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Title: Assessment of semi-empirical potentials for the U-Si system

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Assessment of semi-empirical potentials for the U-Si system

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Introduction

Accident tolerant fuels (ATF) are being developed in response to the Fukushima Daiichi accident in Japan. One of the options being pursued is U-Si fuels, such as the U_3Si_2 and U_3Si_5 compounds, which benefit from high thermal conductivity (metallic) compared to the UO_2 fuel (semi-conductor) used in current Light Water Reactors (LWRs). The U-Si fuels also have higher fissile density. In order to perform meaningful engineering scale nuclear fuel performance simulations, the material properties of the fuel, including the response to irradiation environments, must be known. Unfortunately, the data available for U-Si fuels are rather limited, in particular for the temperature range where LWRs would operate. The ATF HIP is using multi-scale modeling and simulations to address this knowledge gap. Even though Density Functional Theory (DFT) calculations can provide useful answers to a subset of problems, they are computationally too costly for many others, including properties governing microstructure evolution and irradiation effects. For the latter, semi-empirical potentials are typically used. Unfortunately, there is currently no potential for the U-Si system. In this brief report we present initial results from the development of a U-Si semi-empirical potential based on the Modified Embedded Atom Method (MEAM). The potential should reproduce relevant parts of the U-Si phase diagram (see Figure 1) as well as defect properties important in irradiation environments. This work also serves as an assessment of the general challenges associated with the U-Si system, which will be valuable for the efforts to develop a U-Si Tersoff potential undertaken by Idaho National Laboratory (also part of the ATF HIP). Going forward the main potential development activity will reside at INL and the work presented here is meant to provide input data and guidelines for that activity. The main focus of our work is on the U_3Si_2 and U_3Si_5 compounds, because they are the main nuclear fuel candidates. U_3Si_5 is derived from USi_2 in the AlB_2 structure by creating 1/6 vacant sites on Si sublattice. The ordering of these vacancies will not be studied in any detail here.
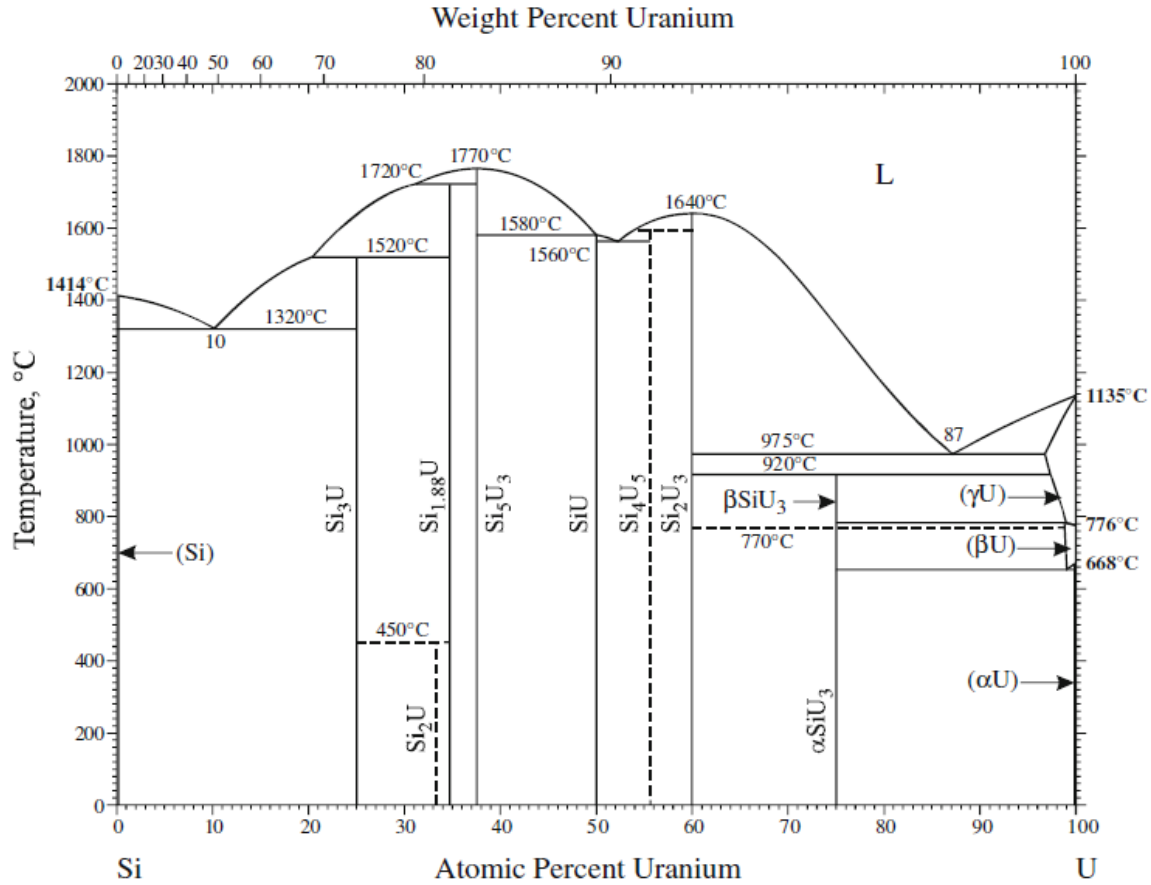
Figure 1: Experimental U-Si phase diagram [1].

