Modeling of tritium trapping effects of vacancy, grain boundaries and vacancy clusters

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Objectives presented in the 1st CRP meeting (Nov. 2013)

"Evaluation of tritium inventory in irradiated W by atomic-scale modeling"

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Our research objectives are

(i) to establish a computational methodology to simulate the tritium behavior in irradiated tungsten which contains radiation defects, then

(ii) to acquire estimates of the tritium inventory in plasma-facing tungsten under some proposed fusion reactor conditions. (>> we gave up this)

To achieve this overall goal, we work on 3 subjects:

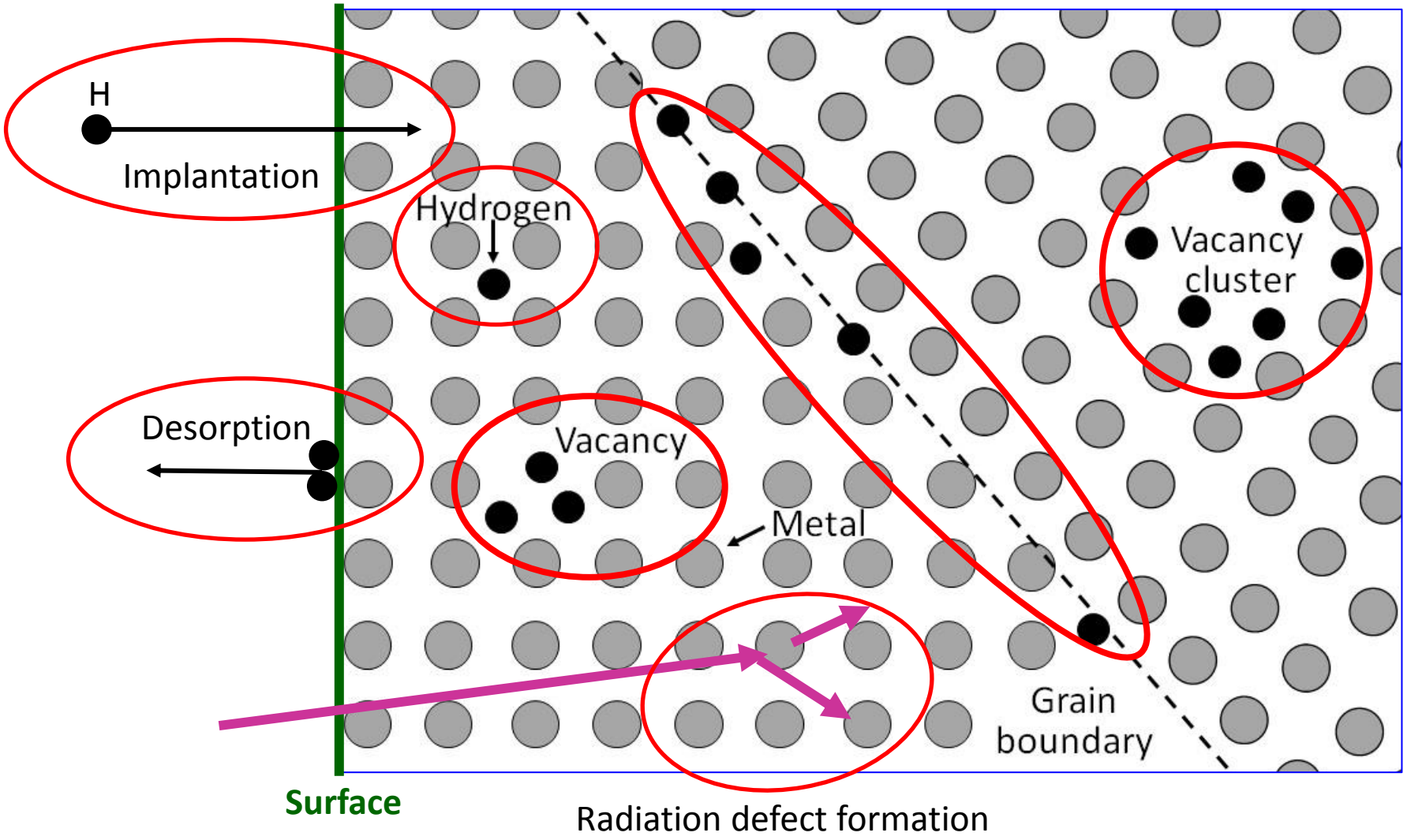
(1) to construct a high-quality potential model for W-H system to simulate behaviors of tritium and defects in W

(2) to establish kinetic models relevant with tritium behaviors in damaged W

(3) to develop a code to simulate tritium behaviors in damaged W

Key fundamental processes for T behavior in damaged W

- ✓ T behavior: ***solution (S), diffusion (D), permeation (P), and release.***
- ✓ To predict it, we need to construct models for fundamental processes.



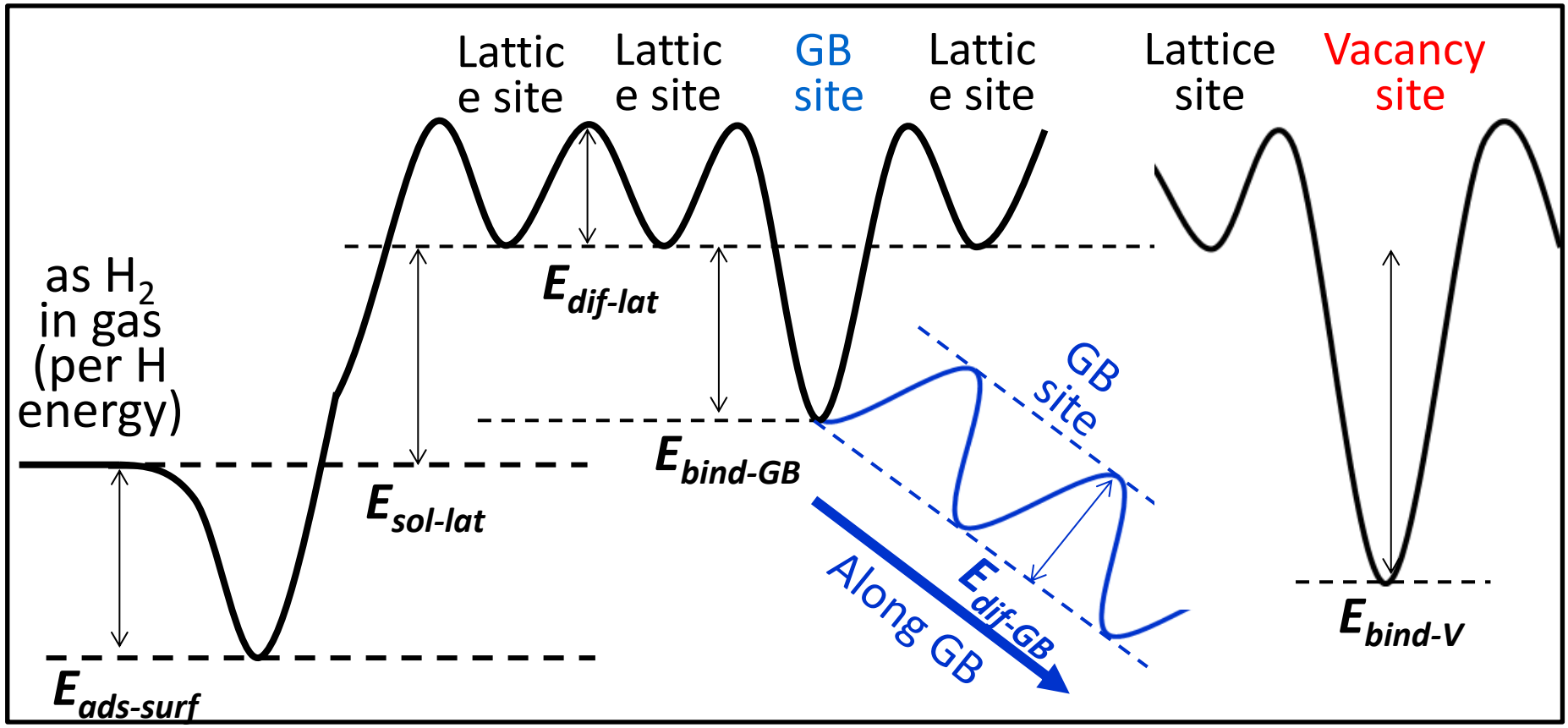
Contents of this presentation

1. Effects of grain boundaries (GBs) on H behavior in W

2. Effects of vacancy clustering on H behavior in W

3. Development of a code to simulate tritium behavior in damaged W

1. Effects of GBs on H behavior in W: difference from effects of V



(eV)	$E_{ads\text{-}surf}$	$E_{sol\text{-}lat}$	$E_{dif\text{-}lat}$	$E_{bind\text{-}V}$	$E_{bind\text{-}GB}$	$E_{dif\text{-}GB}$
W	0.7-0.9[*1]	1.1	0.25[*2]	1.2[*3]	?	?

[*1]K. Heinola et al., Phys. Rev. B 81 (2010) 073409; [*2] K. Heinola et al., J. Appl. Phys. 107 (2010) 11531; [*3] K. Ohsawa et al., Phys. Rev. B 82 (2010) 184117.

1. Effects of GBs on H behavior in W
-thermodynamic model for GBs-

$$A(x) = (xN_H)E_{H-GB}(x) - Tk_B \ln S_{config}(x)$$

where N_H is the number of H atoms in the system and x is the fraction of H atoms trapped by GB.

