Interatomic potential for uranium in a wide range of pressures and temperatures

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Abstract
Using the force-matching method we develop an interatomic potential that allows us to study the structure and properties of $\alpha$-U, $\gamma$-U and liquid uranium. The potential is fitted to the forces, energies and stresses obtained from \textit{ab initio} calculations. The model gives a good comparison with the experimental and \textit{ab initio} data for the lattice constants of $\alpha$-U and $\gamma$-U, the elastic constants, the room-temperature isotherm, the normal density isochore, the bond-angle distribution functions and the vacancy formation energies. The calculated melting line of uranium at pressures up to 80 GPa and the temperature of the $\alpha$–$\gamma$ transition at 3 GPa agree well with the experimental phase diagram of uranium.

(Some figures may appear in colour only in the online journal)

1. Introduction

Uranium is a key component of nuclear fuels. For several decades metallic fuels have been overshadowed by oxide and ceramic fuels. However, nowadays uranium alloys are under active investigation as possible fuels for future fast and research reactors [1–4]. Understanding of the radiation damage effects on the fuel stability is one of the major challenges to be solved on the way to effective and safe fuel design. The description of the radiation damage requires a knowledge of the atomistic mechanisms of defect generation in solids [5, 6]. However, they are still not sufficiently studied for metallic uranium compounds and atomistic models are not mature enough even for pure U.

Uranium has four possible structures: the orthorhombic $\alpha$-U, the tetragonal $\beta$-U, the high-temperature bcc $\gamma$-U and liquid. The crystal structure of the low-temperature $\alpha$-U is presented in figure 1. At temperature $T \sim 935$ K and zero pressure $\alpha$-U transforms to $\beta$-U, which is stable in a very small range of pressures and temperatures. At 1045 K $\beta$-U transforms to $\gamma$-U, then at 1406 K $\gamma$-U melts. Solid $\alpha$-U and $\gamma$-U allotropes and liquid uranium are of the most interest because these structures are directly involved in the technological processes of nuclear fuel operation.

The problem of investigation of the structure and elastic properties of solid uranium has been previously treated using density functional theory (DFT) based \textit{ab initio} calculations. Söderlind [7] has performed \textit{ab initio} calculations of the $\alpha$-U equilibrium volume and bulk modulus within the all electron full-potential method. Later Taylor [8] applied the pseudo-potential developed for uranium by Kresse and Joubert [9] to calculate structure and elastic moduli of both $\alpha$-U and $\gamma$-U. In addition, Taylor has obtained the value of a single vacancy formation energy for the low-temperature
The EAM potential developed in this work. The potential is determined by three functions (see equation (1)): $\varphi$ is the pair potential, $\rho$ has a qualitative meaning of an effective electron density that is induced at the given atom by its neighbour atom, $F$ is the embedding function that introduces many-body effects. The dots represent spline knots.

One can see that $ab\ initio$ methods have been successfully applied to study various properties of solid uranium. However, the application of these DFT based $ab\ initio$ techniques is limited by the maximum computationally possible model size ($\sim 10^2$ atoms) and time length (of the order of picoseconds). Such limitations essentially narrow the applicability of $ab\ initio$ models for atomistic studies of phase transitions, plastic deformations, radiation damage etc. It is the classical molecular dynamics (MD) models that are able to move atomistic description forward to several orders of magnitude larger time and length scales. However, the accuracy of classical MD models is based on the accuracy of the interatomic potentials deployed. In this respect one can mention that the radiation damage studies of reactor materials show relatively more progress in comparison with fuels. The reason for this is the availability of the accurate interatomic potentials for iron and other relevant metals (e.g. [15–26]).

The main general requirement to the interatomic potential is that it should capture all necessary features of the processes under consideration. For example, a correct description of the defect energies’ hierarchy is very important for radiation damage models. If such a potential is at hand, then using current computational recourses it is possible not only to access via direct MD nanosecond and sub-micrometre time and length scales, but to create multiscale models that bridge the gap between atomistic and kinetic scales (e.g. see [27] and [28, 29]).

