

A modified Embedded-Atom Method interatomic potential for uranium-silicide

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Abstract

Uranium-silicide (U-Si) fuels are being pursued as a possible accident tolerant fuel (ATF). This uranium alloy fuel benefits from higher thermal conductivity and higher fissile density compared to UO₂. In order to perform engineering scale nuclear fuel performance simulations, the material properties of the fuel must be known. Currently, the experimental data available for U-Si fuels is rather limited. Thus, multiscale modeling efforts are underway to address this gap in knowledge. In this study, a semi-empirical Modified Embedded Atom Method (MEAM) potential is presented for the description of the U-Si system. The potential is fitted to the formation energy and structural properties of U₃Si₂. The primary phase of interest (U₃Si₂) is accurately described over a wide temperature range and displays good behavior under irradiation and with free surfaces. The potential can also describe a variety of U-Si phases across the composition spectrum.

1. Introduction

Nuclear fuels operate in reactor environments experiencing high temperatures, temperature gradients and mechanical stress under neutron irradiation. This complex and extreme environment, combined with the high power density that allows nuclear fuels to be economical, presents safety challenges during off-normal events and accidents. In addition to innovations in reactor design, research is focused on the development of advanced materials [1] to improve accident tolerance. Accident-tolerant fuel (ATF) [2] is being considered as a potential fuel type for future and existing light-water reactors (LWRs). ATF's aim to provide additional coping time in the event of an accident (such as a loss of coolant accident) due to the inherent properties of the fuel, while maintaining good operational characteristics. Uranium-Silicide (U-Si), and particularly U₃Si₂, is being considered as a fuel candidate in ATFs. U₃Si₂ exhibits both higher uranium density than traditional UO₂ LWR fuel, thus allowing for the possibility of reduced enrichments, fewer assemblies and/or an extended lifetime in the core. U₃Si₂ also possesses a higher thermal conductivity than UO₂, allowing for a lower fuel centerline temperature and more rapid heat removal during off-normal conditions.

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In order for the implementation of U_3Si_2 to become a reality, the scientific community must be able to perform continuum scale descriptive and predictive nuclear fuel performance simulations. To perform such simulations, the material properties of the fuel must be known. Subjecting U_3Si_2 to the in-reactor environment leads to microstructural changes due to the evolution of radiation produced defects, segregation and precipitation of fission products, and mechanical deformation. These changes in fuel microstructure change fuel properties, directly impacting fuel performance and safety. The ability to understand and model microstructural changes throughout the lifetime of the fuel is critical in developing fuel performance modeling codes. However, the current experimental data available for U-Si fuels is rather limited. This includes, but is not limited to, crystal structures [3, 4], phase diagrams [5], thermal conductivity, heat capacity, thermal expansion [6, 7], high pressure diffraction [8], and formation enthalpies [9, 10, 11, 12, 13]). Thus, multiscale modeling efforts are underway to address this gap in knowledge.

One recent investigation involved first principles calculations characterizing a variety of properties in the U-Si system [14]. These calculations have been able to provide insight where experimental information is lacking. However, first principles calculations are limited in their ability to investigate systems larger than a few hundred atoms in size, and are severely restricted in their ability to investigate properties at non-zero temperatures. Thus, although these types of investigations are of critical importance, branching to higher time and length scales is necessary for the investigation of larger, more complex systems. Unlike first principles calculations, molecular dynamics (MD) utilizes interatomic potentials to solve Newton's equations of motion. Thus, MD can be used to calculate relevant properties above 0 K on a nanosecond time and nanometer spatial scale. Information obtained from molecular statics and dynamics simulations can then be input into higher level modeling methodologies such as phase field, kinetic monte carlo or continuum level finite element modeling. In this manner, physics-based multiscale microstructural evolution models can be generated. Thus, development of an interatomic potential to describe the U-Si system is a critical step in branching time and length scales with the longterm goal of developing a descriptive and predictive nuclear fuel performance code.

Very few interatomic potentials have been constructed for uranium-based alloys. This is due to the inherent difficulty in describing the behavior of f-electrons and the mechanical instability of the γ phase of uranium at low temperatures. Several interatomic potentials have been developed for pure uranium [15, 16, 17, 18, 19, 20], with only a few being adapted into alloy potentials for U-Zr [21], U-Al[22] and U-Mo [23]. Based on the functionality of the modified Embedded-Atom Method (MEAM) variants of U and U-Zr [15, 21] as well as their inclusion of fission gases Xe, Kr and He [16], it is determined that this is a suitable potential form to pursue in attempting to describe the U-Si system.

This manuscript presents a MEAM interatomic potential for the description of the U-Si system, with particular emphasis on U_3Si_2 . No interatomic potentials for the U-Si system have been constructed prior to this work.

2. MEAM Theory

The Embedded-Atom Method (EAM) [24, 25, 26] has been shown to predict the properties of alloys and metals quite well. The EAM is the most widely used semi-empirical potential, with applications including calculations of point defects [27], melting [28], grain boundary structure and energy [29], dislocations [30] [40], segregation [31], fracture [32] and surface structure [33]. The basis of the EAM is that the cohesive energy can be expressed in terms of embedding energies. In this view, each atom in the metal is embedded into the electron gas created by the other atoms. The EAM provides a robust means of calculating structure and energetics; however, it is best suited strictly for purely metallic systems with no directional bonding. From the EAM, the total energy of a system of atoms is given by equation 1:

$$E = \sum_i \{F(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} S_{ij} \phi(R_{ij})\} \quad (1)$$

where i and j are the individual atoms of the model [26, 24]. The pair interaction between atoms i and j is given by ϕ [34] and is dependent on the separation between the atoms R_{ij} .

$$\phi(R) = \frac{2}{Z} \{E^u(R) - F(\frac{\bar{\rho}^0(R)}{Z})\} \quad (2)$$

In equation 2, Z is the number of first neighbors, $\bar{\rho}^0(R)$ is the background electron density and $\{E^u(R)\}$ is the per atom energy of the reference structure as a function of nearest-neighbor distance R [35] obtained from the universal equation of state of Rose et al. [33] given in equation 3.

$$E^u(R) = -E_c(1 + a^* + \delta \times (\frac{r_e}{r}) \times (a^*)^3)e^{(-a^*)} \quad (3)$$

with

$$a^* = \alpha(\frac{R}{r_e} - 1) \quad (4)$$

and

$$\alpha^2 = \frac{9\omega B}{E_c} \quad (5)$$

where E_c , r_e , ω and B are the cohesive energy, nearest neighbor distance, atomic volume and bulk modulus, respectively, evaluated at equilibrium in the reference structure. The background electron density is given by:

$$\bar{\rho}^0(R) = Z\rho^{a(0)}(R) \quad (6)$$

where $\rho^{a(0)}$ is an atomic electron density discussed below. The embedding function, F , is given in equation 7 and is the energy required to embed atom i into a system with a background electron density $\bar{\rho}_i$.

$$F(\bar{\rho}) = AE_c \frac{\bar{\rho}}{Z} \ln \frac{\bar{\rho}}{Z} \quad (7)$$

The modification to the EAM is a function of how the electron density at a certain point, ρ_i , is calculated. In the traditional EAM, ρ_i is simply the linear supposition of spherically averaged atomic electron densities:

$$\rho_i^{(0)} = \sum_{j \neq i} \rho_j^{a(0)}(R_{ij}) \quad (8)$$

whereas the MEAM introduces angularly dependent terms to augment $\bar{\rho}_i$ as shown in equation 9 through equation 11 [35, 36].