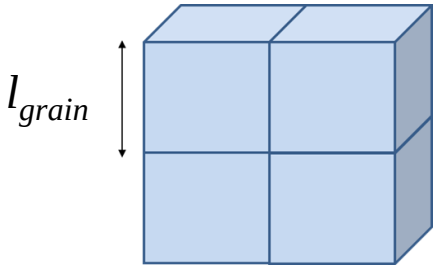
x of equilibrium state is given by $\partial A/\partial x = 0$

$$S_{config}(x) = k_B \ln(W_{H-lattice} \times W_{H-GB})$$

$$W_{H-lattice} = {}_{N_{lattice-site}}C_{N_{H@lattice}} = {}_{N_{lattice-site}}C_{(1-x)N_H}$$

$$W_{H-GB} = {}_{N_{GB-site}}C_{N_{H@lattice}} = {}_{N_{GB-site}}C_{xN_H}$$

(Assumption-1) A specimen is composed of single-size cubic grains.



$$N_{H@\text{lattice-site}} = 12N_{unit-cell} = 12(l_{grain}/l_{lat})^3$$

$$N_{H@\text{lattice-site}} = \frac{6\beta}{2}(l_{grain}/l_{lat})^2$$

where β is the number of GB sites per unit GB plane

1. Effects of GBs on H behavior in W
-thermodynamic model for GBs-

(Assum.-2) Lattice sites are sparsely occupied by H atoms.
(Assum.-3) GB sites are sparsely occupied by H atoms.
(Assum.-4) $E_{bind\text{-}GB}$ and $E_{dif\text{-}GB}$ are independent of the number of H trapped at GB, and we can define effective values of them, which are independent of x and T.
(Assum.-5) Pre-exponential factors for GB diffusion and bulk diffusion are the same.

$$D_{H-GB}[\mathrm{m^2 s^{-1}}] = 1.58\times10^{-7}\times\exp\left(-E_{dif-GB}/k_B T\right)$$

$$D_{eff} = \left\{1+\frac{3\beta l_{lat}\left(\left(D_{H-GB}/D_{H-lat}\right)-1\right)}{3\beta l_{lat}+12 l_{grain}\exp\left(-E_{bind-GB}/kT\right)}\right\}\times D_{H-lat}$$

$$S_{eff} = \left\{1+\frac{3\beta l_{lat}}{12 l_{grain}\exp\left(-E_{bind-GB}/kT\right)}\right\}\times S_{H-lat}$$

$$P_{eff} = D_{eff}S_{eff} = \left\{1+\frac{3\beta l_{lat}\left(D_{H-GB}/D_{H-lat}\right)}{12 l_{grain}\exp\left(-E_{bind-GB}/kT\right)}\right\}\times P_{H-lat}$$

Param.	Definition
l_{grain}	Grain size
l_{lat}	Lattice constant
β	Number of GB sites per unit GB plane
$E_{bind\text{-}GB}$	Effective H binding energy at GBs
$E_{dif\text{-}GB}$	Effective H diffusion barrier along GBs

1. Effects of GBs on H behavior in W
-estimation of some parameters in the model-

(1) β and $E_{bind\text{-}GB}$

- ✓ [Σ5 tilt GB] β = 2; $E_{bind\text{-}GB}$= 1.1 eV (1st atom), 1.0 eV (2nd)
- ✓ [Σ3 tilt GB] β = 6; $E_{bind\text{-}GB}$= 1.2 eV, 1.0 eV, 0.8 eV, 0.3 eV
- ✓ [W(110)/W(112)] $E_{bind\text{-}GB}$= ~1.0 eV

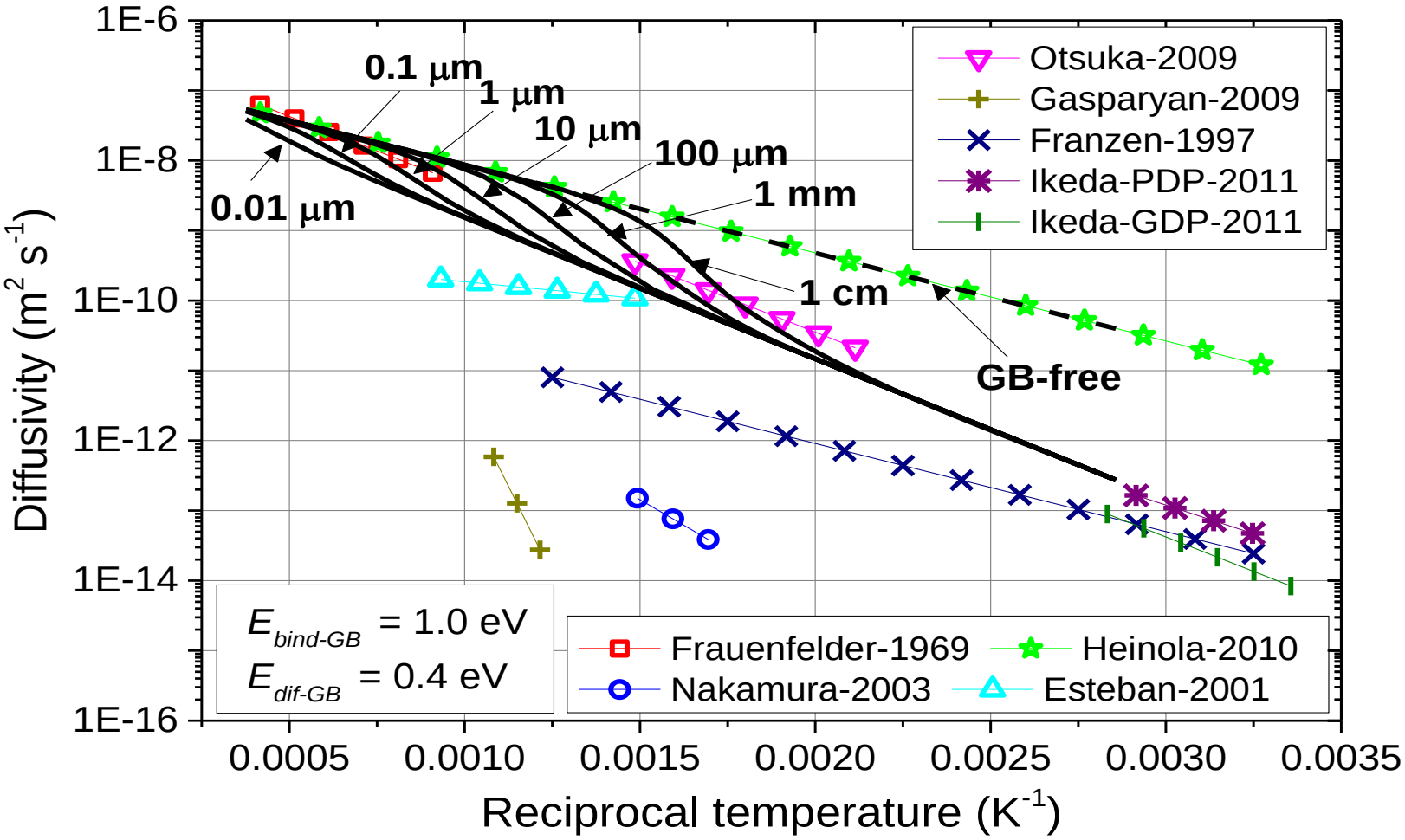
(2) $E_{dif\text{-}GB}$

- ✓ [Σ5 tilt GB] [W(110)/W(112)] $E_{dif\text{-}GB}$<0.2 eV for some paths

*[Σ5 tilt GB] H.B. Zhou et al., Nucl. Fusion 50 (2010) 025016.
*[Σ3 tilt GB] W. Xiao, W.T. Geng, J. Nucl. Mater. 430 (2012) 132.
*[W(110)/W(112)] C. González et al., Nucl. Fusion 55 (2015) 113009.

Parameter	Definition	Value	Uncertainty
β	Number of grain boundary sites for H in unit GB plane	2	High
$E_{bind\text{-}GB}$	H binding energy at gb	1.0 eV	~30%
$E_{dif\text{-}GB}$	H diffusion barrier in and along GB	0.4 eV	High

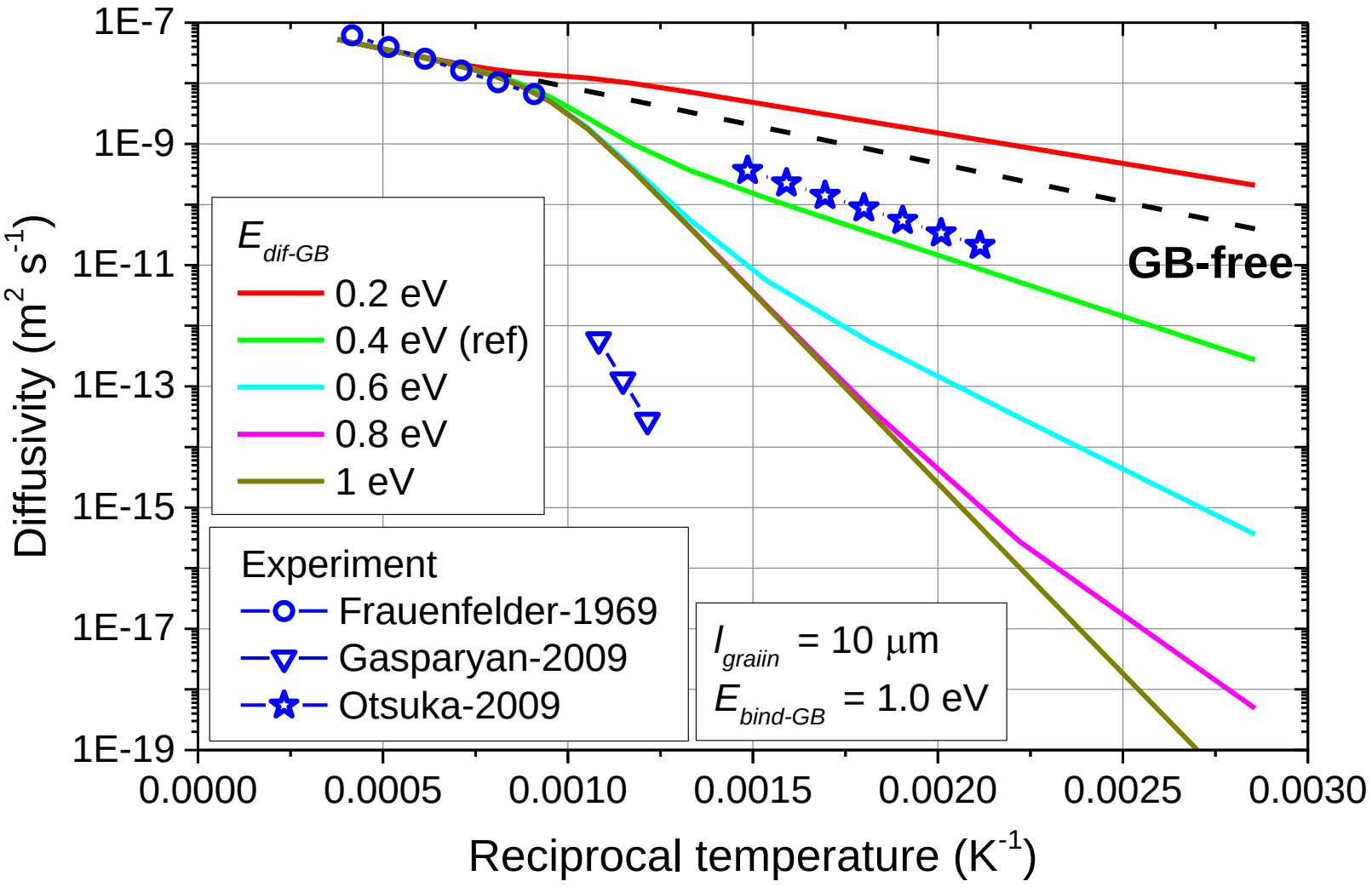
1. Effects of GBs on H behavior in W
-results: effects on H diffusivity-



*The system is equilibrated with $1x10^5$ Pa of H_2 gas.