To our knowledge, there exist three published interatomic potentials for uranium [30–33]. All of them are developed as central-force many-body potentials [34–38] commonly referred to as embedded atom method (EAM) potentials [34, 35]. This type of many-body potential is widely used for simulating the interatomic interactions in metals. In this framework the potential energy of the system can be represented as follows:

$$
U = \sum_{i<j} \varphi(r_{ij}) + \sum_j F(\tilde{\rho}_j), \quad \tilde{\rho}_j = \sum_{j\neq i} \rho(r_{ij}).
$$

This is an empirical model that has only qualitative physical justification based on first principles. The typical shapes of the functions in equations (1) are shown in figure 2. Qualitatively one can consider the first term as a sum of pair potentials $\varphi$ over all atom pairs in the system ($r_{ij}$ is the distance between atoms $i$ and $j$), $\tilde{\rho}$ is an effective electron density that is induced by the neighbouring atoms at the given atom ($\rho$ gives a contribution from each neighbour). Both functions $\varphi$ and $\rho$ are short-ranged and in many EAM models go to zero at the same cut-off radius. A non-linear embedding function $F$ introduces many-body effects. The curvature of $F$ allows us to describe the lowering of the energy of a given atom when the number of its neighbours increases. This is impossible to do using only pair potentials but crucially important for modelling metallic bonding [34–38].

The construction of the above-mentioned potentials for U [30–33] was based on simple analytical forms of the $\varphi$, $\rho$ and $F$ functions. The potential of Pascuet et al [30, 31] was fitted to the lattice constants, the equilibrium atomic volume, the bulk modulus and the cohesion energy of $\alpha$-U. The embedding function $F$ was obtained from the universal features of the equation of state of metals. This potential describes $\alpha$-U at normal conditions and qualitatively reproduces $\alpha$-to-$\gamma$ transition.

The potential developed by Belashchenko et al [32] was fitted to the data on the structure of liquid uranium in the vicinity of the melting temperature and to the results of high pressure impact tests. It gives an accurate description of the thermophysical properties of liquid uranium and bcc $\gamma$-U. The calculated density, self diffusion coefficient of the liquid phase and the melting line are all in good agreement with the experimental data. However this potential is not suitable for low-temperature $\alpha$-U.
The potential of Li et al [33] was fitted to the ab initio results on the U₂ dimer energies, the fcc lattice constant and several other energetic and elastic properties of different structures. Liquid U properties were not considered. Only limited data on the accuracy of this potential were presented in [33]. Therefore none of the existing potentials describes simultaneously the properties of α-, γ and liquid uranium and the corresponding transitions at the acceptable level of accuracy in a wide range of pressures and temperatures. Such a potential is the goal of this work.

2. Construction of the potential

The development of the ab initio DFT methods made it possible to include the ab initio data into the fitting database for potential parameter tuning. Initially ab initio data only supplemented the experimental data. In recent years, however, the interatomic potential fitting has tended to rely exclusively on the ab initio results. Probably the first completely ab initio based approach for potentials’ development was originally proposed by Ercolessi and Adams [39] and called the force-matching method. In the recent work of Fellinger et al on Nb [40] a very detailed explanation of this method was given. Two authors of this work have recently constructed an EAM potential for Mo using the same technique [28]. In the force-matching method the whole developing process is divided into two stages. First the reference database is built. This reference database contains ab initio values of atomic forces, energies and stresses calculated for various atomic structures (so-called configurations). At the second stage the optimization of the EAM potential is performed. It is required to minimize the deviations between the reference ab initio values of forces, energies and stresses and their EAM approximations. The iterative minimization process results in a potential that reproduces the reference data with the best accuracy. We use the force-matching method as described below.

2.1. The reference database

For computation of the reference database we need to create a set of reference structures. These structures represent α-U, γ-U and liquid uranium at different densities. Each reference structure contains about 120 atoms in a simulation box with the periodic boundary conditions in all three dimensions (3D PBC). For each of these structures we perform a short (~1 ps) MD-run with the trial potential [32] and at the given temperature T. This way we introduce thermal displacements of atoms the magnitudes of which reflect the given temperature. The final atomic arrangement after the MD calculation for a given initial structure is one of the required configurations. Classical MD calculations are performed using the LAMMPS code [41].

