Development of a potential model for tritium behavior in tungsten

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✓ This study is performed under IAEA-CRP "Plasma-Wall Interaction for Irradiated W and W Alloys in Fusion Devices".

✓ This study is supported by NRF in Korea, as "Development of tritium inventory evaluation code for damaged tungsten" project.

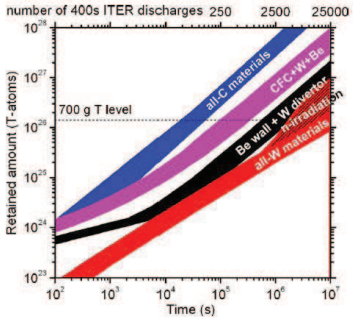
✓ The calculations in this study were carried out using HELIOS supercomputer system at the Computational Simulation Center of the International Fusion Research Center (IFERC-CSC) in Japan.

Background: tritium accumulation in PFC (1/2)

Tritium accumulation in plasma facing components (e.g. W) is considered as a key fusion engineering issue, because

(1) it affects the feasibility and economy of tritium fuel cycle and

(2) the accumulation amount is vital information to make a plasma operation scenario that meets a radiation-safety regulation limit.



*J. Roth et al., Plasma Phys. Control. Fusion **50** (2008) 103001.

Background: tritium accumulation in PFC (2/2)

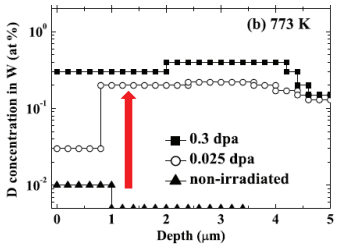
The difficult points in tritium accumulation phenomena are:

(1) Tritium accumulation is largely affected by defect concentration and structure,

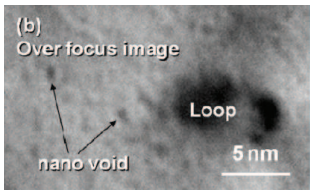
(2) Defect concentration and structure evolve during reactor operation.

Thus, we also need to consider lattice defect behaviors and the effect of defects on tritium behavior.

[Figure] Tritium retention increase due to radiation defects



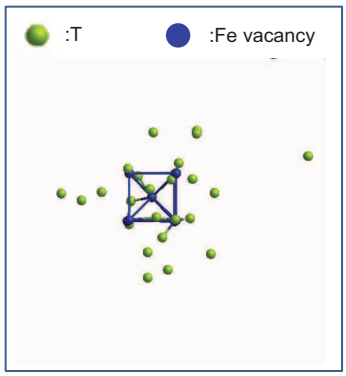
[Figure] Defect cluster (nano-void, loop) formation in irradiated W



*Y. Hatano et al., Nucl. Fusion 53 (2013) 073006.
*H. Watanabe et al., J. Nucl. Mater. 455 (2014) 51.

Motivation and Objectives (1/4) -MD simulation for modeling-

✓ Classical molecular dynamics (MD) simulations should be a vital tool for "tritium in damaged tungsten" study, because we need to understand the evolution of systems which should contain hydrogen-defect complexes and their complicated interactions.



A possible modeling approach ....

✓ (step-1) MD simulation for tritium-defect dynamics in an "imaginary" system (but enough close to real one)

✓ (step-2) Establish rate equations in comparison with MD results

✓ (step-3) Improve rate-equation parameters by using quantum mechanical calculation (DFT)

✓ (step-4) Solve the rate equations to simulate tritium and defect evolution

Motivation and Objectives (2/4) -potential model-

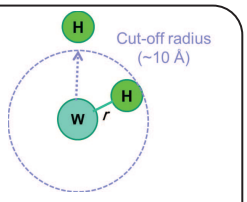
To prepare an appropriate "imaginary" system, we need to prepare a good potential model, which describes interatomic interactions in the system.

(i) **Two-body model** [→ ionic materials]: a function of ***r*** (interatomic distance)

Buckingham potential model

$$U(r) = \frac{q_1 q_2}{r} + A\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}.$$

parameters: A, ρ, C, (q_1, q_2)



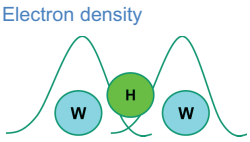
(ii) **Embedded atom model (EAM)** [→ metals]: a kind of many body interaction

$$U_{tot} = \frac{1}{2}\sum_{ij} V(r_{ij}) + \sum_i f(\rho_i).$$

$$f(\rho_i) = \sqrt{\rho_i}, \quad \text{Embedded energy function}$$

$$\rho_i = \sum_{j\neq i} A^2\phi(r_{ij}). \quad \text{Electron density function}$$

3 parameters including A



Motivation and Objectives (3/4) -existing potential models for W-H system

✓ 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].

