Simulation of radiation driven fission gas diffusion in UO_2 , ThO_2 and PuO_2

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Abstract

Below 1000 K it is thought that fission gas diffusion in UO_2 nuclear fuel during irradiation occurs through atomic mixing due to radiation damage. Here we present a molecular dynamics (MD) study of Xe, Kr, U and O diffusion due to irradiation. It is concluded that the ballistic phase does not sufficiently account for the experimentally observed diffusion. Thermal spike simulations are used to confirm that electronic stopping remedies the discrepancy with experiment and the resultant diffusivities predicted lie within the scatter of the experimental data. Our results predict that the diffusion coefficients are ordered such that $D_{\text{O}}^* > D_{\text{Kr}}^* > D_{\text{Xe}}^* > D_{\text{U}}^*$. For all species >98.5 % of diffusivity is accounted for by electronic stopping. Fission gas diffusivity was not predicted to vary significantly between ThO_2 , UO_2 and PuO_2 , indicating that this process would not change greatly for mixed oxide fuels.

1. Introduction

Being the dominant material used as nuclear fuel, the behaviour of UO_2 is of particular importance for the safe and efficient operation of nuclear reactors. Its ability to maintain many of its properties despite extreme irradiation, temperature gradients and chemical changes have made it suitable in this role [1]. However, for the safety of regular burnup fuel and to push for higher burnups, a sound understanding must be achieved of how fission products affect fuel behaviour, such as thermal conductivity [2, 3], microstructure [4] or swelling [5, 6]. A particular problem for nuclear fuel is the release of the fission gases Xe and Kr from the pellet and into the helium-filled clad-pellet gap. This has the combined effect of reducing thermal conductivity and increasing the pressure of the plenum or cladding [7]. Other than causing an increased risk of centerline pellet melting, the high temperatures arising due to poor gap thermal conductivity also give rise to higher mobility and additional release of fission gases [8–10], further exacerbating the problem. A mitigating factor could be an increase in pellet thermal conductivity as the concentration of fission gas in solution in UO_2 is reduced [11]. Nonetheless, an eventual consequence of continued fission gas release is the rupturing of the cladding material and this represents a significant risk for nuclear reactor operation. As discussed by Turnbull *et al.* [12] there are three regimes for gas diffusion: i) higher temperature (> 1500 K) intrinsic diffusion, ii) intermediate temperature radiation enhanced diffusion and iii) the low temperature (< 1000 K) irradiation induced athermal contribution. In the latter case, which is commensurate with temperatures in the periphery of the fuel pellet, it is thought that the atomic mixing, which occurs during damage, drives gas mobility. Höh and Matzke [13] made

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similar observations regarding U self-diffusion in UO_2 and UC. There are two stages of the interaction between radiation and a material: electronic and ballistic stopping [14]. Initially fission fragments interact most strongly with the electrons and deposit energy into the material by raising the temperature of the surrounding lattice it passes through. As the fission fragment slows it begins to interact ballistically with atoms in the lattice causing primary knock on atoms to create cascades. This represents two distinct behaviours that must be treated separately during atomistic modelling by using thermal spike and cascade simulations respectively [14–19]. Although this process has been described as athermal previously, modelling results indicate that this may not be strictly true [14, 19].

The underlying mechanisms for fission gas behaviour, as discussed, are complex and inter-related, whereby the temperature and radiation flux in the pellet have important effects [12]. There has been a strong focus on investigating the impact of fission gas on thermal conductivity [11], fission gas mobility in the bulk lattice or at extended defects [8–10, 20, 21] and the behaviour of fission gas bubbles [22–24]. By understanding and predicting these processes over a range of conditions, in particular a large temperature range, a greater understanding of fuel behaviour can be achieved. However, the accuracy of atomic scale simulations is underpinned by the models and theories upon which they are based. In particular, MD simulations are highly dependent upon the ability of a parameter set to accurately describe the properties of both the host UO_2 (or MOX) and the interaction of fission gas with the host lattice. Previously, Cooper, Rushton and Grimes (CRG) developed a many-body potential for pure actinide oxides and their mixed oxides [25–27], which is capable of accurately predicting a large number of the thermophysical properties of these systems from 300 K to 3000 K. In particular, this is the first instance of an empirical potential being able to reproduce the bulk modulus of UO_2 from 300 K to 3000 K. Recently, Cooper *et al.* [28] have developed complementary potentials designed for modelling Xe and Kr behaviour in UO_2 (or MOX) over a wide range of temperatures, including liquid UO_2 . Therefore, this potential set is suitable for the investigation of the low temperature irradiation induced contribution to fission gas mobility, whereby the lattice exhibits huge variations in local temperature from the background temperature (600 K to 1500 K) to well above the melting temperature at the centre of the radiation damage. The CRG model provides a good description for UO_2 of the melting point and volume change during melting [15], the thermal expansion [25] and the phonon thermal transport. As modelling high energy irradiation events would be sensitive to these properties, the CRG model is suitable for this study. For example, if a potential model over estimated the melting point or the thermal conductivity, the proportion of time spent in the liquid phase for a thermal spike would be underestimated.

