Investigation using atomic scale methods of the transport properties of bulk UO₂ containing defects and fission products

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Summary

The electronic structure calculations and empirical potential methods are developed and assessed for the investigation of fuel performance under irradiation within the F-BRIDGE project. After the review of the relevance of these methods, presented in the first report (deliverable D221), this report contains the results of the investigation of the transport and mechanical properties of bulk UO₂ under irradiation using density functional theory and classical molecular dynamics. Because of their complexity, the fission effects are split in a series of mechanisms that are investigated separately or partially coupled. The information obtained can be used in macroscopic models to simulate fuel performance during irradiation at scales corresponding to reactor operation.

The investigation of the point defects creation, migration, recombination and clustering was the starting point required for the atomistic studies, both in stoichiometric and in non-stoichiometric UO₂. Based on these results, the effect of point defects on some macroscopic fuel properties like the lattice parameter or the diffusion of oxygen and fission gases could be investigated. Existing potential models, as well as a specific potential model developed during the F-BRIDGE project were evaluated. The mechanical properties were determined by empirical potentials for fresh and irradiated fuel and a strong impact of radiation damage was observed on the cracking behaviour under uniaxial stress.

Then, the fission gases location and diffusion were investigated. The solubility of helium being extremely reduced, the investigation of its physical state in the fuel, of the migration mechanisms and of the formation of bubbles is of primary importance for the fuel performance understanding. Finally, the damages produced by displacement cascades, and their interaction with helium bubbles, were characterised.

Approval

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1 Introduction

1.1 Interest of the atomistic methods for the description of UO$_2$ under irradiation

This document presents the results of the investigations of the irradiation effects in UO$_2$ using atomistic methods. The development and validation of the methods used, Density Functional Theory (DFT) and classical Molecular Dynamics (CMD), were discussed in the D221 report (Bertolus et al. 2010).

At the atomic level, each fission generates two kinds of perturbations in the UO$_2$ lattice: point defects (i.e. displaced U and O atoms) appear and foreign atoms (fission products, solid or gaseous) are introduced in the lattice. Moreover, helium is generated in the fuel by decay of some of the fission products. The irradiation effects in UO$_2$ are typical multiscale processes: as irradiation proceeds, the damage and perturbations at the atomic scale are combined and produce effects at the mesoscopic or macroscopic scales: vacancies can combine and produce voids or pores, fission product atoms can form precipitates, interstitials can form dislocations, the stoichiometry of the UO$_2$ matrix can change, the high burn-up structure forms, etc. The thermophysical properties are also affected. This report is restricted to the properties of crystalline UO$_2$ in presence of point defects. The properties of polycrystalline UO$_2$, the effect of extended defects like dislocations, pores, grain boundaries or the formation of the high burn-up structure will be presented in separate reports. The formation and stability of small helium bubbles is however investigated, as this topic is directly linked to the behaviour of helium in the bulk.

Because of its complexity, the investigation of irradiation effects by atomistic effects is usually being split in two coupled sub-problems: the study of the disorder introduced in the positions of the U and O atoms by the displacement cascades, and the study of the behaviour of the solid and gaseous fission products. These two sub-problems are reported separately, but the interactions between them are also presented in the study of the behaviour of helium in damaged fuel and in the simulation of displacement cascades in the presence of rare gas in bulk UO$_2$.

The current document is organised as follows. We first report studies relative to the first sub-problem. Radiation damage starts with fission, generating a displacement cascade consisting in the displacement of thousands of U and O atoms, immediately followed by the recombination of most of these point defects. The simulation of this process requires a good understanding of the properties of point defects, like their creation, interaction, diffusion, recombination and clustering. The stoichiometry of the UO$_2$ matrix has also to be considered, as it is modified due to the oxygen production by fissions and consumption by the oxidation processes (fission products, cladding).

We then report the results of the investigations relative to the second sub-problem. The work focuses on the behaviour of the fission gases Kr and Xe, as well as of He produced by alpha disintegrations. The physical state of these gases is of primary importance for the simulation of the fuel behaviour under irradiation conditions, as gas release and swelling are among the safety criteria which must be evaluated in order to avoid fuel rod failure. The study of the helium behaviour is also relevant for spent fuel storage conditions. Both perfect and damaged UO$_2$ are investigated, as well as various stoichiometries, since damage and non-stoichiometry are always present in real conditions and have a strong impact on the fission gases behaviour.
1.2 Methods used

The methods used were described in detail in the deliverable D221 (Bertolus 2010). Two types of methods were particularly used.

- **Electronic structure calculations : density functional theory (DFT)**
  The properties of matter can be deduced from calculations at the atomic scale by solving the Schrödinger equation. This approach, called *ab initio*, or electronic structure method, considers the interactions between the nuclei and the electrons described by a set of coupled differential equations. The solution to this many body problem can only be obtained using numerical techniques, for instance in the framework of the DFT. In the DFT, the problem is simplified by taking into account the electronic density and the interactions between the electrons, and not all the electrons explicitly. No exact solution exists for the calculation of the energy as a function of the electronic density and the interactions impossible to calculate exactly are gathered in a term called the exchange-correlation term. Various approximations were proposed for the exchange-correlation term, for instance the local density (LDA) or generalised gradient (GGA) approximations, or for strongly correlated systems, the DFT+U method or hybrid functionals.

- **Empirical potentials and classical molecular dynamics (CMD)**
  In classical molecular dynamics simulations, the interactions between the atoms are described in terms of simple analytical functions, called empirical potentials. Pair potentials are very commonly-used potentials usually containing a short-range, a van der Waals attraction, a long-range Coulomb interaction and a covalent bonding term. The parameters of these potentials are determined empirically, by fitting the free parameters to a set of thermophysical properties obtained experimentally or from electronic structure calculations. Several different sets of potential parameters have been proposed as suitable for modelling the bulk and defect behaviour of nuclear oxide fuels. These potentials are combined with the simulation of molecular dynamics, which enables to simulate the evolution in time of a system and to explore its configuration space. This combination is referred to as classical molecular dynamics.

1.3 Structure of the document

This document reports the contributions of the various partners involved in WP2-2 on the investigation of irradiation effects in bulk UO$_2$. It is organised as follows:

First, basic defect properties, in particular point defects formation and migration energies are investigated both by electronic structure calculations, in particular DFT, and classical molecular dynamics (CMD) simulations. The CMD technique is also used to investigate the point defects migration mechanisms and the oxygen diffusion in hypo- and hyper- stoichiometric UO$_2$. The mechanisms required for the understanding of displacement cascade evolution, like the defects recombination range and lifetimes and the defects clusters stability are also considered. The thermal conductivity results are presented in this section.

Then, the incorporation and transport properties of rare gases are investigated by DFT and CMD. The incorporation energies, localisation and transport properties for krypton, xenon and iodine are estimated by DFT. Then the helium diffusion is investigated by CMD in perfect or damaged, hypo- and hyper-stoichiometric UO$_2$. The formation and stability of helium bubbles is simulated. Finally, the xenon incorporation and migration energies are investigated by CMD.

Finally, displacement cascades and thermal spikes are simulated in pure UO$_2$, as well as in presence of helium and xenon. In particular, the concentration of defects remaining at the end of the displacement cascades is calculated as a function of the energy of the initial PKA energy, and the stability of helium bubbles under irradiation is assessed.
2 Investigation of defects formation and migration in bulk UO$_2$ and their impact on structural stability and transport properties

Radiation damage produced by fast nuclear particles has many aspects and stages of its progress (Benson et al. 1963). One way to model advanced stages of radiation damage at the atomistic level is to investigate the creation of a number of oxygen (OFP) and uranium Frenkel pairs (UFP) and the defect evolution in a damaged solid under static or dynamic conditions.

2.1 DFT investigation

The formation energies of various point defects in the fluorite and Jahn-Teller distorted phases of UO$_2$ were calculated in the framework of the density functional theory.

2.1.1 Computational details

Calculations were mainly performed in the DFT+U approximation (Liechtenstein et al. 1995) using Liechtenstein approach together with the fully localized limit of the double counting correction. The U and J parameters of the DFT+U approximation were not fitted, but the 4.50 eV and 0.51 eV values determined experimentally by Kotani et al. using analysis of X-ray photoemission spectra (Kotani et al. 1992) were used. It is now well known that the DFT+U approximation creates multiple energy minima due to the electron localisation (Shick et al. 2001; Larson et al. 2007; Amadon et al. 2008; Jomard et al. 2008; Dorado et al. 2009). We used the occupation matrix control scheme developed in the framework of the project (Dorado 2009) to ensure that the ground states are reached or approached as much as possible in our calculations. The GGA PBE functional (Perdew et al. 1996) was used.

Migration barriers were also evaluated in the GGA approximation using the PBE functional to determine the effect of the electronic localisation on these energies.

All calculations take into account spin-polarization. UO$_2$ is paramagnetic above 30 K and displays a complex non-collinear 3k antiferromagnetic order below 30 K (Caciuffo et al. 1999). These magnetic orders have been approximated by a 1k collinear layered antiferromagnetic order. The SOC is neglected since taking it into account multiplies the calculation times by approximately five and makes the supercell calculations intractable. Calculations were done on a 96-atom UO$_2$ supercell. A 2x2x2 Monkhorst-Pack (Monkhorst et al. 1976) k-point mesh, yielding four k-points in the irreducible part of the Brillouin zone, is sufficient to get converged structural parameters and total energies for this supercell size. The projected augmented wave (PAW) method (Blochl 1994) as implemented in the VASP code was used. A 500 eV cut-off energy, yielding structural parameters and absolute total energies converged to 0.01 Å and 25 meV/atom, respectively, was chosen. Gaussian smearing was used for the treatment of fractional occupancies with a smearing width of 0.1 eV. It has been shown in previous studies (Bertolus 2010) that this parameters yield good results on the structural, electronic and mechanical properties of bulk UO$_2$.

The migration energies of defects were calculated using the nudged elastic band (NEB) method (Henkelman et al. 2000).

2.1.2 Defect formation energies

We have considered point defects as follows: O and U mono-vacancies, O and U mono-interstitials, O$_2$ di-interstitials and Schottky defects (UO$_2$ trivacancies). For the defects involving more than one atom isolated and bound configurations have been investigated. Then, there are at least two O di-interstitial bound
configurations, as shown in Figure 1: one with the two O atoms in neighbouring interstitial sites \(I^O_{\infty}\) and one where the two interstitials share a lattice site with the lattice O \(I^X_{\infty}\). Finally, the bound Schottky defects can take the 3 different configurations represented in Figure 2 depending on the relative positions of the oxygen and uranium vacancies (Dorado, Freyss, et al. 2009).

Figure 1: The two oxygen di-interstitials studied: left with the two extra O atoms in octahedral sites and right the configuration where three O atoms share an oxygen site. Uranium atoms are represented in blue, oxygen in red. The two interstitial atoms and the nearest O atoms are shown in yellow.

Figure 2: The three possible configurations of the Schottky defect. Uranium are represented in blue, oxygen in red, the vacancies are shown in light blue.

The formation energies were calculated as:

- Interstitials \(I_X\) (X=U or U): \(E_{I_X}^{\text{for}} = E_{I_X}^{N+1} - E_{\text{ref}}^X - E_{\text{UO}_2}^N\)
- Vacancies \(V_X\) (X=U or U): \(E_{V_X}^{\text{for}} = E_{V_X}^{N-1} + E_{\text{ref}}^X - E_{\text{UO}_2}^N\)
- Bound O di-interstitial \(I_{OZ}\) (\(I^O_{\infty}\), \(I^X_{\infty}\)): \(E_{I_{OZ}}^{\text{for}} = E_{I_{OZ}}^{N+2} - 2 \cdot E_{\text{O}}^{\text{ref}} - E_{\text{UO}_2}^N\)
- Bound Schottky defects \(S_{1,2,3}\): \(E_{S}^{\text{for}} = E_{V_{\text{UO}_2}}^{N-3} - \frac{N-3}{N} E_{\text{UO}_2}^N\)
- Isolated Schottky defects \(S^*\): \(E_{S^*}^{\text{for}} = E_{V_U}^{N-1} + 2 \cdot E_{V_O}^{N-1} - 3 \cdot \frac{N-1}{N} E_{\text{UO}_2}^N\)
- Bound U Frenkel pair \(FP_U\): \(E_{FP_U}^{\text{for}} = E_{FP_U}^N - E_{\text{UO}_2}^N\)
- Isolated Frenkel pairs \(FP_X\) (X=U or U): \(E_{FP_X}^{\text{for}} = E_{V_X}^{N+1} + E_{I_X}^{N+1} - 2 \cdot E_{\text{UO}_2}^N\)

With:
The results obtained for both UO$_2$ phases are listed in Table 1.

Table 1: Formation energies of point defects calculated using DFT+U for UO$_2$ in the Jahn-Teller distorted structure and in the fluorite structure

<table>
<thead>
<tr>
<th>Point defect</th>
<th>Formation energy (eV)</th>
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<tr>
<td></td>
<td>Jahn-Teller</td>
</tr>
<tr>
<td>Oxygen interstitial $I_O$</td>
<td>0.47</td>
</tr>
<tr>
<td>Uranium interstitial $I_U$</td>
<td>5.72</td>
</tr>
<tr>
<td>Oxygen vacancy $V_O$</td>
<td>5.05</td>
</tr>
<tr>
<td>Uranium vacancy $V_U$</td>
<td>9.56</td>
</tr>
<tr>
<td>Bound di-interstitial ($I_O^0$)</td>
<td>0.43</td>
</tr>
<tr>
<td>Bound di-interstitial ($I_U^0$)</td>
<td>-0.26</td>
</tr>
<tr>
<td>Bound Schottky defect $S_1$</td>
<td>4.07</td>
</tr>
<tr>
<td>Bound Schottky defect $S_2$</td>
<td>3.26</td>
</tr>
<tr>
<td>Bound Schottky defect $S_3$</td>
<td>3.41</td>
</tr>
<tr>
<td>Isolated Schottky defect $S^*$</td>
<td>/</td>
</tr>
<tr>
<td>Isolated Oxygen Frenkel pair $FP_O^*$</td>
<td>5.52</td>
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<tr>
<td>Bound Uranium Frenkel pair $FP_U$</td>
<td>/</td>
</tr>
<tr>
<td>Isolated Uranium Frenkel pair $FP_U^*$</td>
<td>15.28</td>
</tr>
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One can see from Table 1 that the influence of the Jahn-Teller distortion on the formation energies is small and does not exceed 1 eV for all defect considered. This difference, however, is of the same order of magnitude as the formation energy for the oxygen interstitial, which yields a positive energy in the Jahn-Teller structure but a slightly negative one in the fluorite structure. These values contrast with the large negative formation energy for O interstitials which was found using DFT (Freyss et al. 2005) or using DFT+U without any precaution as to the metastable states (Geng et al. 2008; Gupta et al. 2007).

Table 1 also shows that the formation of bound Schottky defects, U Frenkel pair and di-interstitials (especially in the configuration where the 3 oxygen atoms are split over one site) is very favourable. The binding energy of Schottky defects amounts to several eV, as can be seen by comparison with the formation energy of isolated Schottky defects. This had already been observed for the O Frenkel pair by Andersson: the formation energy of the bound Frenkel pair is 3.32 eV instead of more than 5 eV for the isolated one (D.A. Andersson et al. 2011).

The analysis of the charge redistribution induced in the lattice by the point defects shows the creation of U$^{5+}$ or U$^{3+}$ cations for charge compensation. The oxygen interstitial induces the formation of two U$^{5+}$ cations, the oxygen vacancy the formation of two U$^{3+}$ cations and the uranium vacancy the formation of four U$^{5+}$ cations. The position of the U$^{5+}$ and U$^{3+}$ cations relative to the point defect has an influence on the formation energy of the defect and has to be carefully monitored.

2.1.3 Transport properties of defects: migration and activation energies

The migration energies of several elementary migration mechanisms for oxygen and uranium defects have been investigated for the fluorite UO$_2$ structure in the DFT (Dorado et al. 2010) and DFT+U framework
Using the nudged elastic band method, the migration mechanisms considered are as follows:

- vacancy mechanisms, in which an atom moves to a nearest neighbour vacancy of the same chemical specie in the <100> or the <110> directions. In the case of uranium, simple mechanisms, as well as a combined mechanism involving movement of the U vacancy and of the neighbour oxygen atoms were considered.
- a direct interstitial mechanism, in which an interstitial atom in an octahedral site moves to the next nearest octahedral interstitial site.
- an indirect interstitial mechanism (also called interstitialcy), in which an atom in an octahedral site replaces an atom on a neighbouring lattice site, which in turn moves to an octahedral interstitial site. This mechanism is only considered for oxygen atoms.

These migration mechanisms for O and U are represented in Figure 3 and Figure 4, respectively. The corresponding migration energies are reported in Table 2.

![Figure 3: Oxygen migration mechanisms. Up left: direct interstitial mechanism. Up right: indirect mechanism (interstitialcy). Down left: <100> vacancy mechanism. Down right: <110> vacancy mechanism.](image-url)
Figure 4: Uranium migration mechanisms. Left: <110> vacancy mechanism. Right: direct interstitial mechanism.

Table 2: Migration energies of oxygen and uranium defects yielded by the GGA and the GGA+U approximation.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Migration energies (eV)</th>
<th>DFT</th>
<th>DFT+U</th>
</tr>
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<tr>
<td>Oxygen</td>
<td>Direct Interstitial</td>
<td>3.6</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Indirect Interstitial</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Vacancy in &lt;100&gt; direction</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Vacancy in &lt;110&gt; direction</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>Uranium</td>
<td>Direct Interstitial</td>
<td>5.8</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>Indirect interstitial</td>
<td>/</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Vacancy in &lt;100&gt; direction</td>
<td>/</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>Vacancy in &lt;110&gt; direction</td>
<td>4.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Vacancy in &lt;100&gt; direction combined with O displacement</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>

The comparison between the DFT and the DFT+U results show that both approximations give similar qualitative results and that oxygen migration is much more favourable than uranium migration. The influence of the electronic localisation is rather weak for oxygen defects, with differences between GGA and GGA+U energies smaller than 0.5 eV. The effect is more significant on U defects, the differences between GGA and GGA+U energies reaching 1.1 and 2.1 eV.

It should be stressed that one should be careful when determining energy barrier using the DFT+U approximation. One should make sure that the ground state of the system has been reached for each point of the migration pathway calculated and that the energy of the system is varying smoothly along it. The negative migration energy for O previously reported by Gupta et al. (Gupta et al. 2010) is probably due to the fact that a metastable state had been reached for the equilibrium position.

The results of these calculations enable us to determine the precise mechanisms for the O and U migration. In presence of interstitials, O and U migrate through an indirect mechanism, also called interstitialcy mechanism. In presence of vacancies, the migration occurs through jumps in the 100 direction, but for uranium, this migration is combined with significant movement of the nearest neighbour oxygen atoms.

We have compared the results on oxygen migration with available experimental results. The activation energies for O migration obtained from experiments performed in precisely controlled and monitored
conditions by Kim and Olander (Kim et al. 1981) and by Garcia et al. at CEA/DEC during the project (Garcia et al. 2010), as well as the DFT+U values, are indicated in Table 3. Because of the experimental conditions, for the vacancy mechanism, the activation energy is simply the migration energy, while for the interstitial mechanism the activation energy is the sum of the formation and of the migration energy.

