MMSNF

Interatomic potentials accuracy: how do they bridge the scales? U-Mo fuel case

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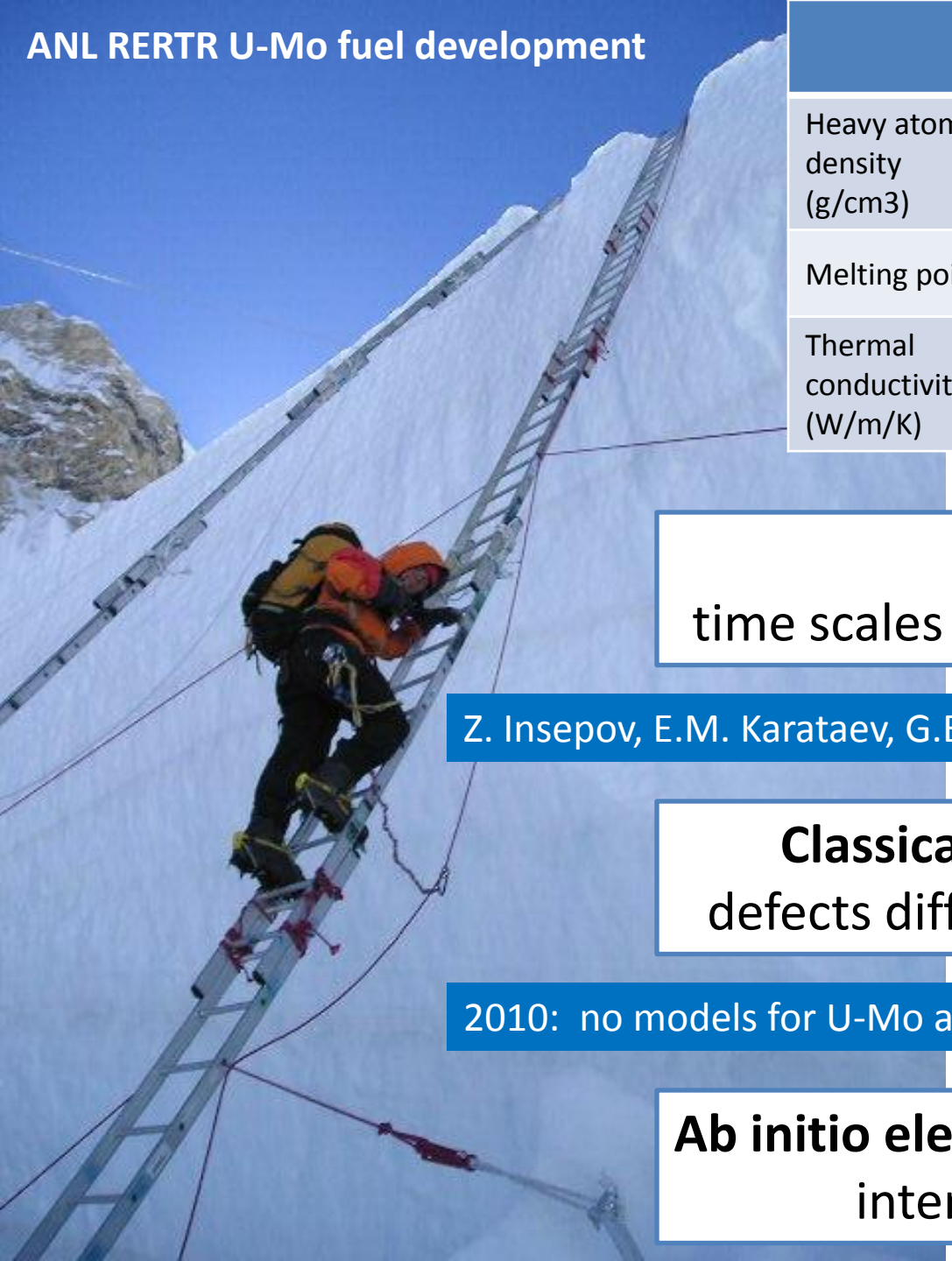
ANL RERTR U-Mo fuel development



	Carbide (U,Pu)C	Nitride (U,Pu)N	Oxide (U,Pu)O_2	Metal (U,Pu)Zr/Mo
Heavy atoms density (g/cm3)	12.95	13.53	9.75	14-15
Melting point	2420	2780	2750	~1100
Thermal conductivity (W/m/K)	16.5	14.3	2.9	14

Rate theory:
time scales of fuel performance codes

Z. Insepov, E.M. Karataev, G.E. Norman, *Z. Phys.* **20** (1991) 449–451

Classical molecular dynamics:
defects diffusion, recombination etc.

2010: no models for U-Mo alloy or pure U, no reliable model for Mo

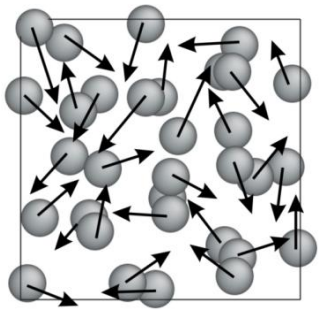
Ab initio electronic structure methods:
interatomic interactions

How would we create a potential model?

What method are we looking for:

1. **Method should be universal (any composition)**
2. **Extendable (impurities, fission products etc.)**
3. **Not limited by the lack of experimental data**
4. **Possibility to improve the accuracy**

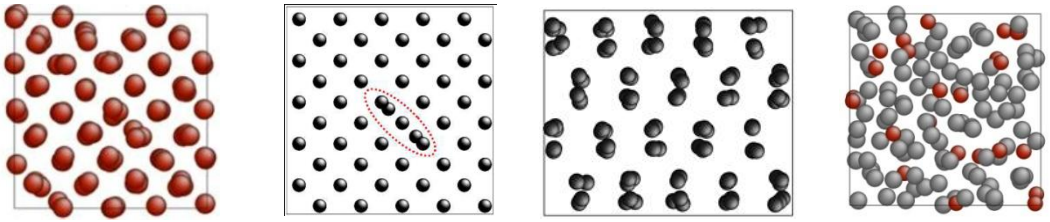
Construction of an MD potential based on DFT



$$E = \frac{\langle \varphi_n | \mathbf{H} | \varphi_n \rangle}{\langle \varphi_n | \varphi_n \rangle}$$

$$\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i}$$

DFT



bcc U **bcc, defect** **α-U** **U-Mo** melt

Force Matching $$Z_F = \sum_{i=1}^{N_a} \sum_{\alpha=x,y,z} \frac{(F_{i\alpha}^{EAM} - F_{i\alpha}^{VASP})^2}{(F_{i\alpha}^{VASP})^2}$$

EAM Potential $$U_i = \sum_{i<j} \varphi_{\alpha\beta}(r_{ij}) + F_\alpha(\bar{\rho}_i),\ \bar{\rho}_i = \sum_{j \neq i} \rho_\alpha(r_{ij})$$

Calculation of diffusion properties and Verification of the potential

Force-matching : F. Ercolessi, J.B. Adams 1994 *EPL* **26** 583 ***VASP:*** G. Kresse 1996 *Phys. Rev. B* **54** 11169

Potfit: P. Brommer, F. Gahler F 2006 *Phil. Mag.* **86** 753 ***EAM:*** M. Daw, M. Baskes 1984 *Phys. Rev. B* 2**9** 6443

Ab initio DFT calculations

VASP package (version 4.6)

PAW pseudopotentials

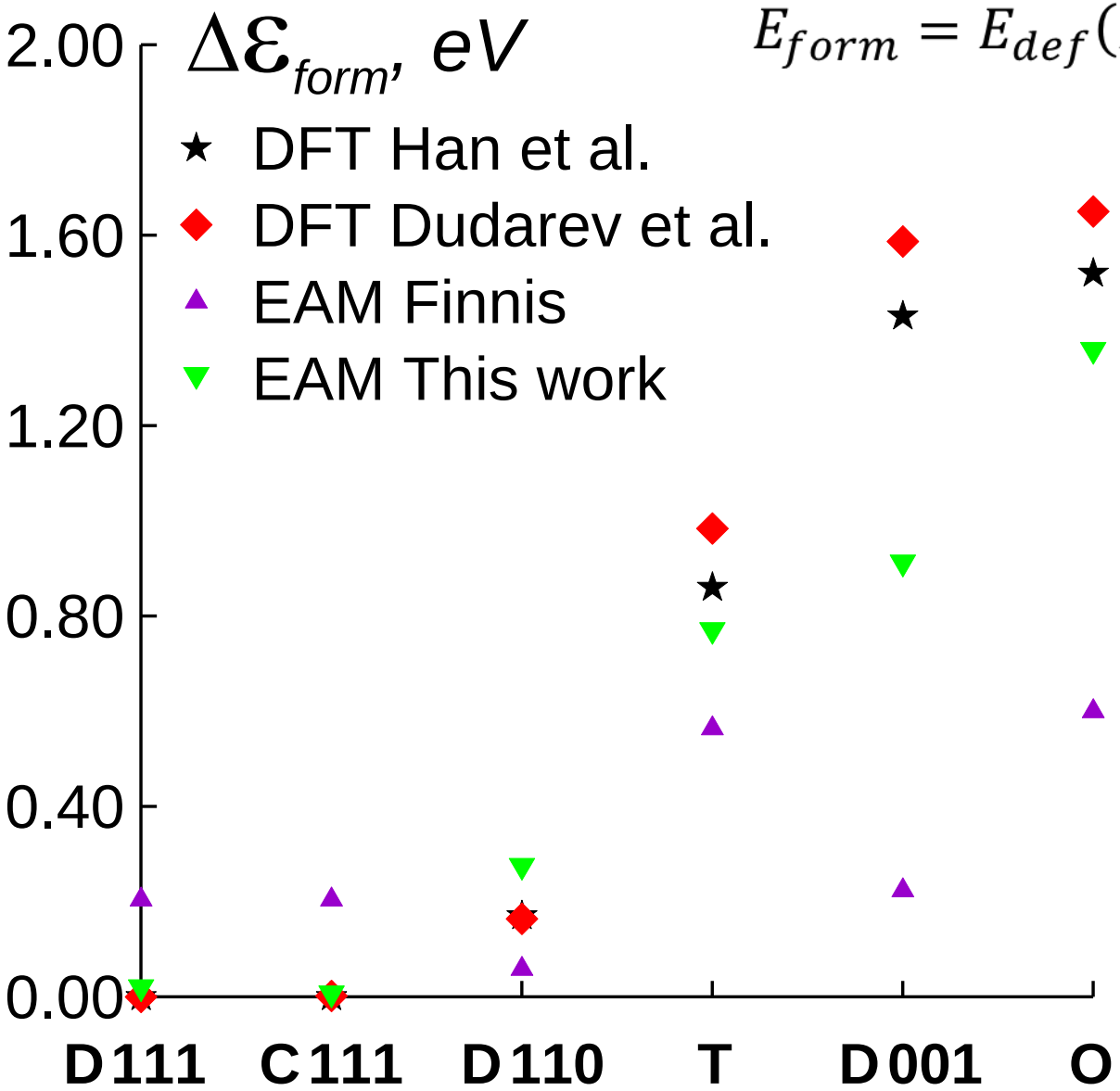
Plane-wave basis cut-off energy of 400 eV