In this work, MD simulations of thermal spikes and damage cascades have been used to investigate the electronic stopping and ballistic phases of irradiation respectively. The relationship between the energy deposited by irradiation and the mean squared displacement (MSD) of Xe, Kr, U and O is used to predict the diffusion coefficient as a function of fission rate. Comparison is made to previous experiments [12, 13] as well as simulations on U mobility during ballistic [19] and electronic stopping [14].

2. Methodology

2.1. Potential model

MD simulations, employing a set of interatomic potentials for UO_2 derived previously [25]¹, are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)

¹Supplementary material describing the use of this potential for use in GULP [29], LAMMPS [30] and DL-POLY [31] are provided at <http://abulafia.mt.ic.ac.uk/potentials/actinides>

[30]. In this model the potential energy, E_i , of an atom i with respect to all other atoms has two components - i) a pair potential description of each system and ii) a many-body embedded atom method (EAM) contribution, using the model of Daw and Baskes [32]:

$$E_i = \frac{1}{2} \sum_j \phi_{\alpha\beta}(r_{ij}) - G_\alpha \left(\sum_j \sigma_\beta(r_{ij}) \right)^{\frac{1}{2}} \quad (1)$$

Where the pairwise interaction between two atoms i and j , separated by r_{ij} , is given by $\phi_{\alpha\beta}(r_{ij})$ (equation 2) and has both long range electrostatic, $\phi_C(r_{ij})$ (equation 3), and short range contributions. The former are calculated using the Ewald method [33] with the Particle-Particle Particle-Mesh (PPPM) implementation of the method being adopted in order to improve computational efficiency [34]. The short range contributions are described using Morse, $\phi_M(r_{ij})$ (equation 4), and Buckingham, $\phi_B(r_{ij})$ (equation 5), potential forms [35, 36]. Where α and β are used to label the species of atom i and atom j respectively.

$$\phi_{\alpha\beta}(r_{ij}) = \phi_C(r_{ij}) + \phi_B(r_{ij}) + \phi_M(r_{ij}) \quad (2)$$

$$\phi_C(r_{ij}) = \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

$$\phi_M(r_{ij}) = D_{\alpha\beta} [\exp(-2\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0)) - 2\exp(-\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0))] \quad (4)$$

$$\phi_B(r_{ij}) = A_{\alpha\beta} \exp\left(\frac{-r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6} \quad (5)$$

Where $A_{\alpha\beta}$, $\rho_{\alpha\beta}$, $C_{\alpha\beta}$, $D_{\alpha\beta}$, $\gamma_{\alpha\beta}$ and $r_{\alpha\beta}^0$ are empirical parameters that describe the pair interactions between atom i and atom j . In comparison to the original CRG model [25] the updated version of the PuO₂ parameters [27] gives an improved description of the melting point of PuO₂.

The second term in equation 1 uses the EAM to introduce a many-body perturbation to the pairwise interactions. The many-body dependence is achieved by summing a set of pairwise interactions, $\sum_j \sigma_\beta(r_{ij})$, and passing this through a non-linear embedding function: $\sigma_\beta(r_{ij})$ that is inversely proportional to the 8th power of the inter-ionic separation (equation 6) and a square root embedding function is used (equation 1), where n_β and G_α are the respective constants of proportionality. The derivation of the parameters and a description of the functional terms used in the EAM component are given in references [25, 27].

$$\sigma_\beta(r_{ij}) = \left(\frac{n_\beta}{r_{ij}^8} \right) \frac{1}{2} (1 + \operatorname{erf}(\kappa(r - 1.5))) \quad (6)$$

In order to prevent unrealistic forces occurring at short separations a short range cut-off using an error function is applied at 1.5 Å that reduces the EAM component gradually (see equation 6). This ensures that there is no discontinuity in the interatomic energy, which would arise from an abrupt cut-off. Buckingham potential parameters for the Xe-U, Xe-O, Kr-U and Kr-O were reported previously [28]. The gas-gas interactions used here were developed previously by Tang-Toennies [37], enabling mixed gas Xe-Kr systems to be studied.

