**Thermophysical properties of U3Si2 fuel: A molecular dynamics study**

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**Abstract**

As a result of the renewed interest in uranium silicide compounds as a candidate for nuclear reactor fuels the extensive knowledge of their thermophysical properties as a function of temperature is required. In this work, we calculated the thermal properties and radiation tolerance of U3Si2 compound within the framework of molecular dynamics (MD) using semi-empirical modified Embedded-Atom Method (MEAM) potential. Thermal expansion, thermal conductivity, heat capacity, and elastic properties are presented as a function of temperature. The thermal conductivity of U3Si2 increases with temperature due to the electronic contribution while the phonon contribution is about ~1.37 W/m-K and ~1.36 W/m-k using non-equilibrium molecular dynamics (NEMD) and equilibrium molecular dynamics (EMD) respectively at 300 K which reduces as temperature increases. Therefore, deployment of U3Si2 as fuel helps to lower the thermal gradients and high centerline temperatures during reactor startup and operation due to the dominant electronic component of the thermal conductivity.

***Keywords:*** *Uranium silicide; ATF; molecular dynamics; thermophysical; MEAM.*

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**1. Introduction**

Uranium dioxide (UO2) is the standard fuel in today’s Light Water Reactors (LWRs). It is subjected to extreme conditions that include high radiation dosage and temperature, which leads to change of thermomechanical and structural properties of the fuel rod during operation. This has a significant effect on the thermal conductivity of the fuel matrix, which decreases as temperature increase due to contribution from phonon scattering. The nuclear accident at Fukushima in 2011 provides the motivation for fuel vendors, in collaboration with national and international regulatory agencies, to consider an alternative fuel that can withstand the loss of coolant for a considerably longer time in the case of an accident. Also, higher efficiency during normal operation is required, however at the same time it would be preferable not making major changes to the present design of the LWRs in near future [1,2].

Binary uranium-silicon compounds such as U3Si2 have attracted a lot of attention as a nuclear fuel material because of some favourable properties compared to UO2. For instance, U3Si2 has a higher thermal conductivity, higher fissile material density and relatively high melting point [3]. The enhanced heat removal capabilities make uranium silicide fuel a promising potential fuel for generation *IV* reactors. However, until recently there has been a limited study on the thermal properties of uranium silicide [4] compared to other properties such as oxidation behaviour [5,6], structural information [7,8], and radiation resistance [9,10].

According to experiments [7,8], U3Si2 has a tetragonal crystal structure (space group 127) with U occupying *2a* and *4h* Wyckoff position while Si occupies the *4g* site. Each U atom is bonded to 4 nearest neighbour Si atoms forming a tetrahedral network as shown in Figure 1. Using a particle swarming optimisation code, Noordhoek *et al*., predicted a new U3Si2 phase with space group number 2 which has not been experimentally synthesized [11].

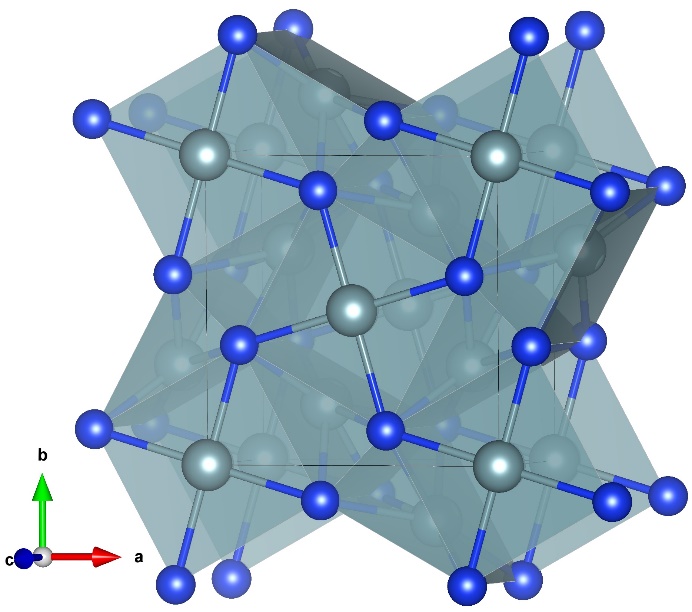


Figure 1: Unit cell of ordered uranium silicide containing 2 formula units of U3Si2 (10 atoms).