Approach

In order to develop a potential for the binary U-Si system we must start from the unary U and Si systems. In this work, we have used a U potential from recent work with INL/GA Tech (M. Baskes) and for Si we used a potential from the literature [2]. The U-Si parameters needed to describe the binary system can either be fitted to available experimental data or to data derived from DFT calculations. Here we used a combination of the two to fit the MEAM cross potential. The MEAM parameters that were fitted or adjusted here are highlighted in red in Table 1 and include the relative electron densities, the heat of formation for the L_{12} reference structure, the distance between atoms in the reference structure and the α parameter for the pair potential between U and Si, which is related to the bulk modulus of the L_{12} reference structure, a cubic repulsive term in the U-Si Rose pair potential as well as the MEAM screening parameters capturing how a third atom screens the interaction between two other atoms. The latter introduces many-body interactions necessary for systems exhibiting complicated crystal structures such as U, Si and several compounds in the U-Si system. These parameters are summarized in Table 1, utilizing the standard notation for MEAM potentials.

Table 1: MEAM cross terms for the U-Si potential derived in this work. The red parameters were adjusted or fitted in this work. All others were left at default values.

```
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kodes(1)='library','library',
repuls(1,1)=0.105,attrac(1,1)=0.105 cmin(2,2,2)=2.0
cmin(1,1,1)=1.0 cmax(1,1,1)=1.9
xncut=2.0,xmcut=6.0,rcut=5.0,nn=.t.,ialloy=1
rozros=1.00,1.7
alphas(1,2)=4.4,deltas(1,2)=-0.5,all(1,2)='L12' res(1,2)=3.046
repuls(1,2)=0.20, cmin(2,1,2)=0.2,cmax(2,1,2)=1.2
cmin(1,2,1)=2.0,cmax(1,2,1)=2.8
cmin(1,1,2)=2.0,cmax(1,1,2)=2.8
cmin(1,2,2)=2.0,cmax(1,2,2)=2.8 &end
```

Red determined from fit to DFT-U and experiments in this work.

Results

In this section we compare predictions from the MEAM potential defined in Table 1 to data obtained from DFT calculations, which were also performed as part of the present study, and experimental data from the literature [3]. The main compounds of interest for fuel applications are U_3Si_2 and U_3Si_5, consequently these two compositions will be scrutinized in more details than others.

Formation energies

The stability of a range of U-Si phases was calculated with reference to α uranium and silicon in the diamond structure using DFT calculations. The DFT calculations applied the GGA+U methodology for the U silicides, where a U value of 1.5 eV was applied to the U 5f electrons (do not confuse the parameter U with the chemical symbol for uranium). This approach predicts the correct structure for U_3Si_2, while regular GGA predicts significant distortions to the lattice in disagreement with experimental diffraction data. Calculations for metallic α uranium did not apply the GGA+U methodology, but rather regular GGA. In order to compare the regular GGA and GGA+U calculations and also improve the accuracy of the calculated formation energies, we applied the approach proposed by Jain et al [4]. The DFT and MEAM data are shown in Figure 2 together with available experimental formation energies [3]. Basic information of the crystal structure of the U-Si compounds in Figure 2 is summarized in Table 2. The DFT calculations agree well with the experimental formation energies across the full composition range. Even though the MEAM potential does a decent job for U_3Si_2 and U_3Si_5, several other phases are predicted to be too stable in relation to the DFT calculations and experiments. Also, there is an alternative U_3Si_2 structure that MEAM predicts to be more stable than the