Figure 1a) shows the variation of the U-O dimer energy (dotted lines) and the lattice energy (solid lines) as a function of U-O separation using the CRG model [25] with $\kappa = 5, 10$ or 20 Å^{-1} (see equation 6). Note that the error function used in the original potential ($\kappa = 20 \text{ Å}^{-1}$) was too abrupt for the short separations created during damage events, giving a kink in the U-O

interaction. It can be seen from Figure 1a) that $\kappa = 5 \text{ \AA}^{-1}$ was a suitable selection for the error function cut-off ensuring smooth U-O interactions. To prevent unrealistic forces at the short separations accessed due to such high energy events, a ZBL potential was splined to the CRG model. Figure 1b) shows the U-O dimer energy (dotted lines) and the lattice energy (solid lines) as a function of U-O separation, whereby the CRG model was splined to the short range ZBL interaction between 0.8 $\text{\AA}$ and 1.6 $\text{\AA}$, 1.0 $\text{\AA}$ and 1.5 $\text{\AA}$ or 1.1 $\text{\AA}$ and 1.4 $\text{\AA}$. The non-splined ZBL and CRG potentials (black dashed lines) are also plotted alongside the splined interactions. It can be seen that the spline between 0.8 $\text{\AA}$ and 1.6 $\text{\AA}$ produced sufficiently smooth interactions, and was used throughout this work.

To demonstrate that the modifications made to the CRG model do not impinge on the ability of the model to reproduce important bulk UO_2 properties, the thermal expansion and bulk modulus (K) have been calculated as a function of temperature. To do so, MD calculations are carried out in the NPT ensemble at a given temperature and a pressure of -0.4 GPa for 20 ps with the volume averaged over the final 10 ps. The pressure is increased at increments of +0.02 GPa until it reaches 0.4 GPa, with the volume again averaged over the final 10 ps at each increment. Using the volumes at 0 GPa the thermal expansion is calculated from 300 K to 1900 K. Additionally, by fitting 2nd order polynomials to the P(V) curves the bulk modulus, K, at 0 GPa was calculated using the following relationship.

$$K = \left(-V \frac{dP}{dV} \right)_{P=0} \quad (7)$$

Where P and V represent the pressure and volume of the system. Figure 2 shows the lattice parameter and bulk modulus as function of temperature using the original CRG potential and the modified CRG model ($\kappa = 5 \text{ \AA}^{-1}$) splined to the ZBL potential. This figure shows that the bulk properties of UO_2 have not been modified by the adjustments to the short range interactions of the potential.

2.2. Radiation damage calculations

The first step was to create a $35 \times 35 \times 35$ UO_2 supercell with 1% U cations randomly replaced with Xe or Kr atoms and 1% O anions randomly removed (to maintain charge neutrality). To enable the O species to migrate to their equilibrated configuration, the system was annealed for 100 ps at 2000 K and then cooled to the temperature of interest (600 K, 1000 K or 1500 K) in the NPT ensemble at zero pressure and using barostat and thermostat relaxation times of 0.1 ps and 0.5 ps respectively. This fully equilibrated $35 \times 35 \times 35$ UO_2 supercell was used as the starting point for subsequent damage calculations.

Five thermal spike calculations were conducted by depositing 30 keVnm^{-1} , 40 keVnm^{-1} , 50 keVnm^{-1} , 60 keVnm^{-1} and 70 keVnm^{-1} of kinetic energy into a cylindrical region (axis in z direction) with a radius of 2.00 nm, 2.95 nm, 3.76 nm, 4.44 nm and 4.98 nm, respectively, at the center of a $70 \times 70 \times 35$ UO_2 fluorite supercell (2,058,000 atoms), i.e. a $2 \times 2 \times 1$ extension of the equilibrated supercells. These radii and energies were chosen based on the post-irradiation experiments of Toulemonde *et al.* [38]. Similar energies and radii have been investigated previously by thermal spikes in MD [14, 18]. The energy was introduced by randomly rescaling the atomic velocities within the cylindrical region to the appropriate temperature with the constraint that the velocities observed a typical Boltzmann distribution. Due to the large energy deposited within the system it was necessary to use a heat bath in the region within 20 $\text{\AA}$ of the x and y periodic boundaries, whereby the atomic velocities within this boundary were rescaled every timestep to the background temperature of interest in the NVT ensemble and the remainder of the supercell is in the NVE ensemble. The use of the boundary thermostat more

