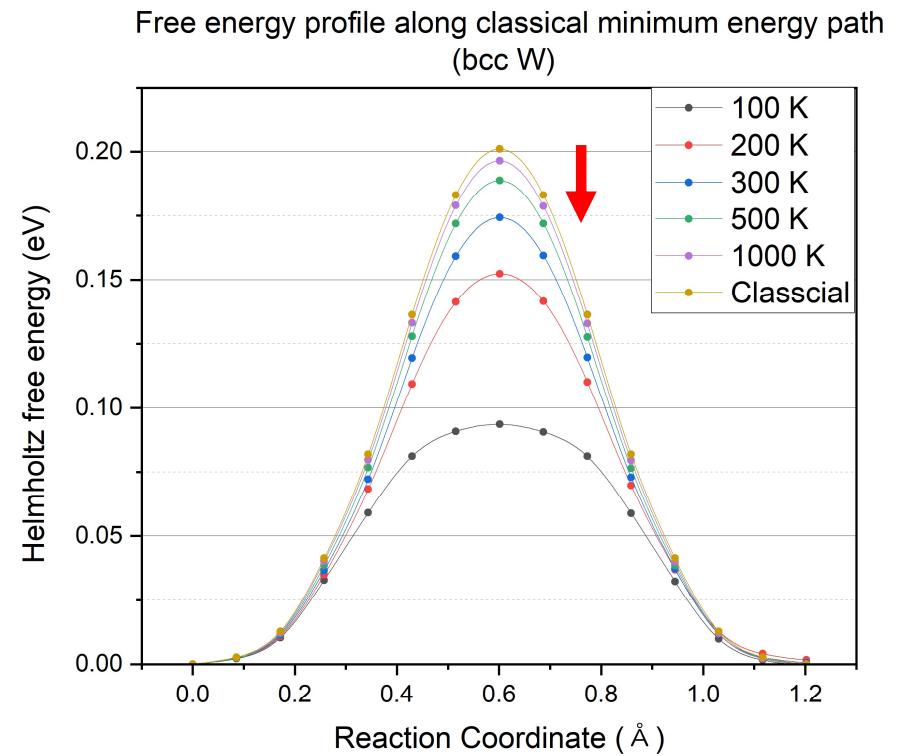
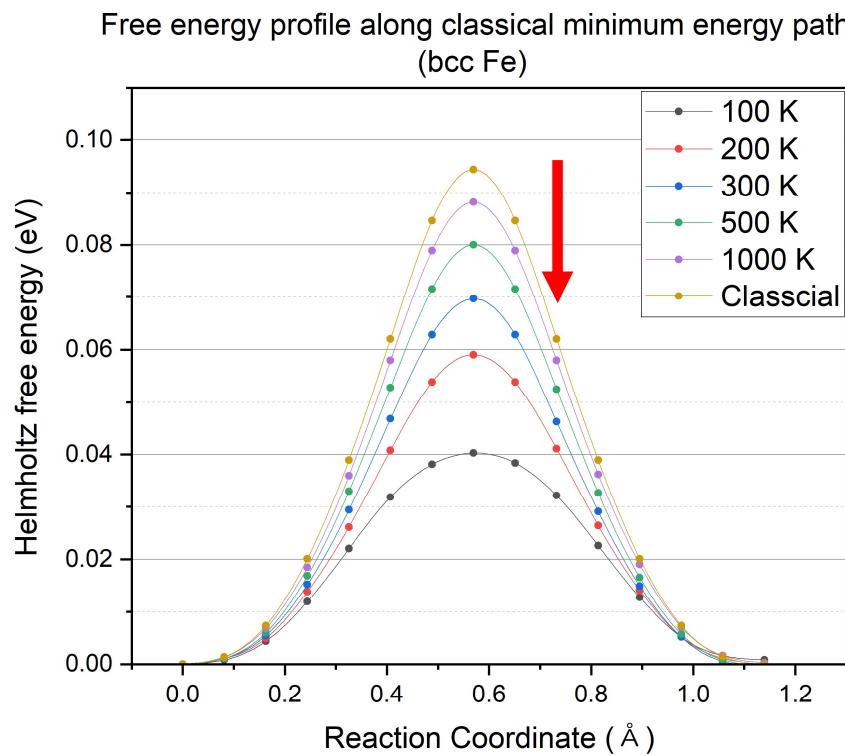
red sphere: centroid of beads