Table 3: Activation energies of oxygen defects yielded by the GGA+U approximation and comparison with experimental results

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>Activation energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT+U</td>
</tr>
<tr>
<td>Indirect Interstitial</td>
<td>0.88</td>
</tr>
<tr>
<td>&lt;100&gt; Vacancy</td>
<td>0.67</td>
</tr>
</tbody>
</table>

It can be seen that both DFT+U activation energies for interstitial and vacancy mechanisms compare very well with the experimental data. The DFT+U results are only slightly overestimated and the energetic order between the two mechanisms is respected. The atomic transport properties of oxygen thus seem well described in UO₂ using the DFT+U approximation.

2.2 Empirical Potentials

In the absence of external constraints (e.g. load, irradiation) on a solid, the equilibrium defect concentration depends on the temperature and on the chemical potential of each species (stoichiometry). The parameters that characterize the equilibrium are the formation energies of intrinsic defects (Frenkel pairs and Schottky defects) and the binding energies of defect clusters. However, when one wants to characterize with higher scale modelling tools the evolution of the defect population, one additionally needs to know the defect production rate, the diffusion coefficient of all defects and the sink strength (where the recombination range also plays a role). The aspects related to thermal equilibrium (formation energy of Frenkel pairs and Schottky defects) have already been discussed in deliverable D221 where a thorough comparison of the values predicted by most potentials was performed.

A model potential developed for stoichiometric UO₂ (Yakub et al. 2007) and adapted to non-stoichiometric UO₂ during the project (Yakub et al. 2010), as well as the potentials of Catlow (Catlow 1977), Yamada (Yamada et al. 2000), Basak (Basak et al. 2003) and Morelon (Morelon et al. 2003) were used to investigate the point defect formation, stability and migration properties, as well as the oxygen diffusion coefficient in both stoichiometric and non stoichiometric UO₂. The defect recombination range (between interstitial and vacancy) and effect of radiation damage were also evaluated. Finally, thermal conductivity calculations are presented.

Three techniques based on empirical potentials were used for the investigation of incorporation and transport properties of rare gases in bulk UO₂:

- Molecular dynamics techniques, in which one follows the time evolution of the system.
- Nudged Elastic Band (NEB) calculations, which simultaneously minimize the energy of a set of intermediate configurations in order to find the migration pathway between two atomic configurations.
- Energy minimizations, in which atom positions are relaxed until an energy minimum is found.

In the last two methods constraints are generally used during the minimizations, fixing e.g. one or more coordinates of an atom. These methods are used as complements to NEB calculations, in order to better visualize the energy surface during migration and to interpret the migration mechanisms operating during the CMD runs.

These techniques have been discussed in more detail in the deliverable D221 (Bertolus 2010) of the F-BRIDGE project.
2.2.1 Investigation of Frenkel pairs in stoichiometric UO$_2$

2.2.1.1 Oxygen Frenkel pairs

A number of individual OFP defects in stoichiometric UO$_2$ were investigated using the potential model of Yakub for stoichiometric UO$_2$ (Yakub 2007). The sizes and identifiers used for the different types of examined defects are listed in Table 4.

The formation energy of the various defects was calculated. Figure 5 represents the energy minimization for the various types of OFP defects. The energy of the defect lattice is plotted here against the displacement of the interstitial ion from the centre of the interstitial site (in units of $R_{OO} = L/2$).

<table>
<thead>
<tr>
<th>Defect identifier</th>
<th>Vacancy-interstitial site displacements</th>
<th>Initial defect size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 $\Delta x_1 / L$</td>
<td>4 $\Delta x_2 / L$</td>
</tr>
<tr>
<td>OFP$_0$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>OFP$_1$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>OFP$_2$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>OFP$_3$</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>OFP$_4$</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>OFP$_5$</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>OFP$_6$</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5: Energy of defect formation plotted against displacements of an interstitial ion from the centre of its interstitial site.

The relaxation curves of the stable (3-3-3) OFP$_1$, (3-3-1) OFP$_2$, and (5-1-1) OFP$_4$ defects ended in the minimum energy points. The relaxation curve of the unstable (1-1-1) OFP$_0$ defect approaches zero energy monotonously. For the (3-1-1) OFP$_3$ (metastable) defect, a plateau is clearly seen. Andersson obtained a significantly lower value (3.3 eV) using DFT+U (D. A. Andersson 2011).
The energy of defect formation is defined for an isolated OFP or cluster and takes as reference the energy of an infinite crystal lattice. All computations involve approximations and simplifications like the Mott-Littleton scheme (Govers et al. 2007) or periodic boundary conditions which affect the computed values. Our calculations are also affected by the finite size of the simulation cell. To estimate the limiting value of the formation energy, a series of simulations with increasing size of the cell were performed. The results (Table 5 and Figure 6) show that the energy of defects formation is affected by the size of the main cell, the values decrease slowly as the size of the cell increases.

Table 5: Formation energy of the OFP$_1$ and OFP$_2$ defects at different sizes of the CMD cell. Comparison with Govers data.

<table>
<thead>
<tr>
<th>Cell size, $N_i$</th>
<th>$E$(OFP$_1$), eV</th>
<th>$E$(OFP$_2$), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>324</td>
<td>5.02</td>
<td>4.71</td>
</tr>
<tr>
<td>768</td>
<td>4.71</td>
<td>4.34</td>
</tr>
<tr>
<td>1500</td>
<td>5.07</td>
<td>4.77</td>
</tr>
<tr>
<td>2592</td>
<td>5.00</td>
<td>4.65</td>
</tr>
<tr>
<td>4116</td>
<td>4.91</td>
<td>4.56</td>
</tr>
<tr>
<td>6144</td>
<td>4.89</td>
<td>4.51</td>
</tr>
<tr>
<td>(Govers 2007)</td>
<td>5.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Figure 6: Energy of defects formation as a function of the cell size.

2.2.1.2 Uranium Frenkel pairs

Simulations of uranium Frenkel pairs were first done under static conditions. A single uranium ion was removed from its lattice site and placed in an interstitial position forming a single uranium Frenkel pair (UFP). The defect lattice was then relaxed to the minimal energy, and the defect formation energy was estimated as a difference between the energies of defect and ideal lattice (at $T = 0$ K). Table 6 illustrates the dependence of the UFP formation energy to the cell size and the separation distance between the two defects (measured
by ions displacements along each coordinate axes in units of minimal distances between the lattice oxygen ions \( R_{oo} = a / 2 = 2.736 \, \text{Å} \). The last value in Table 6 (14.3 eV) is believed to be a reasonable approximation to the energy of infinitely separated uranium vacancy and interstitial \( E_{\text{f(UFP)}} \). The formation energies of UFP calculated by DFT+U (Table 1) are in the same range: from 11.18 eV for bound UFP, to 15.79 eV for isolated UFP. In Table 7 we present the formation energies calculated for the two most stable types of UFP: the UFP\(_1\) defect (characterized by \( x / R_{oo} = 2, y / R_{oo} = 2, z / R_{oo} = 2; R = 4.8 \, \text{Å} \)) and the UFP\(_2\) defect (\( x / R_{oo} = 0, y / R_{oo} = 2, z / R_{oo} = 4; R = 6.1 \, \text{Å} \)). They are in good agreement with the experimental value of 9.5-12.6 eV (Dolling et al. 1965). The comparison with experimental data and other calculations is presented in Table 8.

Table 6: Static UFP\(_{\infty}\) formation energy found using increasing sizes of defects and cells at static conditions, \( T = 0 \, \text{K}, \rho = 10.95 \, \text{g cm}^{-3} \).

<table>
<thead>
<tr>
<th>( N_{ions} )</th>
<th>( x / R_{oo} )</th>
<th>( y / R_{oo} )</th>
<th>( z / R_{oo} )</th>
<th>( E_{\text{f(UFP)}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2592</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>12.8</td>
</tr>
<tr>
<td>12000</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>13.6</td>
</tr>
<tr>
<td>2592</td>
<td>10</td>
<td>12</td>
<td>12</td>
<td>14.1</td>
</tr>
<tr>
<td>12000</td>
<td>10</td>
<td>12</td>
<td>16</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Table 7: Estimation of the formation energy for two uranium defects: UFP\(_1\) (R=4.8 Å) and UFP\(_2\) (R=6.1 Å), calculated for increasing cell sizes (T=0 K, \( \rho = 10.95 \, \text{g cm}^{-3} \)).

<table>
<thead>
<tr>
<th>( N_{ions} )</th>
<th>( E_{\text{f(UFP}_1}), ) (eV)</th>
<th>( E_{\text{f(UFP}_2}), ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>324</td>
<td>10.6</td>
<td>11.0</td>
</tr>
<tr>
<td>2592</td>
<td>11.3</td>
<td>11.9</td>
</tr>
<tr>
<td>6144</td>
<td>11.1</td>
<td>11.7</td>
</tr>
<tr>
<td>12000</td>
<td>11.0</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 8: Comparison of static OFP and UFP formation energies for infinite separation distances with experimental data (Dick et al. 1958) and previous results yielded by electronic structure and empirical potential calculations.

<table>
<thead>
<tr>
<th>Source</th>
<th>( E_{\text{f(OFP)}} ), (eV)</th>
<th>( E_{\text{f(UFP)}} ), (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical potentials (Jackson et al. 1986)</td>
<td>4.76</td>
<td>19.4</td>
</tr>
<tr>
<td>Empirical potentials (Sindzingre et al. 1988)</td>
<td>4.25</td>
<td>16.63</td>
</tr>
<tr>
<td>Empirical potentials (Karakasidis et al. 1994)</td>
<td>4.45</td>
<td>17.42</td>
</tr>
<tr>
<td>Empirical potentials (Meis et al. 2005)</td>
<td>4.5</td>
<td>12.6</td>
</tr>
<tr>
<td>This work, empirical potentials with static conditions</td>
<td>4.7</td>
<td>11.0</td>
</tr>
<tr>
<td>GGA (J. Crocombette et al. 2001)</td>
<td>3.8</td>
<td>10.7</td>
</tr>
<tr>
<td>GGA (Freyss 2005)</td>
<td>3.6</td>
<td>11.8</td>
</tr>
<tr>
<td>This work, GGA+U (Table 1)</td>
<td>5.33</td>
<td>11.18</td>
</tr>
<tr>
<td>Experimental (Dick 1958)</td>
<td>3.0-4.0</td>
<td>9.5 - 12.6</td>
</tr>
</tbody>
</table>
In order to investigate the UFP formation enthalpy as a function of the UFP concentration, we carried out a series of NPT simulations (N = 2592 ions) at fixed temperature T = 2000 K for various numbers of UFP created in the cell. The enthalpy of the UFP formation was estimated as the difference between the enthalpy of damaged and pure UO$_2$ at the same temperature and ambient pressure divided by the number of UFP in the cell. We present in Figure 7 the effect of the UFP concentration on the equilibrium concentration of OFP defects. It can be seen on this figure that the presence of UFP induces the formation of OFP defects. This is due to the large perturbation of the lattice induced by UFP. The ratio between the numbers of OFP and UFP is of the order of two in the range of UFP concentrations between 0.3 and 1.1 %.

![Figure 7: Equilibrium OFP concentration versus percentage of interstitial sites occupied by uranium ions (NPT, N = 2592, T = 2000K).](image)

Figure 7: Equilibrium OFP concentration versus percentage of interstitial sites occupied by uranium ions (NPT, N = 2592, T = 2000K).

Figure 8 presents the CMD simulation results for the UFP formation enthalpy $\Delta H_f^{(UFP)}$ versus the percentage of interstitial sites occupied by displaced uranium ions. At UFP concentrations higher than 0.5 %, the value of $\Delta H_f^{(UFP)}$ stabilizes at approximately 15 eV.

![Figure 8: Enthalpy of UFP formation versus percentage of interstitial sites occupied by uranium ions (NPT simulation, N = 2592, T = 2000 K).](image)

Figure 8: Enthalpy of UFP formation versus percentage of interstitial sites occupied by uranium ions (NPT simulation, N = 2592, T = 2000 K).

The swelling of UO$_2$ containing UFP was also determined. The equilibrium crystal density (lattice parameter) is strongly affected by radiation damage (Staicu et al. 2010). We performed CMD simulations of radiation-damaged UO$_2$ at fixed temperature (T = 2000K) varying the number of UFP created at random. We present in Figure 9 the dependence of the UO$_2$ density on the UFP concentration.
To compare the simulation predictions with experimental data, one needs to estimate the concentration of Frenkel pairs in the swelling experiments. This property is usually measured as a function of the radiation dose accumulated in the sample. There is a difficulty in converting the evolution of a property measured as a function of dose in terms of defect concentration since no accurate model currently exists. It makes the present simulation interesting as a possible candidate for a tool performing such a conversion. As one can see from Figure 9, the material density (i.e. lattice parameter) value varies linearly with the defect concentration in the concentration range studied, from $\rho = 10.32$ g cm$^{-3}$ for pure UO$_2$ to $\rho = 10.14$ g cm$^{-3}$ for 1.2 % UFP. At high temperature, the radiation damage also generates additional OFP defects. According to Figure 7 a single UFP defect is accompanied at $T = 2000$ K by the creation of approximately two extra OFP defects. According to $T = 300$ K we estimated the dilation of the UO$_2$ lattice parameter to be 0.7% per percent (or per $\sim 1.2 \times 10^{20}$ cm$^{-3}$) of UFP created. It is more than the estimated effect of the OFP formation ($\sim 0.2\%$ per each percent of interstitial sites occupied by oxygen ions). Note that the calculation method proposed by (Staicu 2010) (Equation 4), yields a lattice parameter increase equal to 0.58%. The difference between the two values may be due to the neglect of the $2U^{(2+)} = U^{(3+) + U^{(5+)}}$ disproportionation reaction in the model used by Staicu.

2.2.1.3 Frenkel pair recombination

It is generally believed that Frenkel pair recombination plays a key role in the resistance of material under irradiation (Kotomin et al. 1992) and more specifically in fluorite-like structure (Chartier et al. 2005; Chartier et al. 2006; J. Crocombette et al. 2006). To investigate the basic mechanisms of this recovery a series of standard molecular dynamics simulations have been carried out in fluorite structure compounds using rigid ion (Morelon 2003; Van Brutzel et al. 2008; Guglielmetti et al. 2008; Pannier et al. 2009) and core-shell (Meis 2005) potentials.

In these studies the lifetimes of Frenkel pairs have been calculated as a function of the temperature. Separation distances between the vacancy and the self-interstitial up to 1.5 times the conventional lattice parameter have also been investigated. For each separation distance, we will associate in the following a specific rank starting with rank-1 for the closest distance. This can be visualized in Figure 10, Figure 11 and Figure 12. We recall that in the fluorite structure several non-equivalent interstitial-vacancy positions exist for fourth neighbour Frenkel pairs. The two different configurations will be referenced as type-1 or type-2 in the following.
Figure 10: Recombination mechanisms of the 4a site Frenkel pairs plotted in the \{1 0 0\} plane. All the ions represented lie in the plane. Circles represent ions of type 4a. The arrows represent the recombination mechanisms with the numbers indicating the recombination steps. The recombinations of the fourth neighbour FP are indicated by arrows with dotted lines. The recombination of the 2\textsuperscript{nd} and the 4\textsuperscript{th} neighbours of type II are represented in Figure 11 and Figure 12, respectively.

Figure 11: Recombination mechanisms of the 4a and 8c sites Frenkel pairs plotted in the \{1 1 0\} plane. All the ions represented lie in the plane. The left side of the figure is dedicated to the 4a sites and the right side is for the 8c sites. The recombination of the fourth neighbour FP are indicated by arrows with dotted and doubled lines. The recombination for the 4a second neighbour FP are quoted in Figure 12.

Figure 12: Recombination mechanisms of the fourth neighbour 8c site Frenkel pairs plotted in the \{1 1 0\} plane. All the ions represented lie in the plane. For the 4a second neighbours, the first four exchange steps (along de [0 0 1] direction) allow the 8c ions to make enough room around the path for the recombination to occur.
The results of the simulations are summarized in Table 9. In this table the lifetimes are expressed for each rank: (i) either as the maximum time found before the complete recombination if it is temperature independent (ii) or as an Arrhenius function if it is temperature dependent. The mechanism of recombination is specified as well. It is either direct meaning that the self-interstitial recombine directly into the vacancy or indirect i.e. the original self-interstitial displaces one or several other atoms in cascade until the last one recombines into the vacancy.

Table 9: Lifetimes of Frenkel pairs in UO₂

<table>
<thead>
<tr>
<th>Rank</th>
<th>Separation distance</th>
<th>Lifetimes (ps): rigid and core-shell model</th>
<th>Recombination mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2 (a_0)</td>
<td>(&lt; 0.3) (&lt; 0.3)</td>
<td>Spontaneous / Direct</td>
</tr>
<tr>
<td>2</td>
<td>(\sqrt{3}/2 \ a_0)</td>
<td>(3 \times 10^{-2} \exp(1.35/k_B T)) (3 \times 10^{-2} \exp(1.35/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
<tr>
<td>3</td>
<td>(\sqrt{5}/2 \ a_0)</td>
<td>(&lt; 1.1) (&lt; 0.9)</td>
<td>Spontaneous / Direct</td>
</tr>
<tr>
<td>4 type-1</td>
<td>3/2 (a_0)</td>
<td>(3 \times 10^{-3} \exp(1.63/k_B T)) (1 \times 10^{-3} \exp(2.19/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
<tr>
<td>4 type-2</td>
<td>3/2 (a_0)</td>
<td>(5 \times 10^{-3} \exp(1.51/k_B T)) (1 \times 10^{-3} \exp(2.23/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rank</th>
<th>Separation distance</th>
<th>Lifetimes (ps)</th>
<th>Recombination mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\sqrt{3}/4 \ a_0)</td>
<td>(&lt; 0.1) (&lt; 0.1)</td>
<td>Spontaneous / Direct</td>
</tr>
<tr>
<td>2</td>
<td>(\sqrt{11}/4 \ a_0)</td>
<td>(&lt; 0.4) (&lt; 0.3)</td>
<td>Spontaneous / Indirect</td>
</tr>
<tr>
<td>3</td>
<td>(\sqrt{19}/4 \ a_0)</td>
<td>(0.26 \exp(0.18/k_B T)) (6 \times 10^{-2} \exp(0.32/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
<tr>
<td>4 type-1</td>
<td>(\sqrt{27}/4 \ a_0)</td>
<td>(0.42 \exp(0.08/k_B T)) (0.16 \exp(0.11/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
<tr>
<td>4type-2</td>
<td>(\sqrt{27}/4 \ a_0)</td>
<td>(0.27 \exp(0.26/k_B T)) (3 \times 10^{-2} \exp(0.51/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
<tr>
<td>5</td>
<td>(\sqrt{35}/4 \ a_0)</td>
<td>(0.15 \exp(0.30/k_B T)) (1 \times 10^{-2} \exp(0.57/k_B T))</td>
<td>Thermally activated / Indirect</td>
</tr>
</tbody>
</table>

The results show that the recombination of both uranium and oxygen Frenkel pairs is rather complex. The recombination mechanisms are similar in the rigid ion and core-shell models. For uranium, the recombination is spontaneous for the Frenkel pairs of rank-1 and -3. For Frenkel pairs of rank-2 and-4, the recombinations are found to be thermally activated. For oxygen, recombinations are spontaneous for the Frenkel pairs of
rank-1 and -2, and thermally activated for the Frenkel pairs of rank-3 to -5 with different activation energies. According to the results of our simulations, the recombination mechanism can be seen as a succession of vacancy hops along certain crystallographic directions until the spontaneous recombination distance is reached. The lowest recombination activation energies correspond to the migration paths along the [110] direction for the uranium Frenkel pairs and along the [100] direction for the oxygen Frenkel pairs. In all the cases, recombination activation energies are lower than the diffusion migration energies. This means that the recombination process is not a classical thermal diffusion process. The differences between recombination activation energies can be explained by the different migration paths.