Since the growing interest in ATFs in the last few years, some work has been conducted on U-Si alloys focused on U3Si2. Density functional theory (DFT) calculations by Wang *et al.* provided detailed data on the electronic structure [12] and work by Middleburgh *et al.* modeled the formation energies of point defects [13], while White *et al*. developed a feasible powder metallurgy method of preparation and also measured the thermophysical properties of U3Si2 [3]. More recently, Obbard *et* *al.* used *in-situ* neutron diffraction to collect the temperature dependence of lattice parameters and the lattice thermal expansion coefficient was calculated. They observed an anisotropy in lattice expansion at ~1000 oC corroborating the dilatometry measurement of White *et al*. [3, 14]

Beyond the properties of pristine U3Si2, it is essential to understand the underlying behaviour in an extreme environment typical for a nuclear reactor. Our recent work within the framework of DFT explores the mechanism of oxidation from an atomistic perspective [15], while work by Wood *et al*., experimentally showed the oxidation kinetics in the presence of air and steam [16–18]. Furthermore, these authors investigated the possibility of reducing oxidation by alloying of U3Si2 with aluminium due to formation of an Al2O3 passivation layer which can prevent further oxidation [19]. The radiation-induced defects and fission products in a nuclear reactor fuel result in microstructural changes which in turn alters the fuel’s thermophysical properties [20]. Such behaviour is difficult and expensive to determine experimentally. Hence, Beeler *et al*. developed a MEAM potential to model the formation of point defects, formation energy and elastic properties of U3Si2 [21]. The force field developed in Beeler’s work will be used in this work to predict the thermophysical properties such as the heat capacity, thermal conductivity and thermal expansion of U3Si2. Recent *in-situ* TEM observation of Xe ion irradiated U3Si2 indicates that, at normal reactor operation conditions, uranium silicide is stable and no radiation-induced amorphisation was reported [22]. In a similar experiment using Kr ion, Miao *et al*. noticed that U3Si2 is oxidised forming a mixture of nanocrystalline UO2 and a Si-enriched amorphous phase raising concern for radiation assisted corrosion issues [23].

The thermophysical properties such as specific heat, the coefficient of thermal expansion, density and the thermal conductivity of the fuel as a function of temperature are important and must be known in order to effectively model and predict fuel behaviour under normal and off-normal irradiation conditions. In this work, we calculated these properties and evaluate the results obtained by comparing them with the experimental data available in the existing literature.

**2. Computational details**

Molecular Dynamics (MD) simulations, employing a set of interatomic potentials for U3Si2 derived previously by Beeler *et al*. [21] are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [24]. In this model the potential energy , of an atom *i* with respect to all other atoms has two components which are: i) a pair potential description of each system and ii) a modified many-body embedded atom method (MEAM) contribution. The detailed formalism is well described in references [25,26].

The lattice thermal conductivity () of a material is determined by several scattering mechanisms which include isotopic scattering, point defect scattering, three-phonon scattering and grain boundary scattering to name just a few. The value of can be calculated in different ways [27] that includes relaxation time approximation [28], Callaway model [29], Slack model [27], Non-Equilibrium Molecular Dynamics (NEMD) [27], Equilibrium Molecular Dynamics (EMD) with Green-Kubo formalism [30,31] and by solving Boltzmann transport equation iteratively [32]. In this work, we calculated using the MD based methods where the electronic thermal conductivity () was approximated using the Wiedemann–Franz lawrelationship [33].

The computation of thermal conductivity was done using both EMD and NEMD methods for comparison. In the EMD approach, the Green-Kubo method relates the equilibrium fluctuations of the heat current vector, S, to the thermal conductivity tensor via the fluctuation-dissipation theorem. The thermal conductivity in direction α is given by Eq.1 [30,31]

|  |  |
| --- | --- |
|  | (1) |

where is the Boltzmann constant, t is time, and and are the α components of the heat current vector and the heat current autocorrelation function (HCACF). The heat current vector is calculated using the atomic positions and velocities.