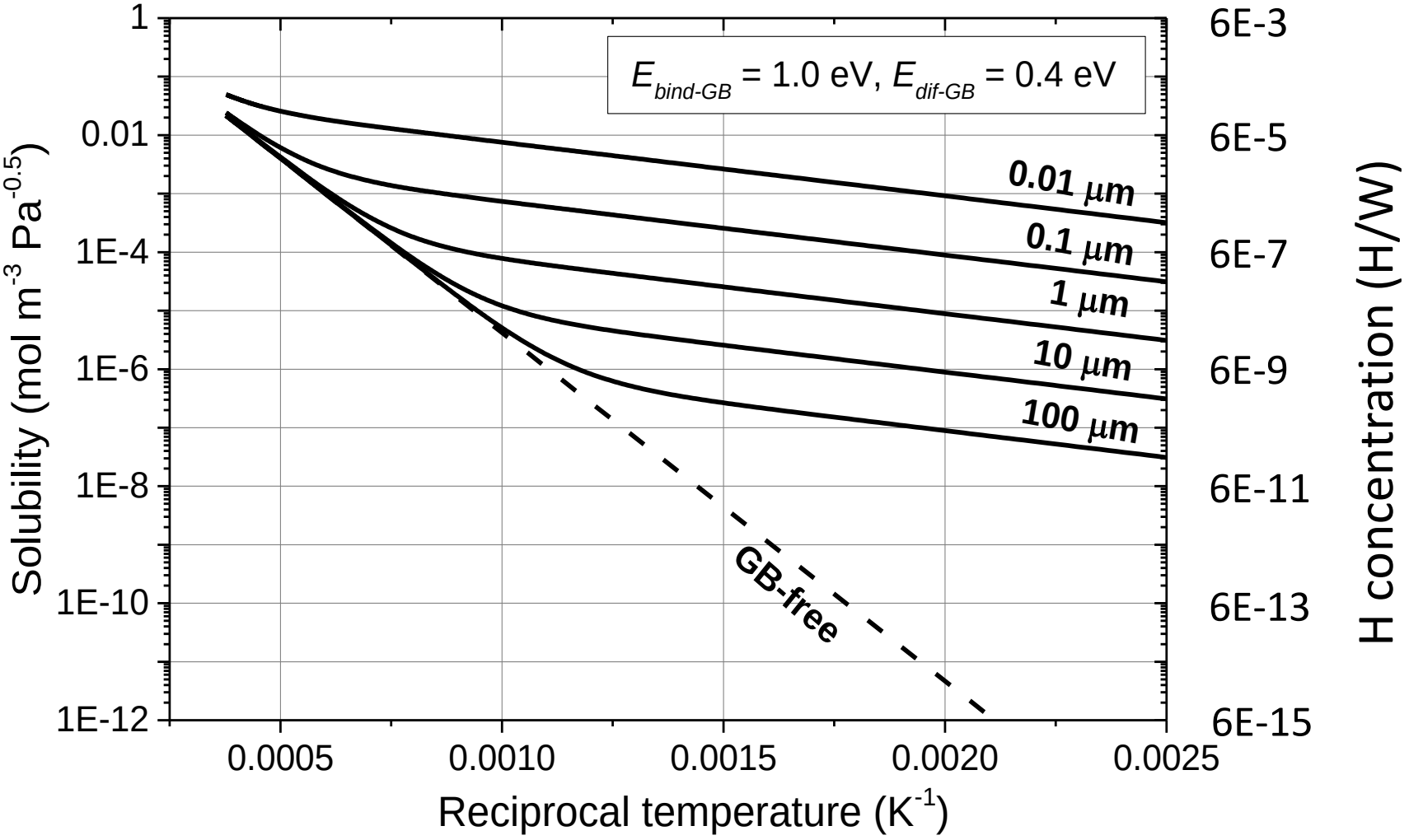
✓ In practice, it is technically difficult to determine $D_{H\text{-}lat}$ at T< 800 K.

1. Effects of GBs on H behavior in W
-results: sensitivity of diffusivity to $E_{dif\text{-}GB}$-



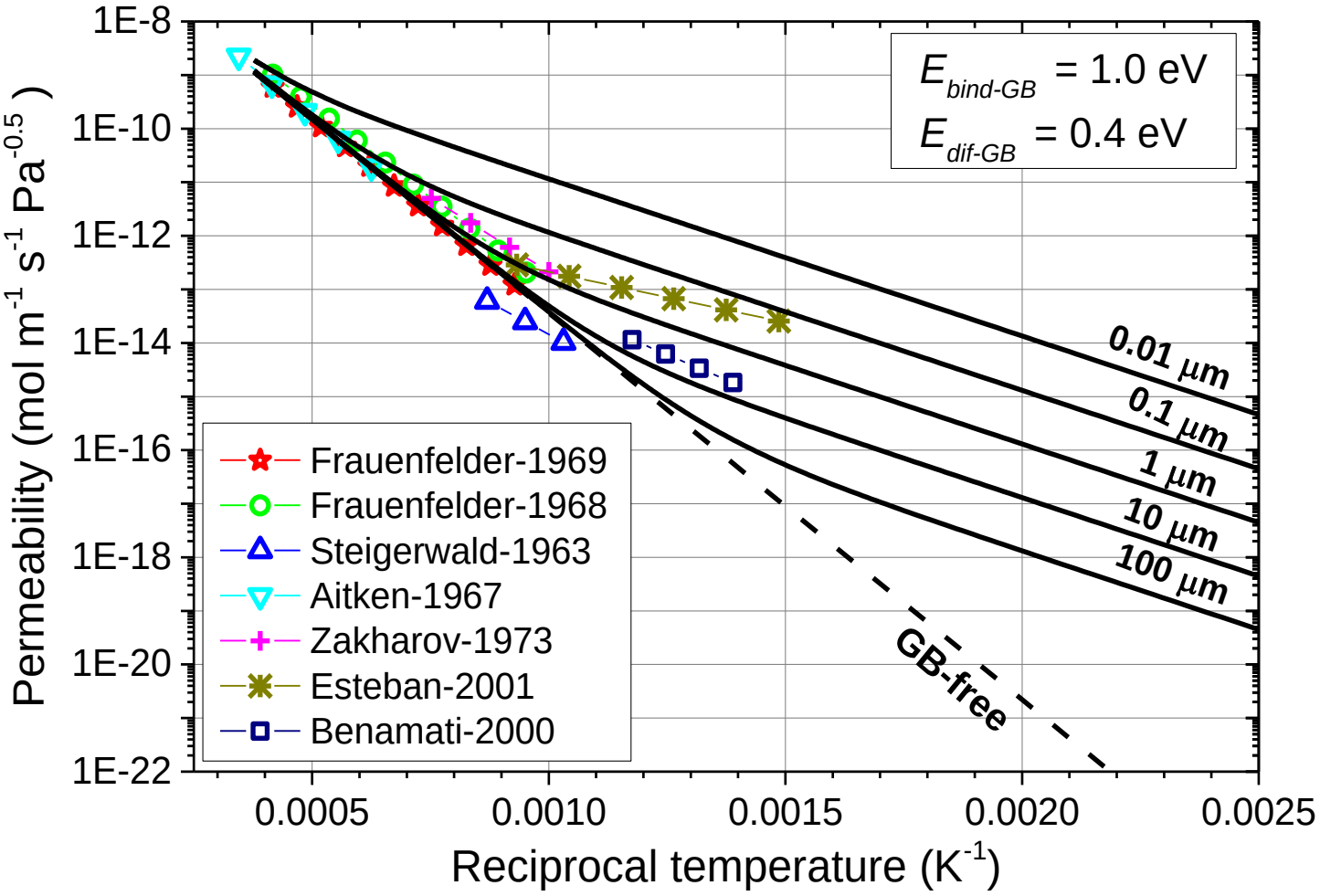
✓ $E_{dif\text{-}GB}$ = 0.4 eV is reasonable in comparison with experimental results.

1. Effects of GBs on H behavior in W
-results: effects on H solubility-



✓ GBs significantly increase T inventory, especially in small-grain materials.

1. Effects of GBs on H behavior in W
-results: effects on H permeability-



- ✓ The deviation seen in experimental data at low temperatures (<1000 K) can be attributed to GB effects.
- ✓ Small-grain materials may increase T leakage.

1. Effects of GBs on H behavior in W
-why GBs change the permeability?-

(i) Defect trapped by which H can still migrate, e.g. grain boundary (GB).

$$S_{eff} = S_{H@lat} + S_{H@GB} = S_{H@lat} / \alpha$$

$$\alpha = S_{H@lat} / \left(S_{H@lat} + S_{H@GB} \right)$$

$$D_{eff} = \alpha D_{H@lat} + (1-\alpha) D_{H@GB}$$

$$P_{eff} = D_{eff} S_{eff} = \left\{ D_{H@lat} + \left((1-\alpha)/\alpha \right) D_{H@GB} \right\} S_{H@lat}$$

(ii) Defect trapped by which H cannot migrate, e.g. vacancy.

$$S_{eff} = S_{H@lat} + S_{H@vac} = S_{H@lat} / \alpha$$

$$D_{eff} = \alpha D_{H@lat} + \underline{(1-\alpha) D_{H@vac}} \sim \alpha D_{H@lat}$$