Then we perform ab initio DFT calculations of reference forces, per atom energies and stress tensors for each configuration using the plane-wave code VASP [42]. To represent the inner electronic structure of uranium we adopt a projector-augmented wave pseudo-potential developed by Kresse and Joubert [9] and previously used by Taylor [8]. The Perdew–Wang 91 exchange correlation functional [43] is also applied. We set the basis plane-wave energy cut-off equal to 500 eV. According to the symmetry of the structures studied we use the following k-point meshes: 3 × 1 × 2 for α-U configurations and 2 × 2 × 2 for γ-U and liquid U. These energy cut-offs and meshes provide converged DFT energies, forces and stresses.

The complete reference database contains 12 054 values of force components, 34 values of the per atom energy and 204 components of the stress tensor. The list of all configurations of the fitting database is given in table 1.

2.2. Fitting of the potential to the DFT reference data

The trial functions ϕ, ρ and F are chosen in the form of cubic splines. The spline knots are adjusted in an iterative way for minimizing the deviations between the reference

**Table 1.** The configurations database. The configurations represent various uranium structures under different conditions. N is the number of atoms in each configuration. The V/V₀ column lists the ratio of the given atomic volume V to the equilibrium experimental volume V₀ of α-U, γ-U [49, 54] and liquid U [32]. The T column lists the temperature value corresponding to the particular configuration. The Δ column lists the average fitting errors for the forces obtained with the resulting EAM potential (see equation (2)).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Structure</th>
<th>N</th>
<th>V/V₀</th>
<th>T (K)</th>
<th>Δ (%)</th>
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<td>900</td>
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<td>3740</td>
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<td>5760</td>
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</tr>
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<td>0.679</td>
<td>5140</td>
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database values and the respective values calculated with the EAM potential. This operation is conducted by the code `potfit` [44, 45]. Then the resulting potential is verified by the test MD calculations of the structure and properties of uranium. Several test properties are compared with the known experimental data. If the agreement is not sufficient we modify the database structures (add or remove configurations, change their ‘statistical weights’ in the minimization scheme etc). Then we repeat the potential generation procedure once more. The optimized cubic splines representing the final potential functions $\varphi$, $\rho$ and $F$ are shown in figure 2. Table 2 presents the final values of the spline knots for all these functions [4]. We determine the average fitting errors for the forces in each reference configuration:

$$\Delta = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{(F_{\text{EAM}} - F_{\text{DFT}})^2}{F_{\text{DFT}}} \right) . \tag{2}$$

where $N$ is the number of atoms in a given configuration, $F_{\text{EAM}}$ is an EAM force, $F_{\text{DFT}}$ is a reference DFT force.

From table 1 it can be seen that for all configurations consisting of 120–128 atoms the values of the errors are about 15–40% (depending on the uranium structure). For the high-temperature rarefied liquid configurations (with 54 atoms in a simulation box) fitting errors are more than 120%. The reason for such significant errors is that the cut-off radius of the potential (6 Å) is obviously insufficient for modelling highly expanded uranium.

### 3. Properties of solid uranium

To verify the potential we carry out MD calculations of the structural, mechanical and thermodynamic properties of the solid structures of uranium and address its phase diagram. Each of these models consists of 2000 atoms in 3D PBC. Additionally we examine the vacancy formation energies in $\alpha$-U and $\gamma$-U.

#### 3.1. Structure and elastic properties

We calculate the lattice parameters at zero pressure, the bulk modulus and other elastic constants of $\alpha$-U and $\gamma$-U with the developed potential. The results are summarized in table 3. The elastic constants $c_{ij}$ are calculated from MD simulations of uniaxial compression of solid $\alpha$-U. The stress components change with deformation in a linear way (see figure 3). The elastic constants can be determined as follows (in Voigt notation):

$$c_{ij} = \frac{\Delta \sigma_{ij}}{\epsilon_{ii}}, \tag{3}$$

where $\Delta \sigma_{ij}$ is the change in the stress component along the $j$-axis providing that the model size $L_0$ is slightly decreased and the corresponding deformation is:

$$\epsilon_{ii} = \frac{\Delta L_i}{L_i}. \tag{4}$$

The bulk modulus is determined from MD simulations of uniform compression and expansion with respect to the equilibrium volume:

$$B = -V_0 \frac{\varDelta P}{\varDelta V}. \tag{5}$$

Here $V_0$ is the equilibrium volume of the solid (at $T \approx 300 \, \text{K}$ for $\alpha$-U and at the $T \approx 900 \, \text{K}$ for $\gamma$-U). The corresponding ‘pressure–volume’ dependence is a linear function of volume. The presented values of the bulk modulus are obtained in the range of $\Delta V/V_0 \approx 0.5–6\%$. The elastic constants and the bulk modulus of $\alpha$-U are within 10–30% of the experimental data. The errors are larger for $c_{12}$ and $c_{13}$.