The EMD simulations were performed using the LAMMPS code [24]. The starting structures were first run for 4,000,000 time steps using an isothermal-isobaric (NPT) ensemble to allow the volume to expand, and then equilibrated under constant volume and energy ensemble (NVE) for 4,000,000 time steps at temperatures of interest. A time step of 0.25 fs was deem fit to maintain energy conservation. To avoid statistical noise during heat flux collection, NVE was run for additional 2,000,000 time steps. Correlation functions were evaluated from the heat current time series.

While in the NEMD simulations, the systems were initially equilibrated using an NPT ensemble with a Nosé-Hoover thermostat and barostat with a damping time of 0.1 ps and 0.5 ps respectively at zero external pressure. Equilibration is achieved when there is convergence in total energy and volume of the system.

These structures are equilibrated for 2 fs for temperatures between 300 K and 1800 K at 15 K intervals with the thermophysical properties (lattice parameter and enthalpy) obtained from averages taken over the final 0.25 fs of the simulation.

The equilibrated structures were also used for thermal conductivity computation using the non-equilibrium MD method. A time step of 1 fs was used throughout the simulation. In the NEMD method [34], kinetic energy can be transferred between atoms from one region of the supercell to another. Here, we used a rectangular supercell (slab) discretized into bins whose length in the *z*-direction is varied from 100–175 unit cells with a constant heat flux, , generated by exchange of atoms between the hot and cold region respectively as shown by schematic illustration in Figure 2. The temperature gradient, , is established between the two extreme temperatures due to the kinetic energy exchange. Eventually, a steady state in thermal gradient is reached where is equal and opposite to the kinetic energy exchange so that the temperature profile remains constant. The phonon thermal conductivity, , is computed using Eq. 2:

|  |  |
| --- | --- |
| , | (2) |

Where the temperature gradient,, is given by Eq. 3:

|  |  |
| --- | --- |
| , | (3) |

Where T is the temperature in Kelvin and is the length of the supercell in the z-direction.

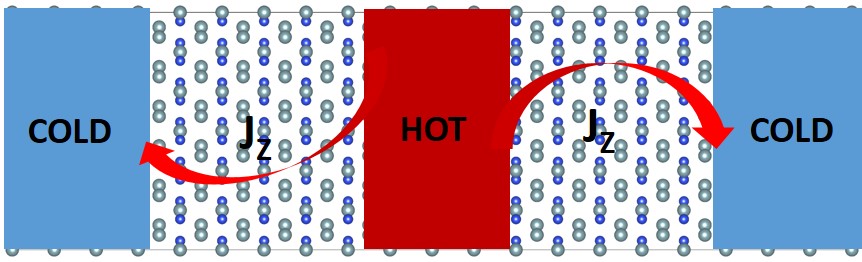


Figure 2: Schematic illustration of the NEMD used to study thermal conductivity of U3Si2. Uranium and silicon atoms are shown by grey and blue spheres respectively.

The was predicted using the Wiedemann-Franz law. The electrical conductivity (required in the Wiedemann-Franz law was obtained using BoltzTraP code [35] and non-self-consistent electronic structure calculated by Quantum ESPRESSO [36] for a dense k points mesh of . Relaxation time at 300 K is evaluated by equating the experimental resistivity 1.05×10-6 Ωm given by Shimizu [37] to calculated from BoltzTraP code. We used as a constant to calculate the thermal conductivity as function given the fact that the experimental resistivity reach saturation point at high temperature.

**3. Results and discussion**

*3.1 Lattice parameter and thermal expansion*

As a preliminary step, we calculate the lattice parameter ‘a’ and ‘c’ as a function of temperature. Not only is it required for all simulations, but also the thermal expansion coefficient α is a simple characteristic that depends directly on the anharmonic terms in the potential. Therefore, it gives a quick indication of how appropriate the interatomic potential is for studying thermal conductivity. The total energies, lattice parameters and volumes were determined by averaging over the last 50 ps of the simulations. The linear thermal expansion coefficient (LTEC) is then given by the relationship:

|  |  |
| --- | --- |
| = | (4) |

where L is the lattice parameter. The derivative of the lattice parameter with respect to temperature, is calculated by fitting a straight line to the lattice parameter at a specific temperature, T, and the points within 15 K on either side (See supplementary material for detailed plots from which lattice gradients are extrapolated) in order to reduce numerical fluctuations. The calculated lattice parameters ‘a’, ‘c’ and cell volume at 0 K are presented in Table 1. Our results are in good agreement with the work by Beeler *et al.* given that the same interatomic potential is used in this work. There is a variation between our MD results and previous DFT + U and experimental measurements. For instance, a comparison with DFT + U calculations from Wang *et al* showed that ‘a’ is underestimated by ~3.1 % and ‘b’ overestimated by 4.88 %.