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

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

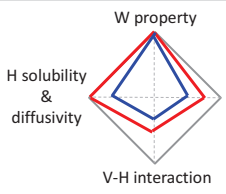
Motivation and Objectives (4/4) -W-H BOP potential quality-

✓ In hydrogen-vacancy interaction energy in W, a large error is brought in both cases: underestimation in BOP-1 and overestimation in BOP-2.

Trapping energy (eV per H)	V_1H_1	V_1H_2	Solution energy
Juslin-BOP	0.59	0.59	0.85
Li-BOP	2.0	2.0	1.03
DFT	1.2	1.2	1.1

*DFT: D. Kato, J. Plasma Fusion Res. SERIES, 8 (2009) 404.

Considering the large error in V-H interaction energy, the quality of both BOP models may be insufficient to simulation "tritium behavior in damaged tungsten" for most phenomena.



Juslin-BOP
Li-BOP

[Short-term objective]
To develop a potential model, which is adequately accurate to simulate "tritium in damaged tungsten".

Then, how to make it? -methods for potential model development -

(1) Defining fitting targets

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

(2) Defining potential formula (and parameters-fitting procedure)

Model frame
- ✓ Two-body
- ✓ Bond-order
- ✓ Embedded-atom

→ Function form (for example in 2 body)
- ✓ Morse
- ✓ Buckingham

There are two main directions to improve the potential formula:

(i) Establish a sophisticated function based on chemical/physical considerations
- ✓ Two-body, EAM, Tersoff-Brenner (BOP), etc.
- ✓ [drawbacks] The available functional space is limited.

(ii) Establish based on mathematical methodologies
- ✓ General purpose atomistic potentials [Review: Eur. Phys. J. B 87 (2014) 152] such as with Gaussian process regression [Phys. Rev. Lett. 104, 136403 (2010) by Dr. Csányi].
- ✓ [drawbacks] More mathematical may cause less physical/chemical meanings

Our approach and target

<Direction-1>
Based on classical theories of Physics and Chemistry
✓ BOP, EAM, etc.

<Direction-2>
Based on mathematical techniques in combination with accurate reference data
✓ Neural network, GAP, etc.

[Our approach] Try to compromise these two points:
(1) using a physically/chemically-sound framework
✓ EAM (+two-body)
(2) applying a more mathematical approach in function parameterization.
✓ Fourier series expansion

The target of our potential model is to create a W-H potential model which
- ✓ Better describes (i.e. closer to DFT) tritium-defect interaction (e.g. tritium trapping energy) than the two existing BOP models.
- ✓ Better describes system dynamics, not only some key energies like tritium trapping energy.

Research steps

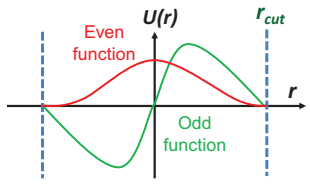
1. Check the validity of methodology for tow-body model frame, where we utilize the concept of Fourier series expansion.
   ✓ The validation test is performed with magnesium oxide (MgO).
2. Extend the methodology to EAM model.
3. Apply the methodology to W system.
4. Apply the methodology to W-H system.
5. (If not adequate enough) Add further terms to expand the available functional space, etc.

1. Two-body potential based on Fourier-series expansion -functional form-

✓ The model function is composed with a finite number of cosine functions having various periodicities:

$$U_{pot}(r) = \sum_{i=0}^{N} a_i \times \cos\left(\frac{i\pi r}{r_{cut}}\right) \quad \left[+\frac{q_1 q_2}{r}\right]$$

where r is an interatomic distance between two concerned atoms, a_i is a set of cosine coefficient to be adjusted, and r_{cut} is the cutoff radius of this potential model (10 Å).



With an even function, the derivative is always converged to 0 at the cutoff radius.