experimental structure, however this is not confirmed by DFT (see below). In summary, even though the formation energies are accurate for the U_3Si_2 and U_3Si_5 compounds the complex bonding in the U-Si system renders a complete description of the phase diagram very challenging. Please note that this is work in progress and the results presented in Figure 2 are preliminary. We are currently addressing the poor formation energy and volume (see below) predicted by the MEAM potential for the USi_2 and U_2Si phases.
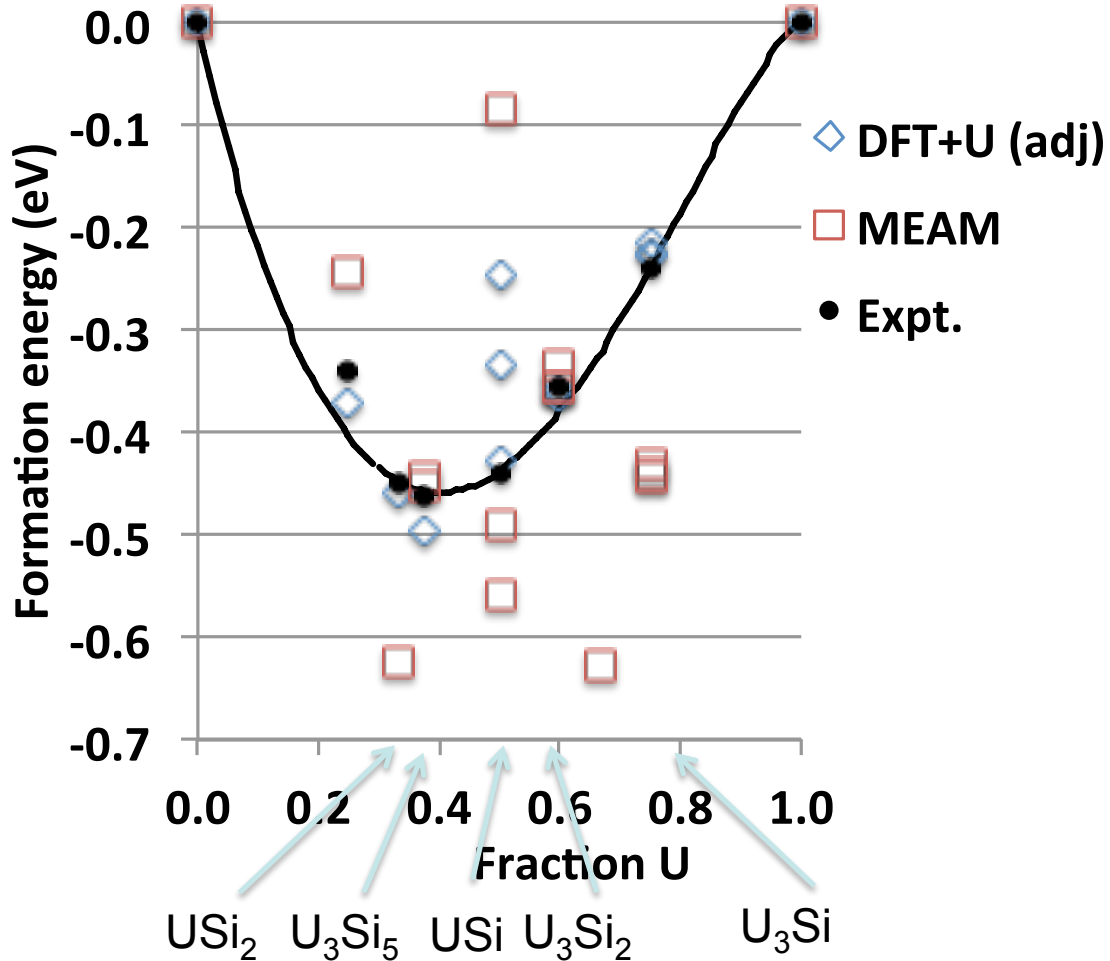

Figure 2: Formation energies for U-Si compounds (with respect to Si in the diamond structure and α uranium) as function of uranium fraction obtained from the MEAM potential, DFT calculations and experimental literature values [3]. The values are normalized per atom. Crystallographic information for the different phases is listed in Table 2.

Table 2: Basic information of U-Si crystal structures investigated by MEAM and DFT calculations in the present study.

Compound	Structure type	X denotes lowest energy structure according to DFT for each composition	Fraction U
α-U$_3$Si	α-U$_3$Si	X	0.75
β-U$_3$Si	β-U$_3$Si		0.75
γ-U$_3$Si	AuCu$_3$		0.75
U$_3$Si$_2$	U$_3$Si$_2$		0.60
USi	NaCl		0.50
USi	CsCl		0.50
USi	FeB	X	0.50
U$_3$Si$_5$	U$_3$Si$_5$	X	0.375
USi$_2$	AlB$_2$	X	0.333
USi$_2$	ThB$_2$		0.333
α-USi$_3$	α-U$_3$Si		0.25
β -USi$_3$	β -U$_3$Si	X	0.25
γ-USi$_3$	AuCu$_3$		0.25