(a) Oxygen Frenkel pair recombination involving significant variations of direction

(b) Oxygen Frenkel pair recombination involving few variations of direction

Figure 13: Lifetimes of two oxygen Frenkel pairs in UO₂ for different temperatures in the core-shell and the rigid-ion model. The data points are the averages of 30 simulations and the straight lines are linear regression fits.

We now turn to a quantitative comparison between the rigid ion and core-shell model. At high temperature (T > 1000 K for oxygen and T > 2500K for uranium), the kinetic energy is so high that the difference between the recombination activation energies associated with the rigid ion and core-shell model cannot be monitored. The Frenkel pair lifetimes (λFP) calculated with the two models are therefore quite similar. At lower temperature (T < 600 K for oxygen and T < 2000 K for uranium), differences arise. In particular, the recombination path of the oxygen atom exhibits significant variations of direction (see Figure 13 in the case of oxygen). The Frenkel pair recombination is then thermodynamically driven and the effect of the polarisability becomes visible. λFP calculated with the core-shell model can then be up to ten times longer than the ones calculated with the rigid-ion model (see Figure 13a). On the other hand, when the recombination path of the Frenkel pair follows a straighter path, the polarisability effects remain negligible (see Figure 13b). The polarisation effects involved in the core-shell description therefore appear to have a different impact depending on the recombination path of the Frenkel pair considered.

2.2.2 Stability of defect clusters

Geometry optimizations of complex defects in urania were carried out using the Morelon potential. As can be seen in Table 10, the binding energies calculated show that point defects tend to aggregate. The aggregation of Schottky defects releases some energy, and this can be seen as the first step for the nucleation of voids. The same behaviour is found for anti-Schottky pairs, which represent the starting point for dislocations.
Table 10: Binding energies of neutral point defects. AS stands for anti-Schottky defects where all the interstitials are first nearest neighbour. S stands for Schottky defects where all the vacancies are first nearest neighbour.

<table>
<thead>
<tr>
<th>Defects</th>
<th>$2I_{O}+I_{U} - AS$</th>
<th>$2AS^- - 2AS^{1st,neig}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{binding}$ (eV)</td>
<td>-3.2</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

The evolution of the binding energy as a function of the aggregation of Schottky defects forming voids of different shapes was also investigated. Results are reported in Figure 14. Wulff (Wulff 1901) shaped voids (corresponding to the thermodynamical equilibrium (Wulff 1901)), spherical voids and {110}-voids show similar behaviour for the sizes of the voids considered herein. The gain in energy for Schottky aggregation saturates around 15-20 Schottky defects. This indicates that 15-20 Schottky voids might be stable in urania, i.e. it is not more favourable to aggregate more Schottky defect into the void. This size (with a radius of 1.3 nm) roughly corresponds to the size of nanocavities observed experimentally in irradiated urania (Sabathier et al. 2008).

The onset of the stabilization of Wulff shaped voids – with respect to the other voids – may be seen (Figure 14) for 30 Schottky voids, in agreement with what is seen experimentally in urania (Castell 2003).

![Figure 14: Binding energies of different shapes of void as a function of the number of S defects.](image)

2.2.3 Defect migration energies in UO$_2$

A series of static calculations of defect migration energies was done with the partly ionic model of Yakub (Yakub 2007) and the results were compared with existing results. The defective lattice was optimized (i.e. relaxed to the minimal energy) and the defect formation energy was estimated as the difference between the energies of defective and ideal lattice at $T = 0K$. A selected ion was then forced to move in small steps along some predefined pathway. At each such step, the rest of the lattice ions (encircled in a simulation cell under periodic boundaries) were relaxed to the minimal energy. The sequence of energy values calculated along this pathway is called "energy profile" in the following. This approach is an alternative to other methods used to find saddle points on the energy hyper-surface, such as the nudged elastic band methos (Gale et al. 2003).
We estimated the static migration energies corresponding to the different mechanisms involving O and U interstitials and vacancies described in section 2.1.3. The migration energies yielded by the Yakub potential for the various mechanisms are listed in Table 11.

Table 11: Comparison of static migration energies (eV) with other calculation results and experimental data.

<table>
<thead>
<tr>
<th>Source</th>
<th>O-vacancy</th>
<th>O-interstitial</th>
<th>U-vacancy along &lt;100&gt;</th>
<th>Direct U-interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Jackson 1986)</td>
<td>0.5</td>
<td>0.6</td>
<td>6.0</td>
<td>8.8</td>
</tr>
<tr>
<td>(Karakasidis 1994)</td>
<td>0.14</td>
<td>0.43</td>
<td>5.1</td>
<td>5.63</td>
</tr>
<tr>
<td>(Govers 2007)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Yamada 2000)</td>
<td>0.4</td>
<td>1.3</td>
<td>6.4</td>
<td>3.9-5.1</td>
</tr>
<tr>
<td>(Govers 2007)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Basak 2003)</td>
<td>0.3</td>
<td>1.3</td>
<td>5.7</td>
<td>5.1-6.4</td>
</tr>
<tr>
<td>(Govers 2007)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Morelon 2003)</td>
<td>0.33</td>
<td>0.7</td>
<td>4.46</td>
<td>5.0</td>
</tr>
<tr>
<td>(Meis 2005)</td>
<td>0.6</td>
<td>-</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>DFT+U results (Table 2)</td>
<td>0.7</td>
<td>0.9 (direct) / 3.2 (indirect)</td>
<td>7.2</td>
<td>7.9</td>
</tr>
<tr>
<td>This work: empirical potentials with static conditions</td>
<td>0.4</td>
<td>1.3</td>
<td>5.0</td>
<td>3.0-4.0</td>
</tr>
<tr>
<td>Experimental (Matzke 1987)</td>
<td>~0.5</td>
<td>0.8-1.0</td>
<td>~2.4</td>
<td>4.4-5.6</td>
</tr>
</tbody>
</table>

- Oxygen vacancy displacement in the <100> direction. These are the lowest-energy events and will be important especially at low temperatures and in an ideal UO$_2$ lattice. The oxygen vacancy migration mechanism has an activation energy of about 0.3-0.4 eV. The calculated value of migration energy only slightly depends on the cell size because short-range forces play the main role in the migration barrier formation. The potential of Yakub (Yakub 2007) predicts a migration energy of 0.4 eV (which compares well with the experimental value of 0.5 eV (Govers 2007)). Yamada's potentials (Yamada 2000) predict a close value (~0.3 eV according our calculations, 0.4 eV according to Govers (Govers 2007)). The comparison with the DFT+U results (Table 2) shows that the energy obtained with empirical potentials and static conditions is lower.

- Interstitial oxygen ion migration. A barrier of approximately 1.3 eV was determined for the direct interstitial oxygen migration. The indirect interstitial oxygen migration mechanism was found to have the same saddle point of ~1.3 eV, in agreement the results of Catlow (Catlow 1977), Jackson (Jackson 1986), and Govers (Govers 2007) that were obtained with very similar potentials. The agreement is less good with the DFT+U results (Table 2), that predict an energy of 0.9 or 3.2 eV, depending on the mechanism.

- Uranium vacancy migration. A static estimation of the uranium vacancy migration energy of 4.7 eV (N = 324) and 5.1 eV (N = 2592) was obtained, in agreement with experimental values 4.4 — 5.6 eV (Govers 2007). The DFT+U results (Table 2) predict an energy of 7.2 eV.

- Uranium interstitial migration in the <100> direction. The energy profile is not continuous and the calculated energy profile reaches first a ~4 eV high value and then falls abruptly to ~3 eV. In DFT+U the most probable path is along <110> and the corresponding energy is 7.9eV (Table 2).
2.2.4 Oxygen diffusion in UO₂

A conceptually simple method to determine the diffusion coefficient is to compute atom trajectories by molecular dynamics techniques. The 3D diffusion coefficient of solute atoms in a matrix can be estimated using the Einstein relation between \( D_0 \) and the mean square displacement \( \langle [r(t) - r_0]^2 \rangle \):

\[
\langle [r(t) - r_0]^2 \rangle = \text{MSQD} + 6D_0 t 
\]

Equation 1

This equation is valid for \( t \to \infty \). The mean square quadratic displacement (MSQD) represents the spread of the ion motion around their equilibrium position, and the second term comes from diffusion itself. MSD curves have been fitted to Equation 1 to derive the diffusion coefficient for each CMD simulation performed. The temperature dependence of the diffusion coefficients \( D_0(T) \) is usually linear in the Arrhenius plot (log \( D_0 \) versus 1/T) giving the possibility to extract the value of the diffusion activation energy \( \Delta H \) and judge about some related quantities like migration energy (Matzke 1987). According to well known theoretical postulates (Frenkel 1926) such a linear dependence is characteristic only of some diffusion mechanisms involving rare activation jumps of ions from one lattice position to another. The question of the linearity of (log \( D_0 \) – 1/T) dependence in superionic phase is still open. At high concentrations of defects, which is characteristic to the vicinity of \( \lambda \)-transition, this mechanism may be different and deviations from Arrhenius behaviour of anion diffusion coefficients were observed near the \( \lambda \)-transition in other fluorite structures like PbO₂.

The oxygen diffusion was investigated using the model potentials of Yakub, Basak and Morelon for stoichiometric and non-stoichiometric UO₂.

2.2.4.1 Diffusion mechanisms

Oxygen and uranium diffusion processes in stoichiometric uranium dioxide involve complicated mechanisms (Catlow 1977). While in sub-stoichiometric solid the oxygen vacancy diffusion and in super-stoichiometric solid the oxygen interstitial mechanisms prevail, in stoichiometric UO₂ the oxygen diffusion mechanism remains unclear. It is generally believed (Catlow 1977), that both mechanisms work here in parallel, making the study of diffusion more complex.

In the present study molecular dynamic simulations are restricted by computers performance to a rather short time period (about 1 ns), and hence in pure UO₂ only the investigation of fast processes like oxygen diffusion at \( T > 2000 \) K and uranium diffusion in the liquid phase are manageable in practice. In the radiation damaged UO₂, as well as in non-stoichiometric solid, diffusion processes are accelerated due to the formation of additional defects, and the low-temperature limits are remarkably lower (about 1000-1200 K). Nevertheless uranium diffusion remains today outside the scope of our dynamical simulations and all the results presented here are related to the self-diffusion of oxygen ions.

The simplified process of the oxygen diffusion in pure UO₂ is considered to consist of two stages. The first one is the formation of a stable OFP defect, formed spontaneously by the thermal motion of ions. The stabilization of the OFP₀ defect by the direct vacancy migration mechanism is presented schematically in Figure 15. This process is characterized by a formation enthalpy of approximately 5 eV. At low temperatures, such events are extremely rare; therefore the concentration of defects and their interaction are negligible. The appearance of a stable OFP initiates two independent diffusion processes: via oxygen lattice vacancy, and via interstitial oxygen ion migration. Both processes are characterized by their migration energies \( \Delta H_m(V_O) \) and \( \Delta H_m(O^-) \).

While the mechanism of vacancy diffusion can be considered as a direct process of lattice ion jumping into the neighbouring empty lattice site, the mechanism of the oxygen interstitial migration is indirect, i.e. involving more than one ion in the elementary act, as shown by the results of DFT (see Table 2) and empirical potentials (Govers 2007).
Figure 15: OFP\(_0\) stabilization by the direct vacancy migration mechanism. Vacancy: green sphere, interstitial oxygen ion: blue, displaced lattice oxygen ion: white.

Our CMD simulations carried out at various temperatures in pure and radiation-damaged UO\(_2\) reveal particular features and specific indirect diffusion mechanisms:

1- Vacancy migration assisted by an instant OFP. This mechanism is similar to direct vacancy migration but the pathway of the displaced ion goes via an intermediate interstitial position. The process is initiated by the interaction of two instant OFP\(_0\).

2- Interstitialcy migration mechanism. It is one of two basic diffusion mechanisms considered in the conventional diffusion model and is well discussed in the literature (Govers 2007; Jackson 1986; Dorado 2011). An oxygen lattice ion, neighbouring to the interstitial one, moves to an interstitial position in the (111) direction, and the initial interstitial moves to the freed lattice position.

3- Interstitial migration via double occupancy. An interstitial oxygen ion crosses the border of an occupied site and replaces the host ion by pushing it to the next vacant interstitial position. This mechanism is observed at high temperatures in pure uranium dioxide and at elevated temperatures in highly radiation-damaged UO\(_2\).

4- Vacancy migration via double occupancy. This migration mechanism starts by an oxygen ion occupying a lattice position. The intruder, when it has enough kinetic energy, displaces the host anion toward the neighbouring vacancy, forming simultaneously another vacancy.

5- Vacancy migration assisted by OFP chains. This migration mechanism was observed at elevated temperatures. A series of OFP\(_0\)-chains appear, causing re-arrangements of lattice ions via interstitial positions. Such a sequence is possible due to the strong interaction of instant OFP\(_0\)-defects, making them more stable and long living (Yakub 2007).

2.2.4.2 Oxygen diffusion investigation using the Yakub potential

The diffusion in stoichiometric UO\(_2\), including the vicinity of the \(\lambda\)-transition taking place around 2000-3000 K was investigated using the interatomic potential of Yakub (Yakub 2007). The results for stoichiometric UO\(_2\) are presented in Figure 16. As one can see from these plots, the low-temperature parts of diffusion follow the Arrhenius law with a slope of \(\Delta H \sim 2.3\) eV. This value is consistent with simulations of Terentyev et al. (Terentyev et al. 2005) (both via vacancy and interstitials) and a bit less than the value recommended by Matzke (\(\Delta H = 2.6\) eV) (Matzke 1987). At the same time we found the high-temperature parts of both diffusion and defect concentration dependencies are essentially non-Arrhenius.
In (Yakub 2009), an extension of the partly ionic model was presented. The method of calibration of the model for a non-stoichiometric uranium-oxygen solid was outlined, including the description of the calibration procedure for the covalent U^{5+}-O^{2-} potential using experimental data on U_{4}O_{9} solid, and the parameterisation of the U^{3+}-O^{2-} potential based on the known enthalpy of disproportionation (2U^{4+} = U^{3+} + U^{5+} reaction). In the ionic model of the non-stoichiometric UO_{2±x} system, the overall neutrality is kept by the disproportionation equilibrium. Any extra (neutral) oxygen atom entering this system ionize up to O^{2-} oxidation level. Two extra electrons needed must come from the surrounding cations, reducing them to lower oxidation level. We suppose the lowest oxidation state is limited by U^{5+}. Correspondingly, in hyperstoichiometric UO_{2+x} (x>0) extra oxygen initiates the following reaction:

\[ \frac{1}{2} O_2 + 2 U^{4+} \rightarrow O^{2-} + 2 U^{5+}. \]

In hypostoichiometric dioxide UO_{2-x} (x<0), the corresponding reduction of the outgoing O^{2-} oxygen ion corresponds to the scheme:

\[ O^{2-} + 2 U^{4+} \rightarrow \frac{1}{2} O_2 + 2 U^{3+}. \]

At temperatures higher than 1000-1500 K, the localized polaron approximation (LPA) fails to describe the behaviour of the cationic subsystem because the polaron hopping process is largely activated (Casado et al. 1994). We therefore apply a free hopping approximation (FHA) (Yakub 2009). In contrast to LPA, where lattice positions of U^{5+} (in hyperstoichiometric system), or U^{3+} ions (in hypostoichiometric case) are fixed, this approximation allows for periodic jumping of electronic holes located on U^{5+} ions or excess electrons located on U^{3+} ions. They jump occasionally into positions of neighbouring U^{4+} lattice ions, whose instant value of electric potential is minimal (for x > 0) or maximal (for x < 0). The frequency of such hopping within FHA is quite arbitrary. The only requirement is that this frequency is high enough to simulate fast continuous fluctuations in the electronic subsystem and imitate cationic disorder (Catlow 1977). It should be much higher than the average frequency of ionic displacements in diffusion process (Yakub 2009). The oxygen self-diffusion coefficients in hyper and hypostoichiometric uranium dioxide computed through CMD are plotted in Figure 17 and Figure 18, respectively.
Figure 17: Oxygen diffusion coefficient in hyperstoichiometric UO$_2$+$x$ solid. Comparison of our simulations (red symbols) with experimental data (Auskern 1961; Hadari 1971; Kim 1981; Contamin et al. 1972; Ruello 2004), and with recent simulations (Terentyev 2005) (via vacancy).

Figure 18: Oxygen self-diffusion coefficient of hypostoichiometric U-O solid. MD simulation data (blue symbols) are compared with oxygen self-diffusion in stoichiometric UO$_2$.00, available experimental data and empirical correlations.
As seen on Figure 17 our predictions for hyperstoichiometric UO$_2$ are in reasonable agreement with high-temperature measurements of Ruello et al. (Ruello 2004). The increase of the diffusion coefficient with increasing $x$, which was observed experimentally (Contamin 1972) and confirmed by Monte Carlo simulations (Murch 1975), is well reproduced by our simulations. It is in contrast, however, with the concentration dependence, following from the measurements of Ruello et al. (Ruello 2004). We believe that this is related to the specifics of “chemical diffusion” experiments (Ruello 2004) with its averaging over zones of different oxygen concentration.

Then, Figure 18 shows that a good agreement is found for hypostoichiometric UO$_2$ with the measurements of Kim and Olander (Kim 1981). Like in the hyperstoichiometric case, oxygen diffusion coefficient tends to increase with deviation from stoichiometry. The overall apparent activation energy (0.7 eV) is in reasonable agreement with the estimations of Hoffmann (Hoffmann et al. 1989) and Olander (Olander 1982).

2.2.4.3 Oxygen diffusion determined with the Basak and Morelon potentials

Standard CMD calculations were performed with a system containing 12 x 12 x 12 conventional unit cells (containing a total of 20,736 ions). Such a large system was needed in order to improve the statistics, averaging the mean square displacements of a larger amount of atoms. The system was first brought to the desired temperature by initializing the velocities from a Maxwell–Boltzmann distribution and applying a re-scaling procedure (every 0.05 ps) for 1 ps. The system pressure was kept close to zero by an adequate choice of the system volume, based on a previous study (Govers et al. 2008). The remainder of the simulation was run in the NVE ensemble. Atom positions were extracted every 0.1 ps during 25 ps, after an additional equilibration period of 4 ps. The diffusion coefficient was then calculated by a least square fitting of the slope of the mean square displacement evolution with time. By computing the diffusion coefficient at different temperatures (from 1000 to 3000 K by steps of 250 K), one can fit the results to an Arrhenius form. In addition to a non-defective host matrix, various non-stoichiometric compositions from UO$_{1.90}$ to UO$_{2.10}$ were simulated by modifying the concentration of oxygen point defects (vacancies or interstitials): 0.5 %, 1 %, 2 % and 5 %. The positions of point defects were chosen at random.