Table 1: Structural properties (lattice parameter a, c (Å) and volume (Å3)) of U3Si2 calculated at 0 K using MEAM U-Si potential and compared to DFT + U calculations as well as experiment.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | a | c | Volume/atom | c/a |
| This work (MD) | 7.078 | 4.064 | 20.561 | 0.574 |
| Beeler (MD) *et al.* [21] | 7.078 | 4.063 | 20.355 | 0.574 |
| Wang (DFT+U) *et al.* [12] | 7.32 | 3.89 | 20.82 | 0.53 |
| Jossou (DFT+U) *et al.* [15] | 7.21 | 3.86 | 20.07 | 0.54 |
| Zachariasen (Expt.) [7] | 7.3151 | 3.8925 | 20.80 | 0.53 |
| Obbard (Expt.) *et al.* [14] | 7.324 | 3.882 | 20.832 | 0.530 |

The average lattice parameters a, c and cell volume ‘v’ as a function of temperature obtained from the MD simulation for U3Si2 are shown in Figure 3a-c. Experimental values are also plotted in the range from 298 K to 1872 K. The lattice parameter ‘a’ and cell volume are underestimated while ‘c’ is overestimated but needless to say that the MD results follow the experimental trend. This is understandable since the interatomic potential model was not fitted with these data. In Figure 3a-c the behaviour of the lattice parameters and cell volume can be seen to be almost linear in the range of 298 - 1800 K approximately.

Figure 3d-f shows thermal strain ΔL/L0 as function of temperature where L is lattice parameters ‘a’, ‘c’ and cell volume ‘v’ for U3Si2 structure. There is a subtle change in the thermal gradient at temperature points which coincidentally marks the onset of change in the LTEC calculated for U3Si2. The underestimation of the LTEC in comparison with experimental data is predictable as the thermal strains are also underestimated especially after ~500 K.



(f)

(e)

(d)



(a)

(b)

(c)

Figure 3: (a-c) Shows variation of lattice parameter and cell volume (d-f) Thermal strain in lattice parameters and in cell volume as a function of temperature.

We compared the LTEC computed from the volumetric strain (αv) with experimental measurement. A fairly good agreement is observed with the data calculated here and the work of Loch *et al*. [38] and Shimizu [37] especially at temperatures above 900 K while underestimation is noticed in comparison to the recent measurement by White *et al*. [3] and Taylor *et al*. [39].



(a)

(b)

Figure 4: (a) Linear thermal expansion coefficients of U3Si2 calculated from volumetric strain (b) anisotropy in linear thermal expansion coefficient in a and c direction as a function of temperature.

The anisotropy reported by Obbard *et al* [14] is not captured by the αv, hence we looked at the directional dependence of LTEC and it is interesting to note that there are three transition regime in the ‘a’ direction at 500, 1300 and 1700 K with LTEC of 9.86, 12.54 and 13.86 × 10-6 K-1 respectively. As shown in the Figure 4b, there is a transition in the ‘c’ direction at 600 K and comparison with recent study where a transition point is established at ~1300 K [14] in agreement with one of the transition point observed in our calculation. This differences might be due to the nature of the MEAM potential since it was not developed for calculating thermophysical properties [21]. It is also well known that thermal expansion can be made up of lattice, electronic, magnetic and vacancy/interstitial compo­nents, depending upon the material and temperature range. All of these factors are not accounted for in the MD model especially the electronic contribution given the metallic nature of U3Si2 [40].

To further explain the observed anisotropy, we compute the c/a ratio which is a measure of the tetragonality of the structure. The change in c/a with temperature is important, because it has a direct influence on the evolution of the LTEC.



Figure 5: The temperature dependence of the ratio c/a of U3Si2.