Atomic volumes

The calculated atomic volumes for the U-Si phases are plotted in Figure 3 and compared to available experimental data. For U$_3$Si$_2$ and U$_3$Si$_5$ we have also listed the lattice parameters in Table 3. The DFT calculations accurately capture the volumes of most phases. Figure 3 plots the volumes obtained from regular GGA calculations. The GGA+U approach predicts slightly higher volumes compared to both GGA and experiments, though the agreement with experiments is still reasonably good (not shown). The MEAM potential predicts most volumes to be higher than the DFT calculations and experiments. The c/a ratio is significantly underestimated by the MEAM potential for U$_3$Si$_5$, which is related to the inaccurate description of the USi$_2$ phase referred to above.
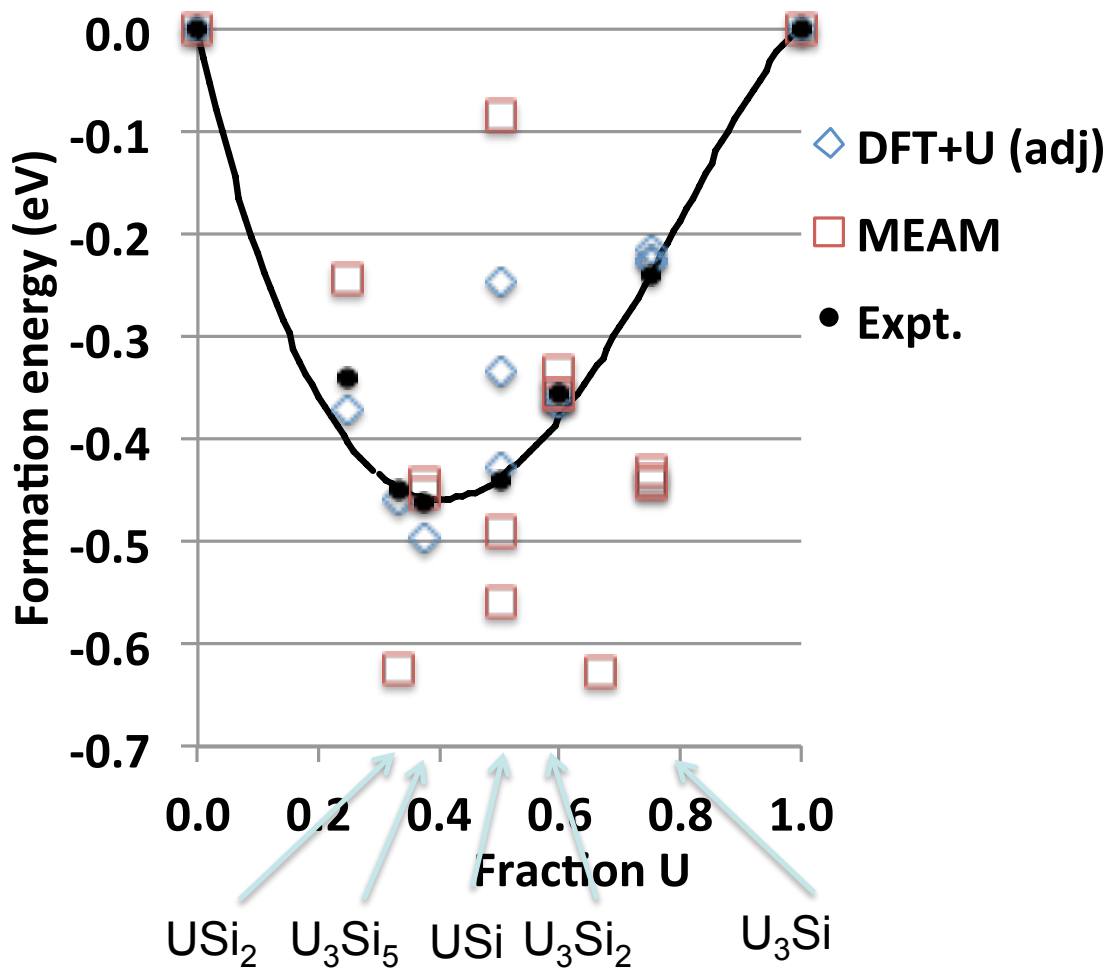
Figure 3: Atomic volumes for U-Si compounds as function of uranium fraction obtained from the MEAM potential, DFT calculations and experimental literature values. The values are normalized per atom. The DFT results refer to regular GGA. The GGA+U approach predicts slightly higher values (not shown). Crystallographic information for the different phases is listed in Table 2.

Table 3: Lattice parameters calculated by the MEAM potential for the U_3Si_2 and U_3Si_5 crystal structures compared to experimental data. The DFT values are not included, but agree well with the experimental data. 'a' values are in Å and the ratios are unit less. The MEAM values marked in red exhibit significant discrepancies.

	U_3Si_2		U_3Si_5	
	MEAM	EXPT	MEAM	EXPT
a	8.51	7.33	4.94	3.84
b/a	1	1	1.73	1.73
c/a	0.539	0.5	0.57	1.05

Elastic constants at 0 K

Table 4 lists the calculated bulk modulus and elastic constants at 0 K for U_3Si_2 and U_3Si_5. Even though the bulk modulus is accurately predicted by the MEAM potential, several of the elastic constants are over predicted compared to the DFT calculations.

Table 4: U_3Si_2 and U_3Si_5 elastic constants calculated by the MEAM potential and DFT. The MEAM and DFT values marked in red exhibit significant discrepancies.

	U_3Si_2		U_3Si_5	
	MEAM	**DFT-U**	**MEAM**	**DFT-U**
B (GPa)	100	81	94	102
C_{zx} (GPa)	79	66	21	**108**
C_{yz} (GPa)	79	66	25	**97**
C_{xy} (Gpa)	**190**	45	52	77
C'_{zx} (GPa)	**113**	49	68	54
C'_{yz} (GPa)	**114**	48	68	51
C'_{xy} (Gpa)	**192**	57	55	75

Point defects

Point defect formation energies were calculated using standard supercell methods for the U_3Si_2 and U_3Si_5 compounds. The results refer to zero pressure calculations and the chemical potentials were defined by the pure elements (Si in the diamond structure and α uranium). The results are shown in Table 5. For U_3Si_2 the MEAM potential agrees well with DFT calculations for both U and Si vacancies, while interstitial and anti-site energies are overestimated. Note that DFT predicts negative formation energy for Si interstitials in U_3Si_2, which is consistent with the slope of the convex hull in Figure 2.