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left\{ \sum_{j \neq i} x_{ij}^{\alpha} \rho_j^{a(1)}(R_{ij}) \right\}^2 = \sum_{j, k \neq i} \rho_j^{a(1)}(R_{ij}) \rho_k^{a(1)}(R_{ik}) \cos\{\theta_{ijk}\} \quad (9)$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha, \beta} \left\{ \sum_{j \neq i} x_{ij}^{\alpha} x_{ij}^{\beta} \rho_j^{a(2)}(R_{ij}) \right\}^2 - \frac{1}{3} \sum_{j \neq i} [\rho_j^{a(2)}(R_{ij})]^2 \quad (10)$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha, \beta, \gamma} \left\{ \sum_{j \neq i} x_{ij}^{\alpha} x_{ij}^{\beta} x_{ij}^{\gamma} \rho_j^{a(3)}(R_{ij}) \right\}^2 - \frac{3}{5} \sum_{j \neq i} [\rho_j^{a(3)}(R_{ij})]^2 \quad (11)$$

Here, the $\rho^{a(l)}$ are the atomic densities which represent the decrease in the contribution with distance R_{ij} and the α, β, γ summations are each over the three coordinate directions with x_{ij}^{α} being the distance ratio R_{ij}^{α}/R_{ij} with R_{ij}^{α} being the α component of the distance vector between atoms i and j [29]. Similar to equation 9, equations 10 and 11 can be put in a form that has a dependence on the angle between atoms i, j and k (θ_{ijk}), and this has been done by Baskes et al. [37]. Atomic electron densities are assumed to decrease exponentially,

$$\rho_i^{a(l)}(R) = e^{-[\beta^{(l)}(\frac{R}{r_e} - 1)]} \quad (12)$$

where $\beta^{(l)}$ are the decay lengths. To obtain the background electron density from the partial electron densities we make the assumption that the angular terms are a small correction to the EAM.

$$(\rho_i^{(0)})^2 = \sum_{l=0}^3 \bar{t}_i^{(l)} (\rho_i^{(l)})^2 \quad (13)$$

where the $\bar{t}_i^{(l)}$ [38] are combinations of model constants t^l that are associated with the atom types of neighbors i .

Many body screening is implemented through a screening function, S_{ik} , that quantifies screening between two atoms i and k due to other atoms in the system, j. The atomic electron densities and the pair potential are multiplied by this function. The screening function depends on all other atoms in the system:

$$S_{ij} = \prod_{k \neq i,j} S_{ijk} \quad (14)$$

where S_{ijk} is calculated using a simple geometric construction. The screening factor S_{ijk} is defined as:

$$S_{ijk} = f_c \left[\frac{C - C_{min}}{C_{max} - C_{min}} \right] \quad (15)$$

Where C is a geometric parameter, and C_{min} and C_{max} are limiting values of C. The smooth cutoff function is:

$$f_c(x) = \begin{cases} 1 & x \geq 1 \\ [1 - (1 - x)^6]^2 & 0 < x < 1 \\ 0 & x \leq 0 \end{cases} \quad (16)$$

A radial cutoff function is also applied to the atomic electron densities and pair potential which is given by $f_c[(r_c - r)/\lambda]$ where r_c is the cutoff distance of 6 Å and λ gives the cutoff region and was chosen to be 0.1. The MEAM has been shown to accurately predict the behavior of complex systems such as plutonium [35] and tin [39]. It should be noted that these equations are for a single component system and can be generalized for a multicomponent system, as was done in [40].

3. Fitting Procedure

In order to create a functional uranium-silicide (U-Si) binary interatomic potential, there must first exist (or be generated) suitable potentials for each individual element. A uranium potential from Moore, et. al [21] is utilized in the fitting. This MEAM interatomic potential performs excellently in describing the body-centered cubic phase of uranium and the alloy behavior of UZr. For the Si MEAM contribution, the initial potential utilized was from Baskes [34]. Upon finding this potential over-predicted the Si-Si dimer distance (reference value of 2.25 Å[41]), the fitting of a new Si-Si potential was undertaken in an attempt to rectify this discrepancy, as well as increasing the vacancy formation energy in diamond cubic silicon. The only MEAM parameters allowed to vary in the Si potential fitting process were β^0 , β^1 , β^2 , β^3 , t^1 , C_{min} and C_{max} . The resulting potential is shown in table 1, with the associated properties of the original and new MEAM potentials shown in table 2. Although the Si-Si dimer distance was unchanged, the formation energy of a vacancy in diamond Si is increased. All other properties are relatively unaffected.

The fitting procedure to develop cross-species parameters (U-Si interactions) involves a reference phase ($L1_2$ U₃Si), a starting guess for MEAM parameters, and is then refined via a script that gives a random step to all relevant MEAM parameters. This updated potential is then input into LAMMPS [42] and a series

Table 1: Silicon MEAM potential parameters

Parameter	Original Si-MEAM	New Si-MEAM
attrac	0	0
repuls	0	0
alpha	4.87	4.87
β^0	4.4	4.4662
β^1	5.5	9.4016
β^2	5.5	13.3826
β^3	8.5	8.6993
alat	5.431	5.431
esub	4.63	4.63
asub	1	1
t^0	1	1
t^1	2.05	2.8841
t^2	4.47	4.47
t^3	-1.80	-1.80
C_{min}	2.0	1.7215
C_{max}	2.8	2.4942

of simulations are performed, the output of which is utilized to calculate a weighted-error summation. The script then either accepts or rejects the prescribed changes to the MEAM parameters based on the reduction of the total weighted-error. The emphasis of the fitting procedure was the U₃Si₂ phase, which possesses a relatively complex crystal structure, with a 10 atom unit cell in space group P4/*mbm*-No. 127, two unique uranium atomic sites (2a (0, 0, 0) and 4h (0.181, 0.681, 0.5)) and one unique silicon atomic site (4g (0.389, 0.889, 0)), as first reported by Zachariasen [3]. The cohesive energy, lattice constants and elastic constants of the U₃Si₂ phase were given priority with respect to the error weighting, and are thus considered the primary fitting targets. A variety of other simulations were performed to fine-tune the potential, the entirety of which is beyond the scope of this paper. The potential parameters are shown in table 3. Screening parameters are given in LAMMPS format (i.e., $C_{max}(I,J,K)$ is a screening parameter when I-J pair is screened by K).