accurately represents electronic stopping in the bulk lattice, mitigating heating of the spike by its periodic image. This ensured that heat was gradually removed throughout the simulation and it returned to the initial equilibrium temperature after 270 ps. By applying the thermostat to the boundary region only it was ensured that the thermal spike was not artificially interfered with. Throughout the thermal spike calculations the MSD for each species was calculated.

Cascade simulations were conducted by selecting a U cation and scaling its velocity in a random direction with a kinetic energy of 10 keV, 25 keV, 50 keV and 75 keV within a $70 \times 70 \times 70$ UO_2 fluorite supercell (4,116,000 atoms), i.e. a $2 \times 2 \times 2$ extension of the equilibrated supercells. The damage cascade was subsequently allowed to evolve in the NVE ensemble until the system returned to equilibrium. The end equilibrium temperature was not sufficiently greater than 600 K to justify the use of a thermostat at the periodic boundaries. This method was repeated 15 times for each cascade energy and the MSD for each species was determined.

3. Results and discussion

3.1. Diffusion during the ballistic phase of irradiation

As discussed in the methodology section, damage cascade simulations were carried out with PKA energies of 10 keV, 25 keV, 50 keV and 75 keV. For each energy 15 PKA directions were chosen randomly so that a statistical average could be obtained. Figure 3 shows the evolution of the temperature profile during a 75 keV cascade (red and blue semi-transparent regions indicate hot and cold respectively, atoms below 600 K have been removed). The opaque spheres indicate displaced Xe atoms, whereby their color identifies the magnitude of displacement relative to the initial configuration. It can be seen that the PKA rapidly recoils and causes branching within the first 0.01 ps. Further branching occurs within the next few ps as the cascade spreads out. By 20 ps it can be seen that significant Xe displacement has occurred and the cascade is beginning to cool down. Finally by 30 ps the cascade energy has more or less fully dissipated and the Xe atoms are permanently displaced from their original configuration. Note that, although not shown here for clarity, there is also displacement of the host U and O ions.

Figure 4 shows the evolution of the number of Frenkel pairs, counted using a Wigner-Seitz analysis, and the MSD of U, O and Xe during the simulation of the 75 keV damage cascade shown in Figure 3. It can be seen that initially the number Frenkel pairs increases and quickly reaches a peak. Subsequently, the lattice recovers leaving residual damage. On the contrary the MSD of all three species increase and, although it oscillates due to shock waves, it does not recover. As the lattice recovers the species settle down at lattice sites displaced from the original configuration; atomic mixing has occurred. The MSDs were averaged over the final 15 ps of the simulations. This was repeated for several PKA energies and the MSD of U, O, Kr and Xe as a function of PKA energy deposited per unit volume is shown in Figure 5. It is clear that O and Kr mix the most during cascade simulations and U the least, while Xe lies in between. Note that as the MSD for a given cascade energy is dependent on the simulations size, it is plotted as a function of energy deposited per unit volume. This will enable direct comparison with the electronic stopping phase discussed below. As will be shown in section 3.3 for 600 K, the ballistic phase contributes very little to the diffusion coefficient and is, therefore, omitted from studies at 1000 K and 1500 K.

3.2. Diffusion during the electronic stopping phase of irradiation

Thermal spike calculations to investigate the electronic stopping phase have been carried out for cylindrical spikes with 30 keVnm^{-1} , 40 keVnm^{-1} , 50 keVnm^{-1} , 60 keVnm^{-1} and 70 keVnm^{-1} . As for the cascade simulations, this results in a very high energy event at the center of the simulation cell that gives rise to significant atomic mixing. Figure 6 shows the high

temperature region of a thermal spike 70 ps after its initiation, semi-transparent spheres indicate the local temperature and atoms at 600 K or below have been removed. The opaque balls represent displaced Xe, whereby the color indicates the displacement relative to the original configuration. The cylindrical shape of the thermal spike is evident and a great deal of atomic mixing has occurred in the middle of the spike where the lattice has melted.