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Table 3. The EAM values of the lattice constants \((a, b, c)\) are presented in Å, \(y\) is given as a relative dimensionless value representing a fraction of \(b\). The atomic volume \((\text{in Å}^3)\), the bulk modulus \((\text{GPa})\), the elastic constants \((\text{GPa})\) and the cohesive energy \((\text{eV})\) of solid uranium structures are shown in comparison with the previous DFT based results and experimental data. The experimental values correspond to \(T = 300\) K for \(\alpha\)-U and \(\sim 900\) K for \(\gamma\)-U. MD calculations are performed at the same temperatures.

<table>
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<tr>
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<td></td>
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<td>2.8361</td>
<td>2.845</td>
<td>2.800</td>
<td>2.8537</td>
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<td>(b)</td>
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<td>5.818</td>
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<tr>
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<td>(y)</td>
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<td>(E_{coh})</td>
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<tr>
<td>(c_{11})</td>
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<td>300</td>
<td>296</td>
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<td>(c_{33})</td>
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<td>320</td>
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<td>267</td>
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<tr>
<td>(c_{12})</td>
<td>109</td>
<td>50</td>
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<td>46</td>
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<td>(c_{23})</td>
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<tr>
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<td>95.0</td>
<td>—</td>
<td>176.0</td>
<td>113.3</td>
</tr>
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</table>

3.2. The normal density isochore of \(\alpha\)-U

As another test we study the behaviour of the low-temperature orthorhombic \(\alpha\)-U under isochoric heating. The obtained ‘pressure–temperature’ dependence compares well with the experimental data [46] (see figure 4). The mean thermal displacements of uranium atoms are not the same for different directions in \(\alpha\)-U. The largest value is observed along the \(a\)-axis where the atoms are arranged closer to each other. This is consistent with the results of the diffraction study of anisotropy of thermal displacements in solid uranium [47].

3.3. The room-temperature isotherm of \(\alpha\)-U

The uranium room-temperature isotherm is calculated in two different ways. First we carry out several independent calculations at the given \(V/V_0\) ratios maintaining all stress

Figure 3. Changes of the components of stress tensor as a function of the compressing deformation \(\epsilon\) (with the indication of the corresponding elastic constants): 1—changes in \(\sigma_{zz}\), compression along the \(z\)-axis (gives \(c_{33}\)); 2—\(\sigma_{yy}\), compression along the \(y\)-axis (\(c_{22}\)); 3—\(\sigma_{xx}\), compression along the \(x\)-axis (\(c_{11}\)); 4—\(\sigma_{zz}\), compression along the \(x\)-axis (\(c_{13}\)); 5—\(\sigma_{xx}\), compression along the \(y\)-axis (\(c_{23}\)); 6—\(\sigma_{yy}\), compression along the \(x\)-axis (\(c_{12}\)).

Figure 4. The normal density \(V = V_0\) isochore of \(\alpha\)-U: 1—experimental data [46]; 2—result of MD calculations with the potential obtained.
components equal to pressure $P$ ($\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = P$). While $V/V_0$ is no less then 0.8 the EAM isotherm is in good agreement with the diamond anvil cell (DAC) experiments, but during further compression the calculated curve becomes somewhat higher than the experimental one. As a second variant, a continuous uniform compression of the $\alpha$-U is simulated. This approach does not allow us to keep all pressure components equal and the crystal structure deforms during the simulation. When $V/V_0 = 0.8$ the difference between $\sigma_{xx}$ and $\sigma_{zz}$ becomes larger than $\sim 20$ GPa and the deformation of the lattice becomes irreversible. It can be noticed from figure 5 that the ‘pressure–volume’ dependence obtained for this irreversibly deformed uranium during further compression is consistent with the experimental data [48, 49].