For the sake of clarity and reproducibility, LAMMPS MEAM-specific parameters are included in table 4. It should also be noted that a non-standard implementation of MEAM within LAMMPS (which relates to modification of the smooth cutoff function) was utilized for the existing U MEAM potential and this subsequent U-Si potential. Please contact the authors to obtain the required modifications in order to accurately utilize the potential.

Table 2: Properties of silicon MEAM potentials. Units are as follows: E (eV/atom), a (\AA), c_{xx} (GPa), E_{form} (eV).

Structure	Property	Original Si-MEAM	New Si-MEAM
Diamond	E	-4.63	-4.63
	a	5.431	5.431
	c_{11}	163.8	165.2
	c_{12}	64.6	64.6
	c_{44}	78.8	95.2
	E_{form}^{vac}	3.858	4.142
FCC	E	-4.065	-4.151
	a	4.100	4.098
HCP	E	-4.067	-4.152
	a	2.904	2.902
	c/a	1.624	1.624
SC	E	-4.337	-4.358
	a	2.622	2.622
BCC	E	-4.316	-4.286
	a	3.145	3.176
Dimer	E	-2.558	-2.546
	a	2.431	2.443

Table 3: Uranium-silicon MEAM potential parameters.

Parameter	U-Si MEAM
E_c	5.36
r_e	3.05
lattce	112
r_c	6.0
attrac	0.1873
repuls	0.0742
alpha(1,2)	4.978
rho(2)	4.151
rho(1)	1
$C_{min}(1,1,2)$	0.124
$C_{max}(1,1,2)$	2.604
$C_{min}(1,2,1)$	2.107
$C_{max}(1,2,1)$	2.741
$C_{min}(1,2,2)$	1.549
$C_{max}(1,2,2)$	2.517
$C_{min}(2,2,1)$	0.985
$C_{max}(2,2,1)$	1.606

Table 4: LAMMPS  MEAM-specific parameters

Parameter	U-Si MEAM
bkgd_dyn	1
nn	1
delr	0.1
ialloy	1
augt1	0
emb_lin_neg	1

4. U-Si MEAM Potential Results

The results for fundamental properties of U_3Si_2 at 0 K are displayed in table 5 and compared to experiments [3, 13] and DFT calculations [14] (DFT+U results from [14] are used for comparison but simply referred to as DFT here). The formation energy and the volume per atom are very accurate. The a lattice constant is slightly underestimated, and the c lattice constant is slightly overestimated. The elastic constants show varying degrees of agreement with DFT predictions. Excellent agreement is shown for G^{xy} and G^{xz} (equations 17 and 18), but significant variance is observed for C_{44} , for example. The resulting bulk modulus, calculated via the elastic constants 19, is overestimated. The bulk modulus was also calculated via the Birch-Murnaghan curve [43, 44], yielding a value of 114 GPa, which is consistent with the calculation of the bulk modulus via elastic constants. A comparison of the elastic constants predicted by MEAM and calculated via DFT are displayed in Figure 1. The blue line represents a 1:1 agreement between MEAM and DFT. It is observed a general overstiffness prediction of the elastic constants, with the exception being C_{44} , which is underpredicted. The root-mean-square error over the nine calculated elastic constants is 35.4 GPa.

$$G^{xy} = \frac{\frac{C_{11} + C_{22}}{2} - C_{12}}{2} \quad (17)$$

$$G^{xz} = \frac{\frac{C_{11} + C_{33}}{2} - C_{13}}{2} \quad (18)$$

$$B = (C_{11} + C_{22} + C_{33} + 2 * C_{12} + 2 * C_{13} + 2 * C_{23}) / 9 \quad (19)$$

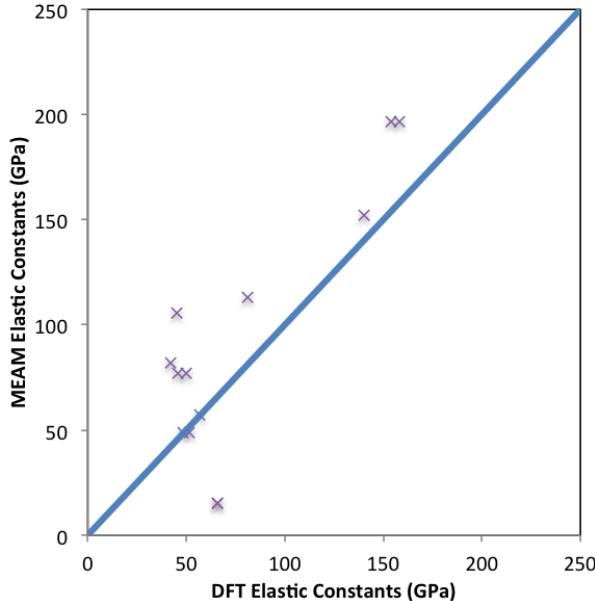


Figure 1: Comparison of U_3Si_2 elastic constants as calculated by DFT and MEAM.

Table 5: Properties of U_3Si_2 at 0 K. Results from the MEAM U-Si potential are compared to experiments¹[3]²[13] and DFT³[14] calculations.

	Reference	U-Si MEAM
E	-0.356 ²	-0.354
V/at	20.844 ¹	20.950
a	7.32 ¹	7.157
c	3.89 ¹	4.090
c/a	0.531 ¹	0.572
C ₁₁	149 ³	196.6
C ₃₃	139 ³	152.3
C ₁₂	49 ³	81.9
C ₁₃	48 ³	77.0
C ₄₄	63 ³	15.3
C ₆₆	46 ³	105.8
B	81 ³	113
G ^{xy}	50 ³	57
G ^{xz}	48 ³	49

The U_3Si_2 structure as predicted by the MEAM potential is shown in figures 2 and 3, compared to the experimental structure [3]. These figures illustrate a supercell of $2 \times 2 \times 3$ unit cells with periodic boundaries. In figure 2 a slight expansion of uranium atoms (red) in the purely uranium plane is observed. Otherwise, agreement is excellent. In figure 3 a minuscule clockwise rotation of atoms in the unit cell with respect to the experimental structure is observed. This alteration is nearly imperceptible, except by analyzing the radial distribution functions (RDFs), as shown in figure 4. The RDF shows that the structure is not capturing the smallest interatomic distance; this is due to the slight expansion in the U plane and the clockwise rotation of U and Si atoms. These minor distortions slightly increase the first nearest neighbor distance by approximately 0.2 Å and slightly decrease the second and third nearest neighbor distances, as shown in Figure 4 in the distance regime of 2.8-3 Å. 