The diffusion coefficients derived from the CMD runs using Basak and Morelon potentials for various temperatures are plotted in Figure 19 and Figure 20 for the hypo- and hyper-stoichiometry regions, respectively. As already observed with the Yakub potential, the low temperature part of the diffusion follows the Arrhenius law and a deviation from this behaviour is observed at high temperatures. A fitting of the lower temperature points to an Arrhenius expression as a function of the deviation from stoichiometry is given in Table 12, together with the comparison with the results presented in the previous section using Yakub potential, as well as with other CMD and experimental results.

A good agreement between the present and literature data is observed on both the prefactor $D_0$ and the activation energy $E_{\text{act}}$ in UO$_{2-x}$ and UO$_{2.00}$. The results obtained using Basak potential show that for highly hypostoichiometric UO$_{2-x}$ ($x > 0.1$), the activation energy is increased, probably due to the large concentration of vacancies and to interactions starting between them. It is much less so for the Morelon potential. The predicted behaviour in the hyperstoichiometric region is very different for the two potentials. Morelon potential predicts an activation energy half of that observed experimentally; while Basak potential predicts still lower activation energy. Detail about the operating migration mechanisms in the various stoichiometry domains will be given in the discussion section.

In stoichiometric fuel, or at high temperature, the oxygen diffusion coefficient presents an activation energy of 2.4 eV (see Table 12, Figure 19 and Figure 20), which is in good agreement with the results of Yakub, of Kupryazhkin and of Matzke. At high temperatures, both potentials predict very similar diffusion coefficients for hypo, hyper and stoichiometric UO$_2$. This is due to the very high mobility, or even to the melting of the oxygen sub-lattice at high temperatures and especially in the vicinity of the $\lambda$ transition. It is seen in Table 12, that the DFT+U results presented in Section 2.1.3 (Table 2) are in a good agreement is observed with the results of Yakub for hypo and hyperstoichiometric UO$_2$. 

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Table 12: Comparison of the derived parameters for the diffusion coefficient to other sources (Empirical potential and DFT+U results, as well as experimental values). The x-dependence column indicates by which function the prefactor of the diffusion coefficient should be multiplied to take into account its variation with x.

<table>
<thead>
<tr>
<th></th>
<th>UO$_{2-x}$</th>
<th>UO$_2$</th>
<th>UO$_{2+x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_0$ cm$^2$/s</td>
<td>$E_{act}$ eV</td>
<td>$D_0$ cm$^2$/s</td>
</tr>
<tr>
<td>(Morelon 2003)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x&lt;0.1</td>
<td>0.00075</td>
<td>0.37</td>
<td>0.5</td>
</tr>
<tr>
<td>x=0.1</td>
<td>0.00100</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>(Basak 2003)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x&lt;0.1</td>
<td>0.00035</td>
<td>0.27</td>
<td>0.3</td>
</tr>
<tr>
<td>x=0.1</td>
<td>0.00045</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>(Yakub 2009)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00003</td>
<td>0.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Other MD sources

(Kupryazhkin et al. 2008)
- **Bulk**: 0.26→0.8 2.6→2.76
- **Surface**: 0.008 1.6

(Govers 2007) 0.2→0.6 0.6→1.3

(Ichinomiya et al. 2009) 0.26 0.9 (single OI 0.14→0.24 (clusters)

DFT+U (Table 2) 0.7 0.9

Experimental results

(Matze 1992) 0.26 2.55 x 0.0045 0.94

(Kim 1981) x 0.00022 0.5 x 0.0045 0.94

(Contamin 1972) x 0.0045 0.94

Figure 19: O diffusion coefficient in the hyperstoichiometry domain. Left: Basak and right: Morelon potentials. The fitting accounts for both intrinsic (high temperature or stoichiometric compound) and extrinsic diffusion (at low temperatures, due to off-stoichiometry).
Figure 20: O diffusion coefficient in the hypo-stoichiometry domain. Left: Basak, Right: Morelon potentials. The fitting accounts for both intrinsic (high temperature or stoichiometric compound) and extrinsic diffusion (at low temperatures, due to off-stoichiometry).

2.2.4.4 Discussion

The main results of the CMD studies obtained in this work on oxygen diffusion are presented in Table 12. Both for the prefactor $D_0$ and for the activation energy $E_{\text{act}}$, the calculated and experimental results are in the same range, but differences can be observed.

Contrary to results obtained with the Yakub potential, Basak and Morelon potentials do not provide the same estimation of oxygen diffusion coefficient between 2000 and 3000 K. Further investigations of the migration mechanism (by NEB calculations) for these potentials has shown that the migration process occurs through a permutation of 4 oxygen atoms position rather than through the formation of Frenkel pairs, as determined for Yakub potential (although both mechanisms should present activation energies that are close to each other).

Lower temperature results could not be exploited for diffusion at stoichiometry because of the too large uncertainties on diffusion coefficient values below $10^{-7}$ cm²/s that are derived from MSD curve (limited due to the system size and simulation times considered in the present work). Indeed, in such conditions, the slope of the MSD was concealed by the fluctuations of the ions mean quadratic displacement around their equilibrium position. Changes associated to a $\lambda$-transition around 2000-3000 K should therefore be investigated with large systems and/or for longer simulation times. In view of the system sizes (20 736 for Basak and Morelon potentials, 324–12 000 atoms for Yakub) and simulation times (25 ps and 10–40 ps) used in both works, similar uncertainties on the results should prevail, and the possible influence of the $\lambda$-transition in that temperature region be considered with caution, as the occurrence threshold could be potential-dependent.

2.2.4.5 Effect of UFP on oxygen migration in UO₂

The formation, interaction and recombination of unstable OFP₀ defects play an important role in many diffusion mechanisms. We performed static calculations to determine how much the presence of radiation damage modelled by artificially created UFPs affects the formation of OFP₀ defects:

- Oxygen interstitial migration. The energy profiles of a lattice oxygen ion displacement in the (111) direction were calculated for pure UO₂ and in the vicinity of a uranium vacancy. The energy profile changes significantly depending on direction of the oxygen approach to the interstitial site (nearer or
When the oxygen displacement is directed toward the uranium vacancy, the creation of an OFP0 defect is less favourable, while when the direction is opposite a uranium-oxygen divacancy is easily formed.

- **Oxygen vacancy migration.** The value of the oxygen vacancy migration energy is strongly affected by the presence of uranium defects. The rather small value of the migration energy is sensitive to the presence of uranium vacancies or interstitials and may be several times higher or lower when a migration process takes place near an UFP. An additional attraction of the interstitial cation placed in the direction of an oxygen ion displacement (i.e. opposite to the direction of the oxygen vacancy jump) – may decrease the static migration energy up to 0.15 eV. The formation of a divacancy, on contrary, makes the migration of the oxygen vacancy less favourable, the migration energy increases up to 1.5 eV. The presence of the uranium vacancy not far from an oxygen vacancy may accelerate the migration of the oxygen vacancy toward the uranium vacancy followed by the formation of a divacancy.

- **Uranium interstitial.** The attraction of two oppositely charged interstitials may affect the oxygen interstitial migration energy. The presence of uranium interstitial may be a hindrance to the oxygen interstitial migration in the direction away from an interstitial cation.

- **Uranium vacancy.** Uranium vacancy-uranium interstitial interaction is largely Coulombic. It has little effect on the uranium direct vacancy migration energy.

The increase in the concentrations of defects in the oxygen sub-lattice caused by radiation damage affects above all the oxygen self-diffusion coefficient. To study the mechanism of this phenomenon we performed a series of MD simulations at the temperature T = 2000K with different levels of radiation damage, modelled by increasing the number of embedded UFP defects. The UFP concentration limit was chosen to include the range of defect concentrations characteristic for the irradiated fuel studied experimentally at JRC-ITU. As it was estimated by (Staicu 2010), the UFP concentration is about 3 \( \times 10^{20} \) cm\(^{-3} \), which corresponds approximately to 1.5 % of the available interstitial sites occupied by uranium ions.

Due to the extremely low equilibrium concentration of oxygen defects in pure UO\(_2\) (Yakub 2007), the temperature T = 2000K chosen is in conventional CMD simulation actually a temperature well below the lower limit of the reliable determination of the oxygen diffusion coefficient. In the simulation of the radiation-damaged dioxide, the OFP concentration gets much higher (see Figure 7), and this limit decreases (depending on the concentration of uranium defects).

The computed oxygen diffusion coefficient is plotted against the UFP concentration in Figure 21.

![Figure 21: Oxygen diffusion coefficient in damaged UO\(_2\) versus the concentration of UFP defects (N = 2592; T = 2000K).](image-url)
As can be observed from Figure 21, this dependence is almost linear for low radiation damage. The initial slope of this dependence is shown by the red line. When the UFP concentration is higher than 1 %, the diffusion tends to stabilize, while both UFP and OFP concentrations continue to grow. Note that the overall rise of the diffusion coefficient due to radiation damage is very large (at least two orders of magnitude for 1% of interstitial sites occupied by uranium atoms). The stabilization is probably due to defect interactions, as the high concentration of UFP induces also a high concentration of OFP (Figure 7).

### 2.2.5 Thermal conductivity of UO$_2$

Thermal conductivity is a fundamental parameter for the safety assessment as it controls the heat removal rate. Three main approaches exist for the calculation the thermal conductivity using Classical Molecular Dynamics. The most popular is the Green-Kubo method, which is based on equilibrium MD (EMD) (Lindan et al. 1991). It is the method used in this work. A second method is the non equilibrium MD (NEMD) (Watanabe et al. 2009) where a heat flow is created in the simulation cell and the resulting temperature gradient is determined, simulating of a real experiment. The thermal conductivity is then calculated from the Fourier law. A third method is the homogenous NEMD, in which a fictive force is introduced to induce a heat current without temperature gradient and the ratio of heat current by the force is used to deduce the thermal conductivity.

Different authors have investigated the thermal conductivity of stoichiometric UO$_2$ as a function of temperature using CMD (Lindan 1991; Kurosaki 2001; Motoyama et al. 1999; Arima et al. 2005; Yamada 2000; Terentyev 2005). The effect of non stoichiometry was investigated by Watanabe (Watanabe 2009). However no systematic study of the effects of radiation damage, Pu or minor actinides addition was performed.

The MD simulations were obtained with a main cell constituted by 6x6x6 unit cells (2592 ions: 864 cations and 1728 anions). One unit cell contains 4 uranium atoms and 8 oxygen atoms. The impact of the choice of the UO$_2$ empirical potentials on the thermal conductivity calculation has recently been investigated by Lunev et al. (Lunev et al. 2011) and it was observed that no available potential reproduces the experimental values over the whole temperature range where heat transport is almost exclusively due to phonons (up to 1700 K). In this work, the pair potential proposed by Arima (Arima 2005), a partly ionic model, was chosen. This potential leads to thermal conductivity values (Figure 22) in good agreement with literature correlations (Harding et al. 1989; Fink 2000) with however an overestimation at low temperatures. This overestimation is likened to the choice of the potentials (Lunev 2011).

The effect of non-stoichiometry on the thermal conductivity was calculated, and compared to experimental data. It was found that, for the same absolute value of the deviation from stoichiometry, oxygen vacancies (hypo-stoichiometric regime) have more influence than oxygen interstitials (hyper-stoichiometric regime). Localised and free hopping polarons were considered. These results are in good agreement with the results obtained by Watanabe (Watanabe 2009).

The influence of the oxygen Frenkel pairs on the thermal conductivity was also investigated. The OFP are created during reactor irradiation (Staicu et al. 2004), but are also present in samples damaged by auto-irradiation (Staicu 2010). The calculations were started at 300K with a main cell of 6x6x6 unit cells containing 0.6% of the oxygen atoms in Frenkel pairs, distributed randomly. When temperature is increased, the OFP recombine progressively, leading to a recovery of the thermal conductivity. In order to obtain more information on the effect of OFP, annealing cycles were simulated, reproducing the experimental procedure used for radiation damage investigations (Staicu 2010). The results are shown in Figure 23 (calculations without polarons). The calculations were performed in the following way: a) the temperature was increased from 300 K to about 500-550 K. At the temperature of about 570 K some Frenkel pairs recombined leading to the increase of thermal conductivity; b) after this first recombination temperature was decreased down to
300 K and then calculations were performed again until the next recombination of Frenkel pairs appeared (at about 610 K); c) then the final cooling down to 300 K was performed and the lattice was heated again until all the Frenkel pairs recombined (at about 750 K). It was found that, in stoichiometric UO$_2$ and for the particular Frenkel pairs configuration considered, Frenkel pairs recombine completely at temperatures between 700 and 800 K. The recovery of the thermal conductivity is in agreement with the experimental observations showing an increase of thermal conductivity when temperature is increased, due to the recombination of OFP (Staicu 2010).

Figure 22: Thermal conductivity of UO$_2$ obtained by CMD and comparison to the correlations of Fink (Fink 2000) and Harding (Harding 1989)

Figure 23: Thermal conductivity of UO$_2$ containing 0.3 % of the oxygen atoms in Frenkel pairs.
3 Investigation of incorporation and transport properties of rare gases in bulk UO$_2$

Among the fission products created during irradiation, the fission gases incorporation and transport properties require particular attention since the fission gases released to the plenum induce pressurisation of the fuel rods. Unlike many fission products rare gases (Kr, Xe) rarely form compounds with other fission products because of their very low chemical reactivity. He atoms are produced in significant quantities in the fuel as a result of alpha decay. The trapping and transport mechanisms of rare gases are investigated in this section.

3.1 DFT investigation

3.1.1 Computational details
The same calculation level and parameters have been used as for the study of defect formation and migration (see section 2.1).

3.1.2 Incorporation energies and localization of Kr and Xe
The incorporation of the krypton and xenon rare gases has been investigated in UO$_2$ using DFT+U (Dorado 2010). The behaviour of Xe in UO$_2$ has also been studied using the GGA approximation (Chartier et al. 2010). The impurities were introduced at various positions in the crystal lattice, in particular the oxygen and uranium substitution sites (V$_O$ and V$_U$), the octahedral interstitial site (Int.) and in three possible Schottky defects (S$_1$, S$_2$ and S$_3$). For each position, the atomic positions and the volume of the 96-atom supercell were optimised.

The incorporation energies are calculated as:

$$E_{inc}^{X} = E_{UO_2}^{X} - E_{UO_2}^{D} - E_{X}^{ref}$$

where
- $E_{UO_2}^{X}$ is the total energy of the supercell containing the fission product,
- $E_{UO_2}^{D}$ is the total energy with a vacant trap site, and
- $E_{X}^{ref}$ is the reference energy of the incorporated element (rare gas dimer).

The incorporation energies obtained are given in Table 13. Positive incorporation energies mean that the impurity is not favourably incorporated in the lattice.

<table>
<thead>
<tr>
<th>Incorporation energies (eV)</th>
<th>Int.</th>
<th>V$_U$</th>
<th>V$_O$</th>
<th>S$_1$</th>
<th>S$_2$</th>
<th>S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>DFT+U</td>
<td>6.6</td>
<td>2.2</td>
<td>5.3</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Xe</td>
<td>DFT</td>
<td>12.0</td>
<td>5.8</td>
<td>9.1</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>DFT+U</td>
<td>9.5</td>
<td>3.8</td>
<td>6.9</td>
<td>1.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

One can first see from the results on Xe shown in Table 13 that the values yielded by the GGA are largely overestimated compared to the DFT+U ones, stressing again the need to take correctly into account the 5f exchange-correlation interactions if one wants to obtain accurate quantitative results. Table 13 also shows that Kr and Xe have a similar behaviour in UO$_2$. First, Xe displays larger incorporation energies than Kr, which is consistent with its larger ionic radius (1.08 and 0.88 Å, respectively). Second, the larger the volume of the host site, the lower the incorporation energy of Kr and Xe. Finally the displacement of neighbouring
atoms is larger for Xe than for Kr, as can be seen in Figure 24. Steric effects are therefore the main contribution to the incorporation of these rare gas atoms in UO₂ as it expected because of their filled electron shell. This is confirmed by the fact that the charge redistribution observed after incorporation in a defect is very similar to that observed for the defect alone.

It is interesting to see that the incorporation energies for Kr and Xe are small in the Schottky defects, with values around 1 eV, suggesting that even if Xe and Kr are not soluble in UO₂ at substitution U or O sites, they will be more easily incorporated in trivacancies.

![Figure 24: UO₂ supercells containing (a) one Kr and (b) one Xe atom incorporated in a U vacancy. Uranium and oxygen atoms are represented in blue and red, respectively. The purple atoms represent the oxygen atoms first neighbours of the rare gas.](image)

3.1.3 Transport properties of defects: Migration and activation energies

Because of the difficulties encountered in the use of the DFT+U approximation due to the occurrence of local energy minima described in the deliverable D221 (Bertolus 2010), the migration of fission products remains to be investigated.

3.2 Empirical potentials

3.2.1 Calculation methods

Based on previous studies (Govers 2007; Govers 2008), two sets of interatomic potentials describing atomic interactions in the host matrix were selected for the calculations involving both He and Xe: Morelon potential (Morelon 2003) and Basak potential (Basak 2003). A third interatomic potential was considered to study Xe: Jackson_2 (Jackson & Catlow 1985b; Jackson & Catlow 1985a). For this potential a specific Xe – host atoms potential was derived by Nicoll (Nicoll et al. 1995). These sets of potentials showed a good agreement with experiments on defect (Govers 2007) (formation and migration energies) and thermal properties (Govers 2008) (lattice expansion, melting temperature), which are essential in view of the calculations we present here.

The interactions involving He atoms (He-O, He-U, He-He) were analysed by Yakub to obtain his new potential model (Yakub 2010), which is also used in this section. Another approach was to obtain these interactions from the work of Grimes (Grimes et al. 1990) based on a Lennard-Jones description and were coupled to the Morelon and Basak potentials for the UO₂ matrix. In view of He low polarisability (Grimes 1990; Parfitt et al. 2008; Govers et al. 2009), He interactions are described in the rigid ion framework rather than using a core-shell model.
3.2.2 Helium diffusion

3.2.2.1 Investigation using Yakub potential

Since the diffusion of He is a slow process a combination of conventional classical molecular dynamics (CMD) and Monte Carlo (MC) methods is applied to accelerate the simulations: a standard CMD simulation is carried out during the equilibration period and at the end of each measurement period, an additional MC-CMD procedure is launched. After the mentioned procedure is over, the standard CMD simulation is continued, starting from the same initial state, which was saved before the MC-CMD procedure started. The overall simulation procedure reproduces the correct probability distributions; nothing is corrupt in the CMD simulation status after the MC-CMD procedure is accomplished, the relative probabilities of the possible dynamical paths and the correlated dynamical events are properly accounted for. The MC-CMD procedure consists of two consecutive steps: “MC step” and “CMD step”. During the “MC step” the He atom obtains a fixed kinetic energy $E$ and the importance sampling consists in selecting the energy value $E$, which is for the dissolved atom sufficient to cross, under favourable conditions, the border between the interstitial site cells.

