

MOLECULAR DYNAMICS STUDY OF MIXED OXIDE FUELS: ISSUES AND PERSPECTIVES

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ABSTRACT

Economically motivated extension of burnup limits of Light Water Reactor (LWR) fuel cycles based on the use of UO₂ fuel and civil MOX causes at the same time the necessity to study further primary effects in highly disturbed polycrystalline lattices which may cause dramatic degradation of physical, chemical and mechanical properties of fuel materials. Apart of "standard" fuels there is vital necessity to evaluate burnup/exposure dependent properties of new candidate fuels for advanced LWR systems or fast reactor concepts.

Molecular Dynamics (MD) simulations were proven to be a successful technique in order to understand the physicochemical properties of standard LWR fuels (UO₂, MOX) and innovative fuels (U-free fuels, inert matrix fuels). Even though MD is today limited to simulation of nanoscale properties, it can be used to investigate beyond what can be measured experimentally, but it needs robust interatomic potentials.

This exercise will focus on basic properties of UO₂, including lattice thermal expansion, heat capacity, Young modulus, cohesive energy and defects energies. We will discuss the completeness of experimental data and further experimental effort that might address observed shortcomings.

KEYWORDS **MOLECULAR DYNAMICS, URANIUM DIOXIDE, INTERATOMIC POTENTIAL, ELASTIC PROPERTIES, DEFECT ENERGIES**

1. INTRODUCTION

More and more models included in codes predicting the behaviour of fuel are based on a realistic description of the underlying phenomena, rather than on empirical correlations. Molecular dynamics techniques, where the system is considered at the atomic scale, can play a major role in this perspective since it can provide parameters for bigger scale models; or even serve to develop models themselves, studying the phenomena at the atomic scale (e.g. identification of the diffusion mechanisms).

SCK-CEN is particularly interested in both aspects, in order to incorporate the results in the code MACROS [36]. The intention is to study the influence of defects, including groups of point defects as found in displacement cascades, on the behaviour of noble gas atoms present in the fuel as fission products. In this article, we will focus on the selection of an interatomic potential (IAP) adapted for UO₂. A set of IAPs found in literature will be used and a comparison with existing experimental data on lattice properties, thermal expansion, elastic properties and point defect energies will be made.

2. MOLECULAR DYNAMICS

2.1. DESCRIPTION

Molecular dynamics (MD) is a computer simulation technique predicting the evolution with time of a system of atoms by integrating their equation of motion (Newton's equations). Configurations (atom positions, velocities etc.) are distributed according to statistical distribution functions. In the frame of MD different statistical ensembles can be reproduced by applying certain conditions to the simulated system: coupling techniques to a thermostat [9] and barostat [37] have been developed to sample other ensemble such as canonical (NVT) or isothermal-isobaric (NPT) ensemble. MD is also used to follow step by step phenomena such as displacement cascades or diffusion mechanisms.

2.2. LIMITATIONS

A MD simulation is based on a classical description of motion which means that electrons are not present explicitly (so called Born-Oppenheimer approximation) and atoms are "point" particles. The potential energy surface is approximated by an analytical function and forces obtained as gradient of potential energy function. Design of the IAP and choice of parameters is often based on a fitting to available experimental data. The main limitation of MD concerns the size of the box we can simulate (up to about a few millions

atoms), and the simulation length (up to a few nanoseconds). Compromises have to be made in order to obtain a reasonable calculation time.

2.3. DETERMINATION OF PHYSICAL PROPERTIES

At each iteration step information about state of the system can be extracted. A set of thermodynamic quantities be directly obtained from MD simulation: total (E), kinetic (K), and potential ($V(r)$) energies, volume (V), pressure (p) and temperature (T). Statistical mechanics provides us with the relation between the fluctuations of these quantities and other macroscopic properties. We used the following relations in this article, with k_B Boltzmann constant, C_V specific heat at constant volume, β_T isothermal compressibility, and C_p specific heat at constant pressure [34]:

$$\left\langle (\delta V(r))^2 \right\rangle_{NVE} = \frac{3}{2} N k_B^2 T^2 \left(1 - \frac{3 N k_B}{2 C_V} \right) \quad (1)$$

$$\left\langle \delta E^2 \right\rangle_{NVT} = k_B T^2 C_V \quad (2)$$

$$\left\langle \delta V^2 \right\rangle_{NPT} = V k_B T \beta_T \quad (3)$$

$$\left\langle \delta(H + pV)^2 \right\rangle_{NPT} = k_B T^2 C_p \quad (4)$$

2.4. INTERATOMIC POTENTIAL

The IAP, from which forces acting on atoms are derived, is the main parameter governing interactions in a MD simulation. An adequate IAP is thus essential in order to obtain a realistic picture of interaction in the system.