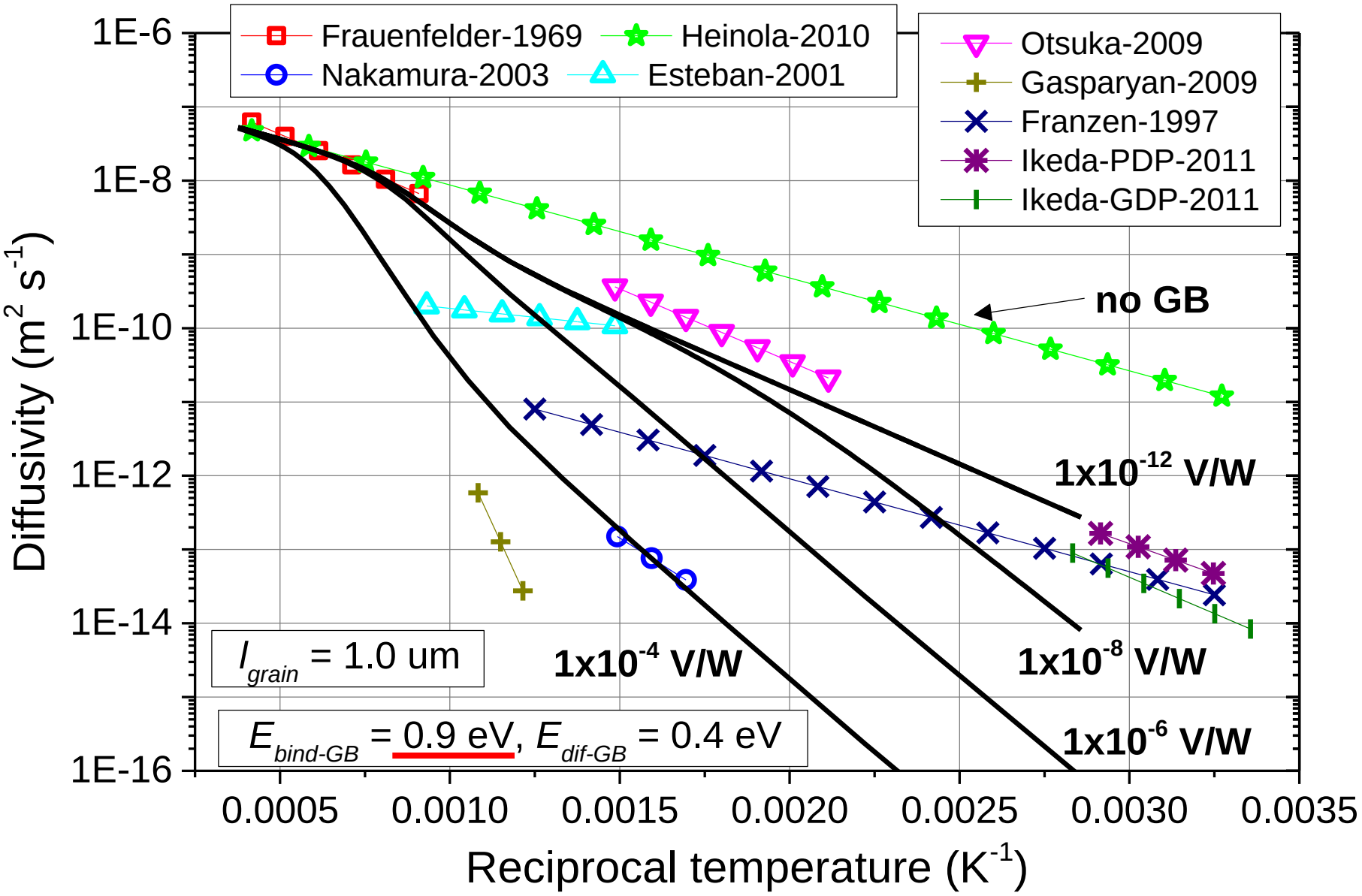
This is the diffusivity of V-H complex, which is negligibly small.

$$P_{eff} = D_{eff} S_{eff} \sim \left(\alpha D_{H@lat} \right) \left(S_{H@lat} / \alpha \right) = D_{H@lat} S_{H@lat} = P_{true}$$

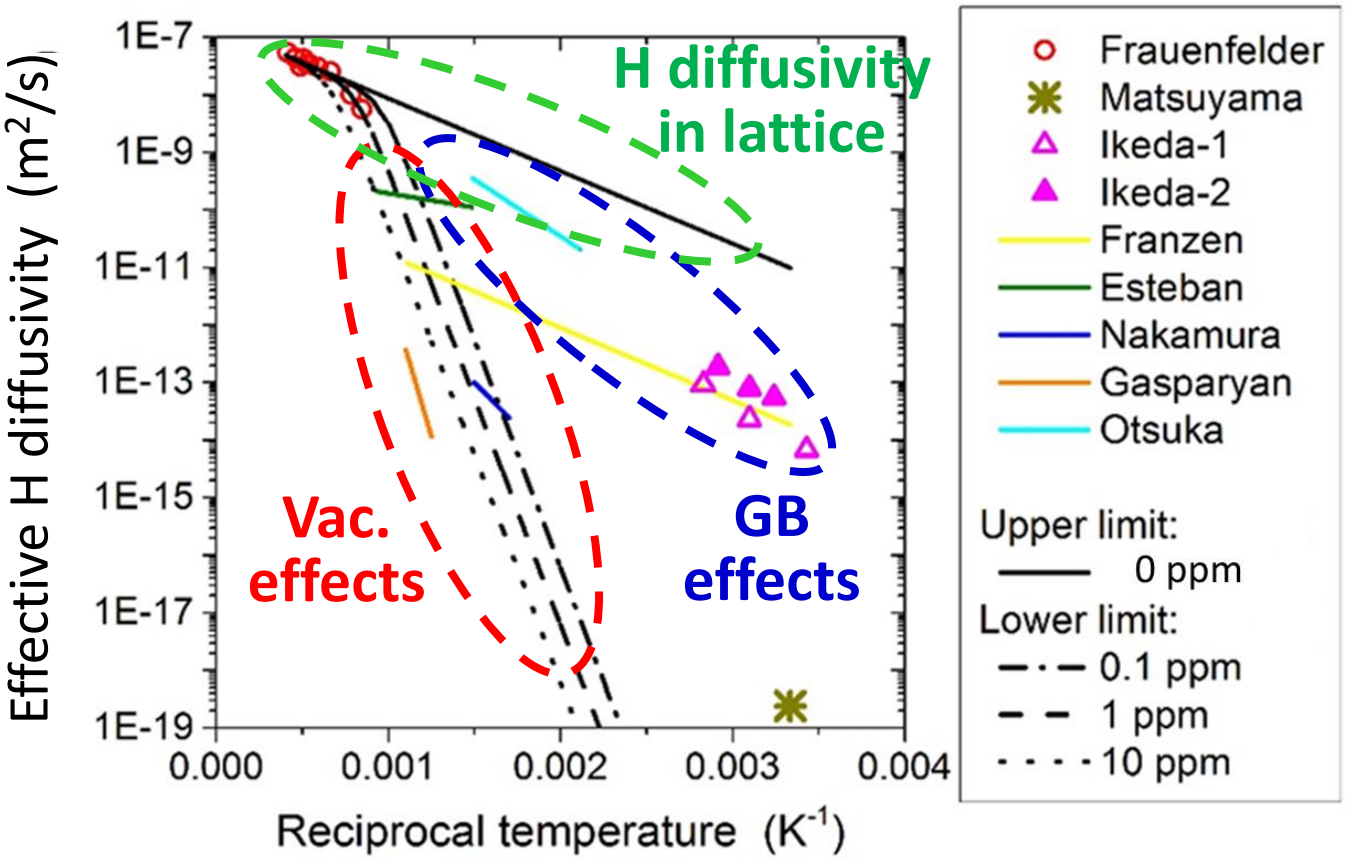
$$\alpha = S_{H@lat} / \left(S_{H@lat} + S_{H@vac} \right) \sim D_{eff} / D_{H@lat}$$

*T. Oda, Fusion Eng. Des. **112** (2016) 102.

1. Effects of GBs on H behavior in W
-synergetic effect of GB and vacancy on H diffusivity-



1. Effects of GBs on H behavior in W
-synergetic effect of GB and vacancy on *D*-



*T. Oda, D. Zhu, Y. Watanabe, J. Nucl. Mater. **467** (2015) 439.

*T. Oda, Fusion Eng. Des. **112** (2016) 102.

- ✓ $E_{bind\text{-}GB}$ = 1.0 eV; $E_{dif\text{-}GB}$ = 0.40 eV
- ✓ GB effects were (unintentionally) considered in many previous studies by using $E_{dif\text{-}lat}$ = 0.39 eV.

Contents of this presentation

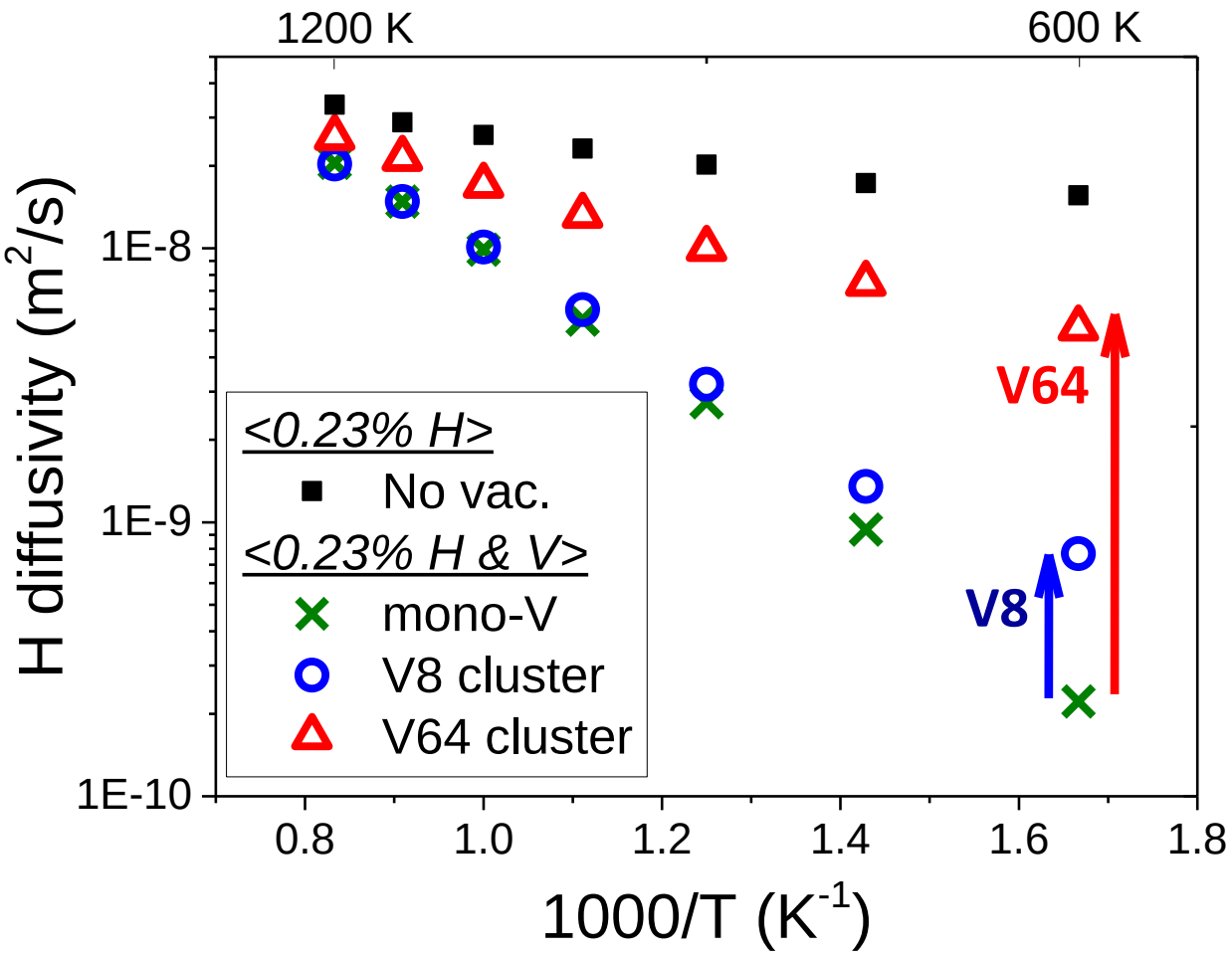
1. Effects of grain boundaries (GBs) on H behavior in W

2. Effects of vacancy clustering on H behavior in W
   - 2.1. Model construction for V clusters in bcc-Fe
   - 2.2. Potential model development for W-H systems
   - 2.3. Effects of vacancy clustering in bcc-W

3. Development of a code to simulate tritium behavior in damaged W

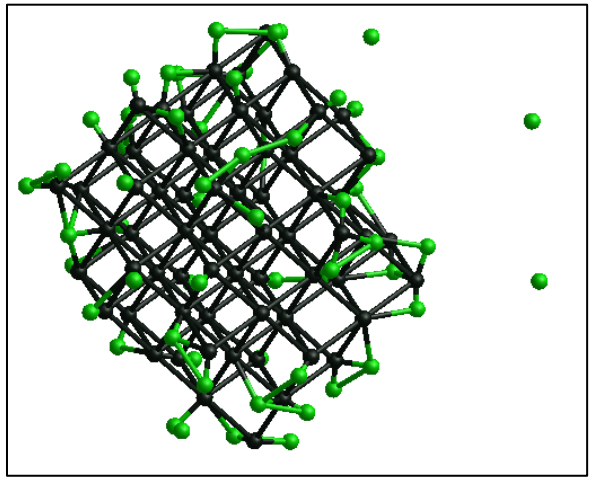
2.1. Model construction for V clusters in bcc-Fe -effects of vacancy clustering on H diffusivity by MD-

MD simulation was performed by using LAMMPS code with Fe-H potential model reported by Ramasubramaniam et al. [Phys. Rev. B 79 (2009) 174101].