Simulations with static conditions were typically carried out on a cell consisting of 2 592 ions ($6a \times 6a \times 6a$). Simulations with dynamic environment (most time consuming) were performed on smaller cells of 324 ions ($3a \times 3a \times 3a$). This circumstance is not crucial because the characteristic size of the diffusion displacement and the lattice parameter have always the same order of magnitude.

In a real oxide fuel, the solubility of He is extremely low and increases with temperature. At the same time, the He concentrations in CMD simulations cannot be kept as low as in reality, due to accuracy requirements, and in order to maintain reasonable simulation times. CMD simulations were therefore performed at several He concentrations, all of them much higher than in the real dioxide, and the results were then extrapolated to lower concentrations.

Some of our high temperature simulation results are presented and compared with the predictions of (Govers 2008) in Figure 25. Despite the increase of the He diffusion coefficient when the concentration of helium increases is significant, which is mainly due to the increase in the equilibrium lattice parameter (swelling), the apparent diffusion activation energy remains approximately constant (2.6 eV). The helium diffusion coefficients calculated by (Govers 2008) from 1500 to 2750K have similar slope but are somewhat higher than the present results.

![Helium self-diffusion coefficient in stoichiometric UO$_2$. Comparison of our MD simulation (1 - He/U=0.093; 2 - He/U=0.019; 3 - extrapolation to He/U=0) with the results of (Govers 2008) (4 - red crosses).](image-url)
The same procedure was applied for the simulation of He diffusion in non-stoichiometric UO₂. It is based on the ‘Free Hopping Approximation’ (FHA) (Yakub 2009). We used the He-He, He-O₂⁻, and He-U⁴⁺ Buckingham-type interaction potentials, corrected on short distances, which were proposed by Yakub (Yakub 2010). The He-U⁴⁺ potentials used in the stoichiometric case were adopted to represent He-U³⁺ and He-U⁵⁺ interactions in non-stoichiometric UO₂. The NPT ensemble was used at four temperatures T = 1800, 2000, 2500 and 2700 K and six values of O/U ratio: three in hyperstoichiometric domain O/U = 2.02, 2.06 and 2.09, and three in hypostoichiometric domain O/U = 1.91, 1.94, 1.98. The results are presented in Figure 26. At low temperatures, the diffusion follows the Arrhenius law. The synthesis of these results is shown in Figure 27, which represents the activation energy (determined from the low temperature portion of the plot) as a function of the deviation from stoichiometry.

According to these results, the static barrier E₀, which determines the low temperature diffusion in perfect UO₂ is significant: about 2.6 eV. This value is very close to the Arrhenius slope of the diffusion curve estimated above (see Figure 25) both at low (2.56 eV) and high concentrations (2.62 eV) in stoichiometric UO₂. As can be seen in Figure 26 and Figure 27 the activation energy decreases when then the deviation from stoichiometry increases. In the hyperstoichiometric solid at O/U=2.09 the apparent helium diffusion activation energy is about 1.3 eV, in the hypostoichiometric system at O/U=1.91 it even becomes less than 1.0 eV (see Figure 27).
The helium diffusion mechanisms in UO$_2$ were analysed. The interaction of He atoms with static lattice ions is characterised by $E(0)$ – the helium incorporation energy (heat of solution). As can be seen in Table 14 (Yakub 2010) the incorporation energy of He atoms in interstitial positions of the UO$_2$ lattice is positive $E(0) = 0.45$ eV. The incorporation in defects (O and uranium vacancies, as well as Schottky defects) is energetically more favourable.

Table 14: Incorporation energies (eV) $E(0)$ calculated of helium in stoichiometric UO$_2$ (Yakub 2010).

<table>
<thead>
<tr>
<th>He atom position</th>
<th>Incorporation energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial site</td>
<td>0.45</td>
</tr>
<tr>
<td>Oxygen vacancy</td>
<td>0.30</td>
</tr>
<tr>
<td>Uranium vacancy</td>
<td>-0.002</td>
</tr>
<tr>
<td>Neutral Schottky trivacancy</td>
<td>0.03</td>
</tr>
</tbody>
</table>

3.2.2.2 Investigation using Basak and Morelon potentials

CMD simulations of the behaviour of He in UO$_2$ were made at temperatures ranging from 1000 to 3000 K by steps of 250 K. Various deviations from stoichiometry were considered in each case to derive an Arrhenius expression for He diffusion in the different stoichiometry domains. They were modelled by creating randomly dispersed oxygen point defects: vacancies and interstitials for respectively the hypo- and hyperstoichiometric regions. The influence of uranium defects has been qualitatively assessed by performing a separate effect study. Their influence on helium diffusion is discussed in a later section.

The He diffusion coefficients derived from the CMD runs are plotted for both Basak and Morelon potentials in Figure 28 and Figure 29 for the hyper- and hypostoichiometry domains, respectively.

It clearly appears on these graphs that He diffusion is assisted at low temperatures by oxygen vacancies, and presents a very low activation energy, around 0.5 eV (see Figure 29). In the high temperature region, as well as for stoichiometric and hyperstoichiometric uranium dioxide, the activation energy presents a higher value, around 2.1 eV. Such behaviour was expected since at high temperature or in absence of structural defects, thermally generated defects dominate with concentrations showing a Boltzmann dependence on both the temperature and the formation energy of the defect. In that case, the activation energy is given by the sum of the migration energy and the formation energy of the assisting defect.

Considering that the vacancy formation energy at stoichiometry can be calculated as half the formation energy of an oxygen Frenkel pair ($E_{\text{OFP}}$), with a value of approximately $\frac{1}{2} \times (3.2 \text{ to } 4.6)$ eV $\sim 1.6$ to 2.3 eV (Govers 2007), a value in the 2 to 3 eV range could easily be explained assuming VO-assisted migration is still operating. However, in that case, a still larger activation energy should be observed in the hyperstoichiometric domain (since the formation energy of a vacancy in UO$_{2+x}$ amounts to $E_{\text{OFP}}$), which is not the case. Therefore, the 2.1 eV activation energy should correspond to a second, intrinsic, migration mechanism. The investigation using NEB and static calculations of the elementary migration mechanisms are presented in the next section.
Figure 28: He diffusion coefficient in the hyperstoichiometry domain. Left: Basak, Right: Morelon potentials

The expression that can be derived for He intrinsic diffusion coefficient, i.e. in the stoichiometric and hyperstoichiometric domain, is as follows:

\[
D_{\text{He,int}} = 0.5 \exp \left( \frac{-2.0\text{eV}}{k_B T} \right) \text{cm}^2 / \text{s}
\]

Equation 2

and for the \(V_O\)-assisted mechanism (hypostoichiometry domain),

\[
D_{\text{He,V}_O} = 0.011 \cdot |x| \exp \left( \frac{-0.5\text{eV}}{k_B T} \right) \text{cm}^2 / \text{s}
\]

Equation 3

where \(x\) is the (negative) deviation from stoichiometry.

Even though we do not expect He diffusion to be enhanced by uranium vacancies because of their lower mobility, (migration energy above 2 eV (Govers 2007)), such defects could influence He mobility through a trapping effect. A CMD study similar to those previously presented was therefore performed using the Morelon potential considering uranium vacancies instead of oxygen ones. When He atoms are located initially in octahedral interstitial sites, no effect of uranium vacancies is observed on the diffusion coefficient. When He atoms are initially located at uranium vacancy sites, however, the diffusion coefficient decreases by 3 orders of magnitude (see Figure 30). This shows the trapping effect of uranium vacancies on He atoms, and could explain the large difference observed for the prefactor of He diffusion derived here and that determined experimentally.
Similarly, only trapping effects are observed when uranium and oxygen defects are inserted. The activation energy appears unchanged although the uncertainties do not enable to derive an accurate value of the activation energy. This observation was made for both randomly distributed uranium and oxygen vacancies, as well as for randomly distributed trivacancies (one uranium and two oxygen vacancies as nearest neighbours).

Figure 30: He diffusion coefficient in presence of uranium vacancies. The trapping effect is clearly visible. Statistical uncertainties on actual D values do not enable to derive an accurate value for the activation energy in presence of uranium vacancies.

3.2.2.3 Determination of He migration pathways by Nudged Elastic Band calculations

NEB calculations were performed to further elucidate the elementary mechanisms of He diffusion. In a first step He diffusion was considered both in a perfect lattice and in presence of one oxygen vacancy. Then, considering the importance of oxygen defects, specific calculations were also made for oxygen migration.

We performed Temperature Accelerated Dynamics (TAD) calculations (Voter et al. 2002) as implemented in the DL_POLY 2.19 software (W. Smith 2006) on a system consisting of 4x4x4 UO₂ conventional unit cells (256 U and 512 O atoms) and containing one He atom in an octahedral interstitial position.

This technique was used to explore the different escape pathways of the He atom from the interstitial position it was initially located in. A jump was recorded if after energy minimization of the system configuration an atom was displaced by more than 1 Å. For each computed jump, a NEB calculation was then initiated between the original and the final configurations. Once a jump has occurred, the configuration returns to the original one and the simulation proceeds in order to explore other possible migration pathways. The TAD simulations lasted 500 ps at 2000 K with an energy minimization (to detect transitions) every 0.05 ps.

The NEB results showed a very good agreement with the migration energies derived from the CMD runs, and enabled us to determine the migration pathway. The calculated migration energies are reported in Table 15. A similar procedure was used to derive the migration energy in presence of an oxygen vacancy. The results are also reported in Table 15.
Table 15: He migration energies between two octahedral interstitial positions (OIS) and between an interstitial position and an oxygen vacancy, NEB calculations with Basak and Morelon potentials

<table>
<thead>
<tr>
<th>Migration mechanism</th>
<th>Basak</th>
<th>Morelon</th>
</tr>
</thead>
<tbody>
<tr>
<td>He_{OIS} $\rightarrow$ He_{OIS}</td>
<td>3.5 eV</td>
<td>2.26 eV</td>
</tr>
<tr>
<td>He_{OIS} $\rightarrow$ He_{VO}</td>
<td>0.42 eV</td>
<td>0.42 - 0.48 eV</td>
</tr>
</tbody>
</table>

Concerning the migration pathway, the results show a migration from an octahedral interstitial site to an equivalent one when no VO is present and a migration to the vacant oxygen site when an VO is in an adjacent place. Considering the small energy difference between both site locations (less than 0.1 eV), a similar migration energy applies to the jump back from the VO site to the interstitial site. The migration pathways are represented in Figure 31 and Figure 32. These results were derived from a large series of energy minimisation calculations, mapping the (x, y) coordination plane with a fine mesh, and in each individual calculation, the x- and y- coordinates of the He atom were kept fixed. The migration energies calculated in this way are in excellent agreement with the NEB calculations, but are approximately 1000 times longer.

The next TAD step usually consists of extrapolating the system evolution at high temperature to a lower temperature. The repetition of such step was not needed here since the various diffusion pathways could be identified and enough statistics were already obtained from the MD runs of section 3.2.2.2 to derive the diffusion coefficient.

Figure 31: Determination of He migration pathway (in green) in perfect UO$_2$ using the Morelon potential. The graph shows the relaxed He position in the z direction as a function of its x and y fractional coordinates. The colour indicates the energy of the configuration relative to the minimum energy configuration. The energy barrier is about 2.3 eV.

Figure 32: Determination of He migration pathway (in green) in presence of one oxygen vacancy, Morelon potential. The graph shows the relaxed He position in the z direction as a function of its x and y fractional coordinates. The colour indicates the energy of the configuration relative to the minimum energy configuration. The energy barrier is about 0.5 eV.
3.2.2.4 Simulation of He gas bubble formation

Based on the models developed by Yakub (Yakub 2010), a simulation was set up for the study of the trapping of He atoms inside defects produced by fast decay products in radiation damaged oxide fuel. Initially 29 Schottky defects forming an approximately spherical void of radius ~ 7 Å were created in the simulation cell containing 2592 ions in the stoichiometric case. To make the simulation feasible, we used a moderate cell size (6a₀x6a₀x6a₀) and a rather high concentration of helium (65, 85, 95 or 128 He atoms in the cell) at temperatures ranging from 1500 K to 3000 K. Two types of initial conditions were employed:

1) He atoms are placed in vacant or interstitial sites inside the void;
2) He atoms are randomly distributed over interstitial sites in the cell.

During the simulation, the diffusion of helium over the cell and the number of helium atoms inside and outside the void were monitored. The general result obtained is as follows: both empty and filled bubbles are stable in stoichiometric UO₂ up to 3000 K. The bubble initially filled by He atoms was found to be the most stable at T > 1500 K in stoichiometric UO₂.

In hyperstoichiometric UO₂⁺x at small x, the bubble is stable up to approximately 2500 K. The helium filled bubble in hypostoichiometric UO₂⁺x (O/U=1.94) remains relatively stable up to 2000-2500 K. Only a few atoms moved away during a very long (~900 ps) simulation run. At higher deviation from stoichiometry and at higher temperatures, fluctuations in the helium configurations increase, the uranium ion migration (vacancy mechanism) is activated and the stability of the bubble decreases. Some uranium vacancies after a long run have been found displaced and the initial configuration and position of the bubble changed. Nevertheless, the tendency to the accumulation of the dissolved He atoms in cavities still persists (Figure 35).

The second type of initial conditions was used to confirm the existence of the equilibrium distribution of He atoms between the spherical cavity (bubble) and the bulk of the uranium dioxide (Figure 36). We studied He atoms diffusing in the bulk of the solid and assembling step-by-step inside the initially empty hollow. Typical examples of the initial and final defects configurations are presented in Figure 33 and Figure 34.

![Figure 33](image_url)

**Figure 33:** Stability of a He gas bubble in stoichiometric UO₂ at T = 3000 K (He/U = 0.1). a) initial configuration: all He atoms trapped inside a bubble; b) final configuration: part of He atoms dissolved in the bulk of solid.
Figure 34: Formation of a He gas bubble in stoichiometric UO$_2$ at T = 3000 K (He/U = 0.1). a) initial configuration: all He atoms distributed at random; b) intermediate (t=45 ps) configuration: part of the He atoms assembled in the bubble. The final configuration (t > 100 ps) is similar to Figure 33b.

Figure 35: He atoms (yellow) trapped inside a bubble at T=2500 K. a) Hypostoichiometric UO$_{2+x}$ (O/U=1.95, 85 He atoms, t=63 ps). b) Hyperstoichiometric UO$_{2+x}$ (O/U=2.03, 65 He atoms, t=37 ps). Oxygen vacancies: green, oxygen interstitials: violet, U$^{5+}$ ions: red, U$^{3+}$ ions: blue, uranium vacancies: grey.

Figure 36: Number of He atoms inside a bubble against the simulation time, in stoichiometric UO$_2$ (NHe= 95, RH=6.5A, T=3000K). Blue: bubble initially filled by He atoms, red: initial random distribution of helium over the cell.
3.2.2.5 Conclusions on the He behaviour

Different calculation techniques involving empirical interatomic potentials were used in the present work to investigate the diffusion of helium and its migration mechanisms in stoichiometric uranium dioxide and for deviations from stoichiometry ranging from -0.1 to 0.1. The simulations predict two migration mechanisms for helium. One of them is active in presence of structural oxygen vacancies and has a low activation energy, around 0.5 eV. NEB calculations have confirmed a vacancy-assisted mechanism, which implies jumps between octahedral interstitial positions and oxygen vacancy locations, and that the observed migration energy corresponds to the barrier between both sites. When there are no extrinsic oxygen vacancies (i.e., in stoichiometric and hyperstoichiometric systems), oxygen vacancies can still be created at elevated temperatures as intrinsic defects. It was, however, found that at elevated temperatures another diffusion mechanism is operative, with direct jumps of He atoms between octahedral sites, with a migration energy around 2.0 eV. This is confirmed by both the MD and the NEB calculations.

Both above-mentioned activation energies were also obtained experimentally (Roudil 2004), (Guilbert 2004), (Ronchi 2004), but the experimental prefactor presents a large scatter, which can, according to our observations, be explained in terms of trapping due to uranium vacancies, or possibly intragranular bubbles.

3.2.3 Xe incorporation

3.2.3.1 Description of the traps

In previous work considering Xe trapping sites (Nicoll 1995), (Catlow 1978), (Ball et al. 1990), Xe most stable defect sites are predicted to be uranium vacancies (as also found in our DFT+U results reported in Table 13) or di- or tri-vacancies. The exact type of defect depends on the stoichiometry, on the Xe concentration and/or on the potential chosen; but in all cases, interstitial positions or substitution on the oxygen sublattice could be excluded. For this reason, only defects containing at least one uranium vacancy have been considered. Energy minimization techniques have been used to determine the effect of both uranium or oxygen vacancies and that of modified valence states of uranium atoms on Xe trapping behaviour. Various defect types have been considered: the isolated V,U, (VO:V,U), (2VO:V,U) (all three non-equivalent configurations of the oxygen vacancies around the uranium one), 2V,U, (VO:2V,U), (2VO:2V,U) (3 different configurations), (3VO:2V,U), (4VO:2V,U).

Charge compensation through valence shifts has been considered for all these defects:
- charge = -1: U^{4+} ⇔ U^{5+} (3 possible configurations);
- charge = 0: no charge compensation;
- charge = 1: U^{4+} ⇔ U^{5+} (3 configurations);
- charge = 2: U^{4+} ⇔ U^{6+} (3 configurations), 2U^{4+} ⇔ 2U^{5+} (4 configurations);
- charge = 3: 3U^{4+} ⇔ 3U^{5+} (3 configurations);
- charge = 4: 2U^{4+} ⇔ 2U^{6+} (4 configurations), 4U^{4+} ⇔ 4U^{5+} (3 configurations).

Electroneutrality is globally achieved through charge compensation at larger distance from the defect and therefore does not affect the reported binding or incorporation energies.

3.2.3.2 Trap binding energy

The approach followed in this work will consist of establishing separately the different components of the trap formation energy because of the scatter among potentials on the prediction of intrinsic defect energies. To better illustrate this point, such values are reported in Table 16 for the three potentials considered in the present work. Polaron, which are intrinsic defects in real systems, cannot be treated as such with empirical interatomic potentials: the treatment implies to move 2 regular atoms «at an infinite distance» from the crystal and reciprocally one U^{3+} and one U^{5+} from there to the crystal. One has then additionally to take into account the 4th and 5th ionization energies of U. For this reason polaron energies will not be reported here.
Table 16: Energies (in eV) of intrinsic defects in UO₂ for all potentials tested. The first value is for clustered defects, the second one when the single point defects are not interacting.