The non-uniform expansion of the ‘a’ and ‘c’ lattice parameters is responsible for the non-linear change in the c/a with temperature as shown in Figure 5 which in turn results in the anisotropic nature of the LTEC in U3Si2. The c/a is overestimated in our calculation but follows the experimental trend especially from 300 to 900 K.

*3.2 Enthalpy and Specific heat*

In this work we determine the enthalpy increment (increase in enthalpy with respect to standard conditions) as a function of temperature, using the relationship. Just like the lattice parameter, the enthalpy increment increases approximately linearly with temperature as shown in Figure 6a. The first derivative of the enthalpy increment with respect to temperature is used to calculate the specific heat capacity at constant pressure due to phonon scattering (harmonic and anharmonic) using the following relationship,

|  |  |
| --- | --- |
| = | (5) |

where n is the number of moles, and the first derivative of enthalpy was calculated by fitting a straight line to the enthalpy (See supplementary material for detailed plots from which enthalpy gradients are extrapolated) at a given temperature T and the data at T±15 K on either side. The molar heat capacity of a metal is the summation of a dilational, harmonic and anharmonic lattice (phonon), and electronic terms. The total molar heat capacity, is estimated by addition of the electronic heat capacity, given by:

|  |  |
| --- | --- |
| , | (6) |



(a)

(b)

Figure 6: (a) The change in enthalpy relative to the enthalpy at 300 K (b) molar heat capacity at constant pressure as a function of temperature.

where is the electronic specific heat coefficient, experimentally determined as 52.0 mJ/mol.K2 [3] and estimated to be 13.2 mJ/mol.K2 from DFT+U calculations [41], and T is the temperature in Kelvin. The calculated values agreed with the Dulong Petit Law value above the Debye temperature. The sum of and components of heat capacity give the total heat capacity, shown as the red and black data points in Figure 6b. In comparison to previous work [14], there is a good agreement at 300 to 900 K especially with experimentally determined. The electronic contribution to heat capacity is quite significant since the Dulong-Petit limit for phonon specific contribution is ~125 J/mol-K. This is consistent with work by Beeler and coworkers who determined at 400 K to be 134 J/mol-K [21] and agree with recently measured value by Antonio *et al*. at 300 K as 149 J/mol-K [4].

*3.3 Elastic constants*

Elasticity describes the physical and internal changes of solid material under the application of stress and strain. The elastic coefficients and moduli can be also linked to the atomic bonding, deformation characteristics and mechanical and structural stability. To investigate the mechanical stability of the intermetallic U3Si2, we computed the elastic constant from ground-state elastic tensor using structures optimised at 0 and 300 K using the scripts provided with LAMMPS code [24]. The calculated elastic constants of a single crystal of U3Si2 are listed in Table 2 along with the reported values from DFT calculations [11,12,41] and experiment [42]. For tetragonal symmetry, there are six independent elastic constants, that is, C11, C12, C13, C33, C44 and C66. The calculated elastic constants of U3Si2 fulfil the Born criteria for mechanical stability [43]. Therefore, it can be said that U3Si2 is mechanically stable at ambient conditions.

While DFT calculations are believed to be more accurate than MD simulations, their high computational cost strongly limits the length and time scales used in such calculations. The bulk and shear moduli here are estimated using the Hill’s model which is an average of the Voigt and Reuss bounds [44] while Beeler *et al.* used only the Voigt bound, hence the difference in bulk modulus. As shown in the Table 2, there is a general softening in the elastic constant as we increased the temperature from 0 to 300 K, and a look at the experimental measurements which are done at room temperature shows that Young's modulus is overestimated in our MD calculation by ~15–20% at 300 K, and ~4–9% at 0 K respectively. There are various deviations in the calculated Bulk moduli in comparison to the measured value of 68.3 and 64.3 GPa from the different set of U3Si2 samples prepared at Los Alamos National Laboratory [42]. It is also important to mention that theoretical calculations assumes a single crystal during simulations while experimental measurements were conducted on polycrystalline U3Si2 samples with possible presence of porosity, grain boundaries and microcracks accounting for the general overestimation in DFT and MD results.