white spheres: imaginary beads

5. Results

5.1. Free energy profiles of classical MEP

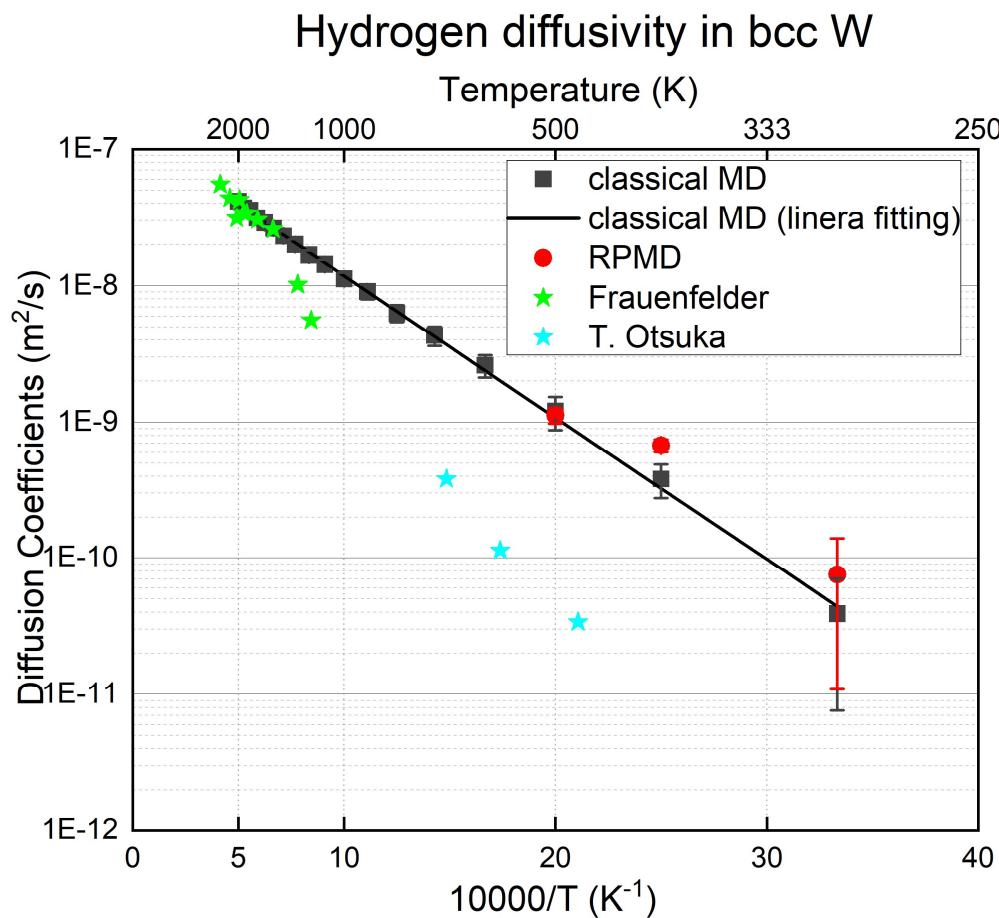
Due to tunneling and zero-point effect (ZPE), **effective** free energy barriers are lowered.