1. Two-body potential based on Fourier-series expansion -parameter optimization-

The evaluation function that should be minimized is:

$$P(a_0, a_1, \ldots, a_N) = \sum_{s}^{\#\ of\ systems} \left\{ \left[U_{s,AIMD} - U_{s,pot}\right]^2 + \sum_{i=1}^{\#\ of\ Atoms} \left[F_{s,i,AIMD} - F_{s,i,pot}\right]^2 + \sum_{i=1}^{6} \left[S_{s,i,AIMD} - S_{s,i,pot}\right]^2 \right\}$$

Then we solve the linear simultaneous equation of the followings:

$$\frac{\partial P}{\partial a_i} = 0 \qquad \text{where } i \text{ is from 0 to } N \text{ (the number of cosine functions)}$$

If $N \to \infty$, it becomes a Fourier series expansion. Due to the completeness, we can obtain "the best function", which is defined as a function having the minimum discrepancy from the targets.

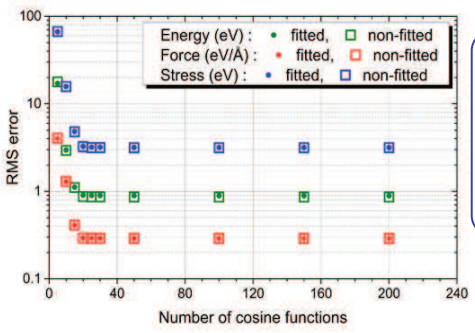
We need to check
(i) error convergence with respect to the number of basis functions (N)
(ii) the performance of the constructed model in statics/dynamics simulations.

1. Two-body potential based on Fourier-series expansion -reference data for fitting: MgO case-

- ✓ *First-principles molecular dynamics* (FIMD) simulations using VASP code:
  - ✓ DFT-PBE with plane-wave basis set and PAW potential.
  - ✓ The MD ensemble is *NVT*.
- ✓ Convergence over the plane-wave cutoff energy and k-point sampling grid were confirmed to about 0.01 eV in relative energy and 0.05 eV/Å in force acting on each atom.
- ✓ In total, 150000 FIMD trajectories of $Mg_{64}O_{64}$ system (supercell of 4x4x4 primitive) were gathered in 300-6000 K.
  - ✓ 150000 energy data; 150000×6 stress data; 150000×128 ×3 force data.

1. Two-body potential based on Fourier-series expansion -Convergence over the number of cosine functions

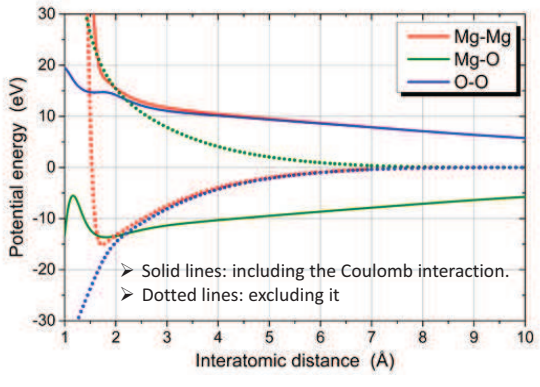
- ✓ This figure shows RMS error convergence with respect to the number of cosine functions involved in the model: 25 cosine functions are enough.
- ✓ Consequently, it is reasonable to say that the method can create the "best function" within two-body model frame (regarding the error from reference data).



Intrinsic errors in two-body frame (with full charge model)
- ➢ 0.88 eV/system in energy (6.8 meV/atom)
- ➢ 0.29 eV/Å in force
- ➢ 3.2 eV in stress

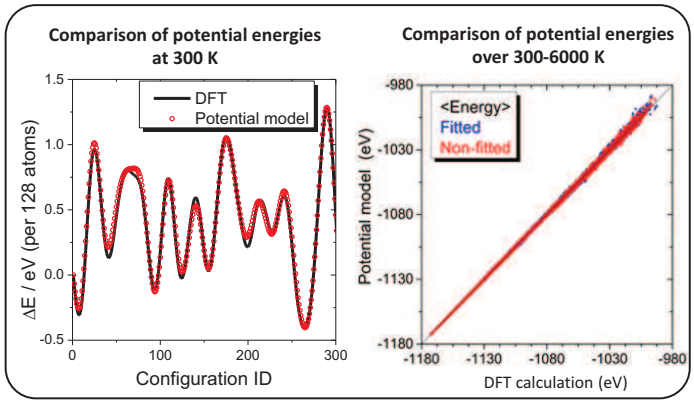
1. Two-body potential based on Fourier-series expansion -shape of constructed potential models-

- ✓ The figure shows the shapes of the constructed potential energy functions.
- ✓ The potential curves are quite smooth (fluctuations is at the order of 0.001 eV), converge nicely at r_{cut} (=10 Å), and are of physically reasonable shapes.