The elastic and thermophysical properties of solid are related through the Debye model. Furthermore, the Debye temperature, is related to many physical properties such as specific heat, elastic constants, and melting point, [45]. The mean wave velocity, in the polycrystalline materials is approximated by [46]:

|  |  |
| --- | --- |
| , | (7) |

where the transverse velocity and the longitudinal velocity. The Debye temperature is then calculated using the relationship [46]:

|  |  |
| --- | --- |
| , | (8) |

where ħ is the Planck's constant, k is Boltzmann’s constant, is Avogadro's number, n is the number of atoms per formula unit, is the density.

The calculated elastic constants can be used to estimate the of solids based on a correlation derived by Fine *et al*. from studying many cubic and tetragonal structures [47]. This is given by:

|  |  |
| --- | --- |
| , | (9) |

Using Eqs. 7–9, the polycrystalline properties of U3Si2 are calculated and are presented in Table 3. These results are also compared to recent DFT result from Wang *et al*. [12]. The calculated value of the 1795.46300 and 1785.65300 K is reasonably close to the experimental value of 1938 K [48] and MD result of 1775 K. This relation provide a quick method for estimating the using the elastic constants calculated in this work. The calculated value of Debye temperature of U3Si2 agrees well with the reported theoretical value of 280.92 K [4]. Although it is overestimated by approximately ~76 (81) K in comparison to recent experimental measurement of 200 K, this is still considered excellent agreement.

Table 2: Elastic constants (GPa), Elastic moduli (GPa) of U3Si2 at 0 and 300 K.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | C11 | C33 | C12 | C13 | C44 | C66 | G | B | E | ν |
| MD at 0K (This work) | 210.23 | 160.20 | 178.90 | 65.75 | 103.10 | 35.40 | 51.09 | 126.67 | 135.13 | 0.32 |
| MD at 0K [21] | 210.2 | 160.2 | 178.9 | 65.8 | 103.1 | 35.4 |  | 134 | \_\_ | \_\_ |
| MD at 300K (This work) | 208.57 | 145.79 | 144.9 | 67.01 | 90.99 | 47.1 | 60.00 | 118.70 | 154.04 | 0.28 |
| DFT at 0K [11] | 149 | 139 | 49 | 48 | 63 | 46 | 53 | 81 | 130 | 0.23 |
| DFT at 0K [12] | 167.26 | 205.31 | 45.63 | 50.34 | 67.49 | 74.09 | 67.68 | 92.01 | 163.06 | 0.20 |
| DFT at 0K [41] | 155 | 142 | 47 | 50 | 65 | 46 | 57 | 83 | 139 | 0.22 |
| Experiment [42] | 137.9 | \_\_ | \_\_ | \_\_ | 53.75 | \_\_ | \_\_ | 68.3±0.5a 64.3±0.3b | 130.4±0.5a 122.9±2.4b | 0.182±0.003a 0.179±0.007b |

Seven U3Si2 specimens labelled a= set A (samples1 – 5) and b= set B (samples 6 – 7) prepared from different feedstocks [42].

Table 3: Theoretical sound velocities (m/s), Debye and melting temperatures (K) of U3Si2 predicted using the elastic properties at 0 and 300 K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (K) |  |  |  |  |  |
| 0 | 4174.17 | 2295.05 | 2558.19 | 276.19 | 1795.46300 |
| 300 | 4125.83 | 2338.76 | 2600.55 | 280.76 | 1785.65300 |
| DFT at 0 [12] | 3865.04 | 2355.32 | 2601.53 | 280.92 | 1541.51300 |

*3.4 Thermal conductivity*

The thermal conductivity of nuclear fuel pellets is an important thermophysical property in nuclear reactors. It is argued in the literature that the high thermal conductivity of metallic systems is mainly contributed by the electrons (*el*) and the phonon (*ph*) contribution is small, hence neglected in some cases [33]. Phonon scattering occurs in three phonon interactions, which result from anharmonicities in the interatomic potential. The other phonon scattering center which contributes to thermal conductivity includes impurities, grain boundaries or local distortions of the lattice. These contributions are not accounted for in this work since their effects are not very significant especially for a systems with small thermal contribution from phonon scattering as we observed in U3Si2.