5. Results

5.2. Hydrogen diffusivity in bcc W

14

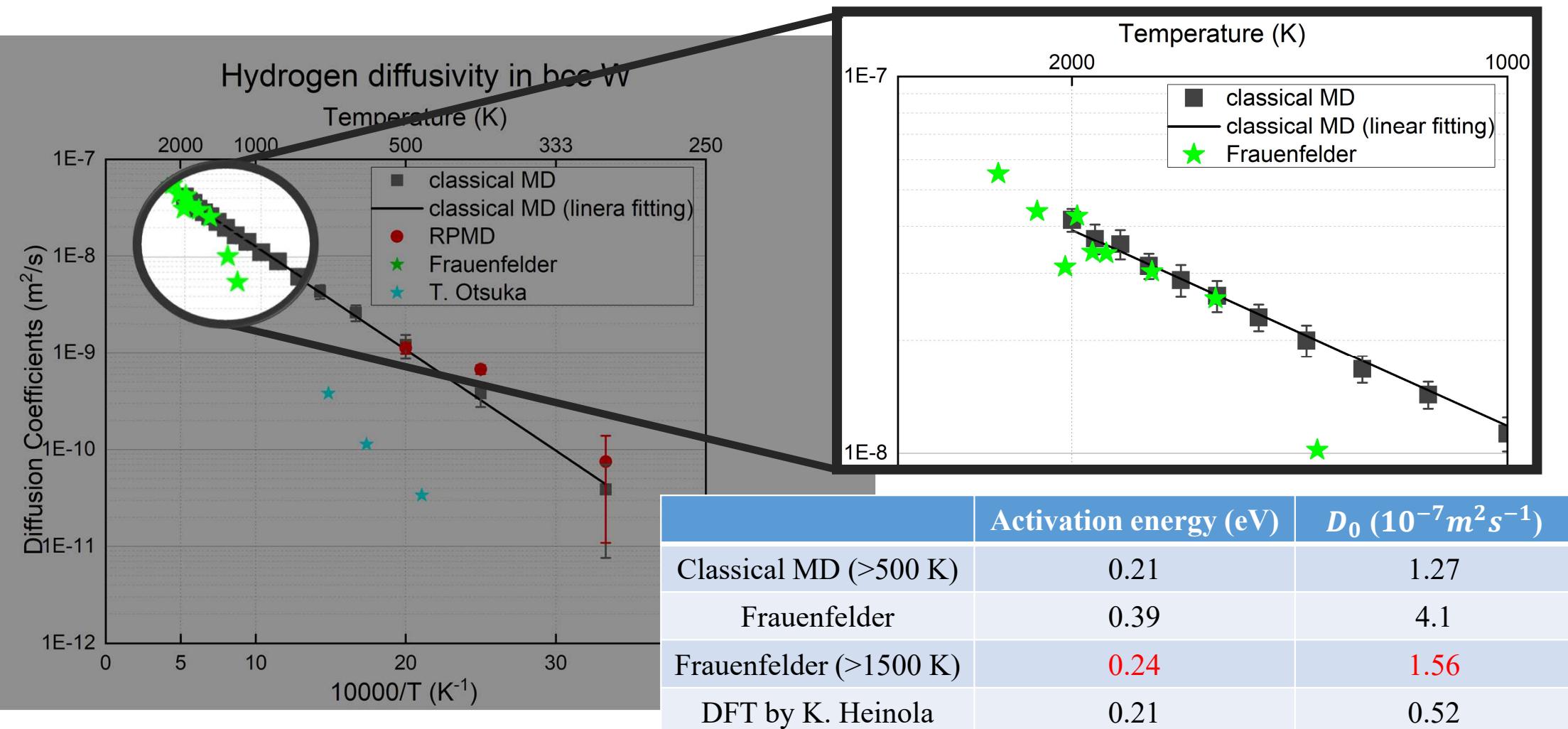


Notes

- Under 1500 K, experimental data seems unreliable because hydrogen diffusion is strongly limited by trapping mechanisms.
 - Nuclear quantum effects could start to be visible below 400 K, although the magnitude is not large even at 300 K
- ∴ Tritium diffusivities at room temperature are expected to be classical at room temperature.