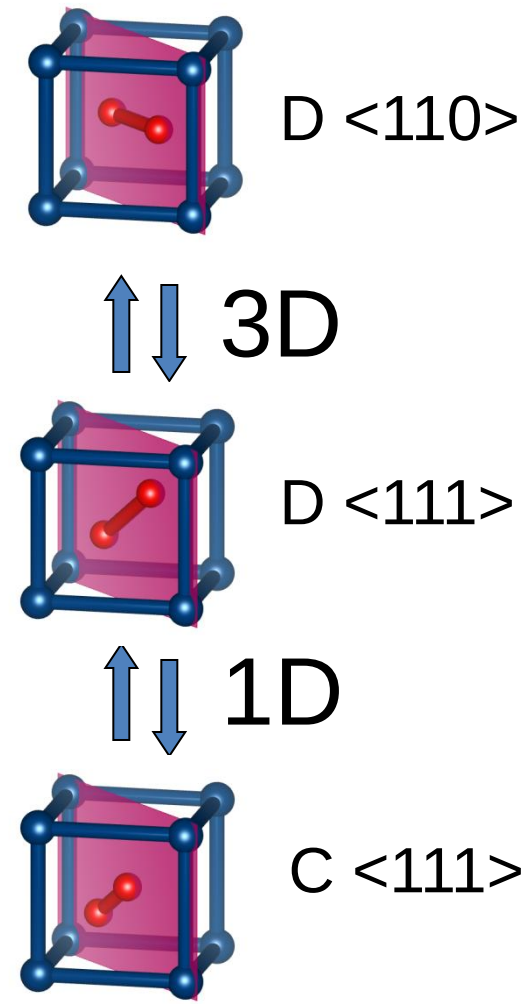
Brillouin zone is sampled with a $3 \times 1 \times 2$ k-point mesh for orthorhombic α-U and a $2 \times 2 \times 2$ mesh for all bcc structures and liquid

PW91 GGA approximation for the exchange-correlation functional

Interstitials in BCC Mo: Formation Energies

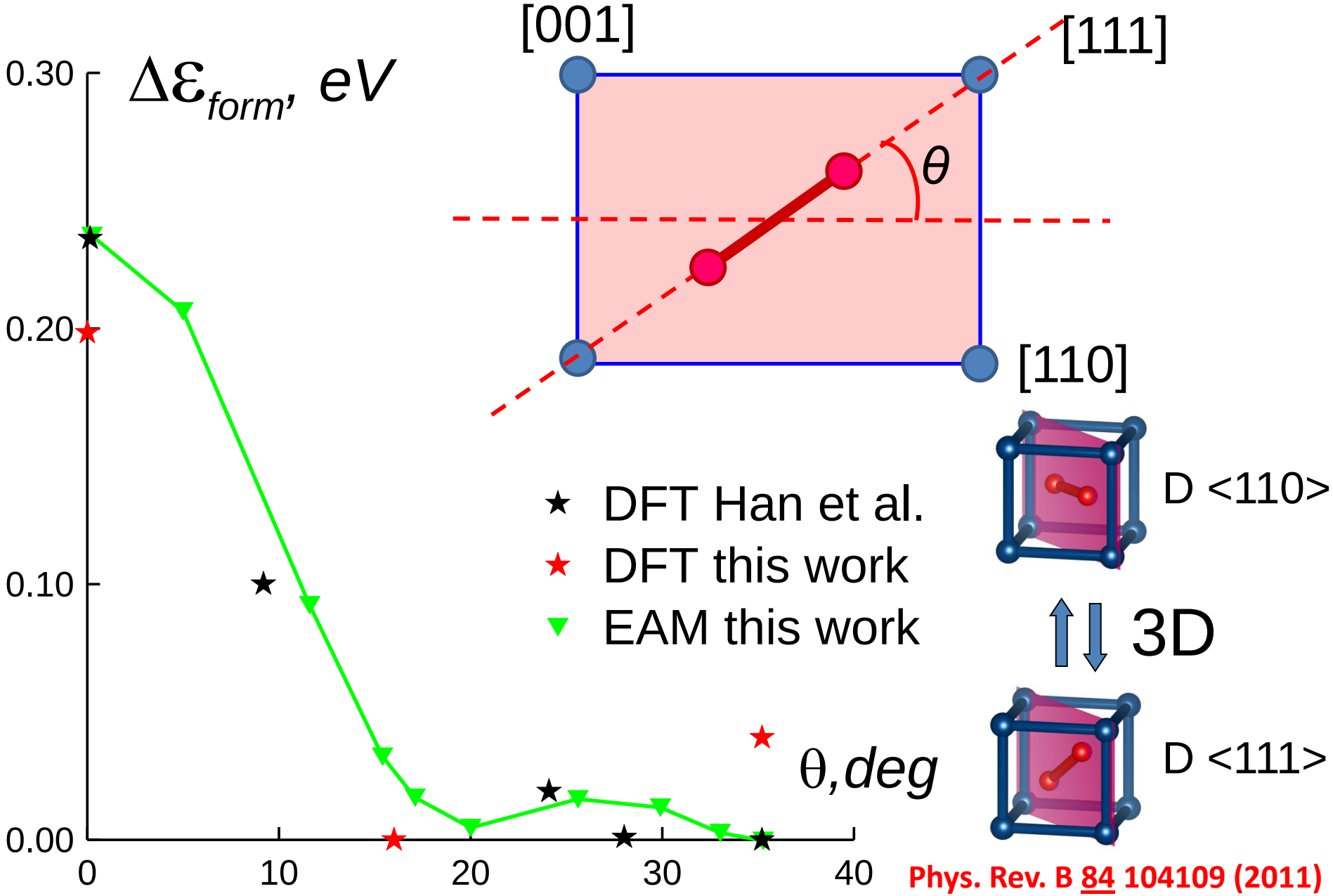
$$E_{form} = E_{def}(N) - \frac{N}{N_{id}} E_{id}(N_{id})$$