Figure 7 shows the evolution of the temperature of the atoms initially in the thermal spike and the MSD of U, O and Xe during the simulation of the 30 keVnm^{-1} thermal spike shown in Figure 6. The temperature of the thermal spike decreases very rapidly as kinetic energy is transferred to lattice melting, thermal expansion and defect generation. As the thermal spike is a high temperature liquid there is rapid displacement of intrinsic and fission gas atoms. Following the initial decrease in thermal spike temperature due to melting/expansion, it begins to cool more slowly through phonon transport to the surrounding lattice. As the thermal spike cools the displacement of atoms begins to stop. After 270 ps the lattice has returned to the background temperature of 600 K and the final MSD for each species is determined.

Figure 8 shows the MSD of U, O and Xe as a function of energy deposited into the lattice per unit supercell volume following 5 thermal spike calculations at 600 K, 1000 K and 1500 K. It is clear that O displacement exceeds that of Kr, which exceeds that of Xe, which exceeds that of U. The relative diffusivity of each species show similar trends to ballistic stopping, although Kr is slightly lower relative to O during electronic stopping. Additionally, Figure 8 shows that the MSD for all species increases at higher temperatures, so the process is not strictly athermal as discussed experimentally [12, 13]. The gradients of Figures 5 and 8 will be used to determine the diffusion coefficients as function of fission rate.

3.3. Calculating diffusion coefficients

Typically fission results in two fission fragments: a heavy fission fragment (HFF) of around 70 MeV and a light fission fragment (LFF) of around 100 MeV. For both fission fragments the majority of the energy is deposited in the lattice by electronic stopping with some residual energy deposited through ballistic stopping. Based on the SCRIM calculations of Wormald and Hawari [14] the HFF deposits approximately 5 MeV ballistically and 65 MeV electronically, while the LFF deposits 2 MeV ballistically and 98 MeV electronically. Therefore, a 170 MeV fission event can be considered as depositing 8 MeV into the lattice through the ballistic stopping and 162 MeV through electronic stopping, as outlined in sections 3.1 and 3.2 respectively. Generally, the diffusion coefficient, D , of a given species is expressed as:

$$D = \frac{\langle x \rangle_{msd}^2}{6t} \quad (8)$$

Where $\frac{\langle x \rangle_{msd}^2}{t}$ is the msd per unit time. Typically D is derived from thermal random walk, however, an equivalent diffusion coefficient, D^* can be related to the fission rate per unit volume, $\dot{F}$, and energy per fission event, E_F , giving:

$$D^* = D_B^* + D_E^* \quad (9)$$

$$D^* = (0.047\epsilon_B + 0.953\epsilon_E) \frac{E_F}{6} \dot{F} \quad (10)$$

$$D^* = A\dot{F} \quad (11)$$

$$A = (A_B + A_E) \quad (12)$$

$$A_B = \frac{0.047}{6} \epsilon_B E_F \quad \text{and} \quad A_E = \frac{0.953}{6} \epsilon_E E_F \quad (13)$$

Where ϵ_B and ϵ_E are the MSD per unit energy deposited in a unit volume of lattice during ballistic stopping and electronic stopping respectively. ϵ_B and ϵ_E , see Figure 9a), are calculated from the slopes of Figure 5 and Figure 8 respectively. The results in Figure 9a) indicate that for a given amount of energy deposited in the lattice electronic stopping results 4-5 times more displacement than ballistic stopping. Furthermore, as SCRIM calculations indicate [14], a much greater proportion of energy ($\approx 95.3\%$) is deposited into the lattice by electronic stopping compared to ballistic stopping ($\approx 4.7\%$), see equation 10. Consequently, Figure 9b) shows that, using equations 9-13, the contribution to A of electronic stopping greatly exceeds that of ballistic stopping. Depending on the species the total value of $A = A_B + A_E$ at 600 K ranges from $1.08 \times 10^{-40} \text{ m}^5$ to $2.43 \times 10^{-40} \text{ m}^5$ (see Table 1), in good agreement with the experimental value of $2 \times 10^{-40} \text{ m}^5$ reported previously [12]. Previously, Martin *et al.* [19] predicted A_B values at 700 K of $9 \times 10^{-43} \text{ m}^5$ for U and $3.4 \times 10^{-42} \text{ m}^5$ for O, in good agreement with our results on ballistic stopping (see Table 1). Wormald and Hawari *et al.* [14], however, used thermal spikes in conjunction with the two temperature model to predict an A_E of approximately $0.2\text{--}1 \times 10^{-41} \text{ m}^5$ for U, about 1-2 orders of magnitude below the experimental value [13] and our predicted values reported in Table 1 and Figure 9.