### 3.4. Bond-angle distribution functions for solid and liquid uranium

In order to understand how the potential reproduces the structure of solid and liquid U we calculate bond-angle distribution functions for several temperatures and compare them with the existing results of QMD simulations [11]. The bond-angle distribution function represents the number of bond angles that the given atom makes with its nearest neighbours. To define what atoms can be considered to be the nearest neighbours for the given atom we set the cut-off radius of $3.9$ Å (equal to the value suggested in [11]). To perform the comparison we build two models of bcc U at low (330 K) and high (1680 K) temperatures as well as a model of liquid uranium at 2150 K. Each model has an atomic volume of $20.45$ Å$^3$/atom. The resulting distributions are compared with the QMD data in figure 6. For each case one can see a good agreement between these two data sets. At 330 K the initial bcc U lattice becomes strongly distorted into a bct-like structure as was shown in [11] ($\gamma$-to-$\alpha$ transition is hindered due to the small system size).

### 3.5. Energy of a single vacancy formation

A proper description of defect formation in the solid state is crucial for radiation damage studies. That is why a single vacancy formation energy is an important basic test of the new potential. This energy is determined as follows:

$$E_{\text{vac}}^t = E_{N-1}^t - \frac{N-1}{N} E_N.$$

Here $N$ is the number of atoms in the model of the ideal crystal lattice without vacancies. $E_N$ is the energy of this ideal lattice and $E_{N-1}$ corresponds to the model that contains a single vacancy. We perform structural relaxations for the models of perfect single crystal uranium with and without a single vacancy for determination of the corresponding energy values. The $\alpha$-U model contains 5200 atoms in the simulation box with 3D PBC. For $\gamma$-U we use 250 atoms and the structural relaxation is performed only for a part of the system in order to overcome spontaneous bcc lattice distortion at low temperatures [12]. The results obtained for both solid structures of uranium are presented in tables tables 4 and 5. For $\alpha$-U the experimental value of the vacancy formation energy is known while for $\gamma$-U it was only estimated by the DFT method.

### 4. Melting and $\alpha$–$\gamma$ transition

We calculate the melting line and the temperature of the $\alpha$–$\gamma$ transition at the given pressure. In both cases we use the two-phase simulation technique (e.g. see [50–53]). Fragments of the simulation boxes are presented in figure 7.

The simulations are performed in 3D PBC. One part of the box is filled by the bcc lattice of uranium atoms and another part is filled with liquid uranium. The total number of atoms is 20 250. The algorithm of the calculation includes equilibration of the system at the given pressure for $\sim 50$ ps. Depending on the temperature and pressure the phase boundary can move or remain stable. In the latter case both phases coexist in equilibrium, which gives the value of the melting temperature at the given pressure.

The structure of the simulation box used for the calculation of the solid–solid $\alpha$–$\gamma$ transition is shown in figure 7(b). The algorithm of the calculation remains the same as described above for melting. The model contains 16 800
Figure 6. Bond-angle distribution functions $g^3(\theta)$ calculated with the EAM potential developed in the present work in comparison with the QMD results [11]. At 330 K the initial bcc $\gamma$-U lattice is strongly distorted into a bct-like structure.

Figure 7. Fragments of the two-phase simulation boxes: the phase boundary between liquid and bcc $\gamma$-U solid (a) and the boundary between $\alpha$-U and $\gamma$-U (b). $\gamma$-U is on the right. Projections of all atoms in the simulation box on a plane are presented in both pictures; arrows show the orientation of the $\alpha$-U lattice.

5. Conclusion

Using the force-matching method we developed a new interatomic EAM potential for uranium aimed at simulation of $\alpha$-U, $\gamma$-U and liquid uranium, the corresponding transitions between them as well as the radiation damage. The results of the performed MD test calculations confirm that it is possible to obtain a good quantitative description of the structure and properties of the solid uranium allotropes using a relatively simple EAM model. The lattice constants, bulk modulus, bond-angle distribution functions, the room-temperature isotherm, normal density isochore and the single vacancy formation energy for $\alpha$ and $\gamma$ structures computed using this potential agree well with the reported experimental and $ab\ initio$ data. The calculated melting line of uranium at pressures up to 80 GPa and the temperature of the solid–solid $\alpha$–$\gamma$ transition at 3 GPa are both in good agreement with the experimental data. Hence this new EAM uranium potential provides an overall quantitative description of the properties of liquid and solid uranium at pressures from 0 to 80 GPa and temperatures up to 2500 K.

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