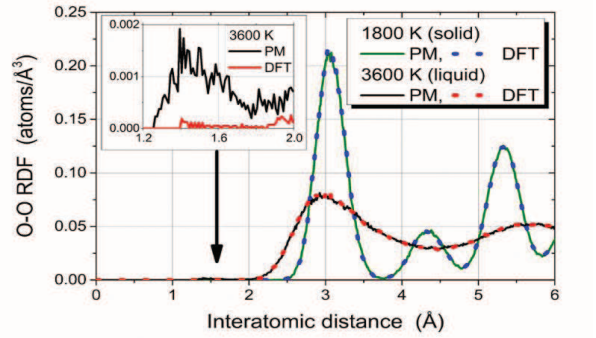
1. Two-body potential based on Fourier-series expansion -Comparison in energy with DFT data-

- ✓ The energies, forces and stresses determined with the constructed potential model well agree with DFT results.



1. Two-body potential based on Fourier-series expansion -performance in simulation-1: RDF-

- ✓ Radial distribution functions (RDF) show good agreement with AIMD results, including both solid and liquid phases. The figure shows O-O RDF at 1800 K (solid) and 3600 K (liquid).
- ✓ The formation of oxygen molecule ion (O_2^-) is also reproduced, although quantitative agreement is bad, which may be a limitation of two-body model.



2. Extension to EAM term -Improvement of mechanical property in MgO-

- ✓ Then, we include EAM term, where embedded energy functions are expanded with cosine series while electronic density functions are fixed.

$$E_{2BODY+EAM} = U(r) + F[\rho(r)]$$

- ➢ $U(r)$: cosine series
- ➢ $F(\rho)$: cosine series
- ➢ $\rho(r)$: no optimization at present

		Exp.	DFT	Potential model (N=50)	
				Two-body pot	+ EAM term
Lattice constant (Å)		4.207	4.261	4.261	4.261
Elastic constants (GPa)	C_{11}	297.0	270.3	267.5	272.4
	C_{12}	95.2	88.5	86.2	89.1
	C_{44}	155.7	140.6	86.2	138.8
Melting point (K)		3098	-	2600-2800	not yet

3. Application to tungsten -Reference DFT data for W-H potential model-

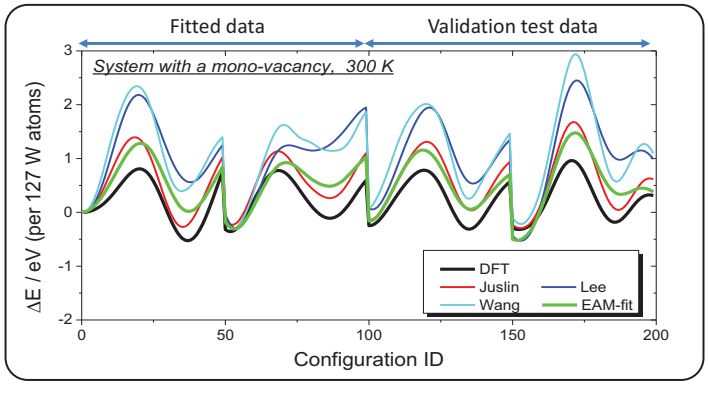
- ✓ As reference data for W-H interaction in damaged tungsten, we have been accumulating DFT data on the following structures.

	Methods	Remarks
bcc-W bulk	MD/MS	Incl. energy response related to elastic constants
bcc-W surface	MD/MS	(100), (110), (111), (211)
bcc-W with vac.	MD/MS	Up to which cluster size?
bcc-W with SIA	MD/MS	Up to which cluster size?
bcc-W with dislocation	MD/MS	Which type?
H in W bulk	MD/MS	Up to which concentration
H in W surface	MD/MS	Up to which concentration; oversaturation.
H in W with defects	MD/MS	Which defect types?
H migration	MS-NEB	In which systems?
Defect migration	MS-NEB	Which defect types?
W polymorphs	MS	fcc, sc, molecules (W_2)
Related molecules	MS	H_2, WH, ….

3. In a defective crystal (including 1 mono-vacancy) at 300 K

There may be limitations in description of defect dynamics (e.g. vacancy) for W, at least in EAM model. To overcome this, we may need

- ✓ (1) enrich the functional form (incl. optimization of electron density function)
- ✓ (2) just focus on key energies such as V-H interaction energy.