Nine IAPs have been taken from the literature, whose properties can be found in table 1. Two types of approaches have been used in the past in order to describe the UO_2 system. The Buckingham-type potential containing two terms, the first one representing repulsion at short distance and the second one the Van der Waals interaction. Its evolution as a function of the interatomic distance r can be expressed as (with A , C and ρ the free parameters):

$$V(r) = A \cdot \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} \quad (5)$$

Bushing-Ida type [41] is obtained adding a Morse type potential, and contains more parameters (A , B , C , D , E , a , r^*):

$$V(r) = A \cdot \exp(-B \cdot (a - r)) - \frac{C}{r^6} + D[\exp(-2E(r - r^*)) - 2 \exp(E(r - r^*))] \quad (6)$$

An atom can be described as a point charge associated with a mass (rigid atom description), or as a charged core bounded by a "spring" (harmonic potential) [40] to a massless charged sphere representing the shell electrons (shell-core description). The last representation simulates polarisability of atoms, but cannot be used for the simulation of displacement cascades because energetic collisions lead to a too large separation of the core and its shell [7], that is the reason why they were treated here as a rigid ions (corresponding to an infinite spring constant), without altering the other potential parameters. The validity of this treatment will be discussed in this article.

Table 1. Characteristics of the potentials used in our simulations

Author	Ref.	Potential type	Shell-core model	Charges	
				Default - O : - 2	Default - U : +4
Basak	[1]	Bushing-Ida	No	O : -1.2	U : +2.4
Busker	[2]	Buckingham	Yes		
Catlow1	[31]	Buckingham	Yes		
Catlow2	[31]	Buckingham	Yes		
Grimes	[2]	Buckingham	Yes		
Jackson	[2]	Buckingham	Yes		
Motoyama	[3]	Buckingham	No		
Van Brutzel	[4,5]	Buckingham	No	O : -1.61...	U : +3.22...
Yamada	[6]	Bushing-Ida	No	O : -1.2	U : +2.4

3. CALCULATION OF PHYSICAL PROPERTIES

3.1. LATTICE PROPERTIES

The first data reproduced concerned lattice properties: lattice parameter at 300 K and its evolution with temperature (thermal expansion). Data were obtained using a MD cell containing 768 mobile atoms, applying a constant temperature algorithm (Nosé-Hoover [9]). The results are plotted on fig. 1. All potentials but Motoyama's one (out of picture range) predict a value for lattice parameter at 300 K within the range of experimental measurements. Only three potentials are close to the experimental curve given by Martin [10]: Basak's one, Van Brutzel's one and Yamada's one; but the first two of them predict the best curvature for a_0 as function of temperature.