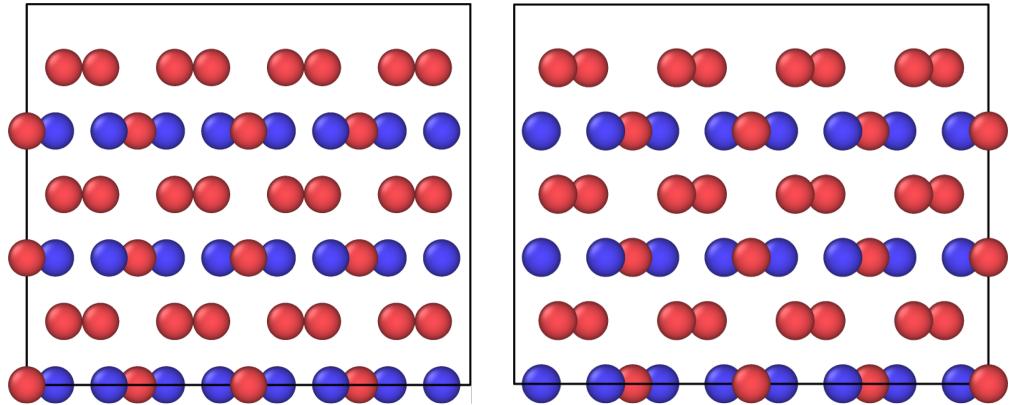


Figure 2: (100) view of the predicted structure (left) and the experimental structure (right) of U_3Si_2 . Uranium atoms in red; Silicon atoms in blue.

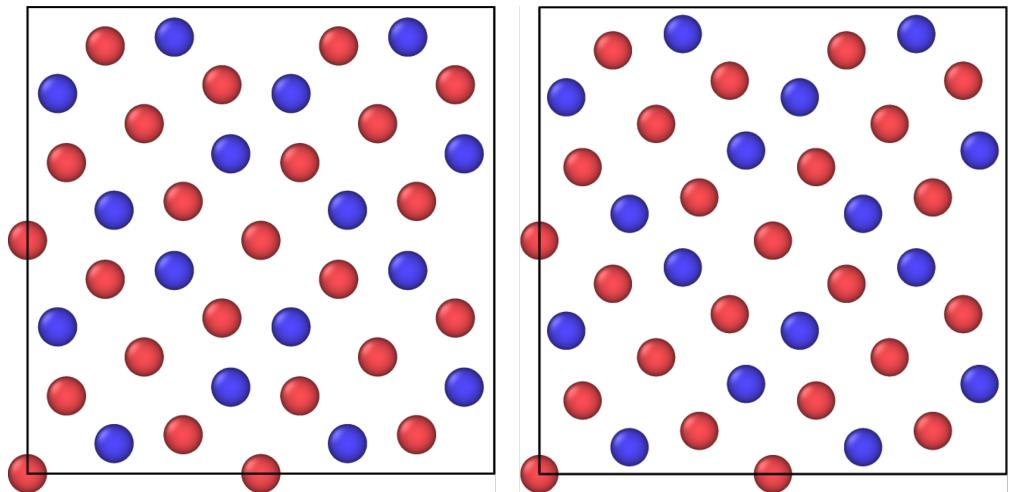


Figure 3: (001) view of the predicted structure (left) and the experimental structure (right) of U_3Si_2 . Uranium atoms in red; Silicon atoms in blue.

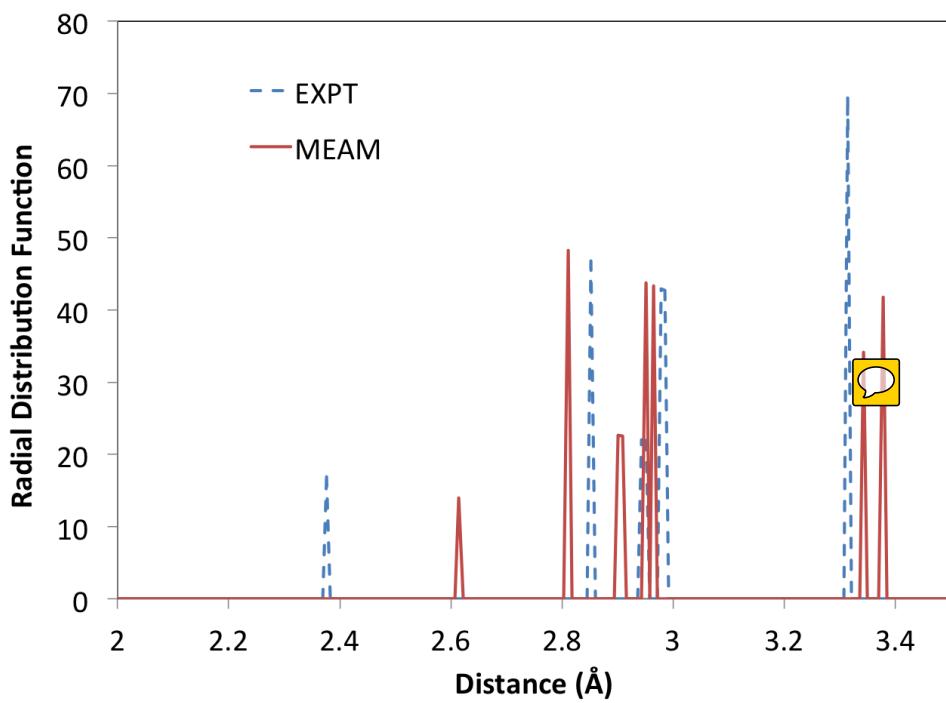


Figure 4: Radial distribution functions of U_3Si_2 , comparing the MEAM predicted structure with the experimental structure.