	U_3Si_2		U_3Si_5	
	MEAM	DFT-U	MEAM	DFT-U
U vacancy	1.72	1.64	2.66	3.44
Si Vacancy	2.13	2.48	1.68	1.48
U interstitial	2.81	0.76	0.94	
Si interstitial	2.04	-0.20	2.50	
U Frenkel pair	4.52	2.31	3.60	
Si Frenkel pair	4.17	2.28	4.18	
U on Si site	3.76	1.70	0.78	
Si on U site	3.14	0.20	2.30	

U_3Si_2 dynamics

So far we have investigated the 0 K properties of U-Si compounds, however the U-Si potential is obviously intended for studying dynamical properties at finite temperature and under irradiation. For this reason we have performed molecular dynamics simulations to identify concerns, such as unexpected phase transformation. Figure 4 plots the energy as function of temperature and Figure 5 the evolution of volume and lattice parameters. The structure of U_3Si_2 at 300 K and 1700 K are shown in Figure 6. The two kinks in the energy vs temperature curve indicate structural phase transformations, which are also visible in the volume and lattice parameters (Figure 6). The lack of experimentally observed transformations as function temperature for U_3Si_2 raises concern regarding the validity of the MEAM predictions.

The structure identified after the two transitions at ~1100 K and ~1500 K was annealed to room temperature and then relaxed at 0 K. The resulting phase turned out to be lower in energy than the original experimentally derived U_3Si_2 structure. The stability of the new structure was investigated by DFT calculations, which did not confirm the result from MD. The DFT calculations still predict the experimental U_3Si_2 structure to be the most stable. Clearly, this is a concern that we continue to investigate.
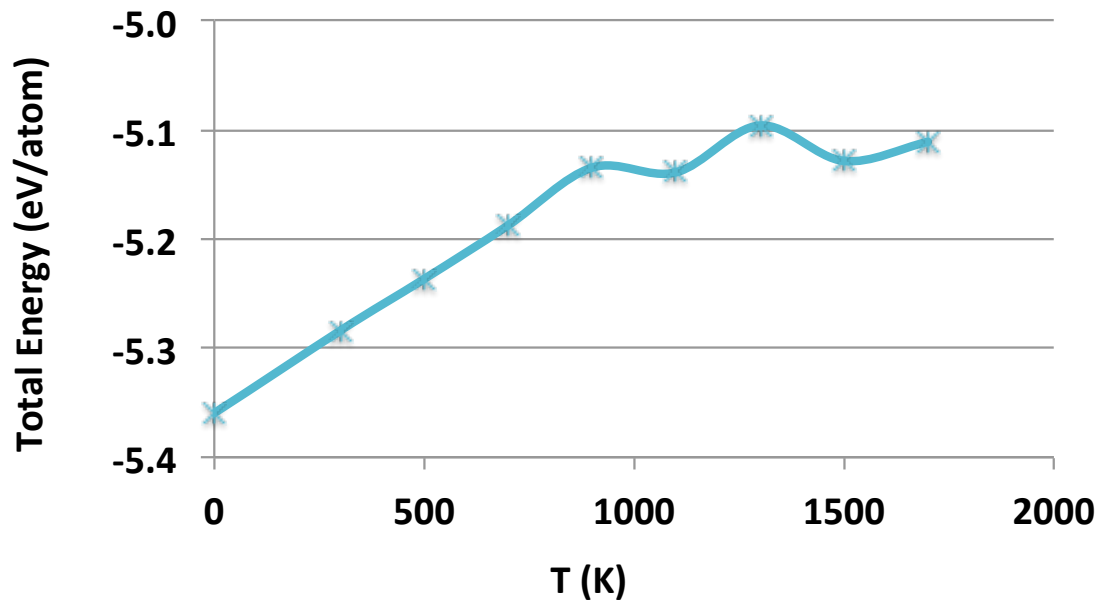
Figure 4: Total energy per atom as function of temperature for U_3Si_2 (MEAM). The two kinks at ~1100 K and 1500 K are caused by structural phase transformations.
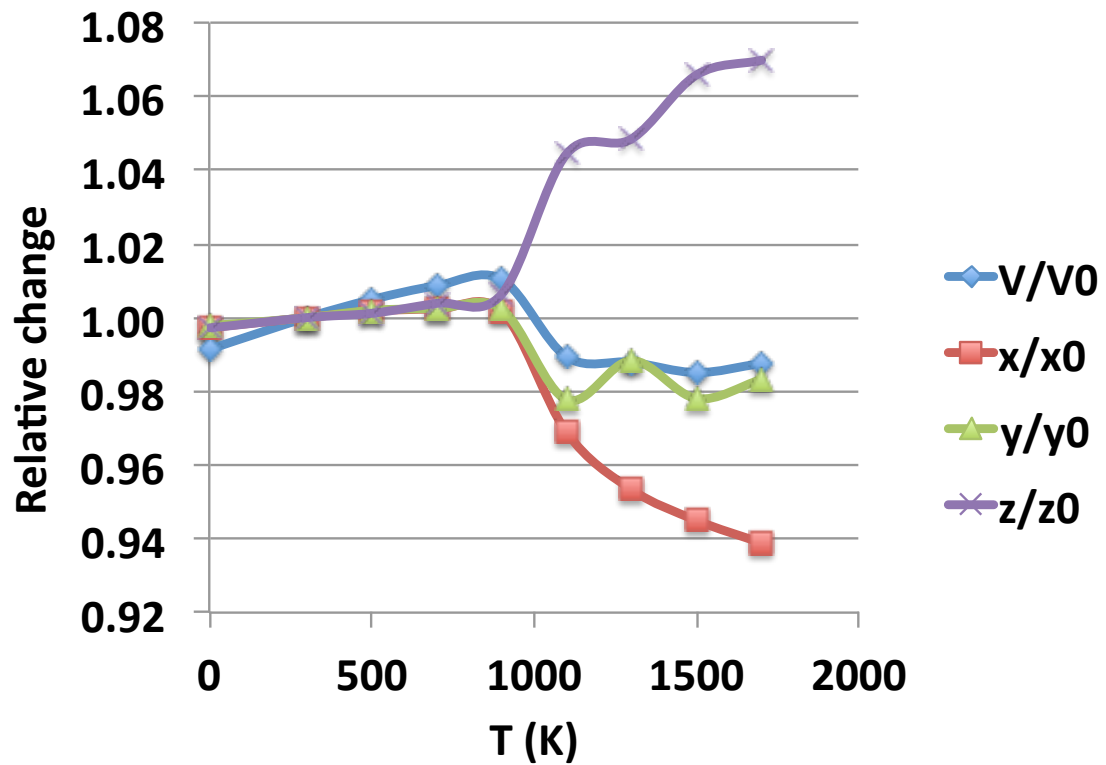