By assuming $\dot{F} = 10^9 \text{ m}^{-3}\text{s}^{-1}$ [12] and using equation 11 the diffusion coefficients at 600 K are also shown in Figure 9b) on the right hand axis. It can be seen that our modeling results lie within the range of experimental data of Turnbull *et al.* [12] for the fission gases and that of Höh and Matzke [13] for U. Although the modeling agrees with experimental results that the Xe diffusion coefficient exceeds that of U, there is disagreement regarding the diffusion coefficient of Kr. While Turnbull *et al.* observed lower diffusion of Kr relative to Xe, the modeling predicts the opposite. However, it can be seen from the error bars in Figure 9b) that there were experimental measurements that exceeded the Kr diffusion coefficients predicted by the model. As a result of experimental uncertainties it cannot be concluded that there is disagreement between the experiments and the model. Due to its smaller size and mass it intuitively makes sense that the Kr diffusion coefficient should be slightly greater than that of Xe.

Although the experimental studies have concluded that the radiation driven diffusion coefficients are athermal, the error is significant enough that this cannot be asserted with a great deal of confidence. Therefore, the diffusion coefficients were also examined at 1000 K and 1500 K by thermal spike calculations (see Figure 8). Given that the ballistic phase contributed so little to the diffusion coefficient at 600 K, cascade simulations were omitted from investigations at 1000 K and 1500 K. Figure 10 shows that the diffusion coefficient is slightly temperature dependent. However, the effect is small and all MD values lie within the error in the experimental studies. It is not surprising that higher temperatures have an effect on atomic displacement during thermal spikes, given that it reduces the temperature gradient between the spike and the surround lattice as well as decreases the thermal conductivity. Both of these effects extend the amount of time the thermal spike spends at high temperature, contributing to a greater MSD per cascade (see Figure 8). A similar effect was predicted by Martin *et al.* [19] for U and O displacement during ballistic damage cascades and by Wormald and Hawari [14] using thermal spikes. The upturn predicted at 1000-1500 K maybe capturing some intrinsic diffusion behaviour seen experimentally. However, without a proper treatment of the background defect concentration for nuclear fuel under irradiation it is not expected to capture the experimental diffusion behaviour at higher temperatures.

Our calculations of A and D^* are based on assumptions about the irradiation environment and radiation interactions with the material. If one wishes to do so, different assumptions based on alternative irradiation environments (e.g. spent nuclear fuel storage conditions) can be used in conjunction with ϵ_B and ϵ_E . Alternatively, these parameters could be coupled with fuel performance and neutronics codes to give the local fission gas mobility based on the irradiation

flux in a specific part of the reactor.

4. Extension to ThO₂ and PuO₂

Having established that the ballistic phase is not significant and that the radiation driven diffusion coefficients are relatively athermal, the electronic phase at 600 K has been investigated for ThO₂ and PuO₂. Using the same methods as outlined in sections 2.2 and 3.2 for UO₂, thermal spikes have been carried out at 600 K on ThO₂ and PuO₂ with Xe and Kr in solution. Throughout the thermal spike calculations the MSD of Th, Pu, Xe and Kr were calculated and by using equations 9-11 (assuming $A_E \gg A_B$) the radiation driven diffusion coefficients were determined. Figure 11 reports the diffusion coefficients for the cations (Th, U and Pu), Xe, Kr and O in the ThO₂, UO₂ and PuO₂ systems. All systems exhibit the lowest diffusion coefficients for the host cation species (Th, U or Pu) and the highest for oxygen. Similarly, all systems also exhibit higher diffusion coefficients for Kr than for Xe. The highest cation diffusivity is exhibited by Pu and the lowest by Th, with U in between. The trend in the cation diffusion coefficients correlates well with the melting temperature of the respective systems, in that ThO₂ has the highest melting temperature and PuO₂ the lowest. This is expected given that the time spent by the ThO₂ thermal spike as a liquid would be lower, leading to less atomic mixing compared to UO₂ or PuO₂. However, for Xe, Kr and O this trend is not continued. The O diffusion coefficient is similar for UO₂ and PuO₂, however the greatest diffusivity is predicted for O in ThO₂. In this case consideration of just the relative melting points is not sufficient to understand the trend. As significant conventional thermal transport is expected for O below the melting point, additional factors may be important such as the diffusion of residual O defects. In the case of the noble gases the small differences predicted for ThO₂, UO₂ and PuO₂ are within statistical significance. It is expected, therefore, that this important gas diffusion mechanism is not affected either by transmutation of U to Pu in conventional fuel or by the use of mixed oxide fuels.