Moving beyond the perfect crystal, the next step in testing the accuracy of the potential is to investigate point defects. Single point defects (vacancy, antisite) were considered as a means of accommodating a change in stoichiometry. The methodology for calculating point defect energetics is outlined in [45]. Point defect energies for the U_3Si_2 system are shown in table 6 and compared to results from DFT [45]. Bound Schottky defects are also shown in table 6. There exist two unique uranium sites in the U_3Si_2 structure. Both U sites are investigated and denoted simply U1 (for the 2a site) or U2 (for the 4h site), as in Remschnig, et al. [4]. The bound Schottky defect consists of two U2 vacancies, one U1 vacancy and two Si vacancies, such that crystallographic accuracy is maintained, as well as the accurate chemical formula. Excellent agreement is observed for the formation energy of the U1 vacancy site. Reasonable agreement is observed for the U2 vacancy and the U2 anti-site defect (Si atom on a U2 lattice site). However, defect formation energies are generally underestimated. The Si vacancy formation energy is substantially underestimated, and this likely leads to the bound and bound Schottky defect energies being substantially underestimated as well.

Table 6: Properties of point defects in U_3Si_2 at 0 K. Results from the MEAM U-Si potential are compared to DFT calculations [45].

	U-Si MEAM	DFT
U1 vac	0.65	0.68
U2 vac	0.90	1.20
Si vac	0.57	1.59
U1 anti	0.25	0.16
U2 anti	0.25	0.35
Si anti	0.34	0.35
Schottky Bound	5. 	7.57

In order to ensure that the potential is not restricted to studying only the U_3Si_2 phase, other phases, experimental and theoretical, were examined that were not included in the fitting procedure. These include the FeB-USi, B1-USi, AlB₂-USi₂, L1₂-USi₃, U_3Si_5 phases and the L1₂, α and β phases of U_3Si . The results are shown in Figures 5 and 6 as the formation energy as a function of uranium concentration and the volume per atom as a function of uranium concentration, respectively. In Figure 5, excellent agreement is observed for the uranium rich portion of the composition range. For U_3Si , U_3Si_2 and FeB-USi, formation energies are nearly identical to those from experiments [13], and DFT calculations [14]. Also, the minimum is observed at USi₂ for the MEAM potential, which matches experiment, and the minimum is observed at $\text{U}^{\text{SC}}\text{Si}_2$ (a distorted USi₂ structure with $\frac{1}{6}$ of the silicon sites vacant) for DFT, which shows reasonable agreement. The energy of USi₂ is slightly lower than what would be consistent with the convex hull behavior shown in experiments [13]. Significant variance is observed for the USi₃ and B1-USi structures. These structures are deemed to be of less importance as they are either far away from the composition range of interest, in the case of USi₃, or not

the low energy structure, in the case of B1-USi. In Figure 6, there exists a general negative parabolic trend in the volume predicted via the USi MEAM potential as a function of composition. This matches the trends from DFT quite well, with the exception being MEAM overestimating the volume per atom of the FeB-USi structure. Per-atom volumes of U_3Si_2 and U_3Si agree incredibly well. Given that only U_3Si_2 was utilized as a fitting target and $L1_2-U_3Si$ was utilized as a reference structure, there is considerable agreement across the entire composition spectrum when comparing MEAM predicted results to the results from DFT calculations. It should be noted that DFT calculations [14] found the presence of another structure for U_3Si_2 that is lower in energy than the experimental structure. This structure was destabilized by the addition of the Hubbard U term, which resulted in the correct prediction of the experimental structure as the ground state. In order to ensure no such low energy structure exists in the MEAM potential energy landscape, this alternate U_3Si_2 structure was analyzed and found to be 0.125 eV/at higher in energy than the experimental structure. Thus, the MEAM interatomic potential is predicting the experimental structure to be the equilibrium phase, which is encouraging.

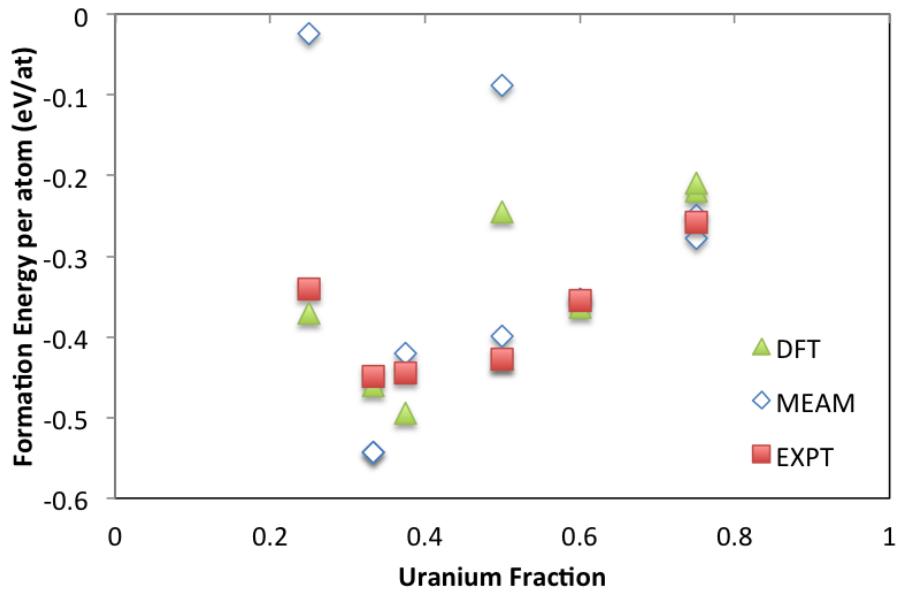


Figure 5: Formation energy per atom as a function of uranium concentration for a variety of phases in the U-Si system compared to DFT calculations [14].

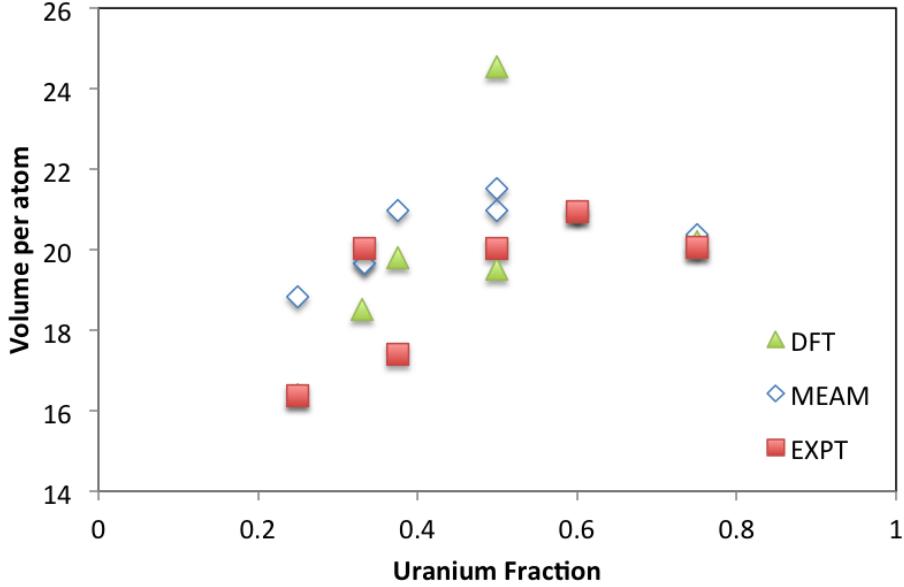


Figure 6: Volume per atom as a function of uranium concentration for a variety of phases in the U-Si system compared to DFT calculations [14]..