Figure 5: Relative change in lattice parameters and volume as function of temperature for U_3Si_2 (MEAM).
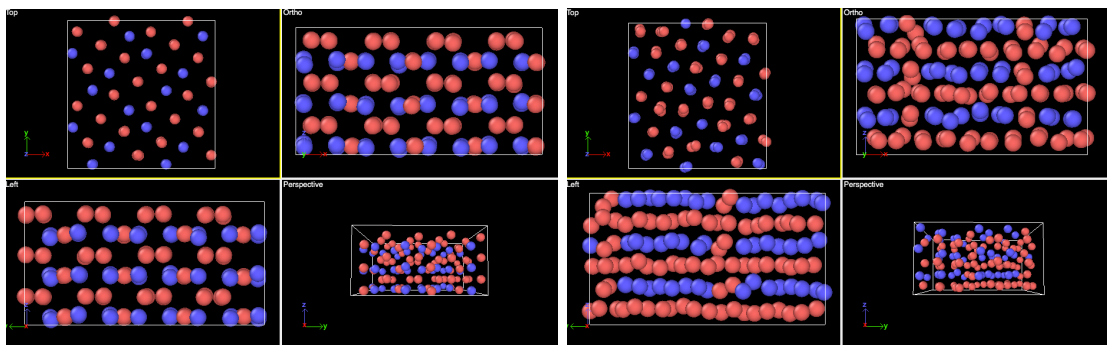
Figure 6: The structure of U₃Si₂ at 300 K (left) and at 1700 K (right) obtained from MEAM MD simulations. Red spheres represent uranium and blue silicon.
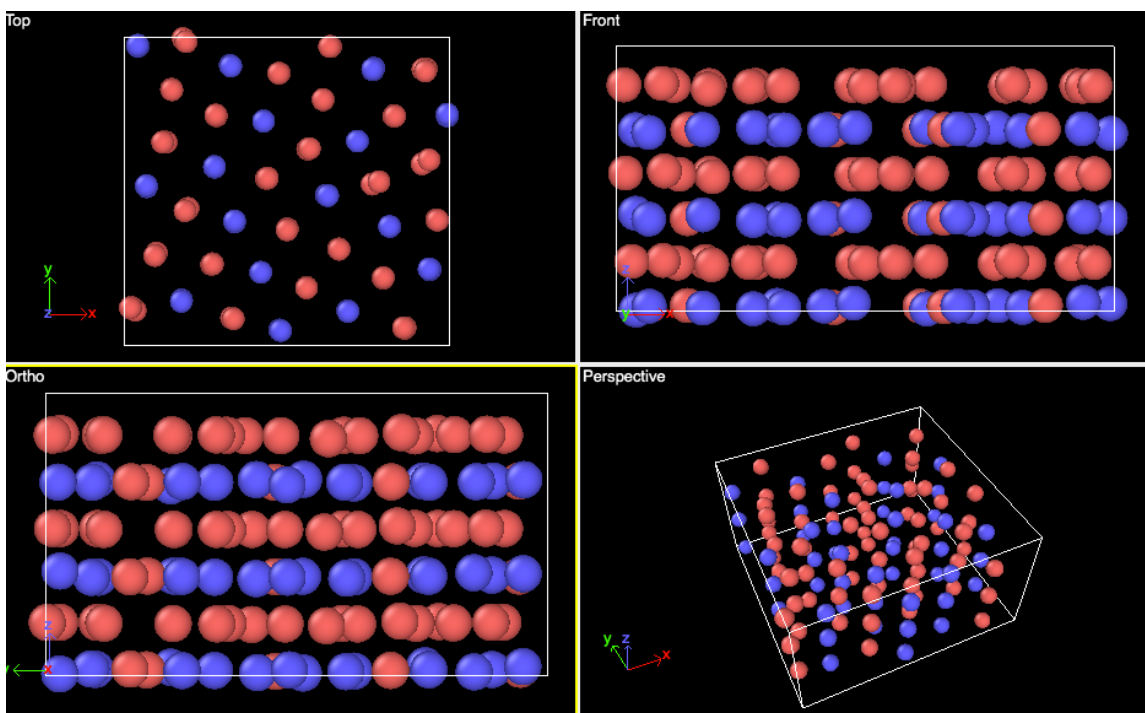

Figure 7: The U₃Si₂ structure predicted to be lower in energy than the experimentally derived structure according to the MEAM MD simulations (after static relaxation to 0 K). This result was, however, not supported by DFT calculations. Red spheres represent uranium and blue silicon.