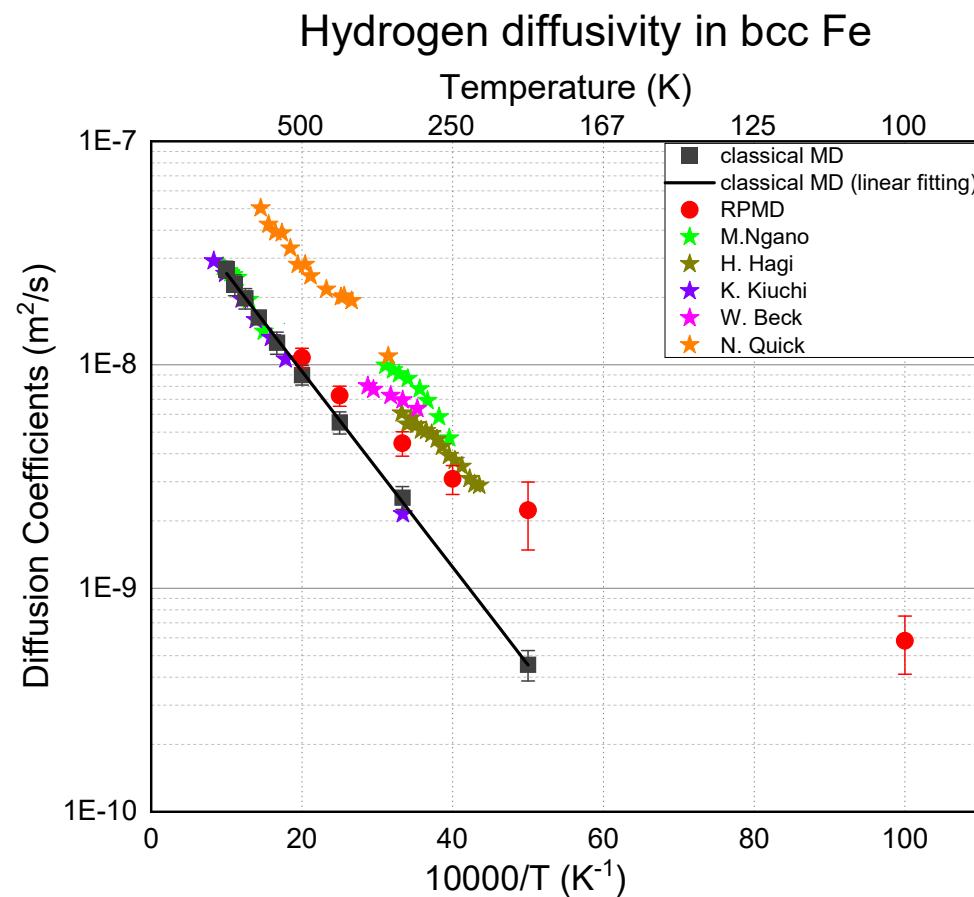
5. Results

5.2. Hydrogen diffusivity in bcc W



5. Results

5.3. Hydrogen diffusivity in bcc Fe

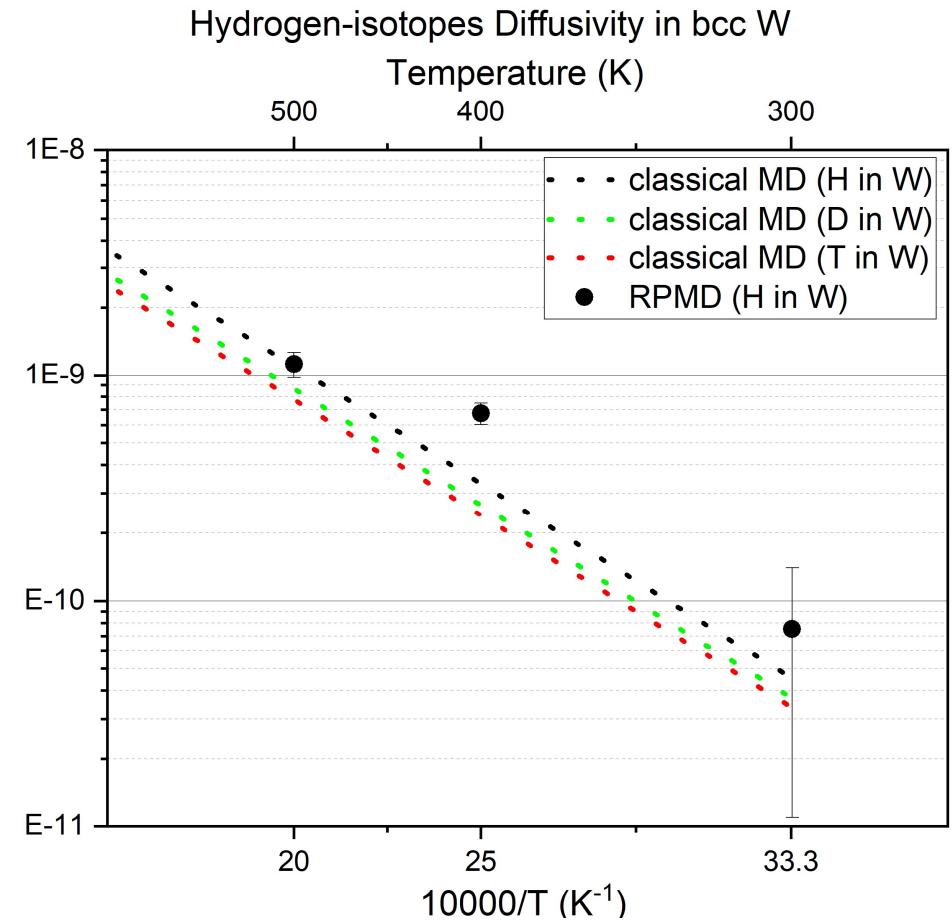
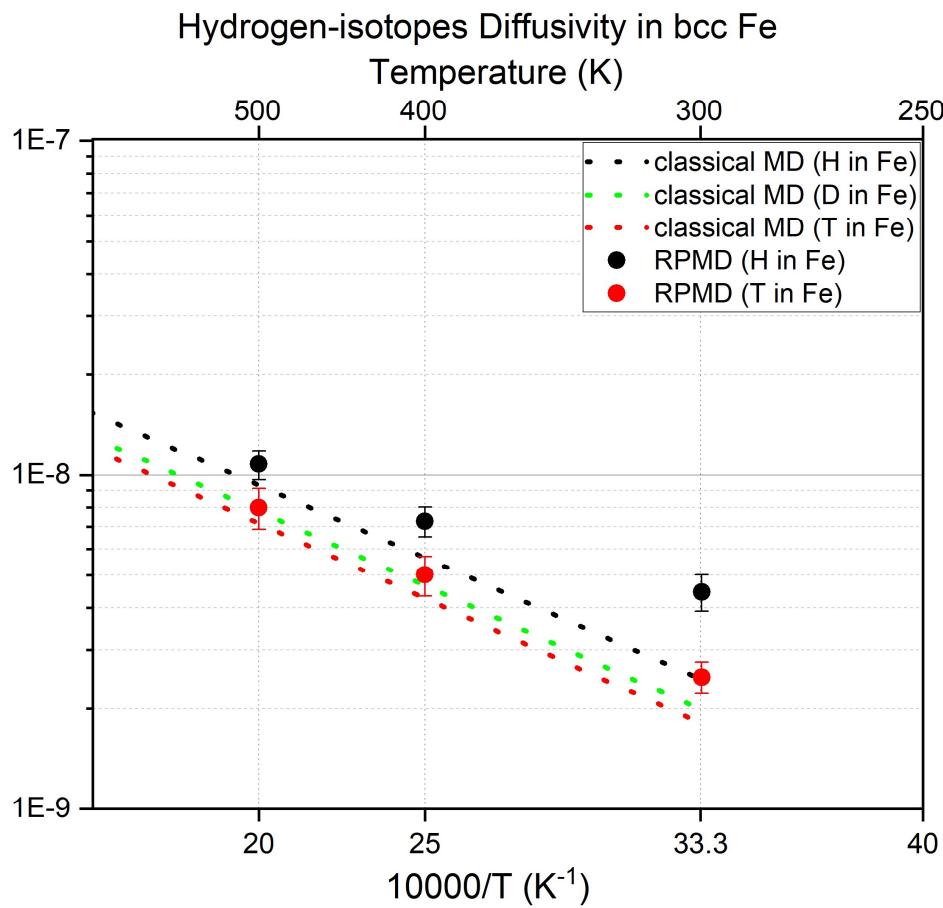


Notes

- Experiment data is widely scattered due to surface and trapping effects.
- Our MTP has good agreement with most of experiments at high temperature.