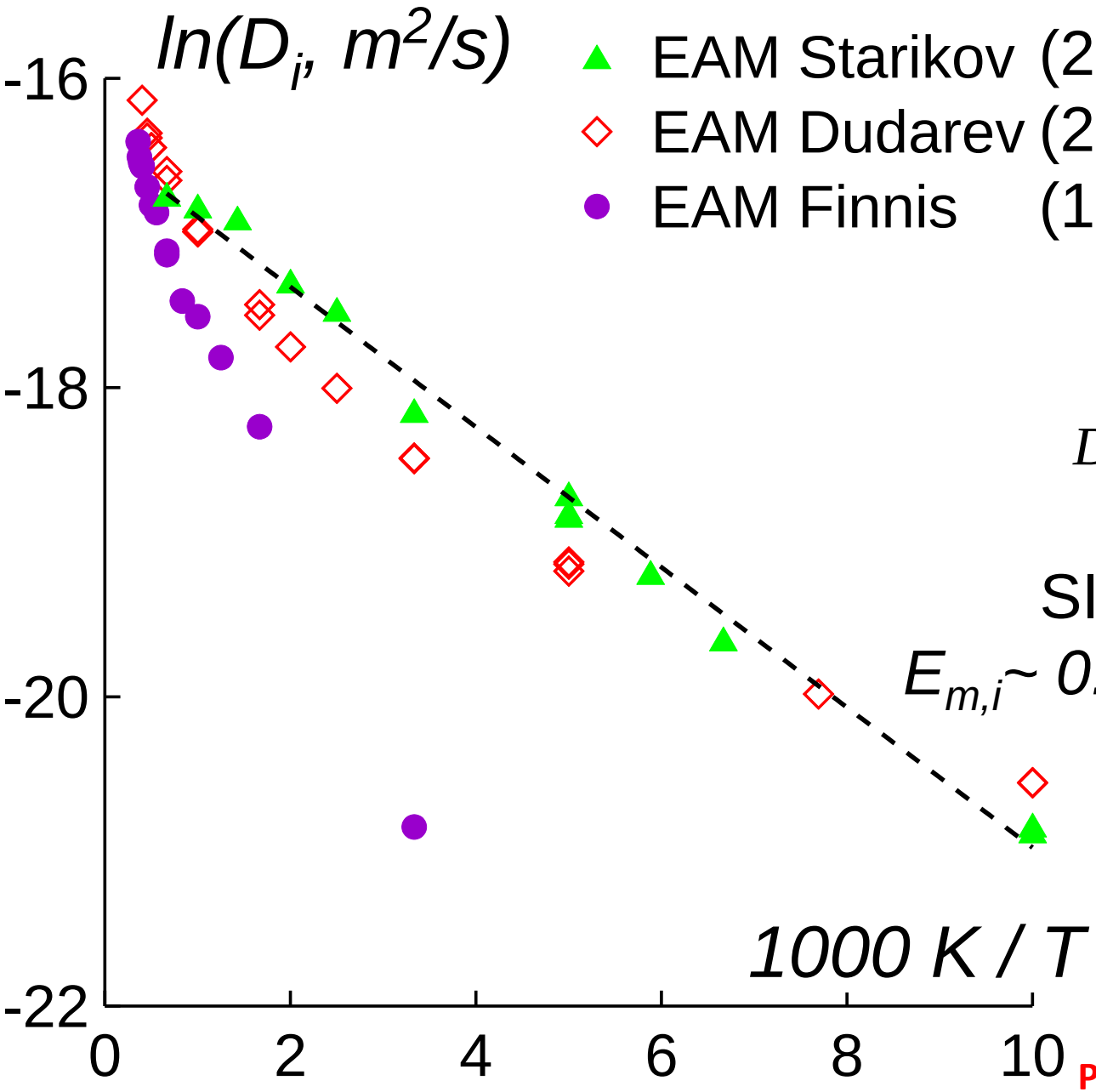
Phys. Rev. B 84 104109 (2011)

3D diffusion: <111> - <110> transformations



Phys. Rev. B 84 104109 (2011)

Diffusion Coefficients of SIA



Line:

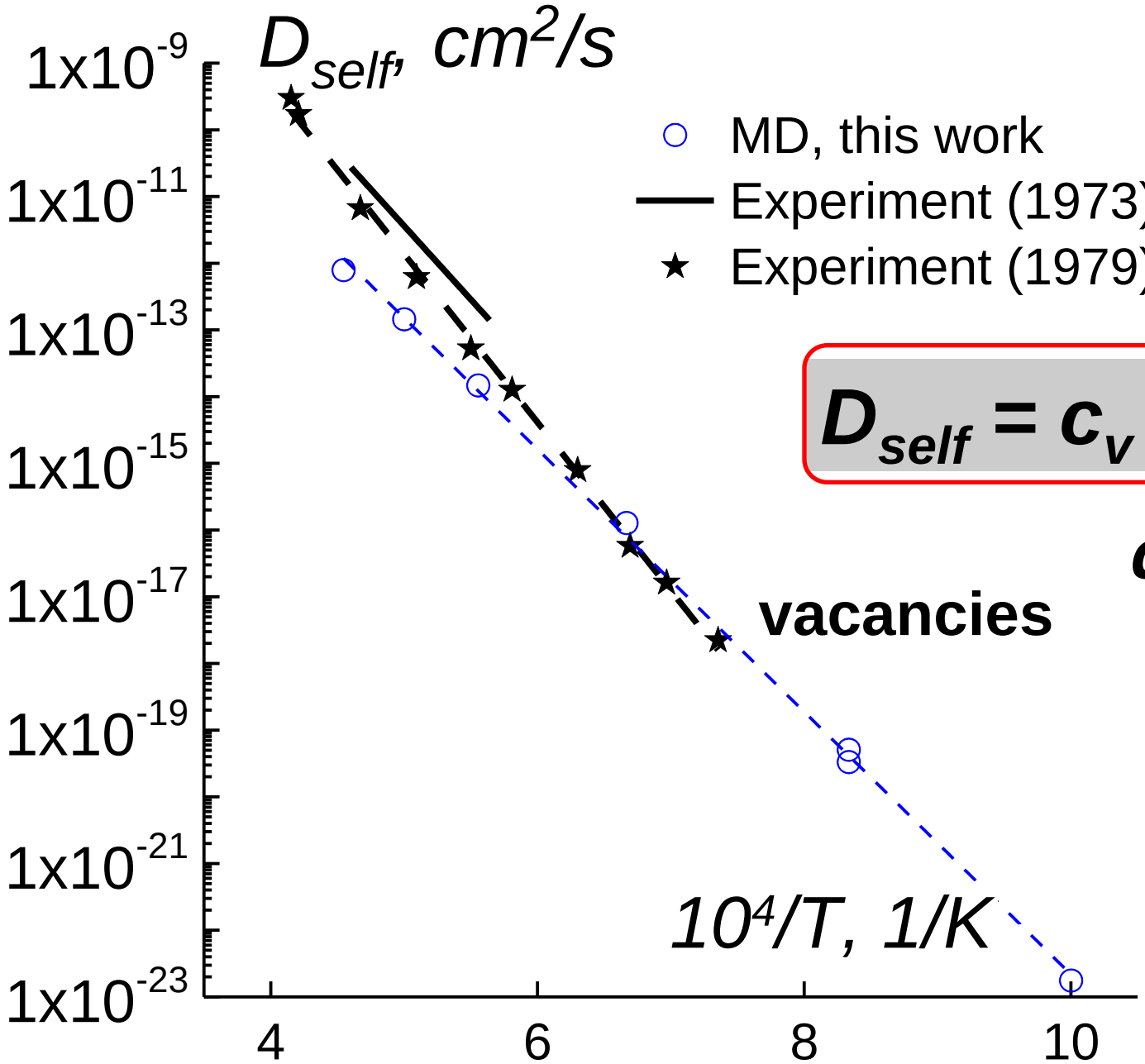
$$D = D_0 \exp\left[-\frac{E_m}{kT}\right]$$

SIA

$E_{m,i} \sim 0.04$ eV

Phys. Rev. B 84 104109 (2011)