Although the ability to accurately predict the properties of a variety of crystal structures at 0 K is a critical step in the generation of a reasonable interatomic potential, being able to accurately model systems at non-zero temperatures is necessary to fully utilize the strength of molecular dynamics in branching the atomistic and mesoscopic time and length scales. Thus, the nature of U_3Si_2 was examined as a function of temperature. A 360 atom ($3 \times 3 \times 4$ unit cells) supercell is equilibrated at a given temperature in an NPT ensemble utilizing a Nose-Hoover barostat and a Langevin thermostat in the Grønbech-Jensen-Farago [46] formalism with a 1 fs timestep. The damping parameters for the Nose-Hoover barostat and the Langevin thermostat are 0.1 and 0.01, respectively. The target pressure is zero with the x , y and z components independently controlled. The systems are equilibrated for 100 ps, with energies and volumes determined by averaging over the final 50 ps of the simulation. The total energy and total volume of the supercell as a function of temperature is displayed in figure 7. It is observed that the structure is stable and behaves predictably as a function of temperature. There are no observed obvious phase changes or discontinuities suggesting potential instabilities. The structure was visually confirmed to be U_3Si_2 throughout the temperature range investigated. The normalized lattice constants are also analyzed as a function of temperature to ensure there exist no structural irregularities. These are displayed in Figure 8. There is expansion of the a and b in equal proportion as temperature increases, suggesting the tetragonal symmetry of the crystal structure is retained. The c shows compression as temperature increases, and thus a decrease in the c/a ratio as temperature increases. The calculated MEAM average linear thermal expansion from 200 K to 1200 K is approximately $15.8 \times 10^{-6} \text{ K}^{-1}$ and the experimental linear thermal expansion is $14-17 \times 10^{-6} \text{ K}^{-1}$ from Shimizu [7] and $16.1 \times 10^{-6} \text{ K}^{-1}$ from White [6]. This is remarkable agreement given that this was not included into the

fitting procedure. The molar heat capacity, given by equation 20, was calculated at 400 K for comparison with White, et al. [6]. The calculated value from the MEAM potential is 120.7 J/mol-K, which compares very favorably to the Dulong-Petit value of 125 J/mol-K and is slightly less than the experimental value of White, et al., which is 150 J/mol-K. It should be reiterated that this thermophysical property was not included into the fitting procedure, and thus this is considered excellent agreement to both theory and experiment. Regretfully, relatively little other experimental data exists for comparison.

$$C_P = \left(\frac{\delta H}{\delta T} \right)_P \quad (20)$$

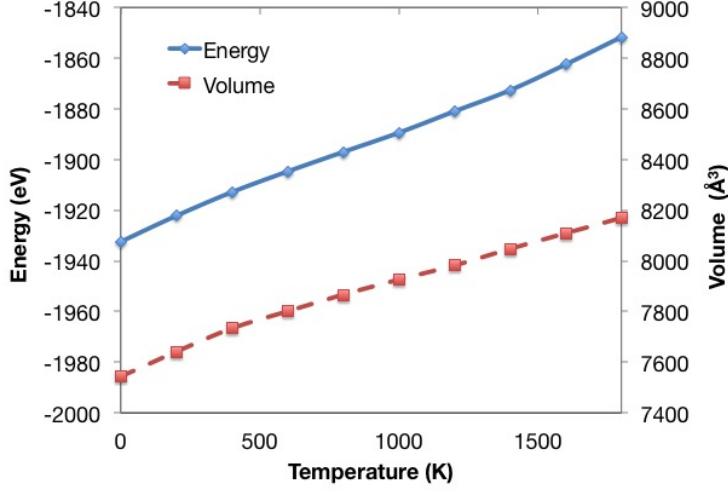


Figure 7: Energy and volume of U₃Si₂ as a function of temperature

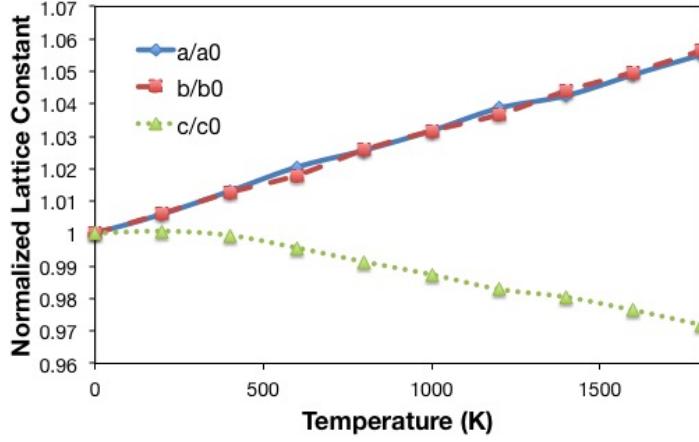


Figure 8: Variation of normalized lattice constants of U₃Si₂ as a function of temperature.

As a nuclear fuel, it is necessary that this potential be able to model U₃Si₂ under irradiation. In order to test the ability of the potential to model radiation damage, a 1 keV cascade is investigated. A 20,000

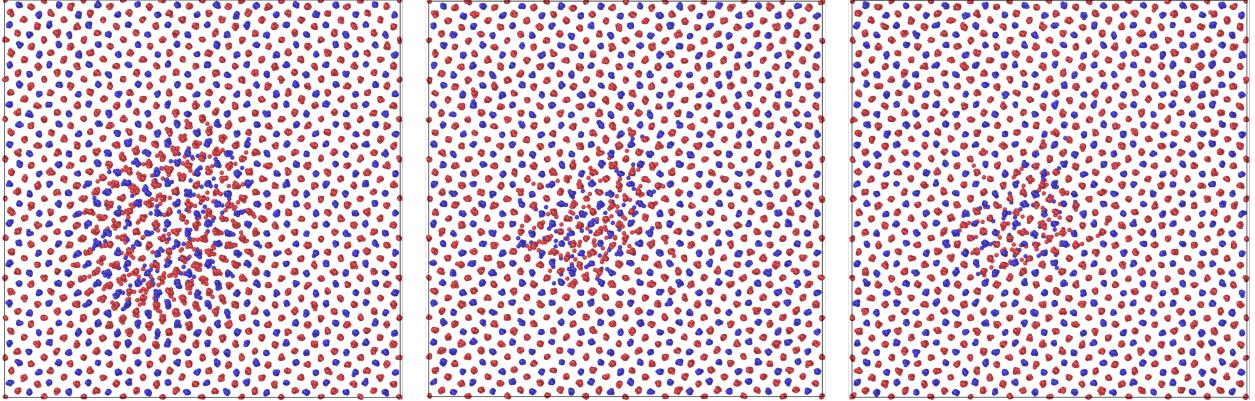


Figure 9: 1 keV cascade behavior of U_3Si_2 at 500 K. The left-most panel is 0.4 ps after cascade initiation; the middle panel is 12 ps after cascade initiation; the right-most panel is 1 ns after cascade initiation.

