MOLECULAR DYNAMIC SIMULATION OF XENON BUBBLE RE-SOLUTION IN URANIUM DIOXIDE

BY

MENGQI HUANG

THESIS

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Master’s Committee:

Professor Robert S. Averback, Chair
Professor James F. Stubbins
This is a comprehensive study of two mechanisms of fission gas bubble re-solution in UO$_2$ by molecular dynamics (MD) simulations: homogeneous re-solution and heterogeneous re-solution. For the homogeneous mechanism, a hybrid approach is employed whereby Monte Carlo (MC) simulations are used to obtain the full recoil energy spectrum of fission gas atoms, and MD simulations are used to build an extensive library of fission gas atom re-solution events. This library is used for calculating a recoil spectrum averaged displacement distribution of fission gas atoms around bubbles. The results show that past estimates of the homogeneous re-solution parameter are very inaccurate. For a better understanding of heterogeneous re-solution, sputtering and the re-solution of Xenon fission gas bubbles due to electronic energy deposition of fission fragments is investigated using MD simulations. First, a two-temperature model (TTM) coupling the electronic (e-) and phonon (p-) system is employed to determine the temperature profile along the tracks of fission fragments. The e-p coupling constant within the model is determined by comparing the sputtering yields deduced from the MD simulations with those obtained experimentally. Next, fission fragments tracks are simulated in a UO$_2$ sample containing one Xenon bubble. At high (dE/dx)$_e$ bubbles are partially re-dissolved, however, for ions with electronic stopping power lower than 34 keV/nm, bubble re-solution is not observed.
Thus, bubble re-solution due to the electronic stopping of fission fragments in UO₂ is likely to be insignificant compared to homogeneous re-solution.
ACKNOWLEDGEMENT

First, I would like to thank my Master’s committee, Prof. Averback and Prof. Stubbins, for reviewing my thesis. Prof. Averback, as my advisor, your comments are invaluable for the whole thesis. And the dedication you shown for your student is wonderful. Prof. Stubbins, thank you very much for being the second reader of my master’s thesis. Your feedback significantly improves my work!

Next, I want to thank my co-worker, Daniel Schwen, who wrote the fantastic 3D TRIM code, and conducted all the MC work. You always gave me very useful suggestions when I needed expert advices!

Last but not lease, thanks to my family and friends who gave me support and care during this process.
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Chapter 1. Introduction

1.1 Motivation

With the development of Generation IV reactor technology, the impact of intragranular fission gas (Xe, Kr, etc.) on the performance of UO$_2$ fuel has gained considerable concern. The presence of fission gas bubbles and their evolution are known to have a detrimental influence on the thermal and mechanical properties of reactor fuels. For example, accumulation of fission gas bubbles in fuels may cause high temperature embrittlement; moreover, release of fission gas from fuels can lead to cladding failure at high burn-up. In view of these deleterious effects of fission gas bubbles in fuels, predicting the evolution of size and population of fission gas bubbles are crucial to improve fuel performance in future reactors.

During the evolution of fission gas bubbles, the fission-fragment-driven re-solution of fission gas atoms from bubbles plays an important role. Presently available bubble re-solution models have been comprehensively discussed in a recent review paper by Olander and Wongsawaeng [1]. These models build on two generally accepted mechanisms: the first one, proposed by Nelson [2] and later termed “homogeneous re-solution”, constitutes the interaction of the fission fragments with fission gas bubbles through energetic collision cascades. Individual fission gas atoms are ejected from bubbles by this mechanism through singular binary collision recoil events. The other, termed “heterogeneous re-solution”, and proposed by Turnbull [3], refers to an interaction of high energy fission fragments with entire bubbles, leading to the instantaneous total or partial re-solution of the contained fission gas into the UO$_2$ matrix.
The elucidation of the dynamics of these two re-solution mechanisms by experiments has been impeded by the small time scale (~ ps) and volume (~ nm$^3$) that characterize a cascade event or a high energy ion track. MD simulation, on the other hand, is highly ideally suited to explore these mechanisms. Therefore, this thesis will use MD simulations to elucidate the two re-solution mechanisms, and obtain quantitative data on the re-solving fission gas atoms for each case.