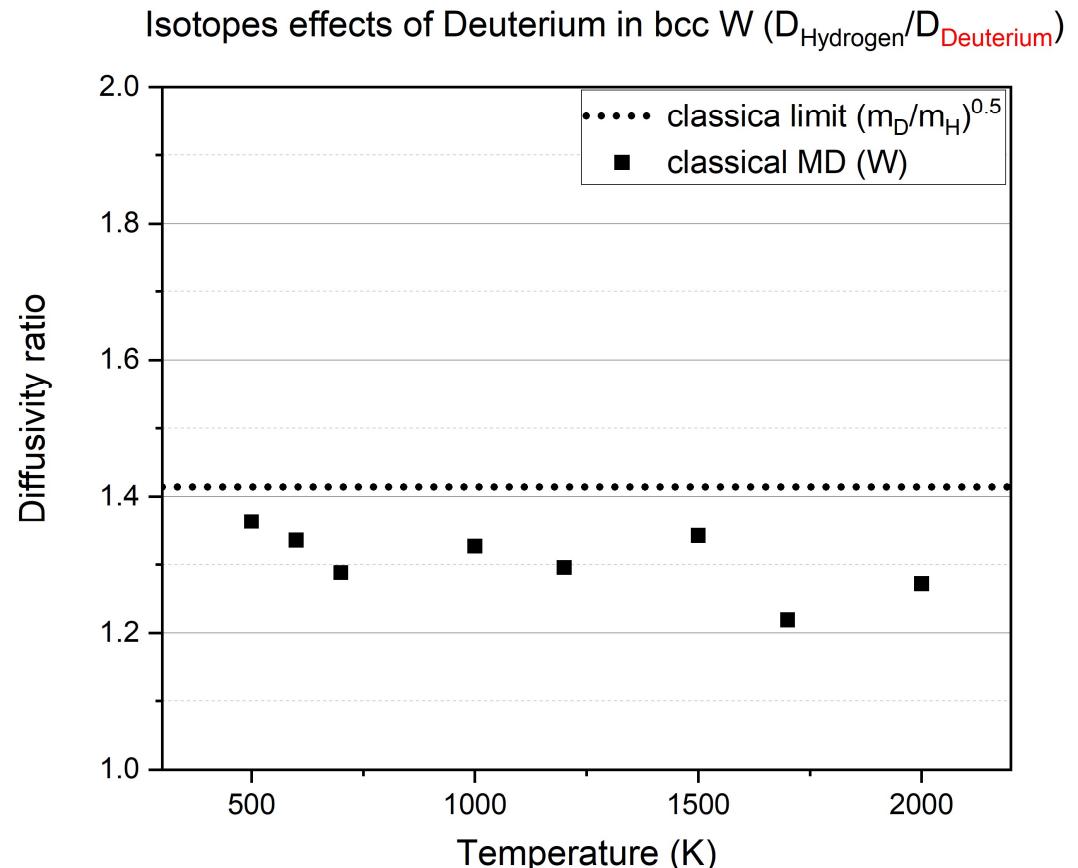
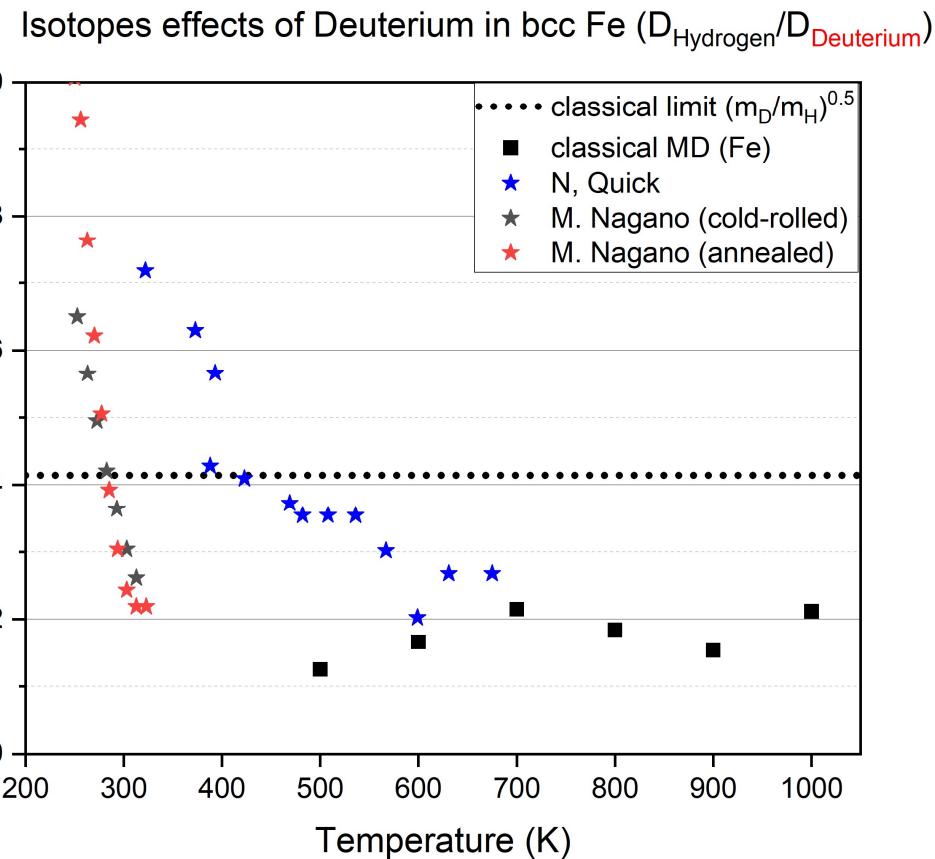
5. Results