Selfdiffusion Coefficients in Mo



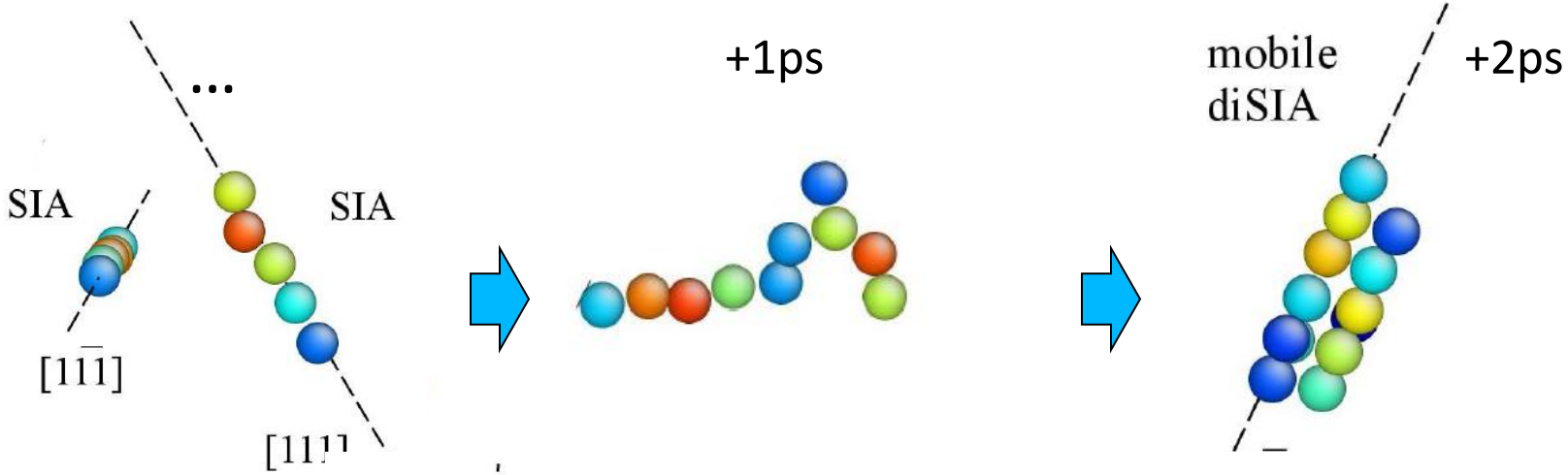
$$D_{self} = c_v D^t_v + c_i D^t_i$$

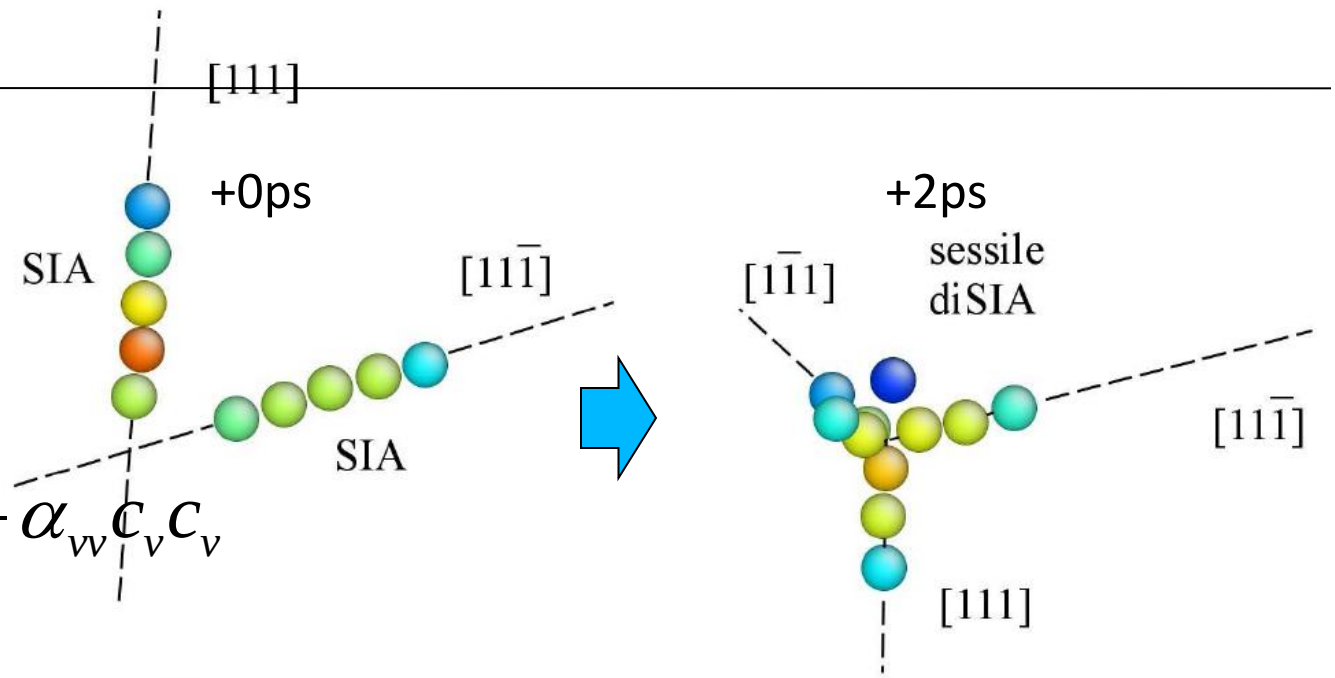
$$c_v >> c_i$$

Diffusion Coefficients of Mo-SIA clusters in Mo

Diffusion Coefficients of SIA Clusters: Dependence on Cluster Size

SIA + SIA reactions and kinetics





$$\frac{dc_v}{dt} = -\alpha_{iv} c_i c_v - \alpha_{vv} c_v c_v$$

$$\frac{dc_i}{dt} = -\alpha_{iv} c_i c_v - \alpha_{ii} c_i c_i$$

J. Nucl. Mat. 425 41-47 (2011)

SIA-Vacancies Recombination

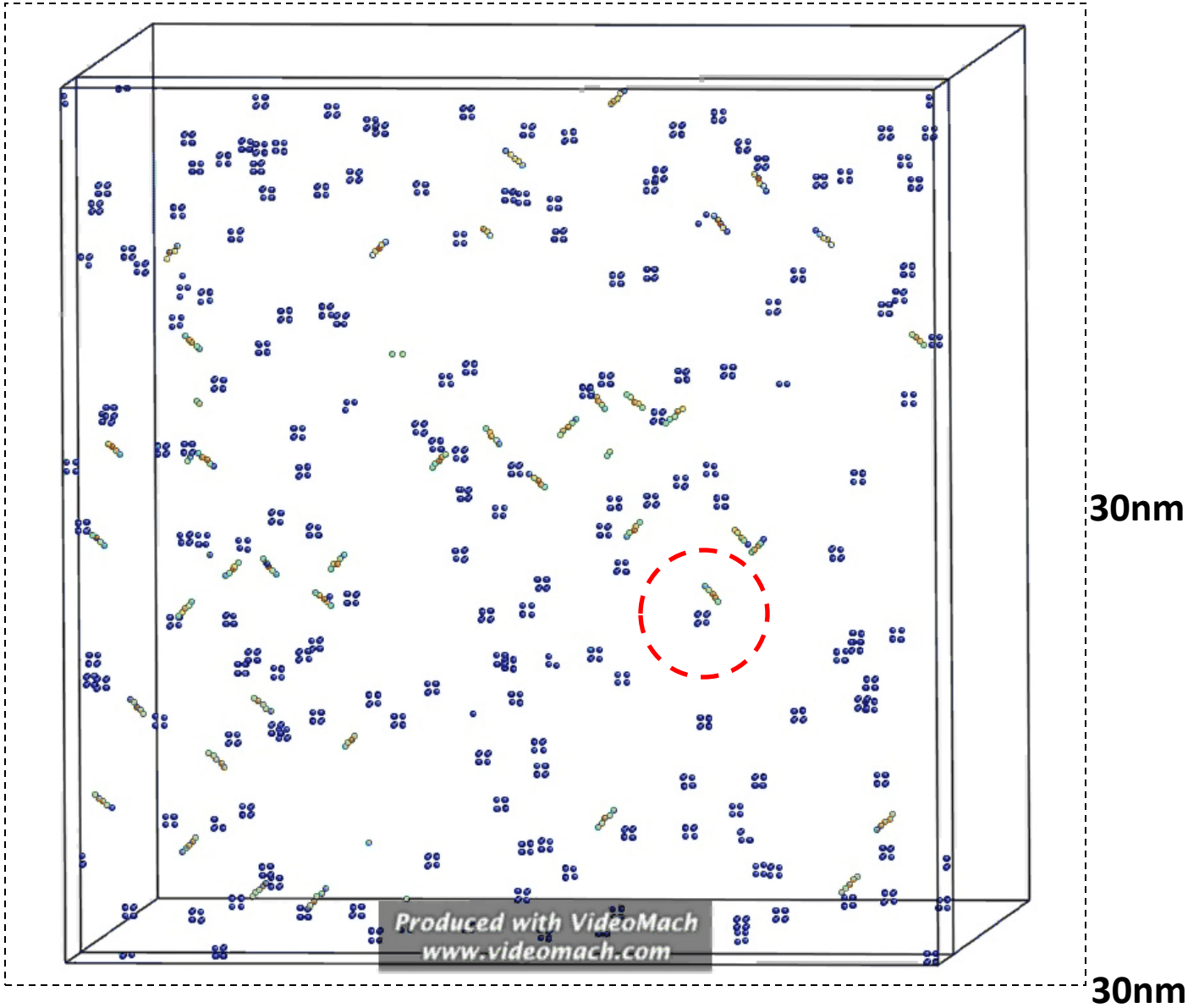
200 crowdions

1000 vacancies

$2x10^6$ atoms

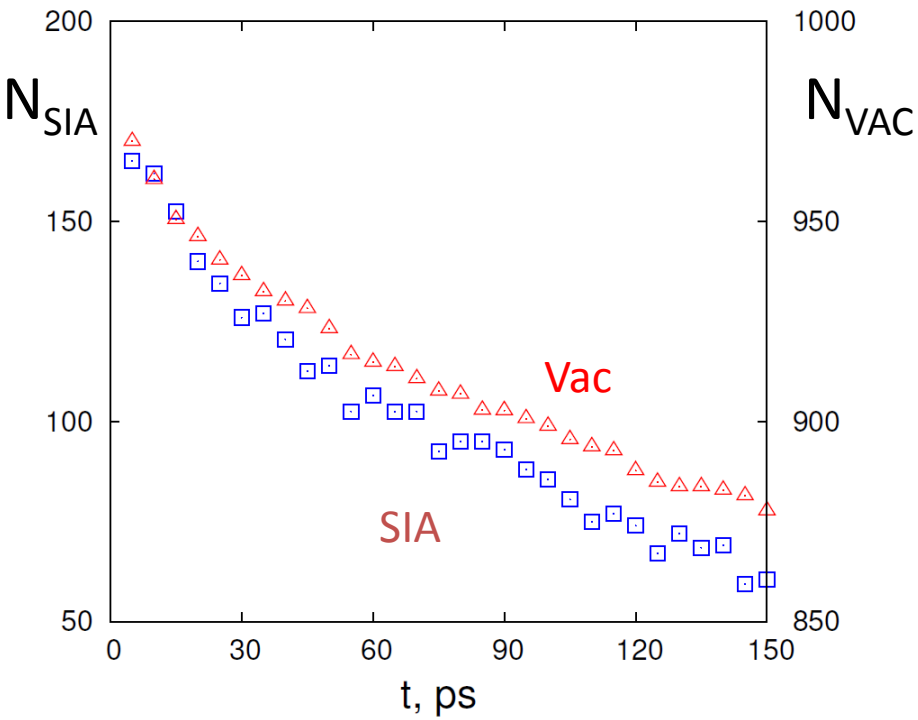
T = 600 K

Colored by potential energy (PE)
(PE>- 6.3 eV)