The total thermal conductivity of metallic nuclear fuel is determined by the combination of the contribution to the thermal conductivity both from electronic and phonon transport as follows:

|  |  |
| --- | --- |
| , | (10) |

where is the lattice or phonon contribution to the thermal conductivity given by

|  |  |
| --- | --- |
| , | (11) |

where *c* is the specific heat due to the phonons, *v* is the group velocity of an acoustic branch and is the mean free path. is the electronic contribution to the thermal conductivity, which can be related to the electrical conductivity using the Wiedemann-Franz law:

|  |  |
| --- | --- |
| = σLT, | (12) |

where L is the Lorenz number which equals L = 2.44 × 10−8 W Ω K−2.

We have calculated the of U3Si2 at temperatures from 300 to 1500 K by the NEMD and EMD simulations respectively. The size of the supercell has a considerable effect on the thermal conductivity calculated using both methods.

In the EMD approach, two sensitivity tests are carried out to obtain converged values of thermal conductivity. The HCACF integral which is directly proportional to the thermal conductivity (see Eq. 4). The normalized HCACF (main figure) and its integral (inset) at 300 and 1200 K is shown in Figure 7a. The HCACF integral converged after 0.90 ns, hence we specify the converged value of the HCACF integral by averaging its value between times of 0.90 and 1.25 ns (the shaded region of the inset).

The number of phonons needed to capture the *ph*-*ph* scattering in the bulk material is dependent on the simulation cell size. This effect is reduced by increasing the simulation cell length until the thermal conductivity reaches a size independent value. In this work, we varied the system size from , and . We have computed the thermal conductivity of U3Si2 using supercells containing 12000, 20160, 31360, and 46080 atoms, all at a temperature of 300 K. These systems correspond to lengths of 4.68, 5.46, 6.24, and 7.02 nm respectively. In Figure 7b we show the computed thermal conductivity obtained by direct integration for 1.25 ns of the HCACF for different choices of simulation cell. We see that the 12000 atom (3.90 nm) system results in the lower value of 0.73 W/mK compared to the simulations at larger system size of 46080 atoms (7.02 nm). However, it is apparent from Figure 7b that the results for are well converged by 31360 atoms (6.24 nm). The same finite size convergence test have been used in previous work [49].



(a)

(b)



Figure 7: (a) Normalized heat current autocorrelation function (body) and its integral (inset) for U3Si2 at 300 and 1200 K. The HCACFs are normalized by their initial values. The shaded region in the inset indicates the time range over which the HCACF integral is averaged to predict the phonon assisted thermal conductivity . Note that the time scale of the inset is 50 times that of the body (b) Thermal conductivity plotted against lateral simulation box dimensions at 300 K. Results converged at supercell length of 6.24 nm.

In the NEMD, it has been shown in the previous study that the finite size of the system can limit phonon mean free path, hence underestimating the thermal conductivity. Furthermore, it is well known that the supercell dimension in the and directions have small effect on the thermal conductivity, but changes along the are more significant [49].



(a)

(b)



Figure 8: (a) The variation of the reciprocal of thermal conductivity as a function of the reciprocal of supercell length for perfect U3Si2 at a range of temperatures. The y-intercepts indicate the reciprocal of bulk thermal conductivity. (b)

A steady-state temperature profile for the largest system (5 × 5 × 175 unit cells) at 300 K in U3Si2.

The linear relationship between and is well described in Ref. [34] and plotted in Figure 8a for perfect U3Si2 structure for a number of temperatures with supercell sizes of, , , and . The y-intercept is used to determine the thermal conductivity of the bulk U3Si2 as shown in Figure 8a. In Figure 8b, a steady state temperature distribution, along the direction of heat transfer, is indicated for the largest system (5 × 5 × 175 unit cells) at 300 K. The figure shows that the temperature at the centre of the supercell is higher than that at the edge. Hence, there is constant heat flow from the hot to the cold region as shown by the schematic diagram of the NEMD setup in Figure 2. The slope of the profile is the temperature gradient of the system. Temperature control can be simulated by addition or subtraction of the non-translational kinetic energies in the heat bath such that momentum is conserved.