1.2 Goal

1.2.1 Homogeneous re-solution

A hybrid approach is employed whereby Monte Carlo (MC) simulations are used to obtain the full recoil energy spectrum of the Xe atoms in intragranular bubbles under fission fragment irradiation, and MD simulations are used to build a library of re-solution events for these energies. While the MC simulations already provide re-solution information, their accuracy is not known, and therefore I choose to verify the data by running full MD simulations within a selected recoil energy window. The lower energy bound coincides with recoils that have a very low re-solution probability, and are therefore unimportant. The upper energy boundary is set by the practicality of running MD simulations. For recoils above this cut-off, and there are only 2% such recoils, binary collision MC simulation are again employed [19]. As I will show, this introduces negligible error into the calculations.
1.2.2 Heterogeneous re-resolution

Fission fragments with high energy first deposit energy in the electronic system, heating the electrons; part of the energy is then transferred from hot electrons to the lattice through electron-phonon coupling. This process produces a cylindrical hot region around the ion trajectory, termed “thermal spike”. Inside the thermal spike, temperatures could easily reach above the melting point of the material, and if the spike intersects a gas bubble, a purely thermally-driven re-solution might take place.

A two-step approach is employed to evaluate the thermal spike as a possible re-solution mechanism. First, a two-temperature model coupling the electronic and phonon system is employed to determine the temperature profile along the fission fragment tracks. The e-p coupling constant within the model is determined by comparing the sputtering yields deduced from the MD simulations with those obtained experimentally. Next, fission fragment tracks are simulated for different values of electronic stopping power in a UO$_2$ sample containing Xe bubbles, and different bubble re-solving behaviors are summarized.

1.3 Thesis Outline

This thesis is partitioned as follows.

Chapter 1 states the motivation and the key goals of this project.

Chapter 2 provides a review of the basic bubble re-solution mechanisms, then demonstrates three key concepts used in thermal spike simulation: electron-phonon coupling, the TTM and the analytical sputtering yield.
Chapter 3 and 4 present the detailed simulation approaches on homogeneous and heterogeneous re-solution mechanisms, and then discusses the simulation results.

Chapter 5 provides a summary of key results and suggests a plan for the future work.
Chapter 2. Background Knowledge

2.1 Bubble Re-solution Mechanisms

Re-solution of fission gas atoms from bubbles in UO₂ matrix takes place by two mechanisms, as shown in Fig.1: (a) the homogeneous re-solution occurs by removal of single fission gas atoms by collisions with fission fragments or recoil U or O atoms; (b) the heterogeneous mechanism describe a complete destruction of a bubble by passing fission fragments. The re-solution phenomenon can be characterized macroscopically by the re-solution parameter \( b \):

\[
b = \frac{\text{re-solved fg atoms}}{\text{(fg atoms in a bubble) \cdot (unit time)}}
\]

(1)

The reciprocal of \( b \) is either the mean time that a fission gas atom spends in a bubble (homogeneous mechanism) or the mean lifetime of a bubble (heterogeneous mechanism) [1].

Fig.1. Schematic picture to illustrate the two re-solution mechanism: (a) homogeneous re-solution, (b) heterogeneous re-solution.
2.2 Electron-Phonon Coupling

The e-p coupling plays an important role in evaluating the thermal spike temperature in electronic stopping power regime. A plot of energy loss as a function of incident energy for Xe ion in UO$_2$ is calculated by TRIM [4] and shown in Fig.2. For a typical swift fission fragment, such as ~70MeV Xe ion, the electronic energy loss is about two orders of magnitude larger than the nuclear energy loss. In this electronic stopping power dominant regime, the energy is first deposited in the electronic system and then is transferred to atoms through the e-p interaction. This process produces a local heating region around the ion trajectory, termed “thermal spike”. As the electronic stopping power becomes dominant, it is necessary to take into account the energy loss due to the heat capacity and heat conductivity of electrons and the inelastic collisions between electrons and phonons, in order to prevent over-estimating the temperature in the thermal spike [5]. All of these quantities can be described by the e-p coupling constant $g$.