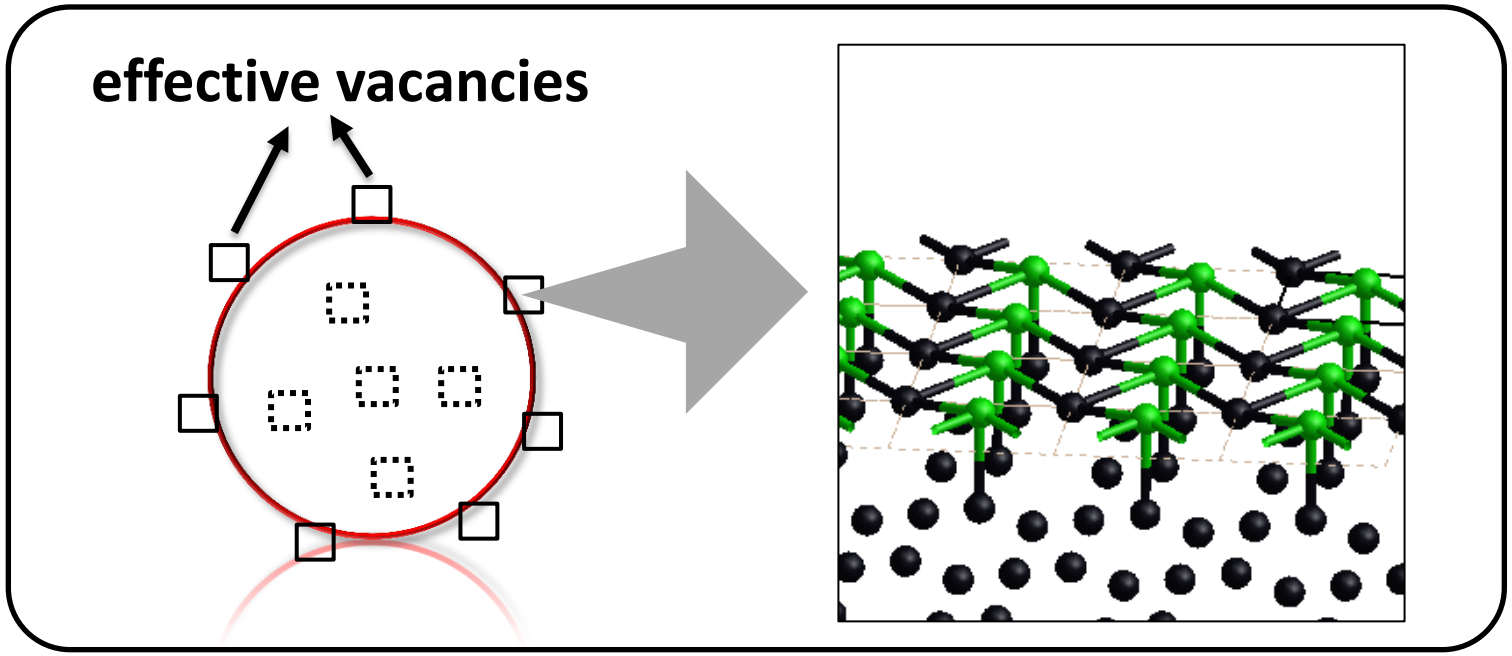
$$\alpha \sim D_{eff} / D_{H@lat}$$

V64 cluster



✓ Vacancy clustering weakens the hydrogen trap effect of vacancies.

2.1. Model construction for V clusters in bcc-Fe
-estimation of the number of trapping sites-



✓ Inner vacancies in a cluster (void) cannot trap H atoms.
  ✓ The surface area of void should be proportional to the number of H-trapping site.

Available H trap sites per void	=	Void surface area	×	H trap site per (100) surface area

2.1. Model construction for V clusters in bcc-Fe

-validation of the model in comparison with MD results-

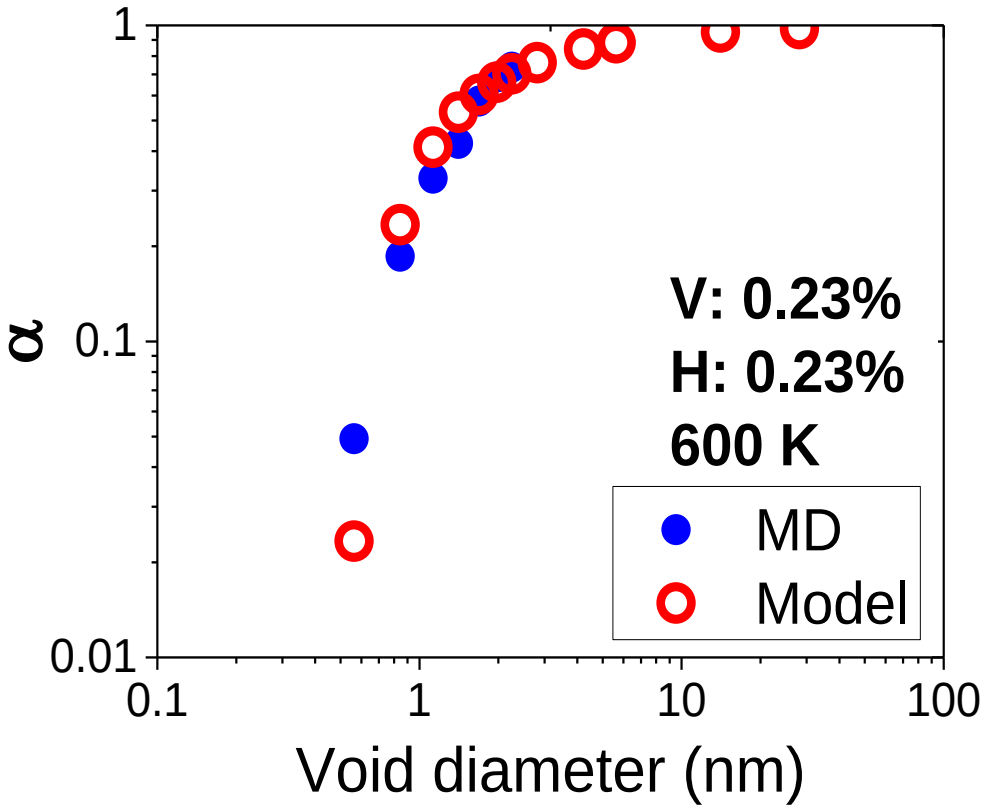
Thermodynamic model based on equilibrium theory

$$S_{conf}(\alpha) = k_B \ln\left(W_{H@lat} \times W_{H@void}\right)$$

$$A(\alpha) = (1-\alpha) E_{H@void} - TS_{conf}(\alpha)$$

$$\frac{\partial A}{\partial \alpha} = 0$$

$$\alpha = S_{H@lat} / S_{eff} \sim D_{eff} / D_{H@lat}$$



- ✓ As the size of void increases, its effect on S_{eff} and D_{eff} are decreased.
- ✓ However, H_2 formation is not considered in this model !!

2.2. Potential model development for W-H systems -motivation-

✓ There are two widely-utilized potential models for tungsten-tritium system: both are Tersoff-Brenner type Bond-order potential (BOP):

- ✓by Juslin in 2005 [N. Juslin et al., J. Appl. Phys. 98 (2005) 123520]
- ✓by Li in 2011 [X.-C. Li et al., J. Nucl. Mater. 408 (2011) 12].

$$E = \sum_{i>j} f_{ij}^{c}(r_{ij}) \left[V_{ij}^{R}(r_{ij}) - \underbrace{\frac{b_{ij} + b_{ji}}{2}}_{\overline{b_{ij}}} V_{ij}^{A}(r_{ij}) \right] \qquad b_{ij} = (1 + \chi_{ij})^{-1/2}$$

$$\chi_{ij} = \sum_{k(\neq i,j)} f_{ik}^{c}(r_{ik}) g_{ik}(\theta_{ijk}) \omega_{ijk} \exp[\alpha_{ijk}(r_{ij} - r_{ik})] \qquad g(\theta) = \gamma\left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h + \cos\theta)^2}\right)$$

✓ Regarding hydrogen-vacancy interaction energy, large errors are brought in both models: underestimation in BOP-1 and overestimation in BOP-2.

Trapping energy (eV per H)	V_1H_1	V_1H_2	Solution energy
BOP-Juslin	0.59	0.59	0.85
BOP-Lee	2.03	2.03	1.03
DFT	1.2	1.2	1.1

2.2. Potential model development for W-H systems -how to make potential models?-

(step-1) Define fitting targets

Materials properties (energetics, elastic, vibrational): ~ 10 targets → Energies/Forces/stresses by DFT calculations: ~ 10^5 or more

(step-2) Prepare model functionals

Model frame
- ✓ Two-body
- ✓ EAM

Function form (for example in two-body)
- ✓ Morse
- ✓ Lennard-Jones

(step-3) Optimize model parameters

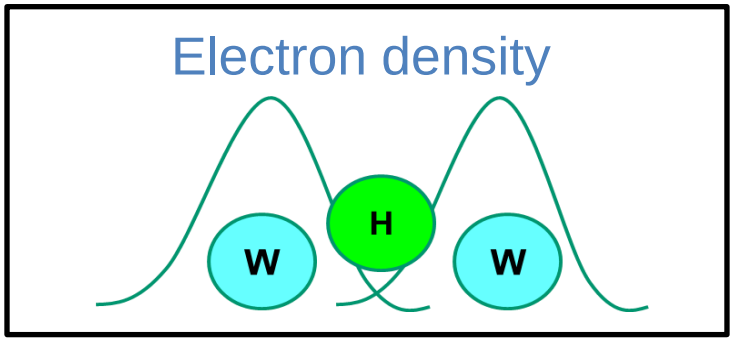
We investigated two type of models.

