Maturity for Molecular Dynamics (MD) Studies of Hydrogen Embrittlement in Fe-C Based Steels

SAND2019-8194C

Xiaowang Zhou, Michael E. Foster, Joseph Allen Ronevich, Christopher W San Marchi

Sandia National Laboratories

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Discussions with A. J. Lew, W. Cai, M. Asta, T. M. Devine, and P. Hosemann are greatly appreciated. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Criteria of Good Fe-C-H Potential

- stable α-Fe, γ-Fe, δ-Fe, and orthorhombic Fe_3C in MD
- energy, volume, and elastic constants of various phases
- energy and swelling volumes of C and H in α-Fe, γ-Fe
- diffusion energy barriers of C and H in α-Fe, γ-Fe
- stacking fault energy of α-Fe, γ-Fe
- hydrogen-vacancy interaction energy in α-Fe, γ-Fe
- hydrogen effects on surface energy of α-Fe, γ-Fe

α-γ-δ phase transformation and Fe3C are challenging

Literature Review

- many EAM, MEAM, BOP, pair, hybrid potentials surveyed
- all potentials are for Fe-C, Fe-H, or C-H binary systems
- only MEAM and BOP are suitable for Fe_3C
- no C-H MEAM exists to construct a Fe-C-H MEAM
- Fe-C, Fe-H, C-H BOPs exist to construct a Fe-C-H BOP
- Two Fe-C-H BOPs were constructed from refs. [1-6]

[1] Kuopanportti et al, Comput. Mater. Sci., 111, 525 (2016)
[2] Muller et al, J. Phys.: Condens. Matter, 19, 326220 (2007)
[3] Juslin et al, J. Appl. Phys., 98, 123520 (2005)
[4] Brenner, Phys. Rev. B, 42, 9458 (1990)
[5] Henriksson et al, Phys. Rev. B, 79, 144107 (2009)
[6] Henriksson et al, J. Phys.: Condens. Matter, 25, 445401 (2013)

Polymorphic Pairstyle in LAMMPS

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\left(1-\delta_{ij}\right)\cdot U_{IJ}\left(r_{ij}\right) - \left(1-\eta_{ij}\right)\cdot F_{IJ}\left(\mathrm{X}_{ij}\right)\cdot V_{IJ}\left(r_{ij}\right)\right]$$

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}(r_{ik})\cdot G_{JIK}(\theta_{jik})\cdot P_{IK}(r_{ij} - \xi_{IJ}\cdot r_{ik})$$

ξ_{IJ}: parameter

$\delta_{ij} = 1\ (i = j)$ or $0\ (i \neq j)$

$\eta_{ij} = \delta_{ij}$ or $\eta_{ij} = 1 - \delta_{ij}$

Potential is defined by η_{ij}, ξ_{IJ}, and the six functions $U_{IJ}(r)$, $V_{IJ}(r)$, $P_{IJ}(\Delta r)$, $W_{IJ}(r)$, $F_{IJ}(X)$, and $G_{JIK}(\theta)$ (for all species I, J, K = 1, 2, …)

X. W. Zhou, M. E. Foster, R. Jones, P. Yang, H. Fan, and F. P. Doty, J. Mater. Sci. Res., 4, 15 (2015).

Generalized Stillinger-Weber Polymorphic Potential

Polymorphic Potential

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\left(1-\delta_{ij}\right)\cdot U_{IJ}\left(r_{ij}\right)-\left(1-\eta_{ij}\right)\cdot F_{IJ}\left(X_{ij}\right)\cdot V_{IJ}\left(r_{ij}\right)\right]$$

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}(r_{ik})\cdot G_{JIK}(\theta_{jik})\cdot P_{IK}(r_{ij}-\xi_{IJ}\cdot r_{ik})$$