atom supercell ($10 \times 10 \times 20$ unit cells) is equilibrated at 500 K for 100 ps in an NPT ensemble with a target pressure of 0 GPa. In an NVT ensemble, a U1 atom is given additional kinetic energy in the [135] direction. The timestep is reduced to 0.2 fs and the cascade is allowed to evolve for 12 ps. The residual damage is then evolved at 500 K for 1 ns utilizing a 2 ps timestep. The state of the cascade and residual damage is displayed in Figure 10 at three different times throughout the simulation. It is observed that the crystal structure is stable and there exists a thermal spike and subsequent annealing stage. At 0.4 ps after cascade initiation, Wigner-Seitz analysis via Ovito [47] shows that there exist 68 Frenkel pairs; there exist 28 Frenkel pairs after 12 ps; there exist 17 Frenkel pairs after 1 ns. By investigating defects on each species sublattice, it can be determined the general nature of the defects generated via this specific cascade. Investigation of the total system at 12 ps shows that there exist 28 Frenkel pairs in the total system. Looking strictly at the uranium sublattice, 23 Frenkel pairs exist. Looking strictly at the silicon sublattice, 23 Frenkel pairs exist. This gives a total of 46 Frenkel pairs. It can thus be determined that in the total system there exist 28 Frenkel pairs and 18 anti-site defects, with the same number of defects on each sublattice. It can be concluded that this potential is displaying reasonable behavior under irradiation and the nature and number of defects can be readily determined. It should be noted that this is not intended to be a full radiation damage study, but simply an example that this potential produces reasonable radiation damage behavior. Radiation damage studies are certainly warranted in the future.

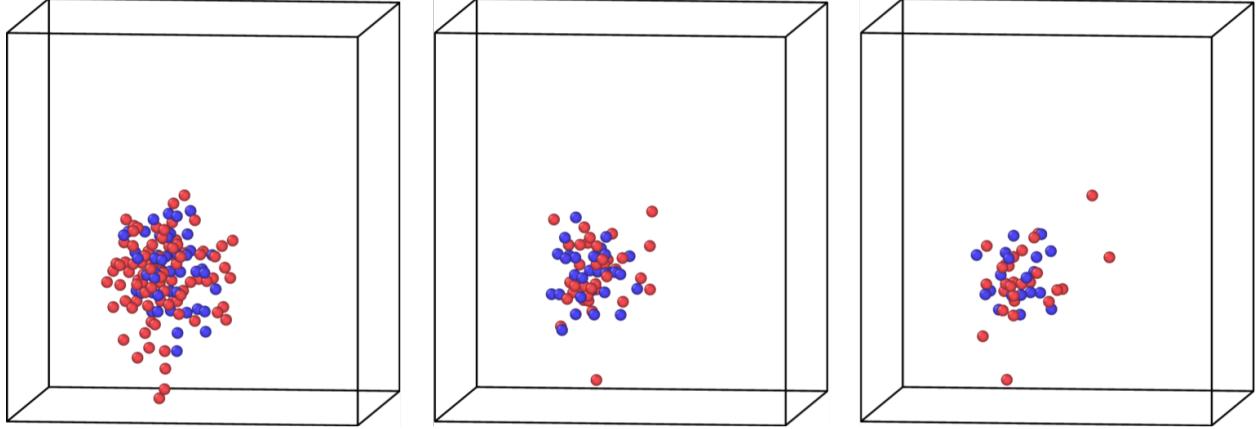


Figure 10: 1 keV cascade behavior of U_3Si_2 at 500 K. The left-most panel is 0.4 ps after cascade initiation; the middle panel is 12 ps after cascade initiation; the right-most panel is 1 ns after cascade initiation.

Another microstructural feature of interest is free surfaces. To ensure the potential is performing adequately with regards to surfaces, two systems are created to investigate both the (100) free surface and the (001) free surface (there exist multiple possible terminations, but in this work all terminuses are created at until cell boundaries). The system with free surfaces is equilibrated in an NPT ensemble at 500 K for 100 ps and the average energy is determined over the final 50 ps of the simulation. The relaxed structures of the (100) and (001) free surfaces are shown in Figure 11 and Figure 12, respectively. The first thing to notice is that the bulk structure remains stable and retains its crystal symmetry. There also exists some surface roughening along the first and second layers of atoms along the free surfaces. The surface energies are determined by equation 21

$$E_{surf} = \frac{(E^* - E)}{2 * A} * N \quad (21)$$

where E^* is the energy per atom of the system with two free surfaces, E is the energy per atom of the perfect crystal U_3Si_2 , A is the area of a free surface (multiplied by two because two free surfaces are present in the system) and N is the number of atoms in the system with two free surfaces. The resultant energy for the (100) surface is 0.99 J/m² and the (001) surface energy is 1.50 J/m². A prior DFT study investigated free surfaces in U_3Si_2 [48]. The surface energy was found to vary from 1.16 J/m² to 1.48 J/m². The 100 surface has a surface energy of 1.48 J/m², while the 001 surface has a surface energy of 1.43 J/m². Given that the physical nature of the surfaces is reasonable combined with the calculation of reasonable surface energies, it is suggested that the interatomic potential performs adequately for free surfaces in U_3Si_2 . Of course, further experimental and computational investigations are required for validation of this predicted surface behavior. To further investigate the performance of the potential, a void is introduced into an equilibrated U_3Si_2 system, and then further relaxed. It is observed that both voids of radius 4 Å (containing 13 vacancies) and 8 Å (containing 93 vacancies, shown in Figure 13) are stable within the structure up to 100 ps (when simulations were terminated). No void collapse is observed, no crystal structure collapse is observed, but