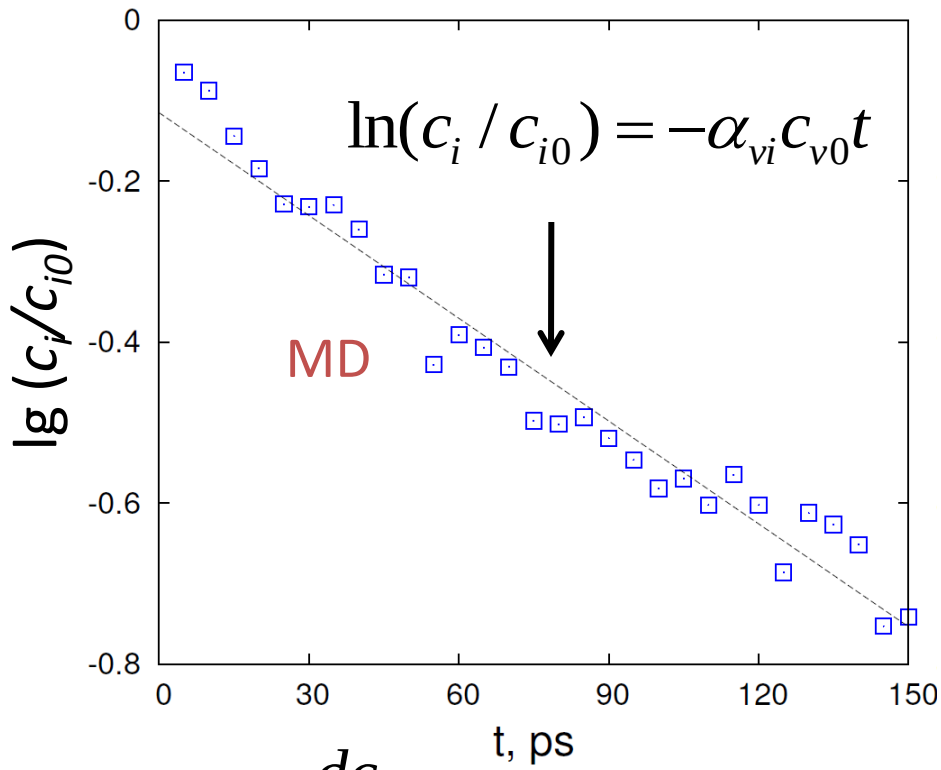
J. Nucl. Mat. 425 41-47 (2011)

SIA-Vacancies Recombination: Reaction Kinetics



T = 800 K

$N_{atoms} = 2x10^6$



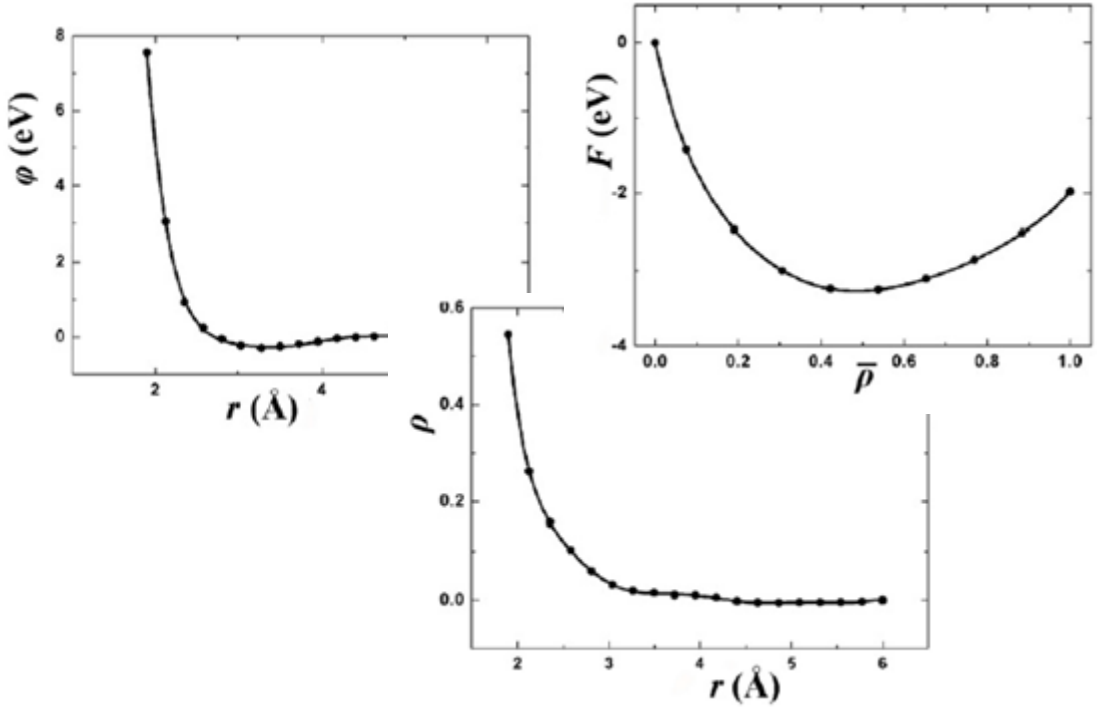
$$\frac{dc_i}{dt} = -\alpha_{vi} c_v c_i$$

α_{vi} - rate constant

J. Nucl. Mat. 425 41-47 (2011)

EAM potential for pure U

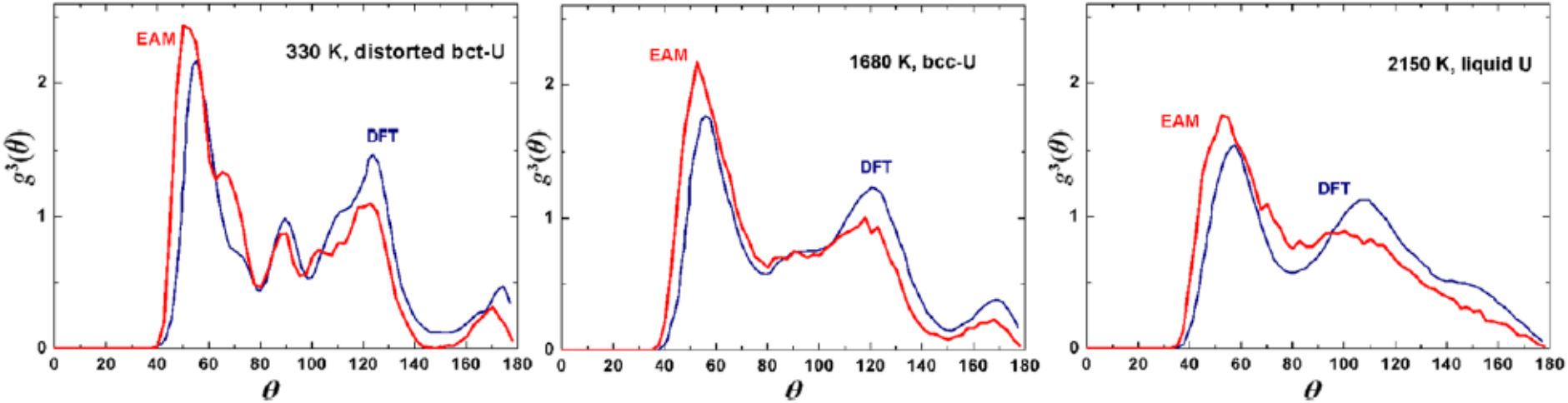
Configuration	Structure	N	V/V_0	T (K)	Δ
1	α-U	120	1.000	900	0.41
2		120	1.000	770	0.41
3		120	1.004	850	0.40
4		120	1.060	990	0.38
5		120	1.000	1300	0.44
6		120	0.940	1200	0.37
7		120	0.902	1600	0.25
8		120	0.850	1600	0.24
9		120	0.827	1700	0.26
10		120	0.827	1100	0.34
11		120	0.902	550	0.35
12		120	1.000	372	0.27
13		120	0.941	340	0.24
14		120	1.061	390	0.27
15	γ-U	128	1.024	1140	0.46
16		128	0.988	1230	0.36
17		128	0.904	2100	0.28
18		128	0.772	3000	0.20
19		128	0.813	2300	0.21
20		128	0.787	2000	0.18
21		128	0.944	1550	0.29
22		128	0.847	1900	0.23
23		128	0.760	3100	0.20
24		128	0.825	1925	0.20
25	liquid U	54	1.293	4300	0.56
26		54	1.448	3077	1.30
27		128	0.934	4000	0.29
28		128	0.769	3740	0.16
29		128	0.934	5760	0.23
30		128	0.679	5140	0.15
31		128	0.748	4700	0.14
32		128	0.790	4000	0.20
33		128	0.734	5900	0.15
34		54	1.293	3417	1.10