U₃Si₅ dynamics

Following the same procedure as for U₃Si₂, we have calculated the dynamics of U₃Si₅ based on the MEAM potential. For this phase both the energy and volume/lattice parameters identify a transition at ~1500 K. There is no transformation for U₃Si₅ in the experimental phase diagram. The vacancies on the Si sublattice make the U₃Si₅ phase complicated. They are ordered at low temperature and disordered at high temperature. According to our preliminary results the vacancies prefer to separate as much as possible from each other at low temperature (0 K). Additional work is required to identify the role of these vacancies in any phase transformations. It is

presently not clear to us if order-disorder reactions have been included in the experimental phase diagram (probably not).
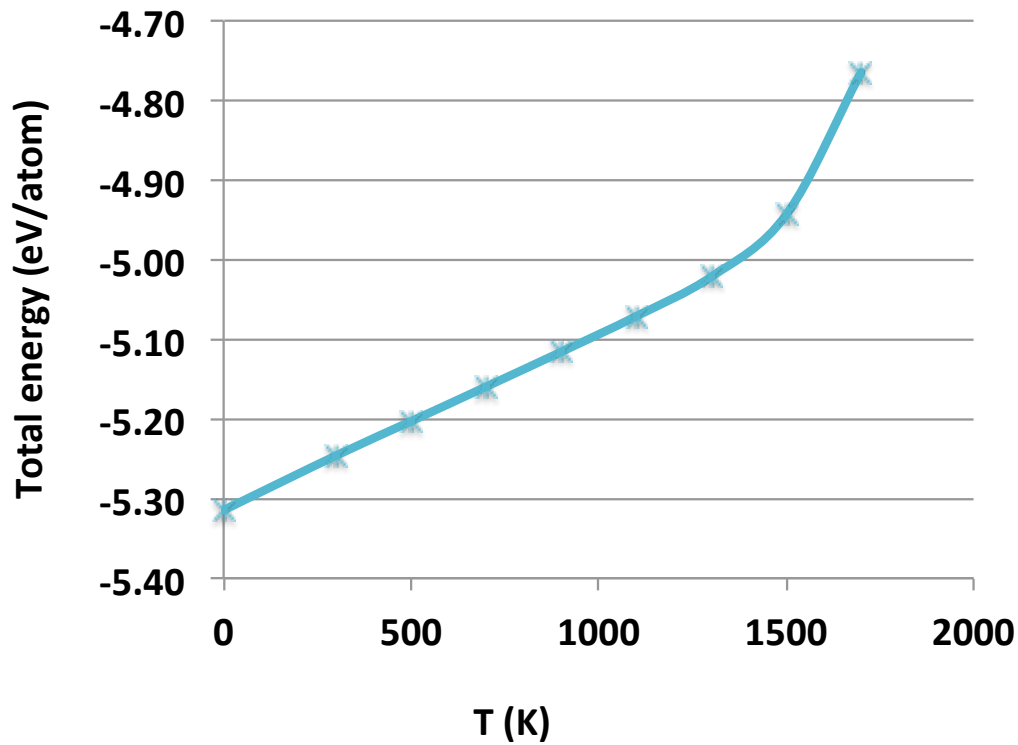

Figure 8: Total energy per atom as function of temperature for U_3Si_5 (MEAM).
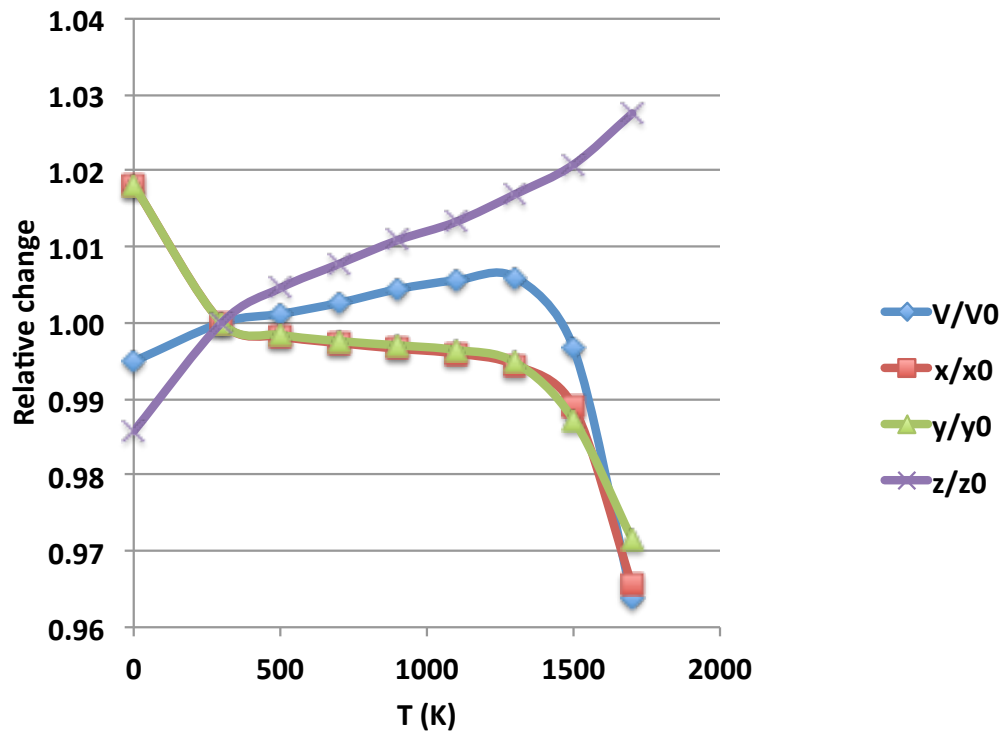