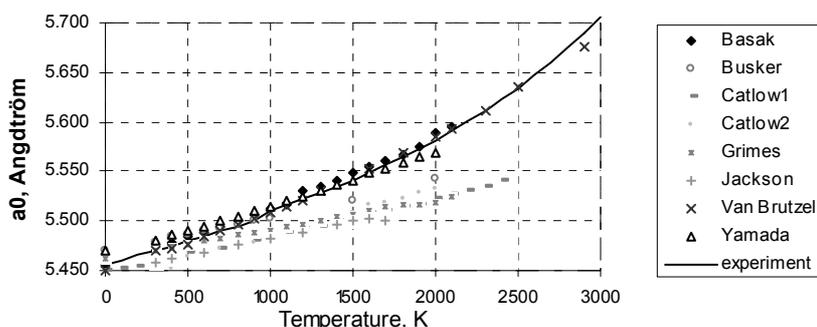


Figure 1. Lattice thermal expansion as predicted by the different potential

3.2. DEFECT FORMATION ENERGIES

Processes of formation and migration of defects in lattice are responsible for transport of atoms in material. Diffusion, segregation and precipitation processes strongly depend on defect properties. Hence it is extremely important to make sure that defects can be correctly reproduced by MD approach. The formation energies of three neutral types of defects were calculated: oxygen/uranium Frenkel pairs and tri-vacancies. The obtained results are summarized in table 2, together with the experimental values found in literature. We clearly see that three potentials (Van Brutzel, Basak and Yamada) provide results which are in agreement with experimental measurements of oxygen Frenkel pair and trivacancy. All potentials overestimate the experimental value obtained for uranium Frenkel pair; at the same time the potentials just mentioned above are closer to the experimental value than the other potentials. However some authors [4,32] think the experimental value is slightly underestimated.

The MD cell size can influence the value of formation energy, because the distortion zone formed by the defects can overlap directly and via periodic boundary conditions [39]. To see a convergence of defect formation energy different sizes of MD cells (the biggest cell contained 2592 atoms) were used. The interaction between vacancy and interstitial was almost negligible above two to three unit cells between vacancy and interstitial (in case of Oxygen Frenkel pair), and recombination radius was found to be 8.2 Å.

Table 2. Prediction of defect energies with all potentials and comparison to experimental data

Potential name	Oxygen Frenkel pair energy, eV	Uranium Frenkel pair energy, eV	Trivacancy energy, eV
Basak	5.36	13.87	6.35
Busker	7.06	25.05	8.52
Catlow1	5.99	23.21	8.31
Catlow2	5.78	20.83	6.15
Grimes	8.28	28.15	10.57
Jackson	6.55	23.25	8.35
Motoyama	7.94	23.14	7.03
Van Brutzel	3.54	13.89	4.84
Yamada	5.58	15.52	8.96
exp	3.1 – 5.4 ¹ [25-30]	8.03 - 9.5 [25, 33]	5.1 - 6.5 ± 0.5 [25, 33]

¹ Note the wide range of experimental values for the oxygen Frenkel pair formation energy.

3.3. ELASTIC AND THERMODYNAMIC PROPERTIES

The most time consuming part of this work was the determination of the elastic and thermodynamic properties of UO_2 , and their evolution with temperature. The methodology to obtain these values was explained in section 2.3. We used finite difference in order to determine specific heat at constant pressure / volume, thermal expansion coefficient, Young's modulus and Poisson's ratio and isothermal compressibility.