Generalized Stillinger-Weber Potential

$$E = \frac{1}{2}\sum_{i}\sum_{j\neq i}\left[V_{IJ}^{R}\left(r_{ij}\right)-V_{IJ}^{A}\left(r_{ij}\right)+u_{IJ}\left(r_{ij}\right)\sum_{k\neq i,j}u_{IK}\left(r_{ik}\right)\cdot g_{JIK}\left(\theta_{jik}\right)\right]$$

$$\begin{cases} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = V_{IJ}^{R}(r) - V_{IJ}^{A}(r) \\ V_{IJ}(r) = u_{IJ}(r) \\ F_{IJ}(X) = -X \\ P_{IJ}(\Delta r) = 1 \\ W_{IJ}(r) = u_{IJ}(r) \\ G_{JIK}(\theta) = g_{JIK}(\theta) \end{cases}$$

Stillinger-Weber Polymorphic Potential

Generalized

$$\begin{cases} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = V_{IJ}^{R}(r) - V_{IJ}^{A}(r) \\ V_{IJ}(r) = u_{IJ}(r) \\ F_{IJ}(X) = -X \\ P_{IJ}(\Delta r) = 1 \\ W_{IJ}(r) = u_{IJ}(r) \\ G_{JIK}(\theta) = g_{JIK}(\theta) \end{cases}$$

Original

$$\begin{cases} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = A_{IJ} \cdot \varepsilon_{IJ} \cdot \left(\frac{\sigma_{IJ}}{r}\right)^{q} \cdot \left[B_{IJ}\left(\frac{\sigma_{IJ}}{r}\right)^{p-q} - 1\right] \cdot \exp\left(\frac{\sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}}\right) \\ V_{IJ}(r) = \sqrt{\lambda_{IJ} \cdot \varepsilon_{IJ}} \cdot \exp\left(\frac{\gamma_{IJ} \cdot \sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}}\right) \\ F_{IJ}(X) = -X \\ P_{IJ}(\Delta r) = 1 \\ W_{IJ}(r) = \sqrt{\lambda_{IJ} \cdot \varepsilon_{IJ}} \cdot \exp\left(\frac{\gamma_{IJ} \cdot \sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}}\right) \\ G_{JIK}(\theta) = \left(\cos\theta + \frac{1}{3}\right)^{2} \end{cases}$$

Tersoff Polymorphic Potential

Polymorphic Potential

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\left(1-\delta_{ij}\right)\cdot U_{IJ}\left(r_{ij}\right)-\left(1-\eta_{ij}\right)\cdot F_{IJ}\left(X_{ij}\right)\cdot V_{IJ}\left(r_{ij}\right)\right]$$

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}(r_{ik})\cdot G_{JIK}(\theta_{jik})\cdot P_{IK}(r_{ij}-\xi_{IJ}\cdot r_{ik})$$

$$f_{c,IJ}(r) = \begin{cases} 1, & r \le r_{s,IJ} \\ \frac{1}{2}+\frac{1}{2}\cos\left[\frac{\pi(r-r_{s,IJ})}{r_{c,IJ}-r_{s,IJ}}\right], & r_{s,IJ} < r < r_{c,IJ} \\ 0, & r \ge r_{c,IJ} \end{cases}$$

$$\begin{cases} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 1 \\ U_{IJ}(r) = \frac{D_{e,IJ}}{S_{IJ}-1}\exp\left[-\beta_{IJ}\sqrt{2S_{IJ}}\left(r-r_{e,IJ}\right)\right]\cdot f_{c,IJ}(r) \\ V_{IJ}(r) = \frac{S_{IJ}\cdot D_{e,IJ}}{S_{IJ}-1}\exp\left[-\beta_{IJ}\sqrt{\frac{2}{S_{IJ}}}\left(r-r_{e,IJ}\right)\right]\cdot f_{c,IJ}(r) \\ F_{IJ}(X) = (1+X)^{-\frac{1}{2}} \\ P_{IK}(\Delta r) = \exp\left[2\mu_{IK}\cdot\Delta r\right] \\ W_{IK}(r) = f_{c,IK}(r) \\ G_{JIK}(\theta) = \gamma_{IK}\left[1+\frac{c_{IK}^2}{d_{IK}^2}-\frac{c_{IK}^2}{d_{IK}^2+\left(h_{IK}+\cos\theta\right)^2}\right] \end{cases}$$