![Graph](image_url)

Fig.2. Nuclear (the red dot line), electronic (the blue dash line), and total (the black solid line) stopping power as a function of ion energy for Xe ion in UO$_2$, calculated from TRIM.
For insulators, \( g \) is generally expressed in terms of electron mean free path \( \lambda \), through the relation: 
\[
\lambda^2 = \frac{C_e \cdot D_e}{g}
\]
[6]. Here \( C_e \) and \( D_e \) are electron heat capacity and diffusivity respectively, and their values will be discussed later in Chapter 2.3. A shorter electron mean free path length \( \lambda \) means that more collisions occur for the electrons to transfer energy to the atoms before diffusing radially outward. More importantly, this stronger e-p coupling will yield a higher lattice temperature at the center of the spike, as a consequence of the more energy transferred from electrons to atoms. The determination of \( \lambda \) value for \( \text{UO}_2 \) system is a key point for this thesis, and will be discussed in Chapter 4.

2.3 Two Temperature Model

Since classical MD simulation do not describe the electronic system and the e-p interaction, an initial temperature profile of thermal spike that takes into account the e-p coupling effect should be manually set as a starting point for the MD simulations. The Two-Temperature Model (TTM) is thus used to calculate the temperature distribution in thermal spikes.

The TTM model, describing thermal spikes induced by swift ions, was revised by Toulemonde et al. [7] to explain the appearance of latent tracks induced in materials by the slowing down of ions in the electronic stopping power regime. In this model, the incident ion first deposits its energy into the electron subsystem on a time scale of \( \sim 10^{-16} \) to \( \sim 10^{-14} \) s [6]. The electrons then transfer energy to the atoms through e-p coupling, which occurs over a timescale of \( \sim 10^{-14} \) to \( \sim 10^{-11} \) s [6]. This heat transfer process produces a cylindrical region around the
trajectory of the energetic ion, where the temperature can often surpass the melting point, $T_m$, of the material.

The TTM describes the temperature evolution of the electronic and atomic subsystems by two coupled differential heat transfer equations in cylindrical geometry [7]:

$$C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r K_e(T_e) \frac{\partial T_e}{\partial r} \right] - (T_e - T_a) \cdot g + A(r, t) \quad (2)$$

$$C_a(T_a) \frac{\partial T_a}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r K_a(T_a) \frac{\partial T_a}{\partial r} \right] + (T_e - T_a) \cdot g \quad (3)$$

where $T$, $C$, and $K$ are temperature, specific heat coefficient and thermal conductivity of the electrons (index $e$) and atoms (index $a$). These equations are non-linear since $C$ and $K$ are temperature dependent. According to Baranov et al. [8], hot electrons in the conduction band of an insulator are expected to behave like hot electrons in a free electron metal. With this assumption, and using the free electron gas model, the value of specific heat is given by:

$$C_e = 3 N_e k_b / 2 \quad \text{at the Fermi temperature, where } k_b \text{ is the Boltzmann constant, } N_e \text{ is the density of electrons excited to the conduction band} [9].$$

Assuming $N_e \sim 5 \times 10^{22} \text{ cm}^{-3}$, $C_e \sim 1 \text{ J cm}^{-3} \cdot \text{K}^{-1}$ [10]. The electron thermal conductivity is described by $K_e = 1/3 \cdot v_F \cdot l \cdot C_e$, here $v_F$ is the Fermi velocity ($\sim 10^8 \text{ cm/s}$) and $l$ is the electron mean free path [11]. Their product is defined as the electron heat diffusivity, given by $D_e = 1/3 \cdot v_F \cdot l$ [11]. At high electronic temperature, by equating $l$ to the interatomic distance ($\sim 0.6 \text{ nm}$), the equation leads to $D_e \sim 2 \text{ cm}^2 \cdot \text{s}^{-1}$ [10]. The other thermodynamic parameters of UO$_2$, such as thermal conductivity, specific heat, density etc. are listed in Table.1 [12].
Table 1: Macroscopic thermodynamic parameters for UO₂ (provided by ref. [12]).