5.4. Arrhenius plots of H-isotopes



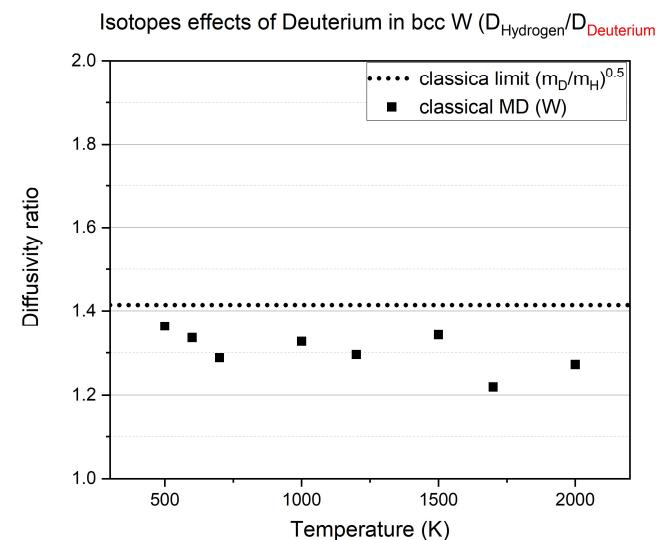
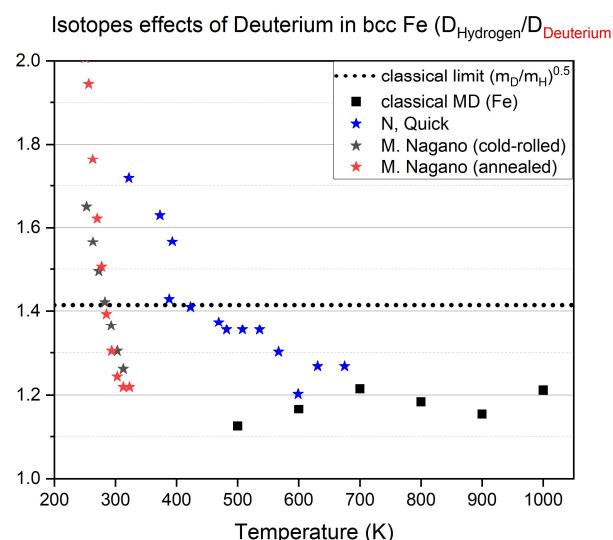
5. Results

5.5. Isotopes effects (Deuterium)



5. Results

5.5. Isotopes effects (Deuterium)



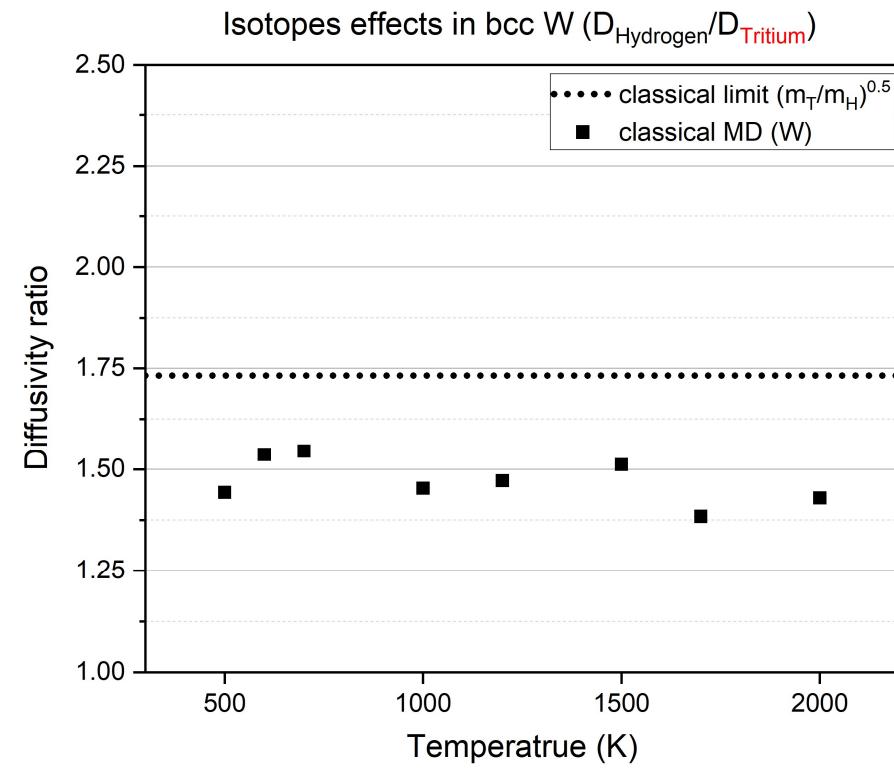
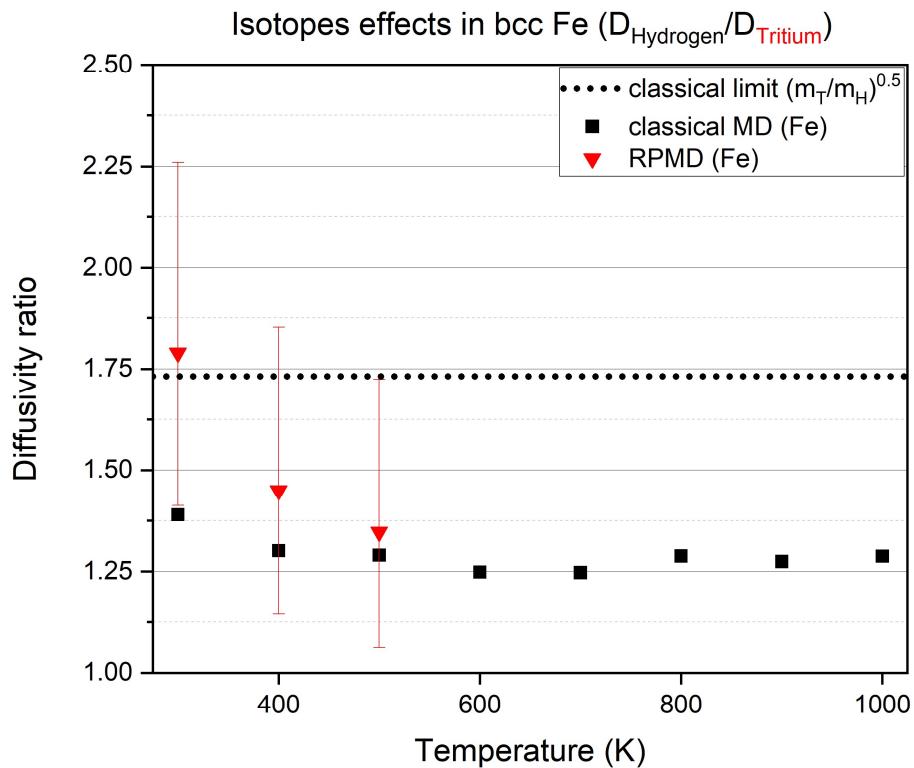
Notes