- ✓ (1) Gaussian Approximate Potential (GAP)
  - ✓ In this model, we do not define potential functions explicitly; instead, we define a statistical model to relate similarities in atomic environments with the potential energy. [A.P. Bartok et al., Phys. Rev. Lett. **104** (2010) 136403; W. Szlachta et al., Phys. Rev. B **90** (2014) 104108]
- ✓ (2) EAM potential, with a systematic parameterization method

2.2. Potential model development for W-H systems -method to construct EAM potential model-

Embedded atom model (EAM): incl. a term depending on electron density

$$E_{EAM} = E_{2B} + \sum_{i}^{atoms} f_{\mathrm{EAM},i}\left(\rho_i\left(\ldots, r_{ij}, \ldots.\right)\right), \qquad \rho_i = \sum_{j}^{r_{ij}<r_{cut}} g\left(r_{ij}\right)$$



For example,

$$f_{\mathrm{EAM},i}\left(\rho_i\right) = \sqrt{\rho_i}$$

$$\rho_i = \sum_{j}^{r_{ij}<r_{cut}} \left(r_{ij} - r_{cut}\right)^3$$

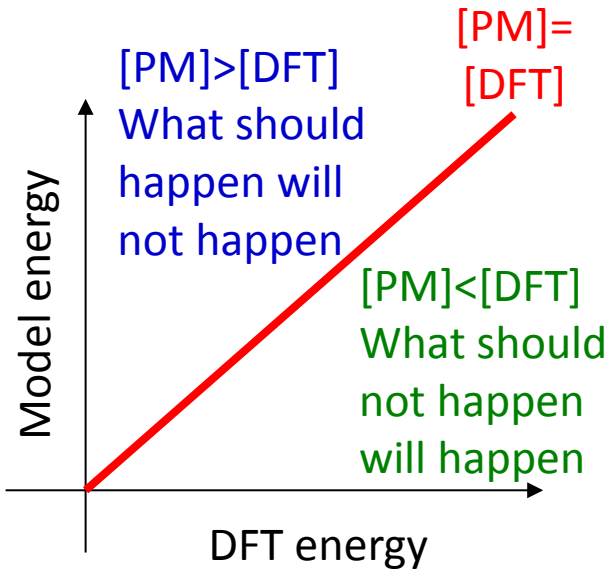
<How to establish an EAM potential model>

(1) Prepare a training set, which is DFT calculation results on energies, forces and stresses.

(2) Expand f_{EAM} function with Fourier cosine series (around 50 terms), with fixing ρ functions.

(3) Perform MD simulations to find configurations that wrongly give lower potential energies.

(4) Conduct DFT calculations with the configurations, and update the training set.



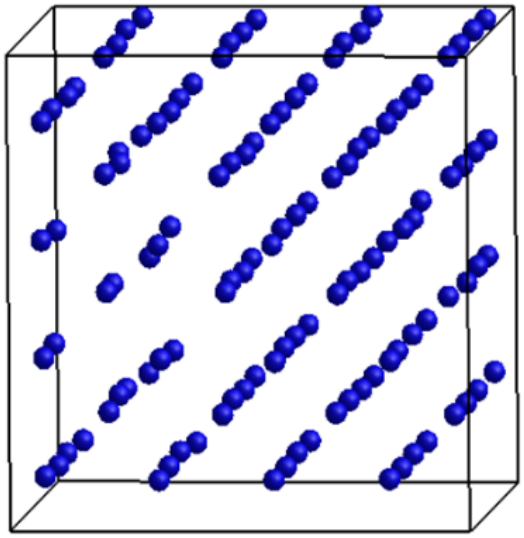
2.2. Potential model development for W-H systems
-DFT calculation results for 'training' potential model-

System	Number of W atoms	Number of H atoms	Temperature (K)	Number of configurations
Perfect crystal	128	0	300, 900, 1500, 2100, …, 5700	8,000 (800 for each temperature)
Interstitial	129	0	300, 900, …, 4500	2,400
Vacancy	127	0	300, 900, …, 4500	3,200
Vacancies (V2)	126	0	300, 900, …, 4500	6,400
Vacancies (V3)	125	0	300, 900, …, 4500	9,200
Vacancies (V5)	123	0	300, 900, …, 4500	6,400
Vacancies (V9)	119	0	300, 900, …, 4500	3,200
Surfaces	12	0	(static calculation)	3,200
Deformation of bcc-W crystals	2	0	(static calculation)	100
W2 molecule	2	0	(static calculation)	100
WH molecule	1	1	(static calculation)	50
H2 molecule	0	2	(static calculation)	50
H in perfect crystal	128	1/2/6/12	300, 900, 1500, 2100	5,600
H in defective crystal: interstitial	129	1/2/6/12	300, 900, 1500, 2100	4,400

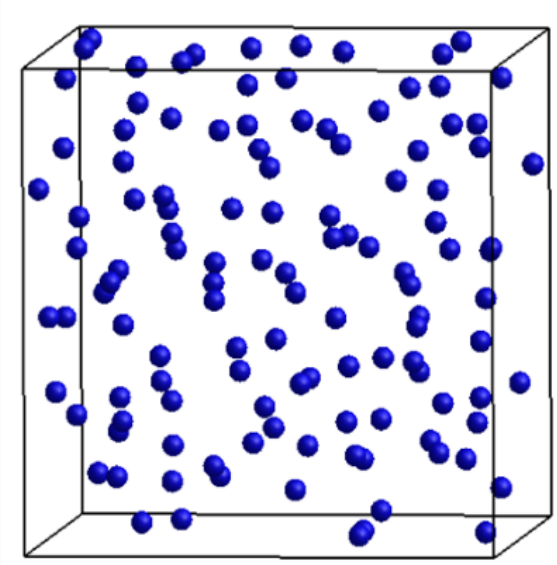
2.2. Potential model development for W-H systems
-DFT calculation results for 'training' potential model-

System	Number of W atoms	Number of H atoms	Temperature (K)	Number of configurations
H in defective crystal: V1	127	1/2/6/12	300, 900, 1500, 2100	5,600
H in defective crystal: V2	126	1/2/6/12	300, 900, 1500, 2100	10,400
H in defective crystal: V3	125	2/6	300, 900, 1500, 2100	3,200
H in defective crystal: V5	123	2/6	300, 900, 1500, 2100	1,600
H in defective crystal: V9	119	2/6/12	300, 900, 1500, 2100	2,000

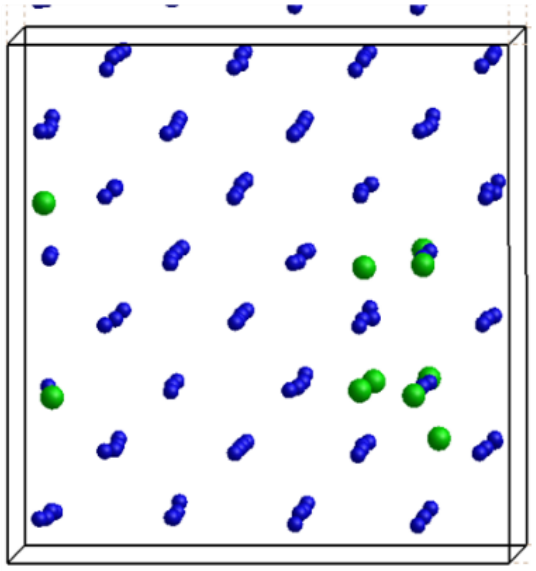
(a) V9 (W119) @ 300 K



(b) V9 (W119) @ 4500 K



(c) V9-H12 (W119H12) @ 300 K

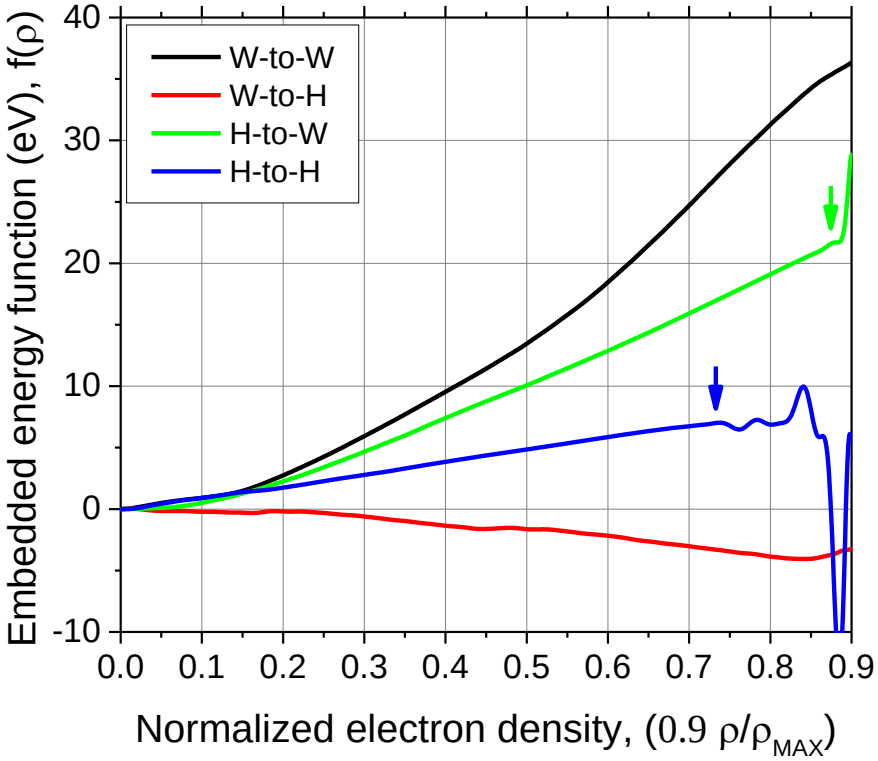


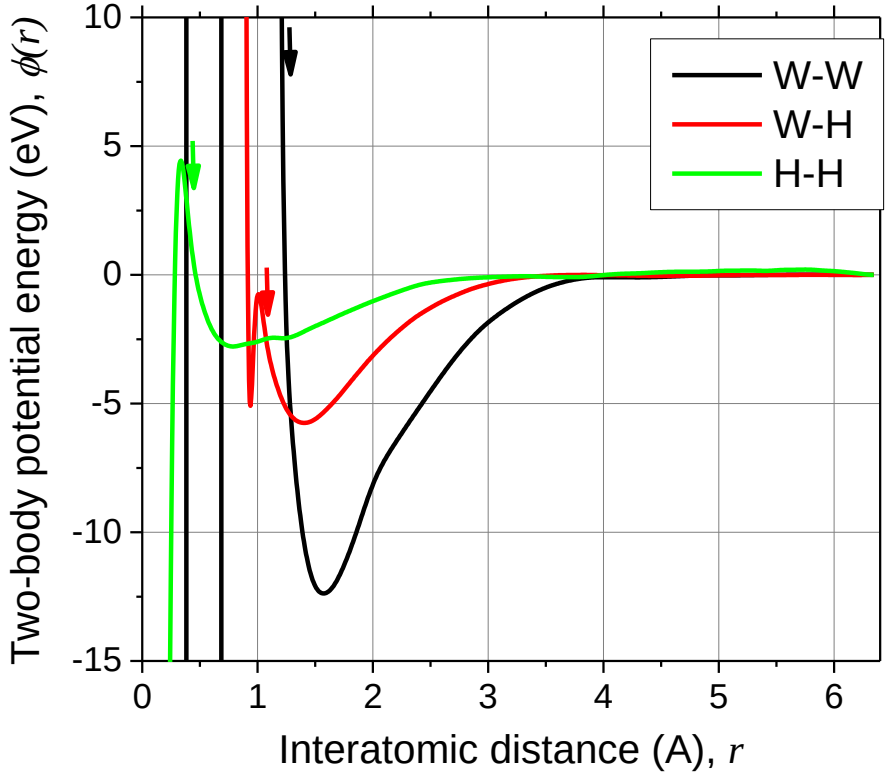
2.2. Potential model development for W-H systems -shape of constructed EAM potential model-