Rockett-Tersoff Polymorphic Potential

$$
\begin{cases}
\eta_{ij} = \delta_{ij}, \xi_{IJ} = 1 \\
U_{IJ}(r) = \begin{cases} A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \le r_{s,1,IJ} \\ A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r) \cdot f_{c,1,IJ}(r), & r_{s,1,IJ} < r < r_{c,1,IJ} \\ 0, & r \ge r_{c,1,IJ} \end{cases} \\
V_{IJ}(r) = \begin{cases} B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \le r_{s,1,IJ} \\ B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r) + A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r) \cdot [1 - f_{c,1,IJ}(r)], & r_{s,1,IJ} < r < r_{c,1,IJ} \\ B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r) + A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \ge r_{c,1,IJ} \end{cases} \\
F_{IJ}(X) = \left[1 + (\beta_{IJ} \cdot X)^{n_{IJ}}\right]^{-\frac{1}{2n_{IJ}}} \\
P_{IK}(\Delta r) = \exp\left[\lambda_{3,IK} \cdot \Delta r^3\right] \\
W_{IK}(r) = f_{c,IK}(r) \\
G_{JIK}(\theta) = 1 + \frac{c_{IK}^2}{d_{IK}^2} - \frac{c_{IK}^2}{d_{IK}^2 + (h_{IK} + \cos\theta)^2}
\end{cases}
$$

J. Wang, and A. Rockett, Phys. Rev. B 43, 12571 (1991).

EAM Polymorphic Potential

Polymorphic Potential

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left[\left(1-\delta_{ij}\right)\cdot U_{IJ}\left(r_{ij}\right)-\left(1-\eta_{ij}\right)\cdot F_{IJ}\left(X_{ij}\right)\cdot V_{IJ}\left(r_{ij}\right)\right]$$

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}(r_{ik})\cdot G_{JIK}(\theta_{jik})\cdot P_{IK}(r_{ij}-\xi_{IJ}\cdot r_{ik})$$

EAM Potential

$$E = \sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N}\phi_{IJ}(r_{ij}) + \sum_{i=1}^{N}F_I\left(\sum_{k=i_1}^{i_N} f_K(r_{ik})\right)$$

$$\begin{cases} \eta_{ij} = 1-\delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = \phi_{IJ}(r) \\ V_{IJ}(r) = 1 \\ F_{II}(X) = -2F_I(X) \\ P_{IK}(\Delta r) = 1 \\ W_{IK}(r) = f_K(r) \\ G_{JIK}(\theta) = 1 \end{cases}$$

Characteristic Properties of the Two BOPs

	α-Fe				γ-Fe			
	BOP I	BOP II	exp.	DFT	BOP I	BOP II	exp.	DFT
a (Å)	2.89	2.89	2.87	2.83	3.65	3.65	3.64	3.64
E_c (eV)	-4.18	-4.18	-4.28	-5.215	-4.15	-4.15	-4.27	-5.140
C_{11} (GPa)	218	218	243	272	206	206	154	----
C_{12} (GPa)	142	142	138	155	141	141	122	----
C_{44} (GPa)	130	130	122	103	101	101	77	----
$E_{C,O}$ (eV)	-6.19	-6.58	----	-5.252	-7.24	-7.60	----	-5.177
$E_{C,T}$ (eV)	-5.87	-5.63	----	-5.236	-6.40	-5.49	----	-5.102
$E_{H,O}$ (eV)	-2.17	-2.17	----	-5.156	-2.58	-2.58	----	-4.988
$E_{H,T}$ (eV)	-2.27	-2.27	----	-5.159	-2.45	-2.45	----	-5.009
$\Omega_{C,O}$ (Å^3)	4.20	2.11	----	11.11	2.69	1.52	----	4.15
$\Omega_{C,T}$ (Å^3)	7.37	1.26	----	10.32	4.13	4.87	----	13.71
$\Omega_{H,O}$ (Å^3)	1.83	1.83	----	4.22	1.55	1.55	----	0.87
$\Omega_{H,T}$ (Å^3)	4.48	4.48	----	4.23	3.37	3.37	----	2.15
$\Delta E_{H\text{-}V}$ (eV)	-0.08	-0.08	----	----	-0.07	-0.07	----	----
E_{usf} (mJ/m^2)	895	895	----	470-590*	260	260	----	>280*
γ_0 (mJ/m^2)	94.0	94.0	2410	2370*	106.6	106.6	1950	2096*
γ_H (mJ/m^2)	90.8	89.1	----	----	104.6	104.6	----	----
$D_{0,C}$ (Å^2/ps)	57.95	59.87	81.0	----	135.3	288.6	7380.0	----
Q_C (eV)	0.72	0.96	0.86	----	1.28	1.80	1.65	----
$D_{0,H}$ (Å^2/ps)	2.76	2.70	11.0	----	223.9	224.6	81.0	----
Q_H (eV)	0.13	0.13	0.12	----	0.98	0.98	0.45	----