5. Conclusions

Understanding the behaviour of fission gases in nuclear fuel is crucial for the safe and efficient operation of nuclear reactors. In particular, fission gas release is a key limiting factor for which a good understanding of the fission gas diffusion coefficient is critical. Using MD simulations the role of radiation damage in the low temperature diffusion of fission gas has been investigated. It was shown by cascade calculations that ballistic stopping is insufficient to account fully for the experimentally observed athermal contribution. Thermal spike calculations showed that electronic stopping accounts for 98.5 % of diffusion. The calculated diffusion coefficients were $1.62 \times 10^{-21} \text{ m}^2\text{s}^{-1}$ and $1.96 \times 10^{-21} \text{ m}^2\text{s}^{-1}$ for Xe and Kr respectively in UO₂ at 600 K. O was predicted to exceed the mobility of fission gas while U did not, giving diffusion coefficients of $2.43 \times 10^{-21} \text{ m}^2\text{s}^{-1}$ and $1.08 \times 10^{-21} \text{ m}^2\text{s}^{-1}$ respectively at 600 K. For all species the diffusion coefficients were predicted to increase slightly with increased temperature, meaning that describing this process as athermal is not strictly accurate. These predicted values lie within the scatter seen in experimental data for Xe, Kr and U [12, 13]. Similar investigations into ThO₂ and PuO₂ predicted that although small changes in cation and oxygen diffusion coefficients are expected, there is no effect on fission gas diffusion. Consequently, the use of mixed oxide fuels is not predicted to have a significant impact on this gas diffusion process. The underlying parameters that couple irradiation environment to the diffusion coefficient of Xe, Kr, Th, Pu, U and O have been predicted and can be coupled to higher level fuel performance codes that provide information about the local irradiation conditions.

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Figures

Figure 1: The change in system energy as a function of U-O separation for a) the CRG potential using $\kappa = 5, 10$ and 20 in the error function and b) using different upper and lower cut-offs for the the ZBL spline with $\kappa = 5$. In both a) and b) for a given set of parameters the change in the lattice energy (dotted lines) and the U-O dimer energy (solid lines) are reported. In b) the pure ZBL (black dashed line) and pure CRG model (black dash-dot line) are plotted alongside the the splines for the U-O dimer.

Figure 2: a) The lattice parameter and b) the bulk modulus as a function of temperature predicted using the original CRG potential (red) as well as the version used in this study with a modified error function cutt-off ($\kappa = 5 \text{ \AA}^{-1}$) and a ZBL spline from 0.8-1.6 Å (blue). Experimental data for the lattice parameter [39] and bulk modulus [40] as a function for temperature are also reported.

Table 1: The ϵ_B , ϵ_E , A_B , A_E , A and D^* parameters for UO_2 from equations 9-11. Subscripts B and E correspond to ballistic and electronic stopping parameters respectively. The A values are based on a fission energy of 170 MeV and assume 95.3 % of this energy is deposited through electronic stopping and the remainder ballistically. D^* values assume a fission rate of $9 \times 10^{-3} \text{ s}^{-1}$. These assumptions can be modified depending on reactor design or local irradiation conditions.