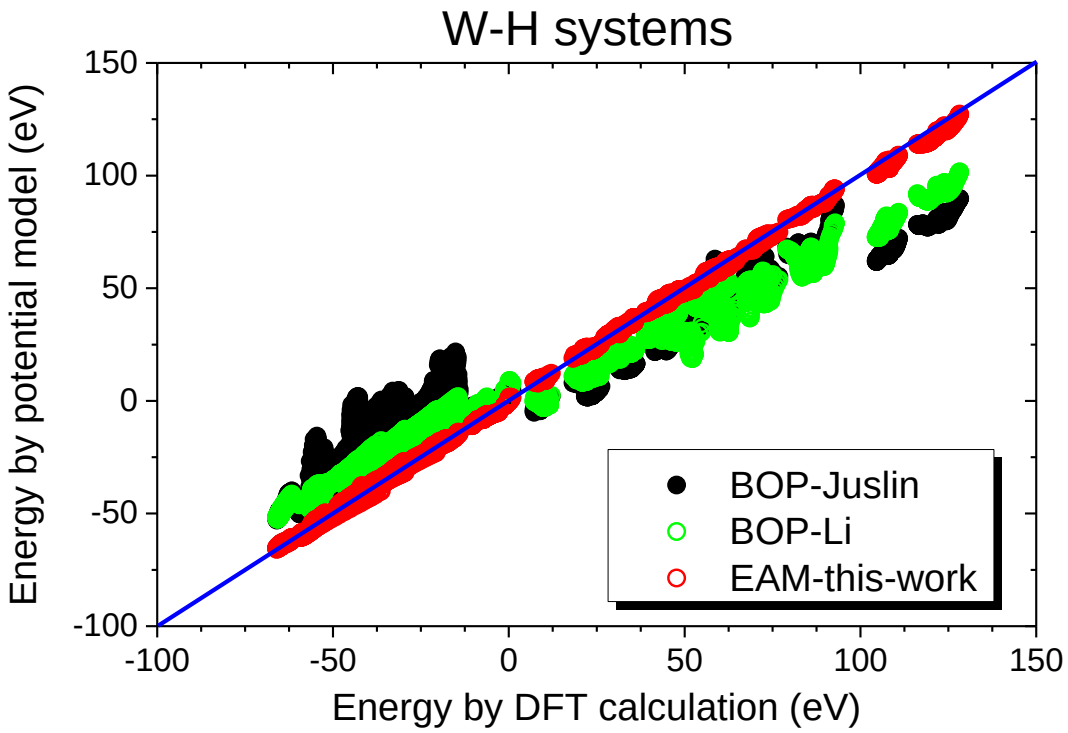
$$U_{EAM} = \frac{1}{2}\sum_{i=1}^{N_{atom}}\sum_{j=1}^{r_{ij}<r_{cut-2body}} \phi(r_{ij}) + \sum_{i=1}^{N_{atom}} f(\rho_i)$$

$$\phi(r) = \sum_{n=0}^{N_{2body}} a_n \cos\left(\frac{n\pi r}{r_{cut-2body}}\right) \quad (\text{for } r < r_{cut\text{-}2body}), \qquad f(\rho) = \sum_{n=0}^{N_{EAM}} b_n \cos\left(\frac{n\pi\rho}{\rho_{MAX}}\right) \quad (\text{for } \rho < \rho_{MAX})$$

$$\rho_i = \sum_{j=1}^{r_{ij}<r_{cut-EAM}} g(r_{ij}), \qquad g(r) = (4.03 - r)^3 \quad (\text{for } r < r_{cut\text{-EAM}})$$





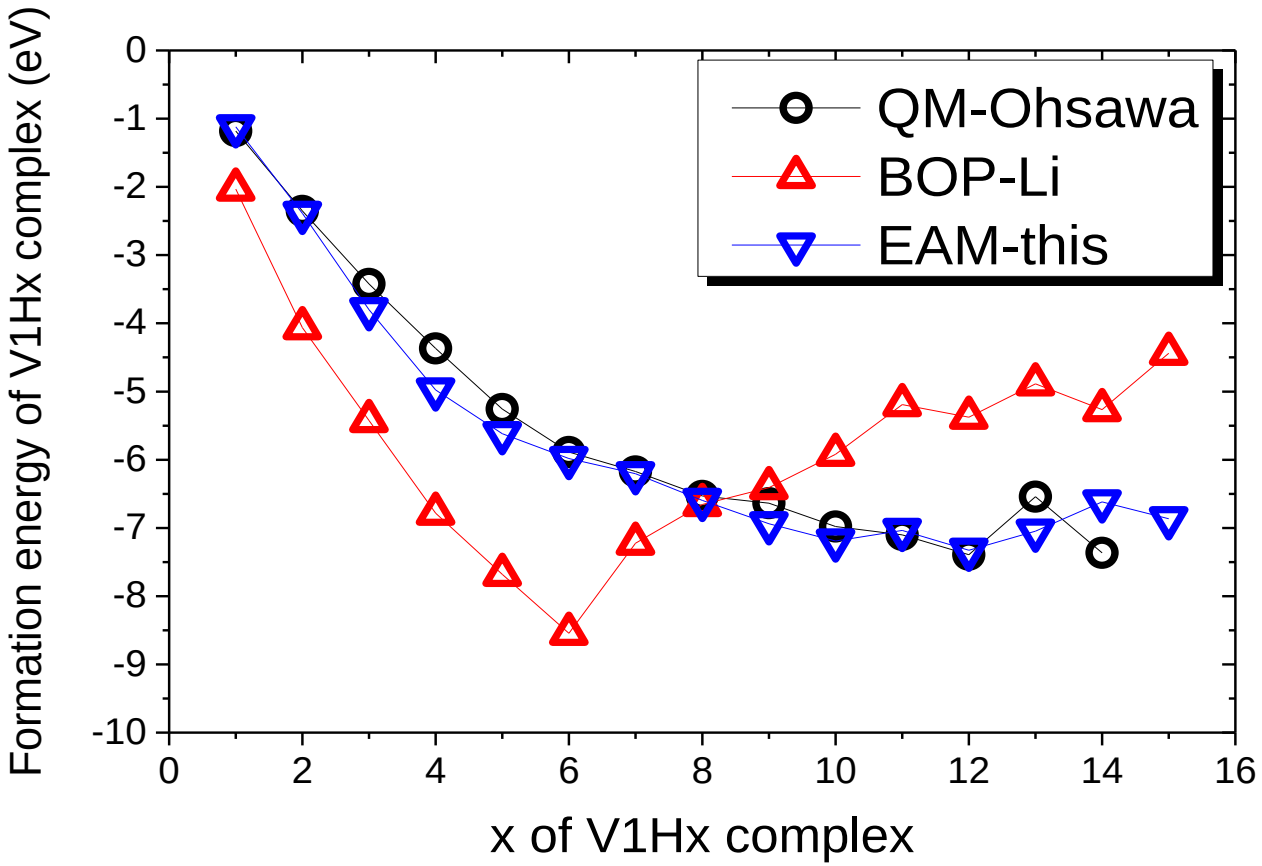


2.2. Potential model development for W-H systems -Comparison of model performance-

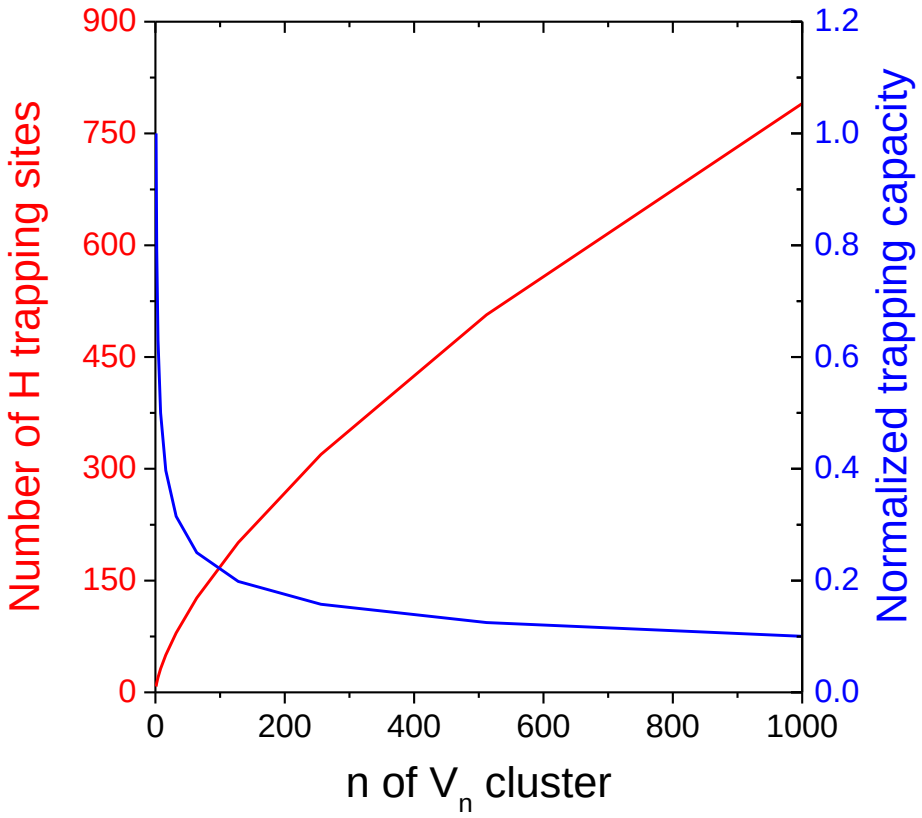
surface-energy	Exp.	QM	BOP-Juslin	BOP-Lee	EAM-Wang	EAM-this
W(100), eV/A2	0.187	0.252	0.090	0.197	0.186	0.200
W(110), eV/A2	0.201	0.205	0.058	0.145	0.159	0.176
defect-energy						
V1 (eV)	3.7	3.27	1.69	3.54	3.60	3.19
V migration (eV)	1.8	1.72	1.77	1.81	1.36	1.49
SIA<100> (eV)	-	12.24	9.29	12.34	10.82	10.02
SIA <111> (eV)	9.06	10.20	10.00	9.55	10.11	10.01
lattice-constant(A)	3.165	3.172	3.165	3.165	3.165	3.172
elastic const. (C_{11}, GPa)	501-521	548	542	515	522	528