Literature experiments [1-13] and literature DFT calculations [14-16]

1. Donnay and Ondik, Crystal Data, 1973
2. Barin, Thermochemical Data of Pure Substances, 1993
3. Simmons, Single Crystal Elastic Constants and Calculated Aggregate Properties, 1965
4. Zarestky and Stassis, Phys. Rev. B, 35, 4500 (1987)
5. Hirth, Metall. Trans. A, 11, 861 (1980)
6. Hayashi and Shu, Solid State Phenom., 73–75, 65 (2000)
7. McLellan and Wasz, J. Phys. Chem. Solids, 54, 583 (1993)
8. Kucera and Stransky, Mater. Sci. Eng., 52, 1 (1982).
9. de Boer, et al, Cohesion in Metals: Transition Metal Alloys, 1988
10. Hirth and Lothe, Theory of Dislocations, 1982
11. Yan et al, Phys. Rev. B, 70, 174105 (2004)
12. Li et al, Philos. Mag., 96, 524 (2016)
13. Yu et al, Appl. Surf. Sci., 255, 9032 (2009)
14. Yan et al, Phys. Rev. B, 70, 174105 (2004)
15. Li et al, Philos. Mag., 96, 524 (2016)
16. Yu et al, Appl. Surf. Sci., 255, 9032 (2009)

Fe_3C Elastic Constants

	(Å)	(eV)	(GPa)								
	a/b/c	E_f	C_{11}	C_{22}	C_{33}	C_{44}	C_{12}	C_{13}	C_{23}	C_{55}	C_{66}
BOP I	5.09/6.52/4.50	-4.95	310	540	352	110	156	154	146	115	126
BOP II	4.96/6.47/4.48	-4.94	319	283	355	37	140	137	112	116	111
exp.	5.09/6.74/4.52	-5.00	----	----	----	----	----	----	----	----	----
DFT	5.03/6.72/4.48	-5.84	377	344	301	133	162	149	172	146	134