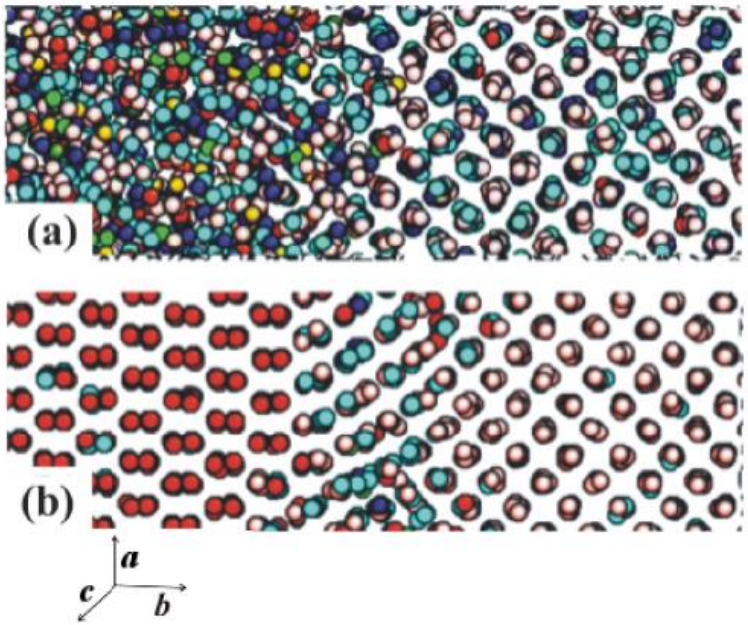


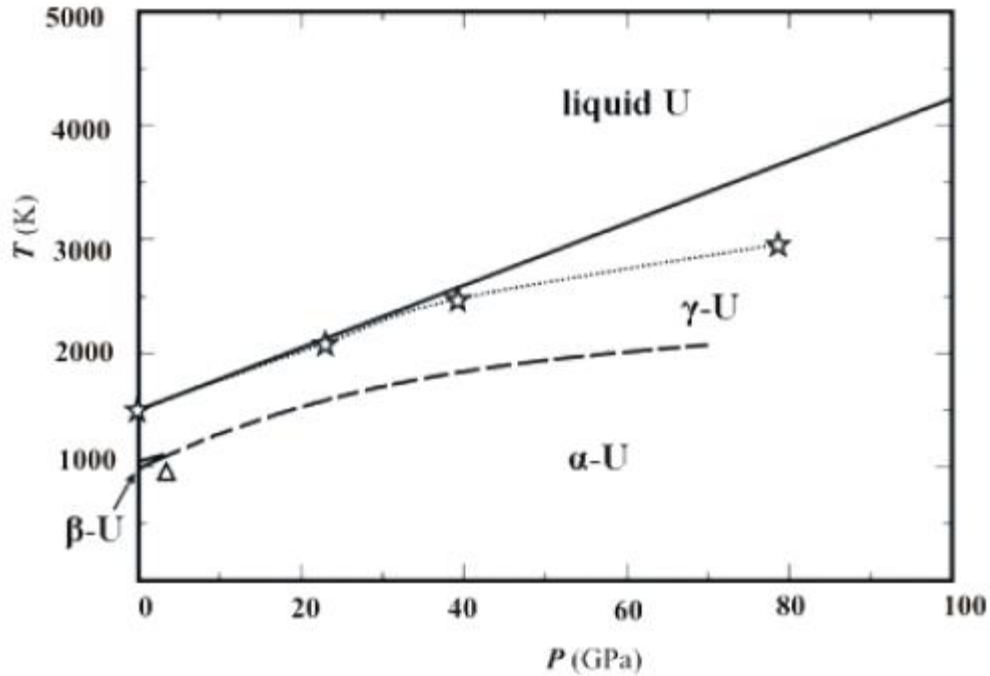
Both α- and γ-phases are stable!

JPCM 24 015702 (2012)

EAM potential for pure U

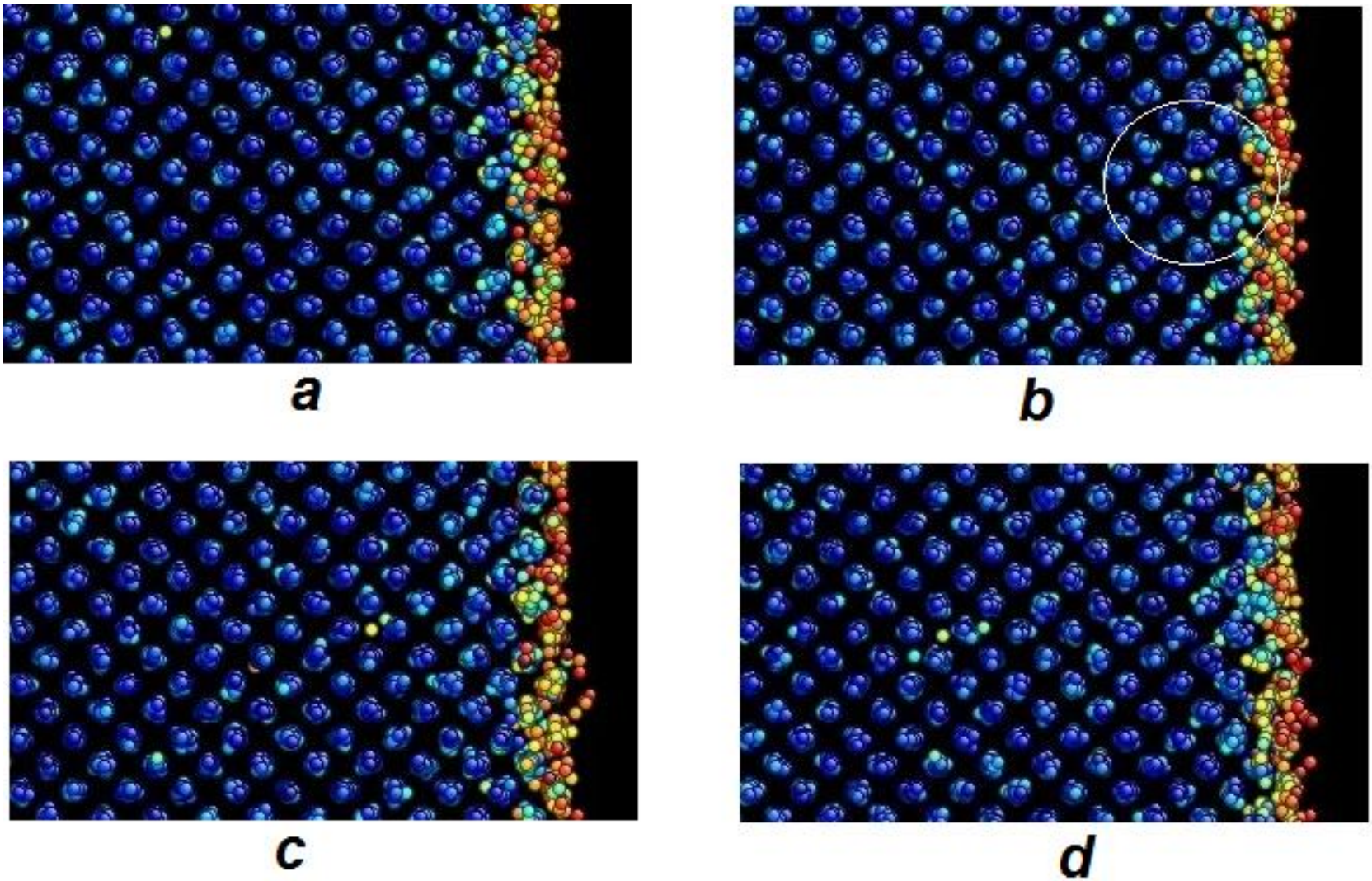






JPCM 24 015702 (2012)