<table>
<thead>
<tr>
<th>Defect energy</th>
<th>Basak</th>
<th>Morelon</th>
<th>Jackson 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky, $E_{\text{Sch}}$</td>
<td>5.4 eV / 10.8 eV</td>
<td>3.9 eV / 8.0 eV</td>
<td>5.6 eV / 11.1 eV</td>
</tr>
<tr>
<td>Oxygen Frenkel pair, $E_{\text{OFP}}$</td>
<td>4.8 eV / 6.0 eV</td>
<td>3.0 eV / 3.9 eV</td>
<td>3.9 eV / 4.9 eV</td>
</tr>
<tr>
<td>Uranium Frenkel pair, $E_{\text{UF}}$</td>
<td>12.4 eV / 17.0 eV</td>
<td>11.9 eV / 15.7 eV</td>
<td>14.7 eV / 19.2 eV</td>
</tr>
</tbody>
</table>

The (formation) energy of the trap, $E_{\text{def}}$, can be expressed as:

$$E_{\text{def}} = E_{\text{form. comp.}} + E_{\text{binding}}$$

Equation 4

Where $E_{\text{form. comp.}}$ is the formation energy of the single isolated point defects present in the trap and $E_{\text{binding}}$ is the binding energy of the trap. The formation energy (under thermodynamic equilibrium) of single isolated point defects depends, in a close system, on the local equilibrium between the formation of Oxygen Frenkel pairs, Schottky defects and polarons.

The binding energies of the different traps are reported in Figure 37. In this figure, for clarity, the traps have been ordered by «type» (corresponding to the number of vacancies present). For each type of vacancy cluster, various charge compensation configuration have been considered, ordered according to the compensation charge they represent. Finally three series of points are represented for each potential, corresponding in each case to the additional substitution of either a U$^{3+}$, no substitution or substitution of a U$^{5+}$ atom to a regular U$^{4+}$. The role of this distinction will become clearer in the subsequent figures, where the migration of these atoms will be studied. The same plotting conditions were applied for consistency.
-1 to +4 (minor increment on the horizontal axis). Local charge compensation is favourable, especially for the highly charged traps (e.g. 2V_U, (V_O:2V_U)).

This figure suggests that neutral defects are favoured, as illustrated by the strong decrease of the binding energy for highly negative defect types (V_U, 2V_U, (V_O:2V_U)) with increasing charge compensation. Similarly when neutrality is reached, the incorporation of additional charges is not energetically favourable. This trend is clearly illustrated in Figure 37. One should recall here that the Figure 37 is only related to the binding energy of the different clusters and does not include the formation energy of their components.

For the 2V_U defect type most configurations are unbound because of the repulsion between both highly negatively charged V_U. This is also true for some of the (V_O:2V_U) configurations. One should probably go to larger charge compensations to stabilize these defects.

3.2.3.3 Xe incorporation energy

A Xe atom was inserted in each defect cluster considered in 3.2.3.2. Migration inside these various traps was considered to occur according to the following mechanisms:

- for defect types containing only one uranium vacancy:
  - the migration of the Xe atom from the vacancy to the nearest interstitial site;
  - the exchange of position between the Xe atom and a regular U atom, whose charge was also varied: U^{3+}, U^{4+} and U^{5+}.

- for defect types containing two uranium vacancies:
  - the migration of the Xe atom between the two uranium vacancies of that defect;
  - the migration of the uranium vacancy around the Xe atom (between two closest neighbour sites), where the migrating uranium charge was also varied: U^{3+}, U^{4+} and U^{5+}.

The latter type of calculation strictly speaking does not simulate Xe migration but will indicate whether the cluster would migrate as a whole, or whether the migration operates through a cyclic process consisting of clustering with a vacancy, migration through the complex and ending the cycle with the dissociation of the cluster. This identification is very important because it could strongly affect the dependence of Xe migration with the uranium vacancy concentration, and hence, its modelling in fuel performance codes.

Following the approach presented in the introduction, the incorporation energy of a Xe atom in the defect has been evaluated in this section, i.e. the energy difference between the energy of the Xe inserted in the trap and the energy of the trap itself, assuming the Xe atom is at an infinite distance from the crystal:

\[ E_{inc} = E_{Xe\ in\ def} - \left[ E_{def} + E_{Xe,\infty} \right] \]  

Equation 5

Where \( E_{inc} \) is the incorporation energy of the Xe atom, \( E_{Xe\ in\ def} \) the total energy of the system when the Xe atom has been inserted in the trap, \( E_{def} \) the formation energy of the trap (without Xe atom) and \( E_{Xe,\infty} \) the reference energy of an isolated Xe atom, taken as zero.

The incorporation energy of a Xe atom (see Figure 38) ranges from 4 to 6 eV in defect types containing only one uranium vacancy. In presence of two uranium vacancies, the incorporation energy is lowered by 1 to 2 eV, and is even lower for the particular configuration (2V_O+2V_U) (1). This tetravacancy consists of two uranium vacancies located at (0, 0, 0) and (½, ½, ½); and the closest two oxygen vacancies, at (¼, ¼, ¼) and (¼, ¼, -¼). These coordinates are relative to the conventional unit cell for the fluorite structure. The latter defect presents the lowest incorporation energy, between 1 and 2 eV depending on the charge modification chosen. These results clearly illustrate that Xe needs large defect sites to be accommodated, as also observed in previous studies.
3.2.3.4 Xe migration energy

In equilibrium, Xe atoms are predicted to be sited at neutral trivacancies in UO$_2$ and UO$_{2-x}$, and in uranium substituted sites in UO$_{2+x}$, as shown in Figure 39. The Xe migration energy was determined by the constraint minimization technique, in various traps, and two cases were investigated:

- Xe migration occurring to the closest interstitial site or between two uranium vacancy sites (Figure 40)
- Xe migration corresponding to an exchange of Xe and U positions or to the migration of a uranium vacancy (Figure 41).

In all cases, three charges have been considered for the migrating atom, namely 3+ (in red), 4+ (in green) and 5+ (in blue). In the first case (Figure 40) Xe migration occurs to the closest interstitial site if only one uranium vacancy is present in the trap; between two uranium vacancy sites when these are present. In the second case, the mechanism corresponds to an exchange of Xe and U positions if only one uranium vacancy is present in the trap or to the migration of a uranium vacancy when two V$_U$ are present in the defect. A similar trend is predicted for all potentials, illustrating the validity of the charge treatment to U atoms for Basak and Morelon potentials.

The migration energies in traps containing only one uranium vacancies are not shown in Figure 40 because of their high value, above 8 eV. It means that the migration mechanisms considered, from a vacancy to an interstitial position or the exchange of position with a regular uranium atom will not occur.

In the case of defect types involving two uranium vacancies, the situation is far different. The migration barrier between these two sites can be calculated using several methods. Crucially however, this is not predicted to be the rate determining step in the migration. The diffusion rate is indeed determined by the recycling of the uranium vacancy (shown in Figure 39c) which has higher migration energy (~3.5-4eV) than
any of the other processes. The motion of a Xe atom between two uranium vacancy sites shows a very low migration energy, between 0.3 and 1.5 eV. This is much smaller than the \( V_U \) migration energy itself, which confirms that the jumps of uranium vacancies are the rate-determining process for Xe migration.

Figure 39: Mechanisms for Xe migration in bulk UO\(_2\): (a) between two uranium vacancies via two oxygen vacancies, (b) the same mechanism without the oxygen vacancies and (c) mechanism showing the recycling of a uranium vacancy.

Figure 40: Migration energy, determined by the constraint minimization technique, in the various traps. Xe migration occurs to the closest interstitial site or between two uranium vacancy sites.

The investigation of the migration of the uranium vacancy in the cluster, “around” the Xe atom (Figure 41) indicates whether the cluster would migrate as a whole or rather through a clustering - dissociation process. Our results show that uranium vacancy migration energy is slightly higher around the Xe atom (~4.5 eV) than in the bulk (~3 eV). On the other hand, the presence of Xe in one type of tetravacancy was energetically very favorable (about 2 eV lower than other types of defects). Such defect cluster could then migrate with a similar or lower activation energy than uranium vacancies through the UO\(_2\) lattice. Both types of migration processes have therefore to be taken into account to determine which one presents the lowest migration barrier.
Figure 41: Migration energy in the various traps determined by the constraint minimization technique. Xe migration corresponds to an exchange of Xe and U positions (case where the only uranium vacancy is occupied by a Xe atom) or to the migration of one uranium vacancy (defects containing two uranium vacancies). Three different charges have been considered for the migrating U atom, they are illustrated in red, green and blue for respectively the 3+, 4+ and 5+ cation.

3.2.3.5 Free energy of Xe incorporation at in nanovoids and bubbles

The free energies of Xe atoms accommodated in nanovoids and bubbles are calculated within the framework of molecular dynamics. Interactions between uranium and oxygen ions in the UO2 matrix are described using the empirical pair potential model of Morelon et al. (Morelon 2003) Xe-Xe interactions are described using the model developed by Tang and Toennies (Tang et al. 2003), derived from an accurate description of van der Waals interactions from different ab inito approaches. The interactions of the Xe with the UO2 take a Buckingham form and are taken from the work of Chartier et al. (Chartier 2010).

Xe free energies are determined using an unusual disintegration procedure, which is based on the Widom method (Widom 1963), and has been used previously to examine He bubbles in β-SiC (Couet et al. 2010). The simulation is performed under constant temperature and volume conditions using a Langevin thermostat and the number of atoms in the simulation other than the target atom remains constant. During our simulations we determine the work generated reducing the Xe interactions with the neighbouring atoms and then integrate this work along the disintegration path to calculate the free energy. The disintegration simulations are performed on all Xe atoms in the system and the average is then the arithmetic mean.

In order to allow compare the free energies of Xe in nanovoids and bubbles to accommodation at point defects a series of simulations of Xe incorporation in point defects are reported in Table 17. For comparison the results of energy minimisation simulations where the forces are modelled using the same pair potential and DFT are included.
Table 17: Free energies of Xe incorporated at point defects in UO₂. The results are compared with data obtained using energy minimisation using both the same potential and DFT.

<table>
<thead>
<tr>
<th>Temp /K</th>
<th>Xeᵢ</th>
<th>Xeᵣ</th>
<th>Xe₀</th>
<th>Xeᵣ₁</th>
<th>Xeᵣ₂</th>
<th>Xeᵣ₃</th>
<th>2Xeᵣ</th>
<th>3Xeᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (0 K)</td>
<td>12.01</td>
<td>5.77</td>
<td>9.14</td>
<td>-</td>
<td>1.2</td>
<td>1.8</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>Emp (0 K)</td>
<td>11.92</td>
<td>5.40</td>
<td>9.34</td>
<td>4.87</td>
<td>4.21</td>
<td>4.64</td>
<td>4.82</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>11.71</td>
<td>5.45</td>
<td>9.27</td>
<td>4.87</td>
<td>4.23</td>
<td>4.71</td>
<td>4.88</td>
<td>8.12</td>
</tr>
<tr>
<td>550</td>
<td>11.54</td>
<td>5.48</td>
<td>9.27</td>
<td>4.87</td>
<td>4.23</td>
<td>4.74</td>
<td>4.91</td>
<td>7.56</td>
</tr>
<tr>
<td>800</td>
<td>11.07</td>
<td>5.56</td>
<td>9.22</td>
<td>4.89</td>
<td>4.23</td>
<td>4.73</td>
<td>4.87</td>
<td>7.05</td>
</tr>
<tr>
<td>1050</td>
<td>10.81</td>
<td>5.56</td>
<td>9.14</td>
<td>4.82</td>
<td>4.24</td>
<td>4.77</td>
<td>4.77</td>
<td>7.18</td>
</tr>
<tr>
<td>1300</td>
<td>10.73</td>
<td>5.64</td>
<td>8.98</td>
<td>4.77</td>
<td>4.64</td>
<td>4.78</td>
<td>5.10</td>
<td>6.24</td>
</tr>
</tbody>
</table>

The results show good agreement with a wealth of other simulation results that show that incorporation at the charge neutral Schottky defect is the most stable incorporation process. As the temperature effect on these free energies appears to be very limited the ordering of the incorporation processes remains unchanged up to high temperatures. As these simulations are dynamic rather than static we are able to make a number of observations of the evolving atoms. Interestingly the Xeᵢ defect is predicted to be metastable and quickly evolves to give a Xe on an oxygen lattice site and an oxygen interstitial bound to it (a similar process has been observed by Liu et al using DFT) (X. Liu et al. 2011). Furthermore, at high temperatures the oxygen sublattice becomes mobile and so the original configuration of the oxygen vacancies in a Schottky defect may no longer be present. Consequently the simulations were restricted to temperatures below 1050 K.

The free energies of Xe atoms in nanovoids and a small (r=6.0 Å) and large (r=10.0 Å) bubble at a series of temperatures are presented in Figure 42.

Figure 42: Plot showing the average free energy of Xe contained in nanovoids and bubbles in UO₂ as a function of the Xe: Schottky ratio.

This figure shows that as the Xe:Schottky ratio inside a nanovoid or bubble increases so does the average free energy of the Xe atoms contained within. The free energy of a Xe incorporated at a Schottky defect is 4.23 eV (indicated in Figure 42 by the dotted line) and for the nanovoid formed from 4 Schottky defects and containing 4 Xe atoms the average Xe free energy is 3.86 eV. The plot also shows that as the size of the bubble increases the free energy decreases for the same Xe:Schottky ratio. Therefore we predict a driving force for nucleation of Xe incorporated at point defects to form Xe containing nanovoids and subsequently bubbles.
At no point in any of the simulations did we observe resolution of Xe into the UO$_2$ matrix, despite the very high pressure inside the bubbles. One of the mechanisms by which the lattice can avoid Xe resolution is for the Xe to push the oxygen atoms on the periphery of the cavity into the lattice thus creating more free volume within the bubble itself. This process is responsible for the decrease in the free energy observed for high Xe:Schottky ratios observed for the nanovoid (see Figure 42).

The free energies of the Xe atoms contained within the bubble are not all the same and in fact there is a very definite distribution of the free energies as shown in Figure 43.

![Figure 43: Spatial distributions of Xe atoms contained within a bubble of 1.2 nm bubble containing 48 Xe atoms (corresponding to a Xe:Schottky 2.5).](image)

What is evident from Figure 43 is that the Xe atoms with the lowest free energy are concentrated at the centre of the bubble and the Xe atoms with the highest free energies are situated at the periphery. This is due to the increased level of interactions between the Xe atoms at the surface and the uranium and oxygen ions of the UO$_2$ lattice.

In order to investigate the influence of the bubble-crystal interface on the behaviour of the Xe contained within bubbles in the UO$_2$ lattice the Xe free energy is plotted as a function of density in Figure 44. For comparison the free energies of pure xenon as a function of the Xe density are also included in Figure 44. For the pure Xenon case, at very low densities the Xe atoms are sufficiently far apart that they are almost non-interacting and so their potential energies are negligible, however as the density increases and the atoms are forced closer together and the free energy begins to increase. As the density increases further the Xe becomes a solid, this occurs at densities of 0.025 mol.cm$^{-3}$ and 0.03 mol.cm$^{-3}$ at 300 K and 1050 K respectively. Once the solid has formed the free energy decreases as the solid approaches its equilibrium density. At densities greater than the equilibrium density the free energy increases dramatically. Within the bubbles in the UO$_2$ the free energy increases much more dramatically than was the case in the pure xenon. This suggests that the gas/surface interface is having a substantial affect on the Xe atoms contained within it. Temperature also appears to have little or no affect on the free energy as a function of density. Importantly there is a substantial difference between the free energy of Xe contained within the bubbles in UO$_2$ and the pure xenon in the range of densities for which bubbles have been observed in spent fuel. This effect is reduced by moving from small to larger bubbles. This suggests that any model which assumes the equation
of state for pure Xe is applicable to fission gas bubbles in nuclear fuels may not be appropriate for small
nanobubbles but may be applicable to larger bubbles.

![Figure 44: Free energy of xenon as a function of the Xe bubble density. Values are plotted for Xe contained
within a bubble in UO₂ and for the pure xenon case. The dotted lines define the experimental densities
(Nogita et al. 1998; Garcia et al. 2006).](image)

In conclusion, our simulations show a driving force for the agglomeration of Xe containing Schottky defects
to form nanovoids and then to combine into small bubbles of up to 10.0 Å. No resolution of Xe from a bubble
into the lattice was observed even when the densities inside the bubble were very high. At high pressures
the Xe atoms in the bubble force the oxygen ions at the bubble periphery into the lattice thus reducing the
pressure inside the bubble and increasing oxygen disorder in the region immediately surrounding the bubble.

Finally we show that the free energy of xenon contained within bubbles in UO₂ is not the same as in a pure
xenon sample at the same pressure in the range of interest as highlighted by experiment. This demonstrates
the limitations of any model that assumes Xe in nano-bubbles in nuclear fuels behaves in the same way as
pure xenon.
4 Investigation of radiation damage in single crystalline UO$_2$

4.1 Simulation of displacement cascades in bulk UO$_2$

4.1.1 Creation of defects (without rare gases)

4.1.1.1 Isotropy of displacement cascades

Displacement cascades were performed using two empirical potentials, the formal charge model of Grimes et al. (Grimes et al. 1991) and the partial charge model of Morelon et al. (Morelon 2003). Time evolution of the number of defects and spatial distribution of defects were recorded (Bishop et al. 2010). For the Grimes potential, the shells were omitted and the formal charges were used with the simple Buckingham potential energy function. Simulations were performed using primary knock-on atom (PKA) energies of 10 keV with both potentials and PKA energy of 0.1 keV and 1 keV for the formal charge model. The purpose of the simulations was to investigate the effect of the initial direction of the velocity of the primary knock-on atom (PKA) on the nature of the resulting damaged region. Previous work in MgO suggests that the crystallographic direction of the PKA may be important in determining the spatial distribution of defects (Cleave et al. 2006), (B. Uberuaga et al. 2005) although displacement cascades in metals have been shown to be more isotropic in nature (Stoller et al. 2000; Hou et al. 2008). In order to account for statistical effects, 10 simulations were performed for each of the 24 crystallographic directions investigated using different equilibrium starting configurations. In total, 960 displacement cascade simulations were performed.

The partial charge model results in more Frenkel pairs than the formal charge model in agreement with the study of Devanathan et al. (Devanathan et al. 2009). The number of Frenkel pair defects appears to be independent from the crystallographic direction of the initial PKA for both potentials at 10 keV (Bishop 2010). The statistical variation in the number of defects is greater than the variation arising from the direction of the PKA as can be seen in Figure 45.

![Figure 45: Number of Frenkel pairs resulting from a 10 keV displacement cascade averaged over 10 simulations, as a function of crystallographic direction of the initial PKA. The partial charge model is shown in black and the formal charge model is shown in red.](image_url)

Other properties such as the peak damage and the spatial distribution of defects (see Figure 46) were measured as a function of crystallographic direction of the PKA. Any hint of anisotropy for the 0.1 keV cascades is masked by the statistical variation in the results for the higher energy cascades when the simulations were repeated.
In conclusion, any possible anisotropy resulting from the initial PKA crystallographic direction is insignificant compared to the statistical variation of the defect properties at higher (and more realistic) PKA energies.

4.1.1.2 Displacement cascades using rigid-ion potentials: impact of the potential used

To measure the impact of empirical potentials on the primary damage state created with MD simulations a set of displacement cascades was carried out with four different rigid ion interatomic potentials: Morelon, Karakasidis, Basak, and Yakub in single crystal UO₂. In order to obtain sufficient statistics, 4 independent cascades initiated with a 10 keV PKA were carried out with each of the interatomic potentials. The type, numbers of defects (Frenkel pairs) and displaced atoms, as well as the spatial distribution of the defects (namely the analysis of the clusters) were analysed. For all potentials no amorphisation was found, only a few Frenkel pairs were created. The number of displaced atoms is also similar for the four interatomic potentials, within the statistical errors. Discrepancies, however, appear in the number of defects created and the clustering of these point defects. The detail of the analysis will be described in the following.