Figure 9: Relative change in lattice parameters and volume as function of temperature for U_3Si_5 (MEAM).
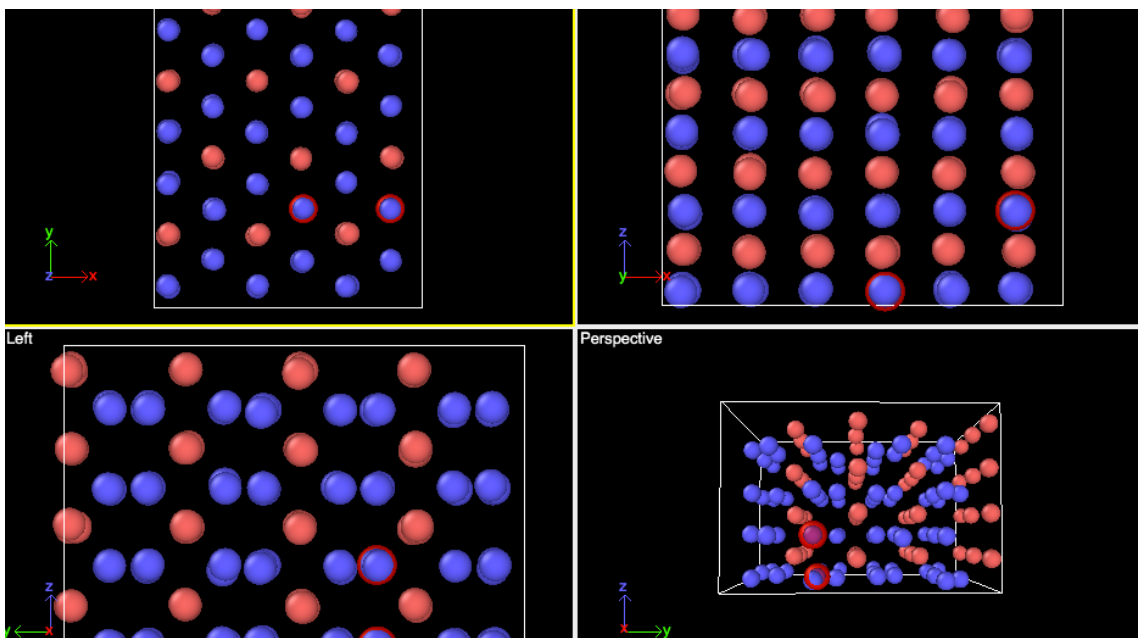
Figure 10: The structure of U$_3$Si$_5$ at 300 K (MEAM). The vacancies on the Si sublattice in the 300 K structure were ordered according to the lowest energy configuration found by a limited search at 0 K. According to the preliminary results the vacancies prefer to separate as much as possible from each other. Red spheres represent uranium and blue silicon.

Conclusions and outlook

This report summarizes the initial steps in developing a semi-empirical Modified Embedded Atom Method (MEAM) potential for the U-Si system and also provides an assessment of the general challenges associated with developing potentials for this system. The MEAM potential was successful in capturing the stability and structure of the two main U$_3$Si$_2$ and U$_3$Si$_5$ fuel candidates. However, the complex bonding in this system gives rise to a complicated phase diagram and the potential fails to accurately predict the stability for some of the other U-Si phases. The MEAM potential also predicts competing stable phases at the U$_3$Si$_2$ composition that have not been confirmed by DFT calculations or experiments. This is going to cause problems in finite temperature molecular dynamics simulations. Additional work is required to resolve these issues. The volumes, elastic constants and defect properties predicted by the MEAM potential also deviate from DFT calculations and experiments for several cases. All of these discrepancies are likely connected and we are currently focusing on improving the description of the volume of the USi$_2$ compound (AlB$_2$ structure), since that seems to be the root cause of many of the observed discrepancies. Despite the challenges that have been identified, our initial assessment of the possibility of developing a reliable U-Si potential has demonstrated some promising results and we are continuing to improve the MEAM potential. The results will also be provided as feedback to the development of a U-Si Tersoff potential at Idaho National Laboratory.

References

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