Experimental data from

1. Fasiska and Jefferey, Acta Crystallogr., 19, 463 (1965)
2. Barin, Thermochemical Data of Pure Substances, 1993

Arrhenius Diffusion Analysis

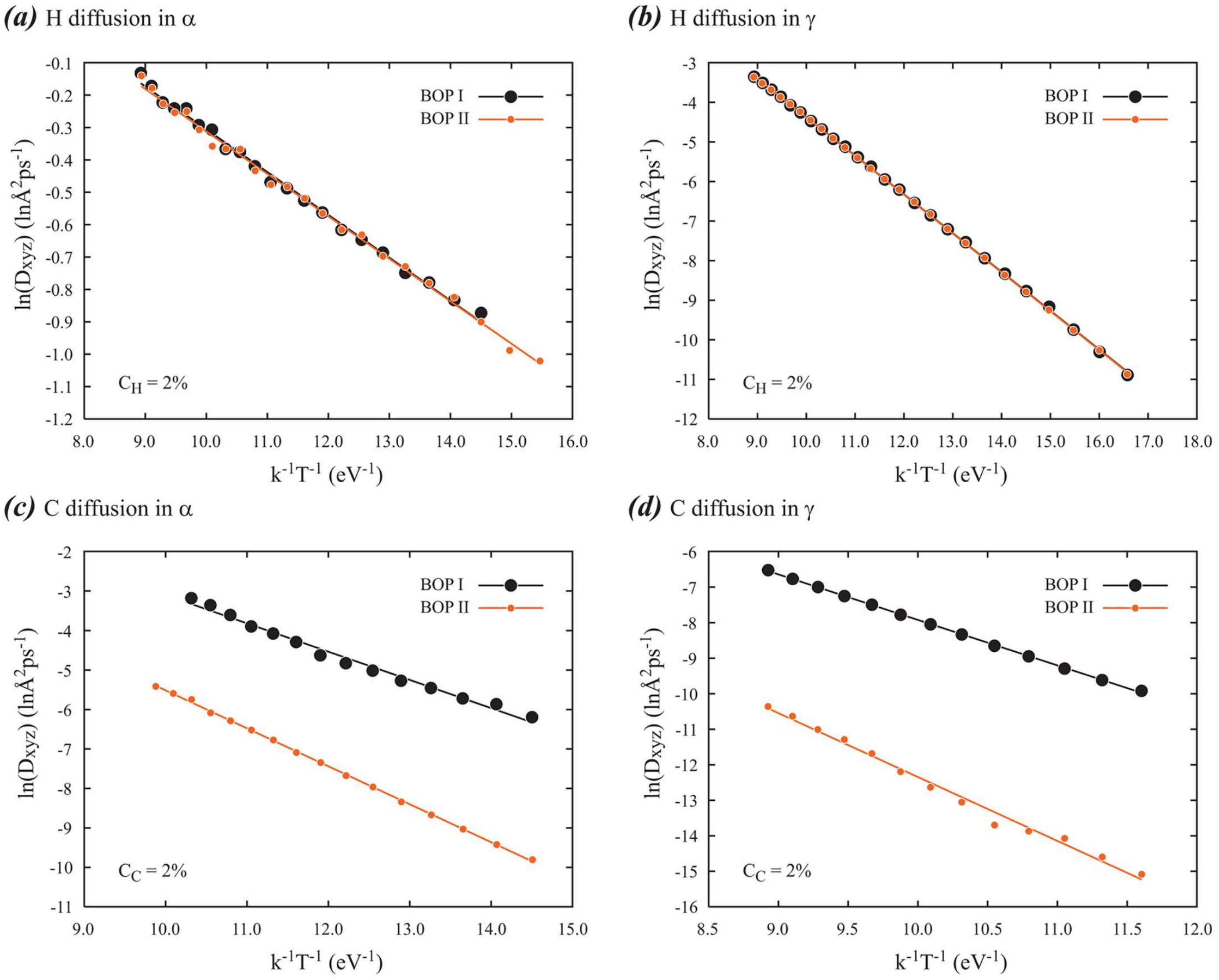
1. MD coordinates output every Δt for total time t >> Δt
2. $\Delta\alpha_{i,j}$: i-th diffusing atom, j-th measurement over kΔt period

$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = \frac{\sum_{i=1}^{N}\sum_{j=1}^{m+1-k}\left[\Delta\alpha_{i,j}(k\Delta t)\right]^2}{N(m+1-k)}$$