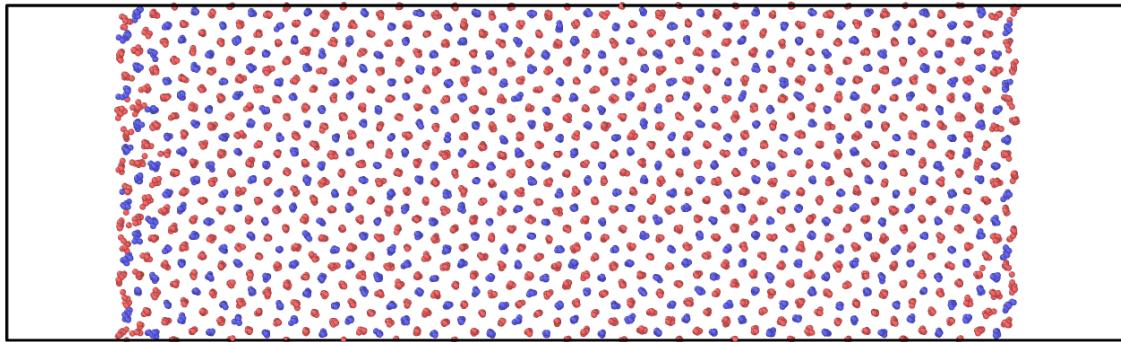


Figure 11: (100) free surface of U₃Si₂ at 500 K after a 100 ps relaxation.

minimal void surface reconstruction does occur. This further reinforces the suitability and stability of the potential for non-equilibrium systems.

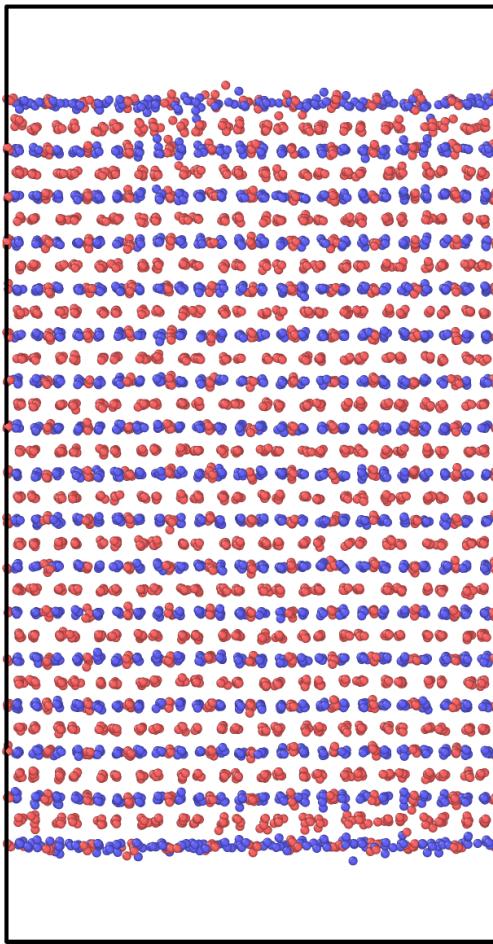


Figure 12: (001) free surface of U_3Si_2 at 500 K after a 100 ps relaxation.

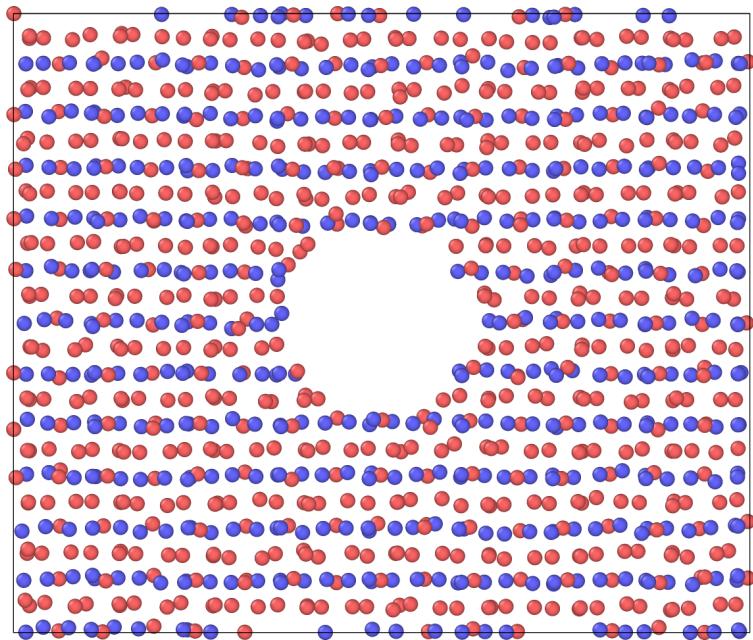


Figure 13: 2D projection of a 3D slice through the a U_3Si_2 supercell at 500 K containing a void with a radius of 8 Å.

5. Discussion

It is the authors' opinion that the potential performs quite strongly for the U_3Si_2 phase with regards to cohesive energy, volume per atom, and elastic constants at 0 K, as well as the thermal expansion and heat capacity at non-zero temperatures. The potential is adequately strong in adjacent U-Si compounds, such as U_3Si and USi . The potential is not suited for describing low uranium content U-Si compounds, such as USi_3 . Also, certain care needs to be exercised when investigating defects utilizing this potential, as important deviations from DFT calculations are observed. Finally, the potential is not intended for investigation of liquid phase U_3Si_2 , as this was not taken into account in the fitting procedure nor fully explored by the authors.

Given the complex nature of the crystal structure of U_3Si_2 , the inherent difficulties associated with the development of atomic potentials for pure uranium, let alone uranium-alloys, it is the opinion of the authors that a suitable interatomic potential to describe the U-Si system has been developed. Provided that the scientific community is continually gaining more knowledge on U-Si alloys via experimentation and first principles examinations, future refinement of the potential should be undertaken once more atomistic and fundamental property information has been gathered. Until such time, this potential can be utilized for the investigation of the U-Si system, in particular U_3Si_2 , at 0 K and up to temperatures of interest for nuclear reactors.

6. Conclusion

A MEAM interatomic potential was developed for the U-Si system. The potential accurately describes 0 K properties of the primary phase of interest (U_3Si_2), including formation energy, lattice constants, elastic constants and a several of point defect properties. The potential can also reasonably predict properties of a variety of U-Si phases across the composition spectrum. The predicted thermal expansion compares excellently to reported experimental values. The interatomic potential was tested by investigating the behavior of U_3Si_2 under a 1 keV cascade, with free surfaces and in the presence of a void. The potential behaves in a reasonable manner in each of these three non-equilibrium cases. This potential can serve as a tool to branch experiments and recent first principles calculations to future longer time and larger length scale simulations.

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