Calculations of thermal concentrations of SIAs

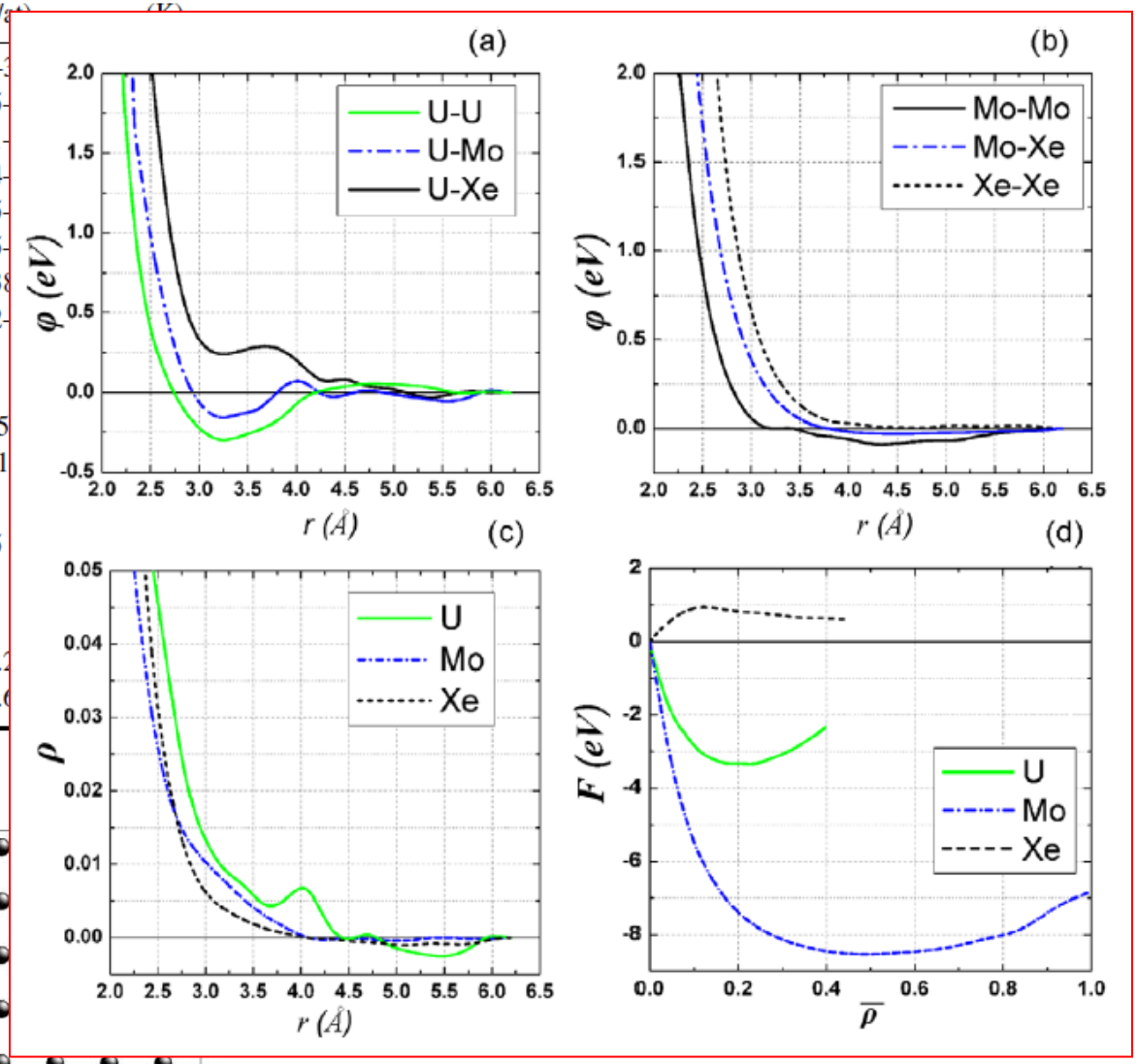


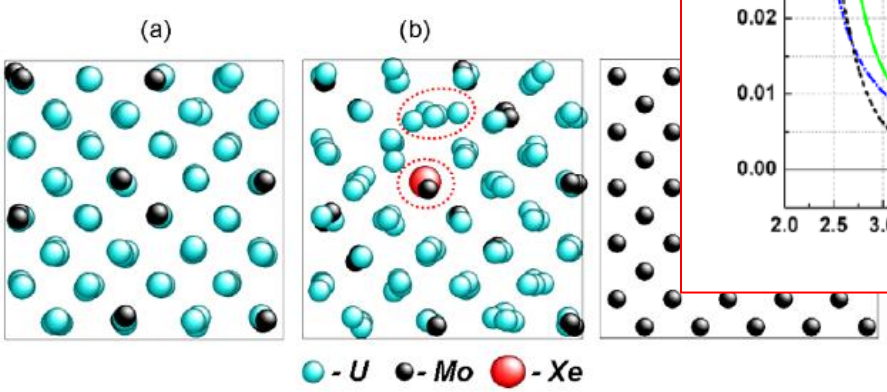
A model of the thin singly crystal film with an open surface

Selfdiffusion coefficient in γ-U

EAM potential for U-Mo with Xe

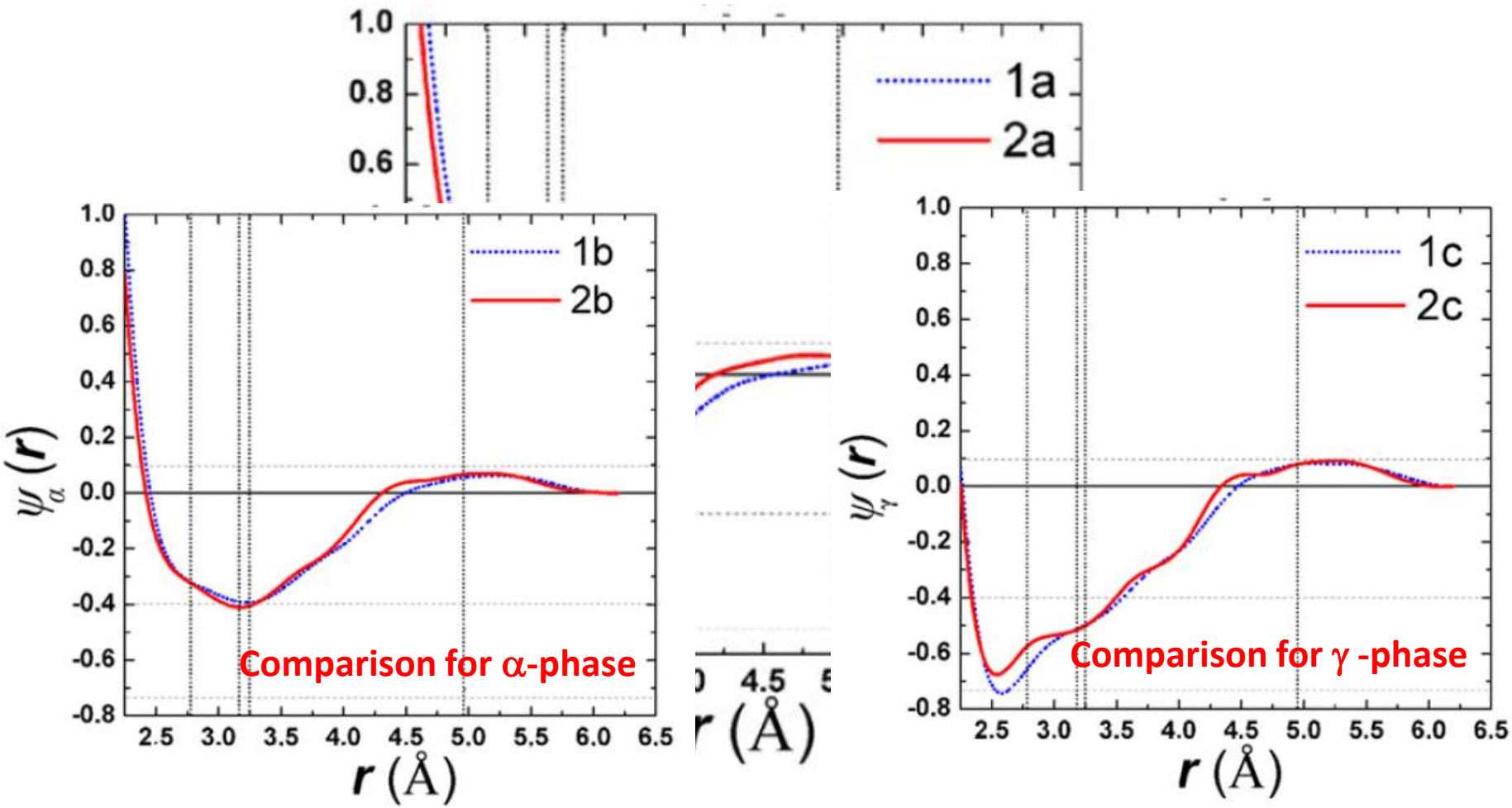
Structure	n	Δ (%)	P_{min}–P_{max} (GPa)	V_{min}–V_{max} (Å^3/a	T_{min}–T_{max} (K)
Mo, bcc	27	21.6	−10–459	8.8–3	
Mo, liquid	4	19.2	3–52	14.5-	
α-U, orth	17	34.3	−3–98	15.1-	
γ-U, bcc	9	31.8	−1–97	15.4-	
U, liquid	11	57.8	−1–102	15.5-	
γ-U–Mo, bcc	14	37.2	−5–62	15.5-	
U–Mo–Xe, bcc	8	41.9	0–52	16.38	
Mo–Xe, disordered	15	23.5	−2–396	11.2-	
Mo–Xe, bcc	5	18.2	6–15	15	
Mo–Xe, fcc	1	29.4	50	24	
Xe, fcc	4	39.5	1–82	14–5	
Xe, disordered	6	51.3	0–8	41–1	
Defect structures					
SIA in solid Mo	8	—	1–5	15.5	
Normalizing structures					
U, 4 at	1	—	0	539	
Mo, 4 at	1	—	0	549.2	
Xe, 4 at	1	—	0	503.6	





Mod. Sim. Mat. Sci. Eng. 21 035011 (2013)

EAM potential for U-Mo with Xe: effective pair format



$$G_\alpha(\overline{\rho}_\alpha) = F_\alpha(\overline{\rho}_\alpha) + k\overline{\rho}_\alpha$$