$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = 2D_{\alpha}t$$

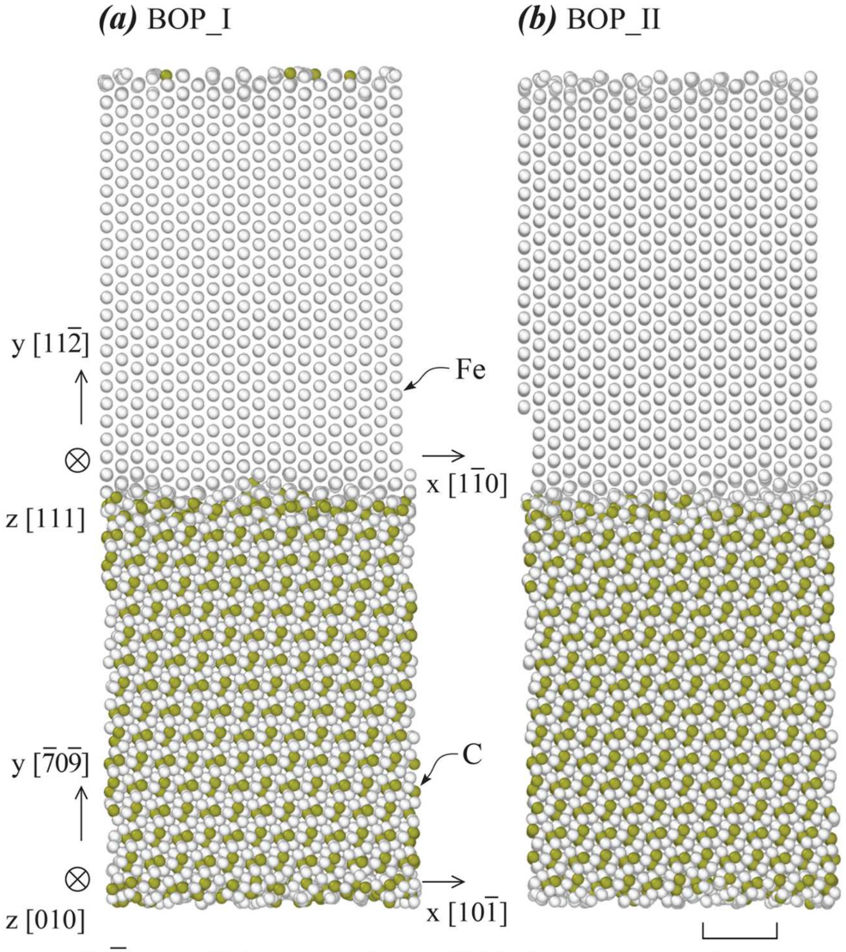
$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 4D_{xz}t$$

$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta y(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 6D_{xyz}t$$



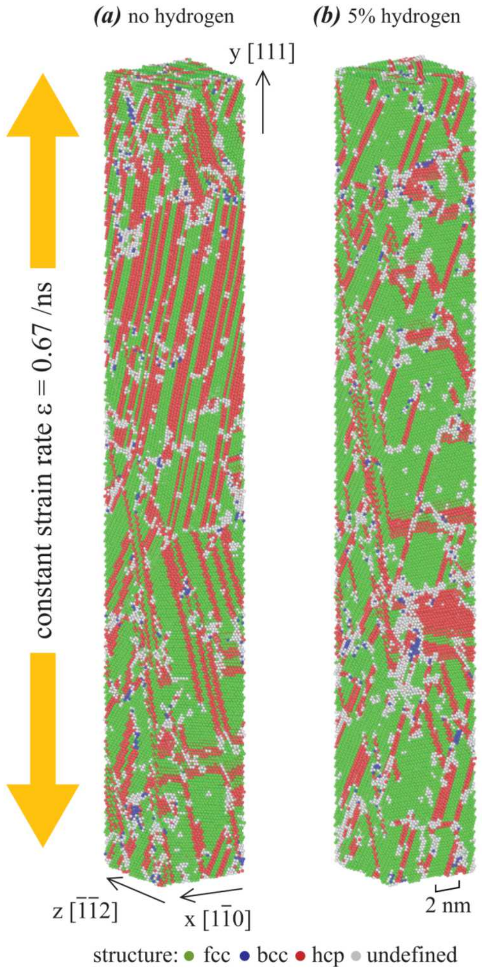
Stringent MD Tests

Stable α-Fe/Fe_3C Interfaces



(11$\bar{2}$)α-Fe//(101)cementite, at 300 K for 5 ns   1 nm

Stable Tensile Tests



Literature Results

- ❑ Capture α-γ-δ phase transformation (Muller et al, J. Phys., 19, 326220, 2007)
- ❑ Capture Fe_3C cementite, Fe_5C_2 Hagg carbide, and Fe_7C_3 Eckstrom-Adcock carbide, with stable temperature way above MEAM (Henriksson and Nordlund, Phys. Rev. B, 79, 144107, 2009)

Summary

- Currently only BOPs can be constructed for Fe-C-H systems without parameterization
- Two Fe-C-H BOPs have been constructed from literature binary Fe-C, Fe-H, and C-H BOPs in polymorphic form
- Molecular statistics indicate that both Fe-C-H BOPs can reasonably study mechanical properties
- Molecular dynamics indicate that they also permit α-γ-δ phase transformation, stable α-Fe/Fe_3C interfaces, and tensile test simulations