<table>
<thead>
<tr>
<th>Thermal properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity $K_a (W \cdot cm^{-1} \cdot K^{-1})$</td>
<td></td>
</tr>
<tr>
<td>Solid (298 K)</td>
<td>0.0889</td>
</tr>
<tr>
<td>Liquid</td>
<td>0.025</td>
</tr>
<tr>
<td>Specific heat $C_a (J \cdot g^{-1} \cdot K^{-1})$</td>
<td></td>
</tr>
<tr>
<td>298 K</td>
<td>0.23</td>
</tr>
<tr>
<td>2500 K</td>
<td>0.5</td>
</tr>
<tr>
<td>3000 K</td>
<td>0.65</td>
</tr>
<tr>
<td>4000 K</td>
<td>0.31</td>
</tr>
<tr>
<td>6000 K</td>
<td>0.36</td>
</tr>
<tr>
<td>8000 K</td>
<td>0.46</td>
</tr>
<tr>
<td>Melting temperature (K)</td>
<td>3150</td>
</tr>
<tr>
<td>Latent heat of fusion (J/g)</td>
<td>289</td>
</tr>
<tr>
<td>Latent heat of vaporization (J/g)</td>
<td>1990</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>10.96</td>
</tr>
<tr>
<td>Liquid</td>
<td>9.6</td>
</tr>
<tr>
<td>Optical gap (eV)</td>
<td>2</td>
</tr>
</tbody>
</table>

The source term $A(r, t)$ describes the energy distribution created by an incident fission fragment in the electronic subsystem. It consists of a Gaussian distribution in time and a radial distribution $F(r)$ of the delta electrons in space, which are obtained from Katz’s delta-ray theory [13]:

$$A(r, t) = b \cdot \left(\frac{dE}{dx}\right)_e \cdot \exp\left(-\frac{(t-t_0)^2}{2t_0^2}\right) \cdot F(r)$$

(4)
Here, $t_0$ represents the time for the electrons to thermally equilibrate ($\sim 4 \times 10^{-15} \text{s}$ [6]). The factor $b$ is a normalization factor, ensuring that the integration of $A(r, t)$ in space and time is equal to the total electronic stopping power $(dE/dx)_e$.

$$
\int_0^\infty dt \int_0^\infty A(r, t) \cdot 2\pi r dr = \left(\frac{dE}{dx}\right)_e
$$

The energy transfer from electrons to atoms is represented by the product of the coupling constant $g$ and the temperature difference ($T_e - T_a$). When the electrons cool below the lattice temperature, they are assumed to be trapped in the lattice, and hence the e-p coupling is suppressed [6]. In my calculations, I reset $g$ to zero to turn off the e-p coupling when $T_e < T_a$.

The two coupled equations are numerically solved by taking into account all these thermodynamic parameters as well as “solid-liquid” and “liquid-vapor” phase changes. Fig. 3 is a typical example, which shows the lattice and electron temperature as a function of time and radial distance along the ion track for a Uranium ion with stopping power of 55.4keV/nm in UO$_2$. The electron temperature reaches the maximum value in a very short time of $\sim 10^{-15}$s, then it decreases rapidly and the lattice starts to be heated by e-p coupling ($\sim 10^{-13}$s). The radius of the local heating zone (temperature higher than the melting point) is about 3nm for this high energy Uranium ion in UO$_2$.

As you might notice, 55.4 keV/nm is extremely high electronic stopping power value. The maximum electronic stopping power for Xe fission fragments in UO$_2$ is only around 30keV/nm. I’ll explain later that for stopping power as low as 30keV/nm, no obvious re-solution events can
be observed in MD simulations. Thus in order to learn the re-solution mechanism, I’ll extrapolate back from high stopping power to low stopping power.
Fig. 3. The radial temperature distribution $T_e(r,t)$ (for electrons) and $T_a(r,t)$ (for atoms) along a 55.4keV/nm Uranium ion track in UO$_2$ as a function of time, calculated from TTM.
2.4 Analytical Sputtering Yield

As mentioned before, the electron mean free path $\lambda$, which is related to e-p coupling constant $g$ by $\lambda^2 = C_e \cdot D_e / g$, is an unknown parameter for the TTM. The value of $\lambda$ is crucial for the evolution of the temperature distribution around the fission fragment trajectory. Ultimately it determines the amount of lattice melting and the re-solution of gas atoms from bubbles, but it can also be linked to directly observable phenomena like track formation and electronic sputtering.