Species	T (K)	ϵ_B ($\text{m}^5 \text{MeV}^{-1}$)	ϵ_E ($\text{m}^5 \text{MeV}^{-1}$)	A_B (m^5)	A_E (m^5)	A (m^5)	D^* ($\text{m}^2 \text{s}^{-1}$)
U	600	1.06×10^{-42}	3.95×10^{-42}	1.41×10^{-42}	1.07×10^{-40}	1.08×10^{-40}	1.08×10^{-21}
Xe	600	1.40×10^{-42}	5.92×10^{-42}	1.86×10^{-42}	1.60×10^{-40}	1.62×10^{-40}	1.62×10^{-21}
Kr	600	1.73×10^{-42}	7.19×10^{-42}	2.31×10^{-42}	1.94×10^{-40}	1.96×10^{-40}	1.96×10^{-21}
O	600	1.83×10^{-42}	8.90×10^{-42}	2.44×10^{-42}	2.40×10^{-40}	2.43×10^{-40}	2.43×10^{-21}
U	1000	-	4.58×10^{-42}	-	1.24×10^{-40}	1.24×10^{-40}	1.24×10^{-21}
Xe	1000	-	6.66×10^{-42}	-	1.80×10^{-40}	1.80×10^{-40}	1.80×10^{-21}
Kr	1000	-	8.73×10^{-42}	-	2.36×10^{-40}	2.36×10^{-40}	2.36×10^{-21}
O	1000	-	9.91×10^{-42}	-	2.67×10^{-40}	2.67×10^{-40}	2.67×10^{-21}
U	1500	-	5.57×10^{-42}	-	1.50×10^{-40}	1.50×10^{-40}	1.50×10^{-21}
Xe	1500	-	7.61×10^{-42}	-	2.10×10^{-40}	2.10×10^{-40}	2.06×10^{-21}
Kr	1500	-	11.49×10^{-42}	-	3.10×10^{-40}	3.10×10^{-40}	3.10×10^{-21}
O	1500	-	11.57×10^{-42}	-	3.12×10^{-40}	3.12×10^{-40}	3.12×10^{-21}

Figure 3: Visualization of a damage cascade with a PKA energy of 75 keV. The U and O atoms are represented by semi-transparent spheres, whereby their color indicates the local temperature (red and blue being hot and cold respectively). Atom with kinetic energy below 600 K are removed. Displaced Xe atoms are represented by opaque spheres, whereby their color indicates the displacement relative to the initial configuration (red indicates displacement greater than 5 Å).

Figure 4: The time evolution of the total number of Frenkel defects in the system (green) as well as the MSD of U (blue), O (red) and Xe (black), during a 75 keV damage cascade.

Figure 5: The MSD of U (blue), O (red), Xe (black) and Kr (grey) at the end of cascade simulations as a function of the PKA energy deposited per unit volume. The labels correspond to the PKA energy. Each point is the average of 15 such simulations.

Figure 6: Visualization of a 30 keVnm^{-1} thermal spike calculation in UO_2 with 1 % Xe, 70 ps following initiation. The U and O atoms are represented by semi-transparent spheres, whereby their color indicates the local temperature (red and blue being hot and cold respectively). Atoms below 600 K are removed. Xe atoms are represented by opaque spheres, whereby their color indicates displacement relative to the initial configuration (red indicates displacement greater than $5 \text{ \AA}$).

Figure 7: The time evolution of the thermal spike temperature (green) as well as the MSD of U (blue), O (red), Kr (grey) and Xe (black), during a 30 keVnm^{-1} thermal spike.

Figure 8: Results for the MSD of U (blue), O (red) and Xe (grey) at the end of thermal spike simulations as a function of the energy deposited per unit volume. Labels correspond to the energy deposited per unit length (stopping power).

Figure 9: a) The predicted MSD per unit energy deposited in a unit volume of lattice for electronic and ballistic stopping at 600 K (slopes of Figures 5 and 8). b) Using the ϵ parameters, assuming an average fission event energy of 170 MeV and that 95.3 % of this energy is deposited electronically, the A parameters for U, O, Xe and Kr are calculated (see equations 10 and 11). By assuming a fission rate of $10^9 \text{ m}^{-3}\text{s}^{-1}$ the diffusivity is also calculated in b) with reference to the experimental data of Turnbull *et al.* [12] and of Höh and Matzke [13], error bars represent the range of experimental data and points indicate the average. Although not plotted in the figure, note also that Turnbull *et al.* report $A \approx 2 \times 10^{-40} \text{ m}^5$.

Figure 10: An Arrhenius plot of the diffusion coefficient predicted by MD for U, O, Xe and Kr at 600 K, 1000 K and 1500 K (solid lines). Experimental data by Turnbull *et al.* [12] and of Höh and Matzke [13] is shown by dashed lines.

Figure 11: An Arrhenius plot of the diffusion coefficient predicted by thermal spike calculations (electronic phase only) at 600 K for cations, O, Xe and Kr for ThO₂ (green), UO₂ (blue) and PuO₂ (red). The experimental data for UO₂ of Turnbull *et al.* [12] and of Höh and Matzke [13] are also plotted, error bars represent the range of experimental data and points indicate the average. Although not plotted in the figure, note also that Turnbull *et al.* report $A \approx 2 \times 10^{-40} \text{ m}^5$.