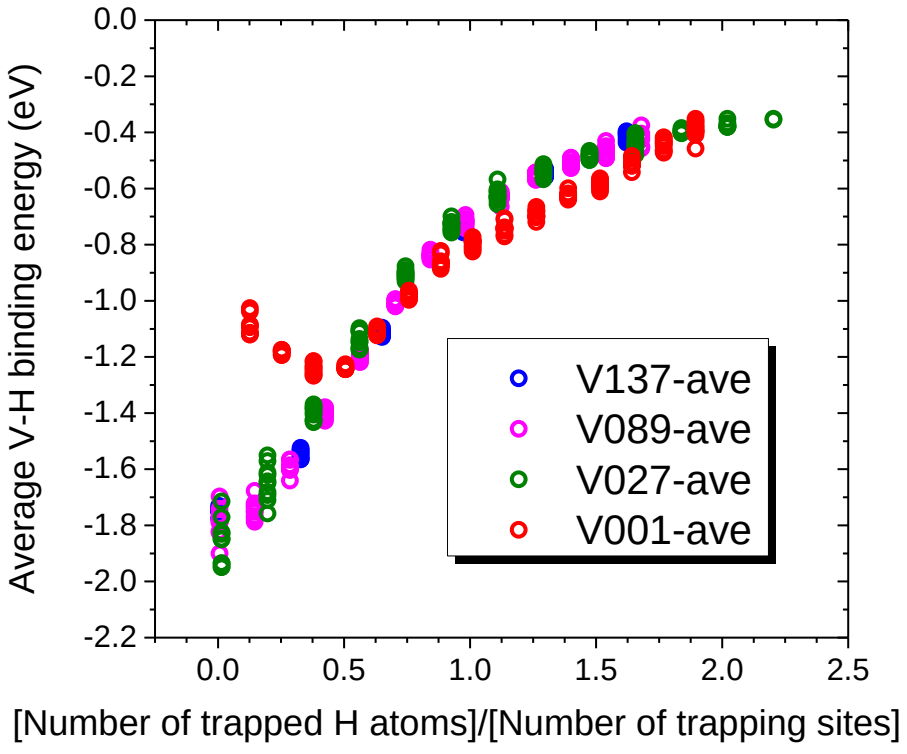
2.2. Potential model development for W-H systems -validation in W-H interaction-

	Exp.	DFT	BOP-Juslin	BOP-Lee	EAM-this
H solution energy	1.1	0.97	0.85	1.03	-1.35
[Tri-site] - [T-site]	0.25	0.205	0.2	0.2	0.215
[O-site] - [T-site]		0.39	0.2	0.32	0.430
V1H1 interaction energy		-1.24	-0.59	-2.00	-1.12

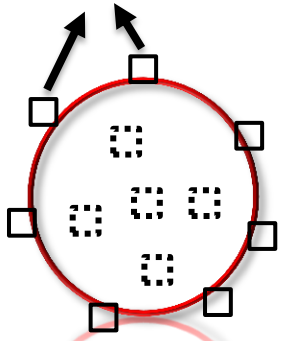


2.3. Effects of vacancy clustering in bcc-W





effective vacancies



- ✓ As the cluster size increases, the trapping capacity decreases in proportional to $n^{2/3}$
- ✓ As the cluster size increases, the maximum trapping energy increases and then soon saturate to be around that for H on surface.

Contents of this presentation

1. Effects of grain boundaries (GBs) on H behavior in W

2. Effects of vacancy clustering on H behavior in W

3. Development of a code to simulate tritium behavior in damaged W

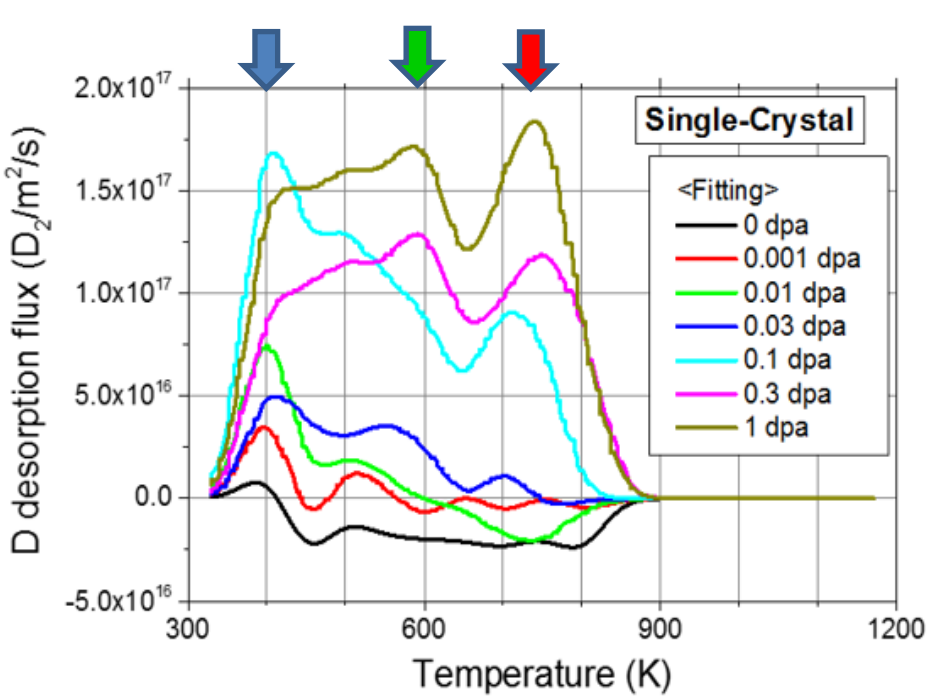
3. Development of a code to simulate tritium behavior in damaged W -kinetic models to be implemented in the code-

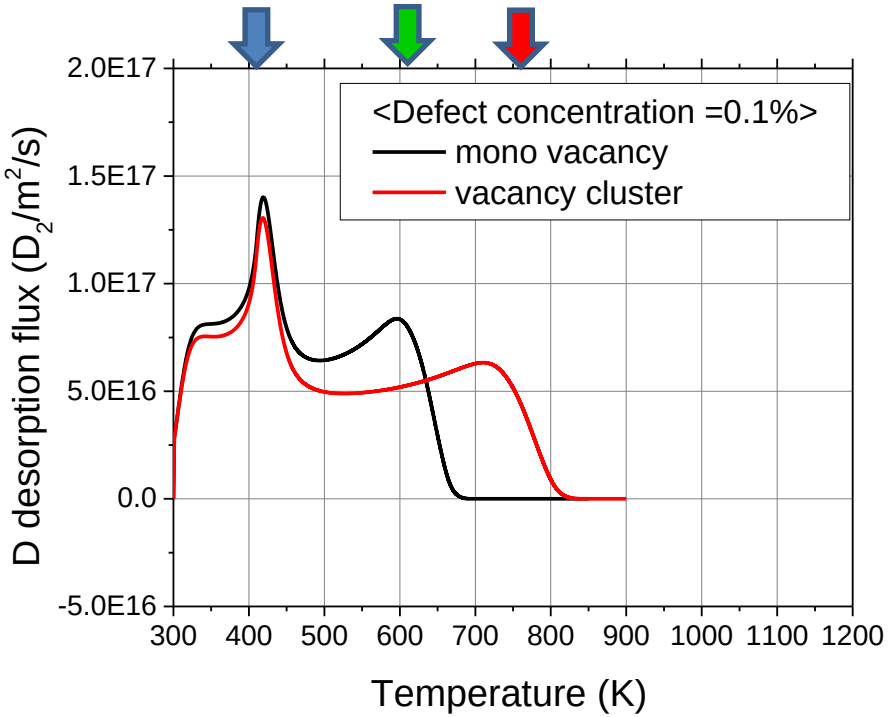
We have recently started to develop a rate-theoretical model to simulate T behaviors in damaged W based on constructed/reported models.

Region	Process	Quality	Method
Surface	Implantation	Δ	Experiment
	Desorption	Δ	experiment
Bulk	Diffusion	○	QM, KMC
	V	○	QM, KMC
	V-cluster effect	○	MD
	Grain boundary effect	○	QM, Thermodynamic model
	dislocations	Δ	QM/MD, Extension of GB effect model
	Radiation defect formation	○	MD
	Defect evolution	-	

3. Development of a code to simulate tritium behavior in damaged W -a benchmark test and application-

- ✓ Experimental data were obtained with single crystals by collaboration with Univ. Tokyo (2.8 MeV W irradiation), and Shizuoka University (TDS experiment).
- ✓ Deuterium ion was implanted by 1keV D_2^+ irradiation with a flux of 1×10^{18} $D/m^2/s$ up to 1×10^{22} D/m^2 at room temperature.
- ✓ Parameters for simulations in our code are defect types (vacancy, what kind of vacancy clusters, etc) and concentrations.





Summary and future works

1. Effects of grain boundaries (GBs) on H behavior in W

- ✓ $E_{bind\text{-}GB}$ = 1.0 eV; $E_{dif\text{-}GB}$ = 0.40 eV
- ✓ GB effects were (unintentionally) considered in many previous studies by using $E_{dif\text{-}lat}$ = 0.39 eV.

2. Effects of vacancy clustering on H behavior in W

- ✓ As the cluster size increases, the trapping capacity decreases in proportional to $n^{2/3}$
- ✓ As the cluster size increases, the maximum trapping energy increases and then soon saturate to be around that for H on surface (1.9-2.0 eV).

3. Development of a code to simulate tritium behavior in damaged W

- ✓ We have started the development. It would be very nice if there are a set of benchmark tests to validate the code….

Summary and future works

(1) Surface processes

- ✓ Reflection coefficient (e.g. blocking effect)
- ✓ Desorption kinetics
- ✓ Adsorption/absorption kinetics

(2) Formation of H_2 gas inside vacancy clusters