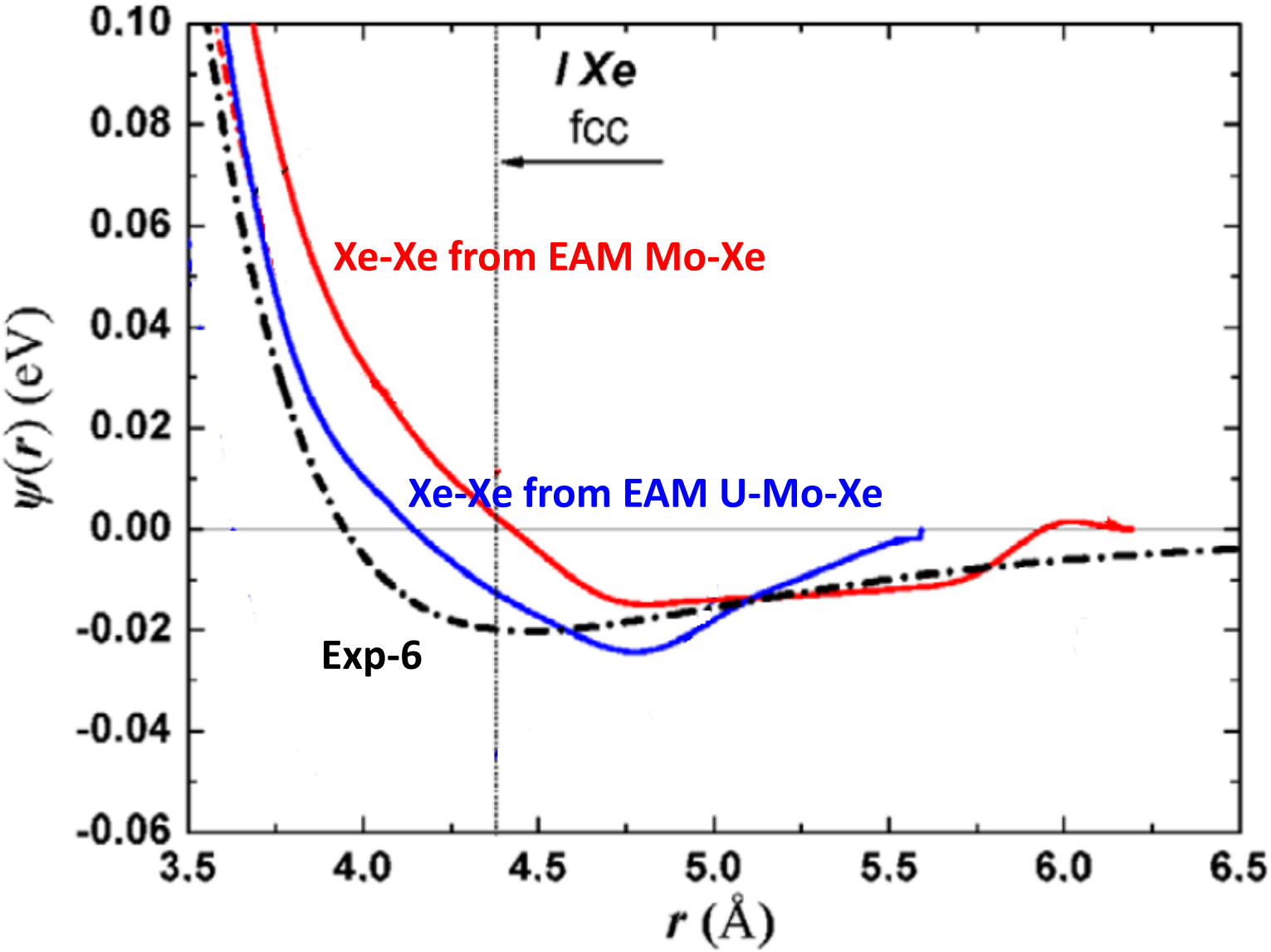
$$\psi_\alpha(r_{ij}) = \varphi_\alpha(r_{ij}) - 2k\rho_\alpha(r_{ij}),$$

$$\alpha = \mathrm{U, Mo, Xe,}$$

where $k = -\mathrm{d}F_\alpha/\mathrm{d}\overline{\rho}_\alpha$ at the given $\overline{\rho}_\alpha = \overline{\rho}_\alpha^0$

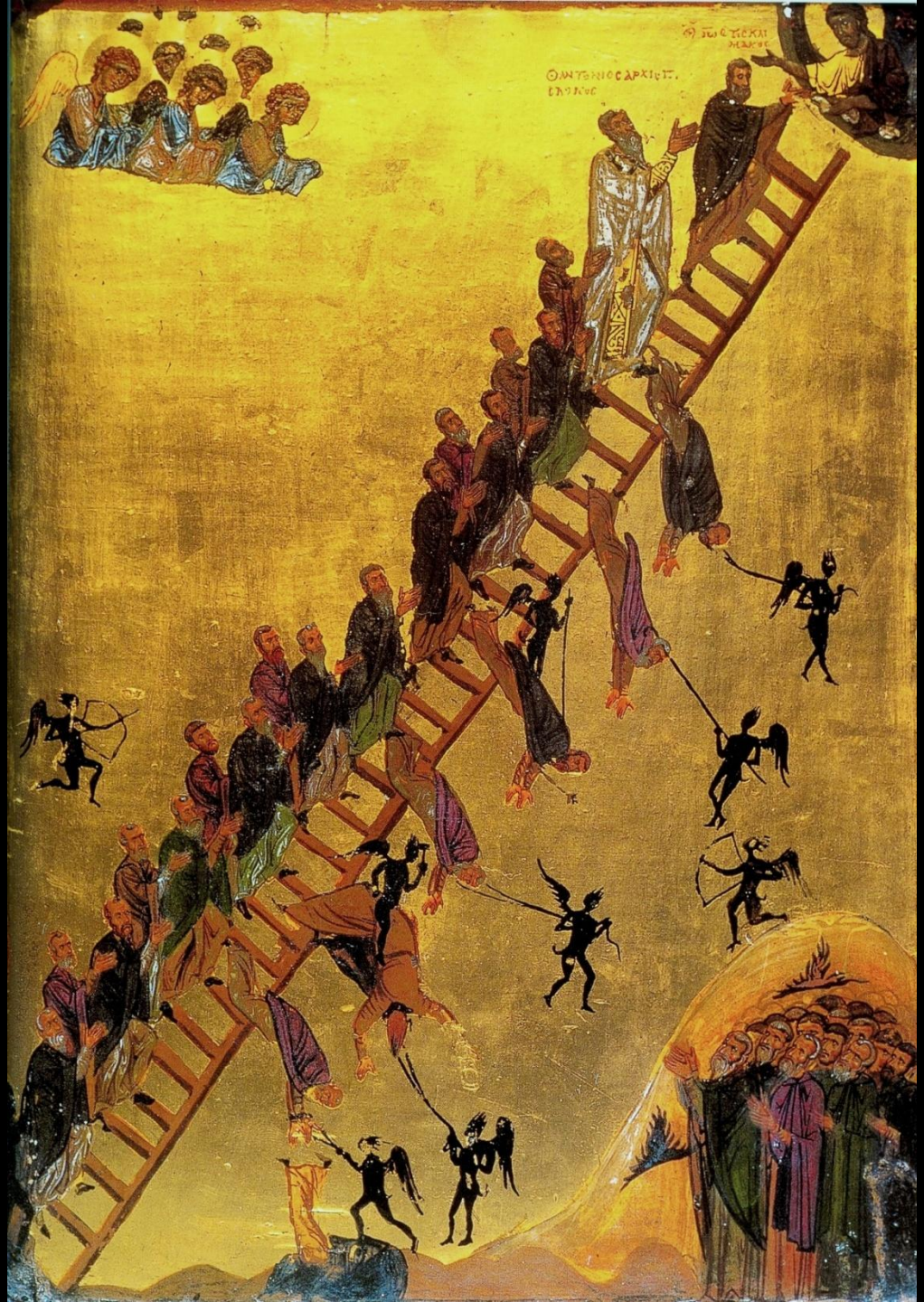
Mod. Sim. Mat. Sci. Eng. 21 035011 (2013)

EAM potential for U-Mo with Xe



Mod. Sim. Mat. Sci. Eng. 21 035011 (2013)

Problem: incorrect trend of SIA formation energies at small Mo concentrations!


ΘΑΝΤΩΝΙΟΣ ΑΡΧΙΕΠ.
ΕΛΟΝΟΣ

ADP non-central symmetric extension of EAM

$$E_i = \underbrace{F_\alpha\left(\sum_{j\neq i}\rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{j\neq i}\phi_{\alpha\beta}(r_{ij})}_{\text{EAM}} + \frac{1}{2}\sum_s(\mu_i^s)^2 + \frac{1}{2}\sum_{s,t}(\lambda_i^{st})^2 - \frac{1}{6}\nu_i^2$$

$$\mu_i^s = \sum_{j\neq i} u_{\alpha\beta}(r_{ij}) r_{ij}^s$$

$$\lambda_i^{st} = \sum_{j\neq i} w_{\alpha\beta}(r_{ij}) r_{ij}^s r_{ij}^t$$

$$\nu_i = \sum_s \lambda_i^{ss}$$

Average error in fitting atomic forces:

	EAM U-Mo-Xe %	ADP U-Mo %
α-U	34	27
γ-U	32	23
Liquid U	58	30
U-Mo	37	25

$$\Delta = \frac{1}{N}\sum_{i=1}^{N}\sqrt{\frac{(F^i_{\text{EAM}} - F^i_{\text{DFT}})^2}{(F^i_{\text{DFT}})^2}}$$

ADP: **Y. Mishin, Mehl *et al* 2005 *Acta Mater* 53 4029**

Comparison of self-diffusion rates of U and Mo in U-Mo alloys

Comparison of self-diffusion rates of U and Mo in U-Mo alloys

Comparison of self-diffusion rates of U and Mo in U-Mo alloys

Summary

1. Multiscale coupling path from ab initio level via classical MD to the rate theory level has been traced on the example of bcc Mo. [PRB 84 104109 (2011) & JNM 425 41 (2011)]

2. EAM model allows to stabilize α-U and γ-U at T > 800K and provides adequate defect formation energies and self-diffusion rate. [JPCM 24 015702 (2012)]

3. EAM model for a ternary system of U-Mo with Xe shows no major change in the U and Mo potentials, Xe-Xe potential is close to the Exp-6 form. However the U-Xe interaction shows a certain peculiarity. [Mod. Sim. Mat. Sci. Eng. 21 035011 (2013)]
   Problem: incorrect trend of SIA formation energies at small Mo concentrations.

4. A non-central symmetric ADP extension of the EAM formalism for U-Mo system allows to overcome this problem and reproduce the decrease in self-diffusion rate due to small admixture of Mo.