- According to the classical rate theory, diffusivity ratio of isotopes should be similar to its square root of mass ratio.
- H. Vineyard mentioned that the classical rate theory is no longer valid in systems where many-body interactions dominate.
- Since many-body interactions were reproduced in our force field, its results are thought to show good agreement to experiments (Fe).
- Because W atom is around 4 times heavier than Fe atom, W-H interaction was expected to be smaller than Fe-H. Thus, D_H/D_T ratios in bcc W were similar to the classical rate theory.

	bcc Fe	bcc W	$(m_{\text{isotope}}/m_H)^{0.5}$
D_H/D_D	1.17	1.30	1.41

5. Results

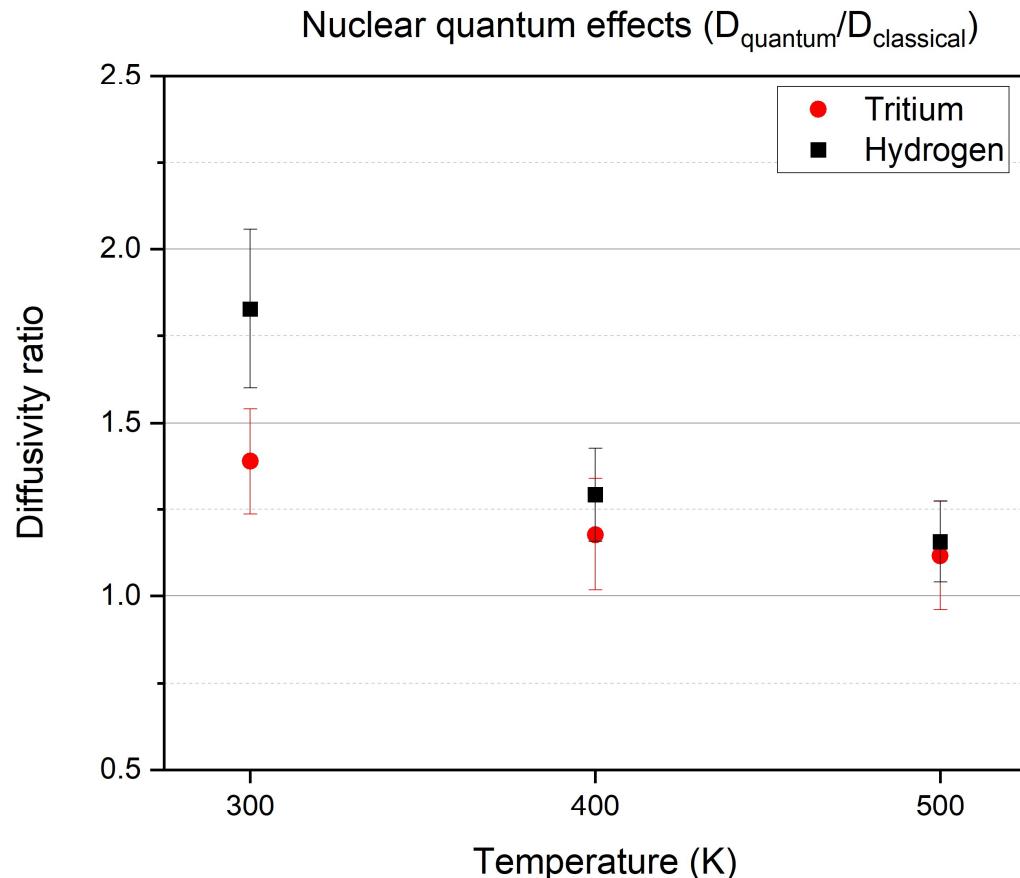
5.5. Isotopes effects (Tritium)



	bcc Fe	bcc W	$(m_{\text{isotope}}/m_H)^{0.5}$
D_H/D_D	1.17	1.30	1.41
D_H/D_T	1.29	1.47	1.73

5. Results

5.6. Classical-quantum crossover temperature in bcc Fe



Notes

- Because tritium is about three times heavier than hydrogen, its nuclear quantum effects were smaller than those of hydrogen.
- Qualitatively speaking, crossover temperature of hydrogen is around 500 K and that of tritium is around 300 K.