1. Two-body potential based on Fourier-series expansion -performance in simulation-2: mechanical property-

- ✓ In mechanical property, fair agreement with experiment and DFT result is also achieved; but not so excellent due to the limitation of two-body framework.
  - ✓ Cauchy relation: $C_{12}=C_{44}$ is wrongly kept.

		Exp.	DFT	Potential model (N=50)
				Two-body potential
Lattice constant (Å)		4.207	4.261	4.261
Elastic constants (GPa)	C_{11}	297.0	270.3	267.5
	C_{12}	95.2	88.5	86.2
	C_{44}	155.7	140.6	86.2
Melting point (K)		3098	-	2600-2800

Research steps

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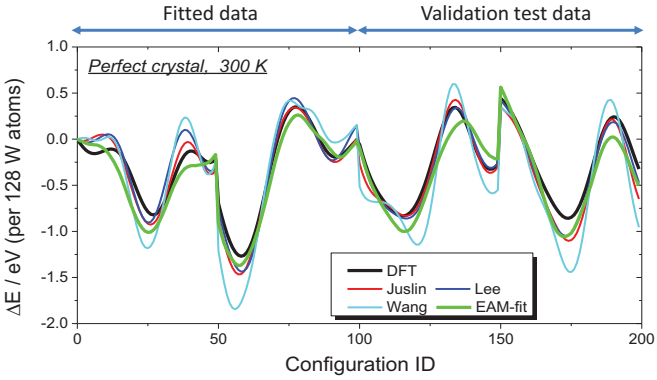
2. Extend the methodology to EAM model.
3. Apply the methodology to W system.
4. Apply the methodology to W-H system.
5. (If not adequate enough) Add further terms to expand the available functional space.

3. Comparison in potential energy in perfect crystal at 300 K



*1:[BOP] N. Juslin et al., J. Appl. Phys. 98 (2005) 123520.
*2:[BOP] X.-C. Li et al., J. Nucl. Mater. 408 (2011) 12.
*3: [EAM] J. Wang et al., Modelling Simul. Mater. Sci. Eng. 22 (2014) 015004.

Another approach ongoing, GAP model (1/2)

Another approach is also ongoing with Gaussian Approximation Potential (GAP) model by Prof. Csányi of Cambridge.

<Direction-1>
Based on classical theories of Physics and Chemistry
✓ BOP, EAM, etc.

<Direction-2>
Based on mathematical techniques in combination with DFT reference data
✓ **Neural network, GAP, etc.**

[Our approach] Try to compromise these two points:
(1) using a physically-sound framework
✓ EAM (+two-body)
(2) applying a more mathematical approach into function parameterization.
✓ Fourier series expansion

Another approach ongoing, GAP model (2/2)

- ✓ GAP method is already applied to W [W.J. Szlachta et al., Phys. Rev. B **90**, 104108, (2014)]
- ✓ Now we are trying to extend it to W-H, possibly W-He as well.

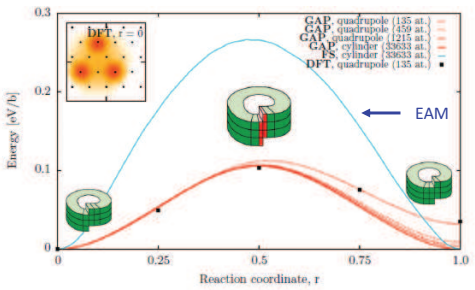


FIG. 4. (Color online) Top: The structure of the screw dislocation along the minimum energy path as it glides. Bottom: Peierls barrier evaluated using GAP and FS potentials, along with single-point checks with DFT in the 135-atom quadrupole arrangement.

Summary

We have been developing a potential model for W-H system, with trying to keep maintaining chemical/physical meanings in the model frame while to applying more mathematically flexible functions in the model.

- ✓ We examined a methodology to construct a two-body potential model based on a Fourier cosine-series expansion.
  - ✓ For MgO, we confirmed this method works appropriately and expects to give us “best” function within two-body frame.
- ✓ We have been extending the methodology to EAM model.
  - ✓ In MgO, we see clear improvement of mechanical property.
  - ✓ In W, there may be limitations in description of defects such as vacancy.
    - ✓ To overcome this, we may need to
      - (1) enrich the functional form (incl. optimization of electron density function) or/and
      - (2) just focus on key energies such as V-H interaction energy.