All the cascades show similar morphology, with branches and sub-branches of displaced atoms (see Figure 47). The sizes of cascades are identical as well. No amorphisation occurs, the fluorite structure recovers within few picoseconds (less than 2 ps), and only few point defects are created at the end of cascades.

Figure 46: The greatest spatial distribution of the defects (measured from the centre of the defective region) for cascades of increasingly larger PKA energy using the formal charge model. (Bishop 2010)

Figure 47: Snapshots of displaced atoms at the end of a displacement cascades initiated with a 10 keV PKA in single UO₂ calculated with two different interatomic potentials: (a) Morelon and (b) Yakub.
Figure 48 displays the number of atoms displaced by more than 1 Å from their original lattice position during the cascade event. For all the interatomic potentials we observe the same standard behaviour. The first peak corresponds to atoms which return to their original position, indicating the time of the so-called thermal spike, which lasts approximately 2 ps. The number of uranium atom displaced is about ten times lower than the number of the oxygen atom displaced, which is really over the stoichiometric ratio. However, the number of oxygen atom displaced with Morelon potential is significantly higher (30%) than with the others interatomic potentials. This means that Morelon potential yields a higher oxygen mobility which facilitates recombination of point defects.

The number of displaced atoms as a function of the distance travelled from their original position during displacement cascade is plotted in Figure 49. The general behaviour is again the same for all the interatomic potentials studied. For both uranium and oxygen atoms the first peak around 0.5 Å (not explicitly shown herein because of the scale difference) corresponds to atoms vibrating around their original lattice position with normal thermal vibration. The following peaks correspond to fluorite lattice positions. Approximately 95% of the displaced uranium atoms move only to either the closest interstitial site at 2.7 Å or to the first nearest neighbour site at 3.9 Å. Only one or two uranium atoms move further than 1 nm. 80% of the oxygen atoms move into their first and second nearest neighbour sites. As for uranium atoms only a few oxygen atoms move further than 1 nm. This identical behaviour for all the interatomic potentials reveals that the same slowing down process occurs during the cascade.

The nature of the point defects created is then investigated. Since CMD simulations are carried out with a constant atoms number and since no antisite defect formation was observed, only Frenkel pairs are created.
For all interatomic potentials, although numerous atoms are displaced only a few percents of those produce Frenkel pairs at the end of the cascade. The others displaced atoms correspond to atoms that have either recombined with vacancies or replaced atoms in a fluorite lattice site through a replacement loop sequence for instance. Table 18 gives the number of Frenkel pairs created at the end of the cascades using the four interatomic potentials.

Table 18: Number of Frenkel pairs found at the end of 10 keV displacement cascades for three different interatomic potentials.

<table>
<thead>
<tr>
<th>Frenkel pairs</th>
<th>Morelon</th>
<th>Karakasidis</th>
<th>Yakub</th>
<th>Basak</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_{FU}</td>
<td>20 ± 3</td>
<td>22 ± 4</td>
<td>44 ± 5</td>
<td>41 ± 8</td>
</tr>
<tr>
<td>N_{FPD}</td>
<td>47 ± 3</td>
<td>55 ± 7</td>
<td>124 ± 9</td>
<td>223 ± 32</td>
</tr>
</tbody>
</table>

While the number of defects created is low for all potentials, the absolute number depends significantly on the potential used. Both the number of Frenkel pairs created and the ratio between the uranium and oxygen Frenkel pairs are different for the four interatomic potentials. The Morelon potential yields the smallest number of Frenkel pairs with a ratio close to 1/2 between uranium and oxygen defects, i.e; the stoichiometric ratio. The maximum number of defects is yielded by the Basak potential with a ratio between the uranium and oxygen defects close to 1/5. The largest difference concerns the oxygen defects.

If we compare the point defect spatial distribution for the four different interatomic potentials clear distinctions appear (see Figure 50 for the Morelon and Basak potentials). For the Morelon potential, few defects can be observed in the Figure 50a. The Frenkel pairs are scattered and do not form any specific cluster. Moreover, vacancies are preferentially created in the centre of the cascade core while interstitials are rather created at the periphery of the sub-cascade branches. However, for Basak potential most of the defects are not isolated. A close analysis of the defects shows that oxygen atoms form cuboctahedral clusters (see Figure 50b). These specific clusters have already been observed by Aidhy et al. (Aidhy et al. 2009) using the Frenkel pair accumulation method and are discussed in this report in section 4.2.1.

These two examples show the limitations of the empirical potentials concerning the description of primary damage state complex structures. Efforts should still be made to design more accurate interatomic potentials which should rely on first principle methods for modelling non-equilibrium processes in UO₂.
4.1.1.3 Displacement cascades: analysis of the defects produced

Several studies of displacement cascades initiated with PKA's energies ranging from 0.5 to 80 keV in single-crystal UO$_2$ were carried out using several empirical potentials (Van Brutzel et al. 2003; Van Brutzel, Rarivomanantsoa, et al. 2006; Van Brutzel & Rarivomanantsoa 2006; G. Martin et al. 2009; Devanathan 2009). All the results presented herein have been found with Morelon interatomic potential (Morelon 2003).

Whatever the initial energy of the PKA, no amorphisation of the matrix appears at the end of the cascade. This result is in good agreement with all the experimental studies (Matzke et al. 1966; Stout et al. 1988) which reveal no amorphisation even under high doses of irradiation. It is interesting to state here that amorphisation in other ceramic matrices either with direct impact amorphisation (i.e. Zircon matrix) or with accumulation of point defects (i.e. Silicon Carbide matrix) has been found with MD simulations (Devanathan 2009). This indicates that this simulation method is sensitive enough to reproduce even for small PKA energies the main material's behaviour for primary state damage.

All the atom trajectories are recorded during a cascade event, thus statistics on displaced atoms and point defects creation can be established. Figure 51 displays the evolution with time of the total number of displaced atoms, the number of Frenkel pairs (pair of vacancy and self-interstitial atom), the number of atoms returning to their initial lattice position, and the number of replacements occurring (i.e. an atom taking a lattice position which was not its original lattice position) during a displacement cascade initiated with a 20 keV PKA. This simulation shows that one PKA can displace up to 20000 atoms during a thermal spike. However during the subsequent relaxation only 5000 atoms do not return to their original lattice position. Of these 5000 atoms, most take another atoms lattice position leaving only about one hundred stable Frenkel pairs. Thus numerous interstitial-vacancy recombinations take place in the very short time of the cascade. It is believed that these recombinations play a key role for the resistance against amorphisation in fluorite structure (Van Brutzel 2008; Guglielmetti 2008; Pannier 2009).

The influence of the PKA's initial energy on the primary damage state has been studied and directly compared with the theoretical model (NRT) developed by Norton, Robinson, and Torrens (Robinson 1972; Torrens et al. 1972). This model is used to count the number of point defects, $N_{\text{NRT}}$, created as a function of the energy and is defined as follows:

![Figure 51: Number of displaced atoms, Frenkel pairs created, replacements, and atoms returning to their original lattice position as a function of time during a displacement cascade initiated with a 20 keV PKA](image-url)
\[ N_{\text{NRT}} = \frac{0.8}{2} E_d \]

where \( E_d \) is the average value of the threshold displacement energy (herein 30 eV for UO\(_2\) (Soullard et al. 1978; Soullard 1985). The number of Frenkel pairs created at the end of a cascade is plotted as a function of the PKA initial kinetic energy in Figure 52. It is clear that the number of point defects created by MD simulations is significantly less than the number predicted by NRT theory. For instance, at 80 keV NRT theory predicts 2133 point defects whereas MD simulations find only 380 point defects, i.e. 5.5 times less. This discrepancy has already been found for several other metallic materials: Cu (Diaz 1992), Fe (Stoller 1995), Ni\(_3\)Al (Turbatte et al. 1996), Ti and Zr (Gao et al. 1995). The difference probably stems from the fact that NRT theory does not properly account for recombination during the annealing process and the thermal spike.

![Figure 52: Total number of Frenkel pairs created at the end of displacement cascades versus the initial PKA energies: MD results and calculation with the NRT law.](image)

The acceleration of the atomic mobility during the radiation events can be extracted from these simulations. Indeed, under radiation, particle diffusion can be accelerated through two different mobility mechanisms: (i) ballistic collisions occurring during the displacement cascades, called a-thermal diffusion and, (ii) thermal diffusion accelerated via the additional point defects created during the cascades. The first mechanism is really difficult to observe experimentally despite several attempts (Höh et al. 1973; Turnbull et al. 1982; Hocking 2001). However, MD simulations naturally provide information on the atomic mobility. The a-thermal diffusion coefficients are obtained by multiplying the mean square displacement per cascade with the cascade frequency. For the second acceleration mechanism, the extra diffusion is obtained multiplying the stationary additional point defect concentration with the diffusivity of the thermal point defects. It appears that under long-term storage conditions, the a-thermal diffusion coefficient is always inferior to \(5.5 \times 10^{-31}\) m\(^2\)/s and the mobility of the defects is inferior to \(10^{-37}\) m\(^2\)/s. In-reactor conditions, the estimated self-diffusion coefficients are considerably less than to those determined experimentally under the same conditions. Hence it is probable that nuclear collisions and associated ballistic mixing do not provide an explanation for the observed movement of atoms under normal operating conditions. Details of these calculations can be found in the following references (Van Brutzel et al. 2007; G. Martin 2009).

To fully characterize the primary damage state, the spatial distribution of point defects has been analyzed. For all PKA energies and empirical potentials studied, the spatial distribution of the main point defects is heterogeneous. Vacancies are preferentially created in the centre of the cascade core whereas interstitials are created preferentially at the periphery of the sub-cascade branches. As an illustration the Figure 53 displays the point defects after a cascade is initiated with an 80 keV PKA. This heterogeneous distribution stems from the fact that during MD cascade simulations no noticeable diffusion of point defects was
observed. Therefore, most vacancies created in the cascade's core during the collision phase rapidly form large stable clusters. On the other hand, interstitials, which are created at the end of the thermal spike, and preferentially at the periphery of the sub-cascade branches, form smaller size clusters. However, the size and the exact composition of each cluster depend strongly on the interatomic potential used (Devanathan 2009). For instance, interstitial clusters created with a Morelon potential are constituted mainly of anti-Schottky defects, which can lead ultimately to the formation of dislocation loops (G. Martin et al. 2010). Whereas, interstitials clusters created with Yakub potential for instance are mainly comprised of oxygen interstitial. Furthermore, as already mentioned, no mobility of point defects are observed during the short time (only few picoseconds) of the cascade simulation. The possible recombination or clustering of point defects is then not taken into account. Therefore, development of new methods such as accelerated dynamics (Sorensen et al. 2000) or damage accumulation process are needed to study the mobility and the stability of point defects.

![Spatial distribution of point defects after a cascade initiated with 80 keV PKA energy.](image)

Figure 53: Spatial distribution of point defects after a cascade initiated with 80 keV PKA energy. Uranium interstitials: grey spheres (IU), oxygen interstitials: red spheres (IO), uranium vacancies: green spheres (VU), oxygen vacancies: blue spheres (VO).

4.1.1.4 Displacement cascades using a shell model

In the core shell models, each ion is divided into a positively charged core and a negatively charged shell. The core and shell are then allowed to relax independently except for their interaction via a harmonic force constant. The inclusion of core-shell polarisability has been shown to improve the transferability of a potential set, particularly in the prediction of elastic properties (Govers 2007; Govers 2008).

Previous damage cascade simulations in UO₂ have employed only rigid-ion potentials. This is because during high energy events the trajectory of the ions can cause an ion core to become very close to a neighbouring shell unit. Since there is no short range repulsive term acting on the core, the core-shell unit can become separated due to the strong Coulomb attraction of the neighbouring ion. This highly unphysical separation of the core and shell is sometimes referred to as the “polarisation catastrophe”. The aim of the first part of this work is to investigate the influence of shell model polarisability on the results of radiation damage cascades by modifying the core-shell model to mitigate the impact of the “polarisation catastrophe”. In the second part, the self-healing of the UO₂ matrix after a cascade event is simulated using an unmodified core-shell model. During the initial phase of the cascade where most of the defects are created a rigid-ion model is employed.

The number of defects formed during a displacement event can be estimated from the threshold displacement energy using the model of Kinchin and Pease. The Kinchin-Pease model predicts that for energies above a threshold displacement energy (E₀) and below the cut-off energy loss by electron stopping (Eₛ), the number of ions displaced (v) as a function of the PKA energy (T) is inversely proportional to the E₀.

This relatively simple model has been demonstrated to be surprisingly good at predicting the typical defect
populations that are comparable to those obtained from molecular dynamics simulation. According to this simple model, calculating $E_d$ for uranium and oxygen ions in UO$_2$ should give an indication of the number of defects created during a cascade and hence a measure of the radiation tolerance of the material. In particular, the effect of polarisation can be estimated without the need to perform computationally challenging high energy MD simulations by assessing the change in $E_d$ due to the inclusion of core-shell polarisability.

The first set of simulations presented here examines the difference between the threshold displacement energies determined using the Grimes and Catlow potentials and the same potential models with core-shell polarisation removed. In order to investigate the impact of core-shell polarisation, it is essential to ensure the chemistry of the system is identical except for the inclusion of the core-shell model itself. For both models a ZBL function was splined to the interactions between ions in order to avoid the dispersion term of the Buckingham potential dominating the interactions and allowing the atoms to become unphysically close. The core-shell model was augmented by the inclusion of a very short range repulsive exponential function between ion cores and the cores and shells of separate ions for distances less than 1 Å. This modification is in the spirit of Chen et al. (Chen et al. 2009).

For both models, simulation supercells containing 768 atoms were equilibrated at 300 K for 5 ps. Various properties of the system (i.e. lattice parameters and potential energies) were closely monitored. It was found that there was no significant change in the equilibrium properties of the system resulting from the removal of core-shell polarisability or the short range modifications to the potentials. After equilibration, five uranium and ten oxygen ions were randomly selected to be PKAs. These PKAs were then given speed in eight different directions to investigate the influence of direction on threshold displacement energy. For the oxygen ion two sets of calculations were conducted due to the different environments of the O$^{2-}$ ion in [111] and [T11] direction of the UO$_2$ fluorite structure. The threshold displacement energy was determined in each direction by increasing the energy with which the PKA is initiated in 5 eV steps until the ion is displaced. An ion is said to have been displaced and therefore the threshold displacement energy has been reached if the PKA does not return to its initial lattice site within 1 ps.

The threshold displacement energies as a function of the crystallographic direction are plotted for a uranium ion in Figure 54 and for an oxygen ion in Figure 55. Figure 54 shows that the displacement threshold energy for a uranium ion has been reduced from an average of 130 eV for the rigid-ion model to 100 eV for the model including core-shell polarisability. A similar trend is observed for oxygen ions where $T_d$ is reduced from...
50 eV to 34 eV upon inclusion of the core-shell polarisability (see Figure 55). A likely explanation for the reduction in the threshold displacement energy is that the core-shell unit becomes polarised during the displacement, stabilising the transition state and thus lowering the threshold displacement energy.

![Figure 55: Threshold displacement energies for oxygen PKAs. Each block represents 10 simulations. The black data represents the rigid ion model and the red data shows the modified core-shell model data.](image)

Whilst it is clear that the introduction of core-shell polarisability decreases the threshold displacement energy on average, the effect of direction is less clear as is apparent in Figure 54 and Figure 55. A notable exception is the uranium PKA in the [110] direction where the threshold displacement energy is increased upon inclusion of core-shell polarisability. Each bar in Figure 54 and Figure 55 corresponds to the mean ± one standard deviation. In some crystallographic directions there is a wide distribution in the data, particularly for the highly symmetric directions (i.e. [111] for oxygen PKAs). This wide variation in the data demonstrates the importance of statistical sampling in molecular dynamics simulations.

The results of this first set of simulations have shown that the inclusion of dipole polarisability in the uranium dioxide model reduces the average threshold displacement energies. For uranium the average threshold displacement energy was reduced by 23 % and for oxygen the value was 32 %. The significance of this observation of lower threshold displacement energies can be best understood in the context of the Kinchin-Pease model. According to Kinchin-Pease the effect of lowering the threshold displacement energy by 30 % would lead to an expected increase in the number of ions displaced in the cascade by 42 %. This suggests that the radiation damage cascade simulations performed thus far employing a rigid-ion model may be underestimating the degree of damage in the matrix following a radiative event.

The recombination phase of a displacement cascade is not modelled by the simulations described so far. Therefore this issue was addressed independently by a second set of simulations. The goal was to investigate how the inclusion of polarisability effects into the model affects the types, number and distribution of defects remaining after a damage cascade. To this end simulations of displacement cascades with a PKA energy of 10 keV were run with a rigid-ion (Morelon 2003) and a core-shell model (Meis 2005) in a simulation box containing 253 unit cells of pristine UO₂. The simulation conditions were similar to those described in (G. Martin 2009). In particular, the initial cubic box was firstly relaxed applying isobaric-isothermal conditions (NPT ensemble) for 20 ps. In the next step a uranium ion was selected as the PKA and accelerated to initiate a cascade event. A thermostat was applied to the atoms close to the box walls within a 3 Å thick layer by rescaling the velocities of these atoms to maintain the target temperature of 700 K within this region of the simulation box. A variable time-step algorithm was employed to ensure the stability of the simulation, i.e. the fastest atom was not allowed to move more than 0.04 Å between two consecutive molecular dynamics steps. The cascade simulations were run with the CP2K program package (http://www.cp2k.org).
The first stage of the displacement cascade (ballistic phase) was carried out using the rigid-ion potential in both cases to avoid the "polarisation catastrophe" described above using an unbiased core-shell model. After approximately 0.75 ps, the calculation was carried on using either the rigid-ion or the core-shell model. The evolution of the number of displaced uranium and oxygen atoms for both models is shown in Figure 56 and Figure 57, respectively.

Figure 56: Distributions of uranium atom displacements at different times after the onset of a displacement cascade using a rigid-ion (black) and a core-shell (red) model.

Figure 57: Distributions of oxygen atom displacements at different times after the onset of a displacement cascade using a rigid-ion (black) and a core-shell (red) model.
The distributions of uranium and oxygen atom displacements share a similar evolution for both models. While the distribution evolves rather smoothly at $t = 1$ ps after the onset of the displacement cascade, some distinct patterns appear only 2 ps after the beginning of the cascade. The displaced atoms occupy one of two possible crystallographic sites, i.e. an original lattice site or an interstitial octahedral site. The distribution of displaced atoms then features several maxima where the displacement distance corresponds to atom-atom or atom-octahedral site distances in the UO$_2$ matrix, as found previously (G. Martin 2009). This evolution occurs overall at the same pace for uranium and oxygen atoms in both using the rigid-ion and the core-shell model. It might take place at a slightly earlier time for oxygen in the core-shell model (see Figure 57) but this effect remains marginal.