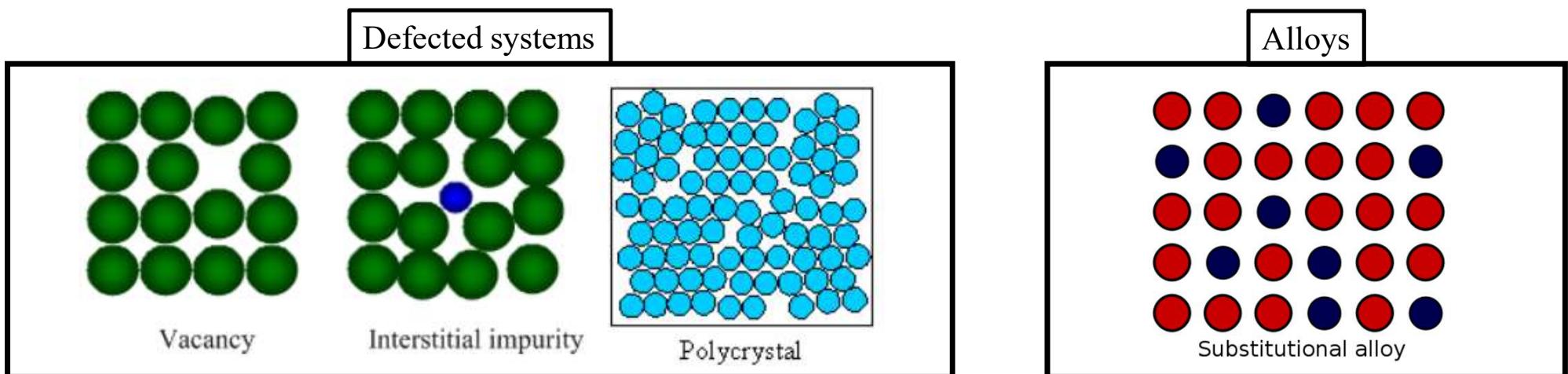
6. Conclusion

- By generating moment tensor potentials (MTPs) in reference to DFT calculation results, accurate and fast force fields were prepared for the nuclear quantum effects of hydrogen diffusion.
- In bcc W, nuclear quantum effects of hydrogen were relatively small even at 300 K, so tritium diffusivities can be reasonably approximated by a classical one at room temperature.
- The classical rate theory failed to estimate hydrogen isotope effects, while our MTP showed good agreement to experimental data of D_H/D_D ratio. Also, its deviation from the classical limit of tritium was larger than that of deuterium.
- In bcc Fe, classical-quantum crossover temperature of hydrogen is around 500 K, and that of tritium is around 300 K.

6. Conclusion

Potential value of machine-learning PIMD (ML-PIMD)

- Although only perfect bcc crystal systems were treated in this presentation, our methodology can be further applied to more complex systems with a **high level of transferability**.



7. Acknowledgement

- I would like to express my deepest gratitude to my supervisor, Prof. Oda for his careful instructions.
- Furthermore, we are indebted to the HPCI of Japan for providing computational resource of supercomputer Fugaku.
- We would like to acknowledge Dr. shiga for his kind explanations about the PIMD code.
- Finally, we would like to thank Prof. Kimizuka in Nagoya University for active discussions .

8. References

- [1] Beck W., Bockris J. O'm., McBreen J. and Nanis L. Hydrogen permeation in metals as a function of stress, temperature and dissolved hydrogen concentration Proc. R. Soc. Lond. A290220–235 (1966)
- [2] Basinski, Z. S. Series A, Mathematical and Physical Sciences, Volume 229, Issue 1179, pp. 459-467 (1955)
- [3] B.N. Dutta, phys. stat. sol. 8, 2253 (1963)
- [4] F. H. Featherston and J. R. Neighbours, Phys. Rev. 130, 1324 (1963)
- [5] Frauenfelder, Journal of Vacuum Science & Technology 6, 388 (1969)
- [6] H. Hagi, Transactions of the Japan Institute of Metals: 1979 Volume 20 Issue 7 Pages 349-357
- [7] H. Kimizuka, H. Mori, and S. Ogata, Phys. Rev. B 83, 094110 (2011).
- [8] Ivan S Novikov et al 2021 Mach. Learn.: Sci. Technol. 2 025002 (2021)
- [9] George H. Vineyard, J. Phys. Chem. Solids. Vol. 3. pp. 121-127 (1957)
- [10] J.J. Adams, J. Appl. Phys. 100, 113530 (2006)
- [11] K. Heinola, J. Appl. Phys. 107, 113531 (2010)
- [12] Kiuchi, K. Kiuchi, R.B. McLellan, The solubility and diffusivity of hydrogen in well-annealed and deformed iron, Acta Metallurgica, Volume 31, Issue 7, 1983, Pages 961-984,
- [13] M. Nagano, Y. Hayashi, N. Ohtani, M. Isshiki, and K. Igaki, Scripta Metall. 16, 973 (1982)
- [14] M. Nagano, Transactions of the Japan Institute of Metals, Vol. 22, No. 6 (1981), pp. 423 to 429 Diffusion
- [15] Quick, Nathaniel R. and Herbert H. Johnson. "Hydrogen and deuterium in iron, 49–506°C." Acta Metallurgica 26 (1978): 903-907.
- [16] Shapeev A V, Moment tensor potentials: A class of systematically improvable interatomic potentials Multiscale Model. Simul. 14 1153–73 (2016)
- [17] T. Otsuka, Application of Tritium Tracer Technique to Determination of Hydrogen Diffusion Coefficients and Permeation Rate near Room Temperature for Tungsten, Fusion Science and Technology, 60:4, 1463-1466 (2011)