Having computed the thermal conductivity of U3Si2 using the NEMD and the EMD method, we are now in a position to directly compare the results. For the NEMD at 300 K, extrapolation to = 0 yields a value of of 1.37 W/mK. The EMD method gives a result of 1.36 W/mK for a system at 300 K. The predicted thermal conductivities from the two methods are plotted against temperature from 300 – 1500 K in Figure 9a (main). Unlike the Boltzmann Transport Equation (Lattice dynamics and MD) prediction methods, there are no major assumptions inherent to the EMD and NEMD methods other than the choice of the interatomic potential, which is consistent here. The predicted thermal-conductivity values from the EMD and NEMD methods are in good agreement, generally within ~6% (except at temperatures of 900 and 1200 K) where the predictions are within 10%. Previous work by others have also found that EMD and NEMD thermal-conductivity predictions are consistent [49,50]. Our MD results compare reasonably well with recent work by Antonio *et al.* who predicted a from 0 – 350 K with a value of 1.99 W/mK at 300 K which is overestimated compared to our EMD (1.36 W/mK) and NEMD (1.37 W/mK) results respectively [4].

This is a good evidence that either method can be applied to compute bulk thermal conductivity in perfect crystalline solids. It is important to note that the many-body MEAM potential used here is not developed with a special focus on thermophysical properties of U3Si2.



(a)

(b)

Figure 9: (a) of U3Si2 using EMD and NEMD approach (b) as a function of temperature.

We further explored the directional dependence of as shown in Figure 9a (inset), which shows the variation as a function of temperature. The lattice thermal conductivity exhibits significant directional anisotropy with the ratio of to ranging between 0.82 at 300 K and 0.39 at 1500 K. This implies that anisotropy in thermal conductivity decreases as temperature increases. Anisotropic behaviour may be attributed to differences in group velocity, anharmonicity, and scattering phase space along the different directions [51]. It is well known that the longitudinal sound velocity () and the transverse sound velocity () are primarily harmonic parameters while their ratio is an anharmonic quantity which depends on the ratio between the axial and shear rigidities of interatomic bonds [52]. We find that the value of is 1.76 which is a deviation from isotropic behaviour. This implies that the anisotropy in the of U3Si2 should be ascribed to its anisotropic sound velocities amongst other factors that have not been explored in this work.

In metallic system like U3Si2, it has been shown that at the low temperature i.e. T , only phonon scattering, *ph–ph*, plays a role in the thermal conductivity calculation [33,53] while in the T regime, *el–el* interaction is the main contribution, hence it is not surprising to have low at 300 K given the fact that the has been determined to be ~200 K [3,4,54]. Low contribution means that as temperature increases, degradation in thermal conductivity is not a big concern in U3Si2 fuel, since increases and the reduction in is minimal and should be less than the of ~2 W/mK. It is also interesting to note that the calculated conductivity (Figure 9b) agrees with recent experimental results for U3Si2 [3] while values reported by Shimizu is lower which might be due to the defects in the structure and method of measurement [37].

**4. Conclusion**

In summary, we have performed a systematic molecular dynamics study to investigate the temperature dependent thermophysical properties of U3Si2 using the MEAM potential. Based on the equilibrated structure of U3Si2, we systematically analyze its thermodynamic properties and obtain the values of its thermal expansion coefficient, bulk modulus, and heat capacities at different temperatures, which are in good agreement with corresponding experimental measurements. A comparison of calculated molar heat capacity with experimental data show reasonable agreement with experiments. Due to the anisotropy in lattice strain with temperature, we noticed an anisotropic behaviour in the in-plane and cross-plane LTEC which has been experimentally observed. The agreement between our calculations and experiments also proves the validity of our methods and model, and the effectiveness of the MD method employed in this work.

In addition, we also calculated the lattice assisted thermal conductivity of U3Si2 and to be sure whether the results are affected by artefacts of the methodology we have used both the EMD (Green–Kubo) and the direct (NEMD) methods respectively. The Green–Kubo method was also used for all predictions of the directional dependence of the in-plane and cross-plane, for which application of the direct method is impractical. The total thermal conductivity calculated is slightly underestimated compared to a recent experiment by White *et al* [3]. Unlike other metallic fuel such as UB2 where there is significant, U3Si2 has a less than ~2 W/mK, which means that above the Debye temperature, the thermal gradient is mainly driven by which increases with temperature. Hence, ‘ drag’ on the at reactor’s operating temperature is insignificant compared to uranium diboride or similar fuel type.

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