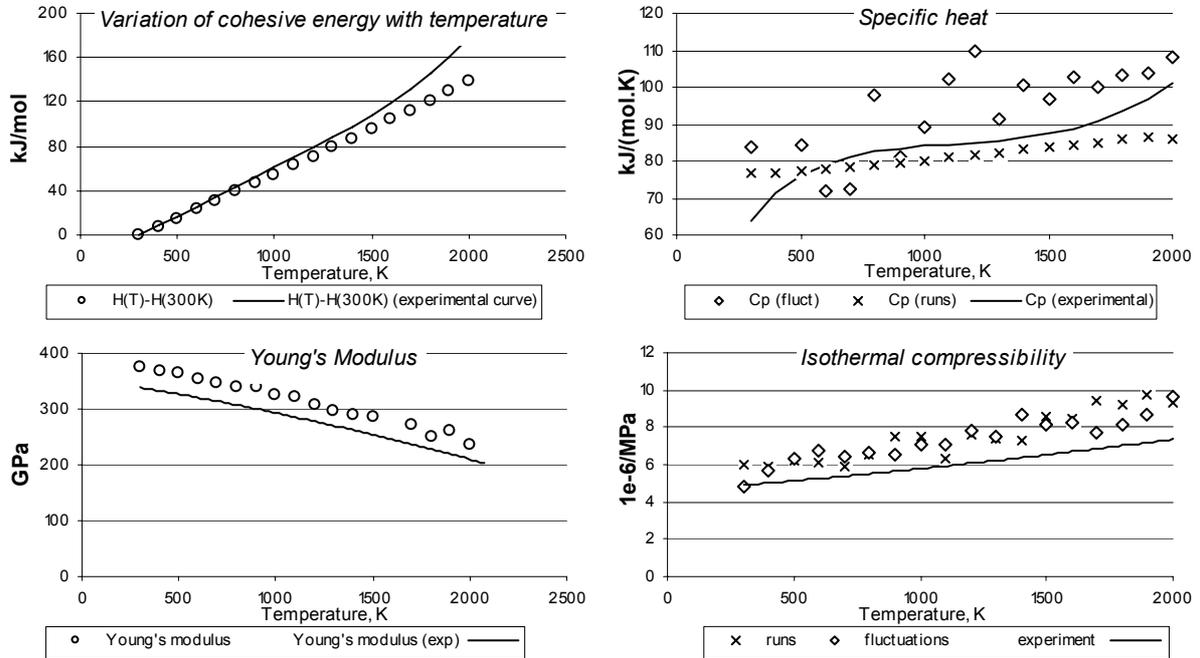


Figure 2 Elastic and thermodynamic properties calculated with Basak's potential – Comparison to experiment

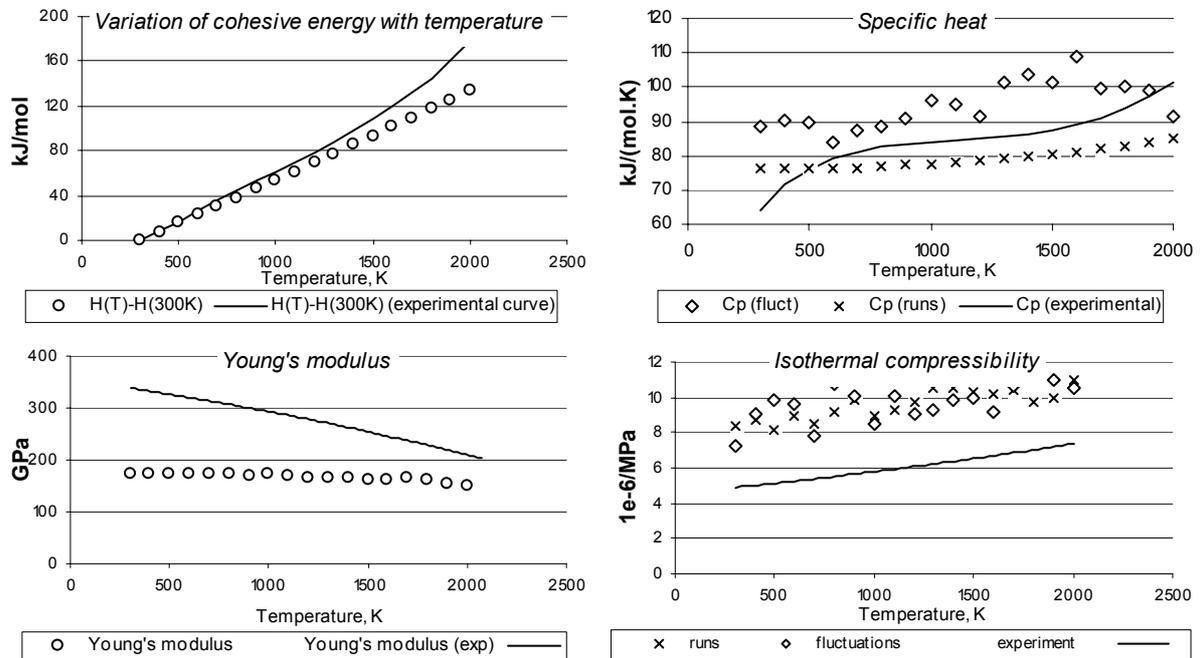


Figure 3. Elastic and thermodynamic properties calculated with Van Brutzel's potential – Comparison to experiment

Fluctuations theory was used for isothermal compressibility, specific heat at constant pressure or volume. These last calculations are quite long, hence only three IAPs have been chosen to perform calculations (Basak and Van Brutzel), plus one initially presented with a shell-core model (Busker). We assume this last IAP is representative of the other shell-core potentials, because they have shown the same tendency in the

previous simulations (see section 3.1&3.2). Since Basak's IAP is an "improved" version of Yamada's one, large difference between them should not be expected. Initial system of atoms was equilibrated during 50ps and measurements have been performed within next 100ps that allows collecting acceptable statistics and good the precision for averages.