In order to investigate further the evolution of the structure during the displacement cascade, the UO$_2$ fluorite lattice was decomposed into Voronoi polyhedra centred on U, O and interstitial octahedral sites in order to determine the total number of defects. Two adjacent defects are considered belonging to the same defect clusters, if they are closer than the distance between two interstitial sites (~5.5 Å). Figure 59 shows the defects present in the simulation box at $t = 5$ ps after the start of the displacement for both the rigid ion and the core-shell model. At this stage the total number of defects amounts to 202 and 144 in the rigid-ion and the core-shell model, respectively.

Figure 58 shows the evolution of the number of defects and of clusters of defects for both models.

![Figure 58: Evolution of the number of defects (left) and clusters of defects (right) for the rigid-ion and the core-shell model.](image)

These numbers are higher for the rigid-ion model, which would imply that the self-healing of the UO$_2$ matrix occurs more rapidly using the core-shell model, i.e. when polarisability effects are also considered. This result does not follow the trend observed in a previous study of recombinations of Frenkel pairs (see part 3.2.1.1) which revealed that the recombination times were equal or higher using a core-shell model compared to a rigid-ion model. However, the average recombination time of a single specific defect like a Frenkel pair in a pristine UO$_2$ matrix can hardly be compared to the situation shortly after a cascade event when a partial melting of the structure takes place and introduces a significant amount of disorder. This disorder in the material includes all kinds of defects and even defect clusters, whereas the recombination time of a single Frenkel pair at moderate conditions ignores for instance any interaction between defects completely.

On the other hand, this result is in line with the results from the first set of simulations presented in this chapter, which reveal a lowering of the threshold displacement energy when polarisability effects are included. Lower energy barriers should also facilitate a faster self-healing of the fluorite crystal structure, because the recombination of defects should take place successfully with an increased rate.
This effect seems to be even more pronounced for clusters of defects. Their relative stability is obviously favoured using a rigid-ion model due to the lack of polarisability effects in these models. However, these results are rather preliminary, because they are derived from a single cascade simulation. At least a few tens of such cascade simulations are needed to provide a reasonable statistics. Moreover, the temperature control during the cascade simulations is a delicate issue. It is not easy to ensure similar conditions both for the rigid-ion and the core-shell model cascade simulation. Nevertheless, the presented studies give a clear indication that polarisability effects are important for a more realistic description of the defect creation rate during the initial phase of a cascade event as well as for the defect recombination rate during the self-healing phase.

4.1.2 Cascades in presence of rare gases

4.1.2.1 Rare gases distributed in the bulk

Displacement cascades have been performed using the Morelon potential (Morelon 2003) in the presence of fission gas atoms. Helium atoms were distributed randomly throughout the simulation cell at the interstitial position at a concentration of 0.3 at. %. The helium interactions were described by a simple Lennard-Jones interaction potential. Simulations were initiated with a uranium PKA of 10 keV in 24 crystallographic directions. However, clustering of the atoms was not observed during the displacement cascade, or after the event, at the timescale of the simulation.

Simulations were also performed with xenon atoms at a concentration of 0.3 at. %. The simulation was performed with the atoms distributed randomly throughout the simulation cell at the interstitial positions. 24 crystallographic directions were used for the uranium PKA, with energies between 10 keV and 100 keV. In addition, simulations were performed with the atoms located at randomly distributed neutral trivacancies. As with the helium simulations, clustering is not observed at the timescale of the simulations.

4.1.2.2 Resolution of helium from bubbles

The interaction of helium bubbles with a uranium PKA was investigated by Parfitt et al. (Parfitt 2008). The uranium and oxygen interactions were described using simple Buckingham potentials, the helium-ion interactions using simple Lennard-Jones potentials and the helium-helium interactions using the potential of Beck (Beck 1968).
It was found that gas resolution occurred via two mechanisms. Firstly, energetic recoil during the ballistic phase and secondly via leakage into the highly defective region of UO$_2$ at the bubble surface; damage assisted resolution. Examples of these mechanisms can be viewed in Figure 60.

Figure 60: Displacement cascade simulation where a uranium PKA interacts with a small over-pressurised helium bubble. a) The PKA is initiated. b) Ballistic phase; He is emitted via energetic recoil. c) Damage assisted resolution; He is absorbed into the highly defected region. d) Final configuration at 25 ps where helium is trapped in the disordered region of UO$_2$. (Parfitt 2008).

Helium bubbles of increasing density were investigated and resolution was observed in all cases by both the damage assisted and ballistic mechanisms as can be seen in Table 19.

Table 19: Average resolution observed for helium bubbles of increasing density. The resolution occurred via energetic recoil (ballistic) and thermally activated leakage into the disordered region (thermal). (Parfitt 2008)

<table>
<thead>
<tr>
<th>No. He atoms</th>
<th>Atomic density Per UO$_2$</th>
<th>No. resolved He atoms</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>250</td>
<td>0.31</td>
<td>2.2(1.8)</td>
</tr>
<tr>
<td>500</td>
<td>0.61</td>
<td>2.5(2.6)</td>
</tr>
<tr>
<td>750</td>
<td>0.91</td>
<td>7.4(5.2)</td>
</tr>
<tr>
<td>1000</td>
<td>1.22</td>
<td>8.3(5.5)</td>
</tr>
<tr>
<td>1250</td>
<td>1.52</td>
<td>10.5(5.5)</td>
</tr>
<tr>
<td>1500</td>
<td>1.83</td>
<td>25.7(11.5)</td>
</tr>
<tr>
<td>1712</td>
<td>2.08</td>
<td>30.0(8.7)</td>
</tr>
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</table>
The probable mechanism of resolution (i.e. damage assisted or ballistic) was determined by monitoring of the resolved atoms' kinetic energy throughout the simulation. The amount of total resolution was found to increase with increasing bubble density; however, it is unclear if the distribution between the two resolution mechanisms varies as a function of bubble pressure too.

4.1.2.3 Resolution of Xe from bubbles

Displacement cascades simulations were performed in bulk UO$_2$ in the presence of low, medium and high density xenon bubbles of radius 20 Å and 25 Å (Govers, Bishop, et al. 2010). The position of the uranium PKA was chosen in order that the peak damage coincided with the location of the rare gas atoms, approximately 58 Å from the centre of the bubble. The gas atoms were carefully monitored in order to see if any were resolved into the UO$_2$. The PKA was initiated with successively higher kinetic energies of 10 keV, 20 keV and 50 keV.

It was found in the majority of the 63 simulations (68 %) that no resolution was observed. The maximum resolution was 3 atoms be emitted from the bubble which occurred in only two simulations as can be seen in Table 20 and Table 21. The xenon atoms that were resolved were emitted via a ballistic mechanism only. There was no significant increase in the average kinetic energy of the gas atoms in the bubble nor was leakage into an amorphous region observed (the damage assisted mechanism, section 4.1.2.2), as seen with the helium atoms in the previous study (Parfitt 2008).

Table 20: Number of xenon gas atoms resolved into bulk UO$_2$ from a 20 Å radius xenon bubble as a result of a displacement cascade (Govers 2010).

<table>
<thead>
<tr>
<th>Xe atoms</th>
<th>10 keV</th>
<th>20 keV</th>
<th>50 keV</th>
</tr>
</thead>
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<tr>
<td></td>
<td>[110]</td>
<td>[210]</td>
<td>[561]</td>
</tr>
<tr>
<td>400</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 21: Number of xenon gas atoms resolved into bulk UO$_2$ from a 25 Å radius xenon bubble as a result of a displacement cascade (Govers 2010).

<table>
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<th>Xe atoms</th>
<th>10 keV</th>
<th>20 keV</th>
<th>50 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[110]</td>
<td>[210]</td>
<td>[561]</td>
</tr>
<tr>
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</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1500</td>
<td>0</td>
<td>2</td>
<td>0</td>
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</tbody>
</table>

In conclusion, for displacement cascade simulations at energies where electronic effects are not yet significant, there is no significant xenon resolution into the bulk. Therefore, thermal spike simulations at higher energies were investigated in order to investigate xenon gas resolution, see section 4.2.3.
4.2 Thermal shocks and spikes in bulk $\text{UO}_2$

4.2.1 Defects concentration and clusters after a thermal shock

Below we present some MD simulation results related to the evolution of the defects concentration after a thermal shock (a short heating period) followed by quenching (fast drop of temperature). This method can be used to simulate the relaxation processes observed in radiation-damaged fuel (Gale 2003) as an alternative to the simulation of displacements cascades (Van Brutzel 2006).

Following such a concept, we designed a dynamic simulation on a large CMD cell containing 12000 ions which started at the temperature well above the melting temperature. This temperature was kept to destroy the oxygen sublattice for a short period only. To avoid melting of uranium sublattice this period should be very limited (less than 2-3 ps). After, the temperature was dropped (suddenly or step by step) to the room value.

During the whole simulation, we monitored the number of OFP defects in the cell. It rises quickly during the thermal shock period up to ~40 % (relative to the number of uranium or interstitial sites). In Figure 61 we present the evolution of the OFP number in the course of this period.

After the thermal shock period the temperature was dropped and the simulation cell was annealed at $T = 1000$ K for ~ 4 ps. During this period the concentration of defects decreases by a factor thirty and after a short period of irregular behaviour (∼1 ps) the defect relaxation processes follow the exponential decay law with a relaxation time of $\tau = 1.84$ ps (Figure 62).

At the last stage of the simulation, the decay of defects in the solid was quenched at $T = 300$ K. The defects concentration stabilizes at ~1.5 % (see Figure 63). The structure of defects clusters obtained was already discussed. Along with stable isolated oxygen vacancies and interstitials, a few large metastable globular clusters appear (Figure 64).

![Graph showing OFP number during thermal shock period](image)

**Figure 61**: Evolution of the OFP number during the thermal shock period.
Figure 62: Relaxation of defects during an annealing period at $T = 1000$ K. An exponential decay law with relaxation time $\tau = 1.84$ ps is observed.

![Graph showing relaxation of defects](image)

Figure 63: Stabilization of the defects concentration at the last stage of the simulation.

![Graph showing stabilization of defects](image)

We used a big simulation cell, containing up to 12000 ions, to study the geometry and energetics of the different defect clusters, which may appear spontaneously during such computer experiments. Two types of globular clusters, obtained after a few picoseconds of thermal shock at $T = 4000$ K and instant quenching to $T = 1000$ K, are shown in Figure 64. The first one has a lattice ion in the middle (not shown), the second one is interstitial-centred. Both types of clusters have non-zero negative net charge.

![Images of artificial clusters](image)

Figure 64: Artificially created perfect interstitial-centred globular clusters a) 12 int + 8 vac; b) 13 int + 8 vac. Ions in their lattice positions are not depicted for clarity reasons.
The total energy of a globular cluster is rather high (from 10 to 30 eV). However, it is noticeably less than the sum of energies of the separated defects. The value of formation energy calculated per defect is usually 3-5 times less than the OFP formation energy (~5 eV).

By introducing additional UFP defects one may study the stability and interaction of uranium interstitials and vacancies with oxygen defects. An example of a combined uranium-oxygen defect cluster is shown in Figure 65. This cluster is negatively charged.

4.2.2 Defects created by thermal spikes

Thermal spikes are the result of fast ions (energy above 100 keV) interactions in materials. These interactions occur mainly through electronic excitation (Hayashi et al. 1997); this energy is mostly evacuated through photon emission, but part of it will still be released locally to the lattice because of electron-phonon interactions. Although the recoil range of fission fragments (typically 6 to 9 µm) is presently out of the range of MD capabilities and although electronic excitations cannot be modelled with such techniques, a simplified approach is possible in which only one slab, perpendicular to the thermal spike axis, is modelled with periodic boundary conditions. Atoms present in a cylindrical zone of a few nanometres (in most cases considered: 4 nm) along the thermal spike axis were given higher kinetic energies (a few eV per atom) to simulate local heating due to electronic effects. The present study has been limited to thermal spikes along the <100> direction. The system had a size of 48 conventional unit cells in the x- and y- directions (perpendicular to the thermal spike axis) and 12 conventional unit cells along the z-axis (along the thermal spike direction). The latter choice is the result of a compromise between computing time and periodicity effects due to boundary conditions.

The system similar to that used for the PKA simulations (section 4.1) has been first equilibrated at 1000 K. For the simulation of thermal spikes, the system has been thermostatted on the x- and y- borders, over a few atomic layers using a pseudo-Langevin thermostat for simulations performed with the DL_POLY 3.09 code. The source code has been slightly modified to impede thermostating on the z-faces (crossing the thermal spike). The Moldy code (Refson 2000) has no border thermostat and has therefore been modified to simulate thermal spikes. The procedure chosen consisted of resetting border atoms velocities according to a Maxwell-Boltzmann distribution every 50 to 200 ps (according to the border thickness), which enable energetic shock-waves emitted from the thermal spike to fully enter the border region and to be efficiently damped. Shorter time intervals were observed to provide inefficient damping, because of the reflexion of shock-waves on the border layer.

Based on a recent review of interatomic potentials for UO$_2$ (Govers 2007; Govers 2008), Morelon potential (Morelon 2003) has been chosen in the present work to describe host ion (O and U) interactions.

For all the thermal spike simulations the same behaviour is observed. The first stage of the thermal spike consists of the melting of the inner cylindrical zone, after less than 0.1 picoseconds. Due to the difference in local density between the melted zone and the fluorite lattice, a shock-wave is emitted rapidly from this zone.
The melted zone grows faster in the \( <100> \) direction, which leads to the formation of a square shape melted core with edges along the \( <110> \) direction. Then solidification phase occurs and last for approximately 50 picoseconds. During this phase residual damage appears, nevertheless no amorphisation of the fluorite matrix remains at the end of the thermal spike. However, different types of damage are observed according the initial energies. For a linear energy transfer equal to 4 keV/nm no defects were found. The fluorite structure is perfectly reconstructed. For a linear energy transfer equal to 16 keV/nm only a few point defects (Frenkel pairs) are found distributed randomly in the box. For a linear energy transfer equal to 66 keV/nm misalignments in the fluorite structure are observed, leading to the apparition of dislocation loops (see Figure 66). These dislocation loops are stable and are characterized as nanometric edge dislocations with Burger's vector along the \( <110> \) direction.

![Figure 66: Snapshot of the primary damage state after a thermal spike initiated with a linear energy transfer of 66 keV/nm. Dislocation loops appear with burger's vector along the \( <110> \) direction.](image)

These results are consistent with experimental observations. However, some phenomena like the electronic component for thermal conductivity and electron phonon coupling are neglected with this MD approach. Further investigation with other models such as the one developed by Duffy et al. (Duffy et al. 2009) including these phenomena could bring more accurate description on the thermal spike primary damage state.

4.2.3 Thermal spikes in presence of xenon

The system similar to that used in the previous section, but containing a Xe bubble, has been first equilibrated at 1000 K. The parameters for the Xe-host atoms and Xe-Xe interactions were taken from the work of Geng et al. (Geng 2008). Although Geng potential was originally developed in combination with
Basak potential (Basak 2003), its use together with Morelon potential was shown to provide good results both in terms of defect formation energy and Xe migration energy (Govers, Lemehov, et al. 2010).

Sixty-six simulations of thermal spikes have been performed with an initial thermal spike radius of 4 nm. The kinetic energy of U and O atoms inside the thermal spike has been varied between 2.5 and 10 eV/atom, simulating an energy transfer to the lattice (e.g. by a fission fragment) ranging between 10 and 42 keV/nm. Three bubbles sizes have been considered, namely of 1.2, 2.0 and 2.5 nm radius, corresponding respectively to 138, 767 and 1505 UO$_2$ molecules. For each bubble size, different densities were considered in order to also study the influence of this parameter on the re-solution rate.

The observed number of re-soluted atoms is illustrated in Figure 67 for all types of bubbles.

![Figure 67](image)

**Figure 67:** Number of re-soluted Xe atoms as a function of the thermal spike energy, plotted for different bubble sizes and gas density in the bubble. The regression line is provided in Equation 6.

At low energy deposition rate in the lattice, no re-solution has been observed (in agreement with the study of Huang et al. (Huang et al. 2010)). However, re-solution has been observed at an energy deposition rate of 15 keV/nm. The series of simulations indicate that the number of resolved atoms increases almost linearly (at least over the range covered in our simulations) with the thermal spike energy:

$$N_{at.re-sol.} = 1103 \cdot (E_{av./at.} - 3.17)$$  \hspace{1cm} \text{Equation 6}

where $N_{at.re-sol.}$ is the number of re-solved atoms and $E_{av./at.}$ is the average initial energy (in eV) per atom in the thermal spike. Interestingly, no dependence of this quantity with the bubble size nor with the number of gas atoms they initially contain has been observed.

Figure 68 shows a snapshot from a typical simulation. Partial resolution of a 1.2 Å (118 Xe atoms) bubble after a thermal spike is observed; the deposited energy was 6.4 eV/atom (27 keV/nm).
5 Conclusions

Various properties and processes related to the behaviour of UO$_2$ under irradiation were investigated at the atomic scale using electronic structure calculations (DFT+U) and empirical potential methods associated to molecular dynamics (CMD). Because of the complexity of the fission effects, a comprehensive simulation including all the effects at representative time and geometric scales is not possible, but these methods provide valuable information for the understanding and quantification of different elementary processes associated to the fuel burn-up. Such information can be used in mesoscopic and macroscopic models to simulate fuel performance during irradiation at scales corresponding to reactor operation.

The investigation of the points defects creation, migration and recombination was the starting point required for the atomic scale studies. The interaction between point defects and the formation of clusters (in particular Willis cluster) were simulated for the oxygen Frenkel pairs (OFP), present not only in non-stoichiometric UO$_2$ but also in UO$_2$ at high temperatures. The existence of uranium Frenkel pairs, which is a characteristic of radiation damage, induces the formation of OFP that can cluster to form more extended defects. Based on these results, the effect of point defects on some macroscopic fuel properties like the lattice parameter, the diffusion of oxygen and fission gases, or the thermal conductivity could be investigated. The effect of non-stoichiometry on these properties, which is relevant in irradiated fuel because of the expected changes in the fuel matrix stoichiometry due to the fissions, could also be determined by CMD simulations and was found to be in good agreement with the experimental data. Existing potential models, as well as a specific potential model developed during the F-BRIDGE project for non-stoichiometric fuels and taking into account the charge transfers, were applied.
Rare gas behaviour in UO$_2$ was also investigated by DFT+U and CMD. The solubility of helium being extremely reduced, the investigation of its physical state in the fuel, of the migration mechanisms and of the formation of bubbles is of primary importance for the fuel performance understanding. In particular, the diffusion coefficients of helium were determined in stoichiometric and non-stoichiometric fuel, which demonstrates the capability of atomistic methods to obtain results usable at a higher scale. Here again, interaction potentials from the literature, but also a new potential model developed during the project, were evaluated. The Xe and Kr incorporation, as well as the Xe migration and clustering mechanisms, which lead to the formation of bubbles under irradiation, were investigated by CMD.

Finally, the damages produced by displacement cascades were characterised. The formation and stability under irradiation of helium bubbles submitted to displacements cascades could be assessed, including for instance the effect of helium atoms re-solution. This kind of simulation provides input data for an improved modelling of these processes by mesoscopic models based on reaction rate equations.
6 References


## 7 Annex: Document approval by authors’ organisations

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