We clearly observe (fig. 2) that predictions based on Van Brutzel's IAP are quite far from experimental measurements with regard to elastic properties, but thermodynamic properties (specific heat and cohesive energy variation with temperature) close to experiment, except in the high temperature region (above 1500K), where electronic effects start to play a role. Good agreement for experimentally measured elastic properties have been found for results given by Basak's IAP (see fig. 3), and we can make the same remark about thermodynamic properties.

4. DISCUSSION OF THE AVAILABLE EXPERIMENTAL DATA

4.1. LATTICE PARAMETER AND THERMAL EXPANSION

The generally adopted value for the lattice parameter of stoichiometric UO₂ at standard conditions of temperature and pressure is $5.470 \pm 0.002 \text{ \AA}$ [11,12, and 33].

Lattice thermal expansion has also been extensively studied, and two very important reviews have been made, by Martin [11] and Fink [13]. Empirical expression for lattice parameter as function of temperature was derived using experimental measurements, one should emphasize that the uncertainty of that curve was quite low.

4.2. ELASTIC PROPERTIES

We have compared the theoretical results to two elastic curves: the evolution of isothermal compressibility and Young's modulus with temperature. Experimental data on the dependence of isothermal compressibility on temperature was found only in one source [14 For Young's modulus, many experimental data are available for polycrystalline specimens [e.g. 15-22] but we found only two for a monocrystal [23, 24]. For both mono- and polycrystalline its value is decreasing with rising of temperature [15, 16].

4.3. DEFECT FORMATION ENERGIES

Defect formation energies are more problematic, because of the large range of experimental values (from 3.1 to 5.4 eV [25-30]) obtained for oxygen Frenkel pair energy, (8.03 and 9.5 [25, 33]) for uranium Frenkel pair energy and (5.1 and 6.5 [25, 33]) for trivacancy formation energy. Moreover, the obtained values of trivacancy energy are subject to discuss in [4, 5, and 32] and are perhaps underestimated. It is thus difficult with such an experimental range of values to assess the validity of all potentials, even if it allowed us to dismiss many of the available ones.

5. CONCLUSION

The objective of this work was to select an IAP adapted for UO₂. We performed a large number of simulations in order to assess the validity of IAPs available in the literature, by comparison to experimental data.

Compromises on MD cell size and simulation length were made in order to run all simulation in a reasonable computing time. Since the convergence was checked, no artificial effects are expected.

The first observation, based on lattice thermal expansion is that the proposed treatment of shell-core potentials is not appropriate, especially at high temperature. Motoyama's IAP predicted a too low value for lattice parameter and was also rejected. Three potentials remain in "competition": Basak, Van Brutzel and Yamada. The first two of them could also predict the good curvature of lattice parameter evolution with temperature (and thus thermal expansion coefficient).

When we consider elastic properties, Basak's potential provides results in agreement with experiment, while results obtained with Van Brutzel's potential are away from the experimental points. The situation was different for defect properties: in that case Van Brutzel's potential gave the best agreement with experimental data, while Basak's potential was close to the upper limit of the experimental range of values for the energy of formation of oxygen Frenkel pair. This can be explained by the fitting procedure for the two potentials: Basak based his fitting on elastic properties (isothermal compressibility) and Van Brutzel on defect properties (energy of formation and migration).

With regard to uranium Frenkel pair formation energy, the predictions were in all case above the experimental values, but we could clearly see that the three just mentioned potentials are much closer to this value than all other ones.²

We have thus two good interatomic potentials, one reproducing accurately the elastic properties (Basak) and relatively good defect formation energies, the other one just the defect properties (Van Brutzel), but at the centre of the interval of experimental values. The remaining interrogations arise from the defect energies measurement. We could dismiss a large part of the available potentials whose predictions were much too high; but the prediction of oxygen Frenkel pair energy made with Basak's potential is still inside the experimental range, but above most of the experimental values. One question remains: can we use this potential for the simulation of defects or more complex events? The second point is: are uranium Frenkel pair formation energies correctly predicted or not? The answers to these questions require cooperation with experimentalists.

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² A strange observation can be made on the charges attributed to ions: the best predictions for defect energies appear for potential using non-formal charges (O: -2 and U: +4). However, we don't think there is a correlation between these two observations, but rather than the general form of the well of the potential play the major role. Note that a very recent potential [35] also based on a shell-core description of atoms gives an accurate value while the charges remain formal.