Attempts have been made to determine the free parameter $\lambda$ by fitting calculations of ion track damage using the TTM model to experimental data. For example, by assuming that track damage in UO$_2$ becomes visible in a transmission electron microscope (TEM) only after the spike temperature exceeds the melting temperature, Wiss et al. suggested $\lambda = 6.0$ nm [14]. In a later paper, Toulemonde et al. revised this previous analysis by assuming visible track damage required a spike temperature equivalent to the sublimation energy. Using this criterion, $\lambda$ is found to be 4.0 nm [10]. However, the nature of the track damage in UO$_2$, sources for the TEM contrast, and relationship between the two, are not yet well understood. These facts make the track formation criteria somewhat speculative.

In this thesis, I adopt a similar procedure for determining $\lambda$, but I consider sputtering data to avoid the ambiguities involved in both defining track damage and relating spike temperature to track damage. This procedure has several advantages: (1) sputtering yields have been measured experimentally; the results are quantitative, and (2) MD simulations can be performed on sputtering to provide a direct connection to the experiments.
Before reporting the sputtering results of the MD simulations, I calculate sputtering yields using the Sigmund thermal spike model [15]. This will be useful later for scaling my MD results.

In the Sigmund model, the evaporation flux \( \Phi(T_a(r, t)) \) is given as a function of the lattice temperature at the surface, \( T_a(r, t) \):

\[
\Phi(T_a(r, t)) = N \sqrt{\frac{kT_a(r, t)}{2\pi M}} \exp\left(-\frac{U}{kT_a(r, t)}\right),
\]

where \( N \) is the atomic density, \( M \) is the molecular mass of the target, and \( U \) is the sublimation energy per sputtered molecule, which is assumed equal to the surface binding energy [6]. \( T_a(r, t) \) is obtained using the TTM. The total sputtering yield \( Y_{tot} \) is obtained from the integral of \( \Phi(T_a(r, t)) \) over time and space:

\[
Y_{tot} = \int_0^\infty dt \int_0^\infty \Phi(T_a(r, t)) \cdot 2\pi rdr
\]

Note that this model assumes evaporation from a planar surface and the temperature is taken from a bulk calculation. Furthermore, the model neglects sputtering of clusters larger than a single formula unit and the possible formation of craters.
Chapter 3. Homogeneous Re-solution

3.1 Overview

The focus of this chapter is to demonstrate the homogeneous re-solution mechanism, and to obtain quantitative data on the re-solution of Xe atoms using computer simulations. A hybrid approach is employed whereby Monte Carlo simulations are used to obtain the full recoil energy spectrum of the Xe atoms in intragranular bubbles under fission fragment irradiation, and MD simulations are used to build a library of re-solution events for these energies.

3.2 MC Simulations

For the MC part of the study, a new binary collision model (BCM) code was created by Daniel Schwen [19]. It is based on the published TRIM algorithm [4] and uses the Ziegler-Biersack-Littmark (ZBL) universal potential [20]. The software is designed, however, to treat arbitrary sample geometries and arbitrary irradiation conditions, as opposed to the fixed layer geometry and external, monoenergetic, fixed-angle irradiation employed by TRIM [4]. In either domain of the sample–Xe bubble or UO₂ matrix–the scattering events are determined randomly based on the appropriate scattering cross sections. Neither lattice structure nor defect accumulations are taken into account. Schwen used this BCM software [21] to simulate samples of UO₂ containing randomly dispersed spherical bubbles of Xe. The typical properties of the intragranular bubble population (provided by ref.[1]) used in the calculations are summarized in

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1 This chapter includes a published paper: D. Schwen, M. Huang, R. S. Averback, P. Bellon, J. Nucl. Mater. 392 (2009) 35. Both MC simulations and the 3D-TRIM in this chapter, including Fig.5, Fig.6 and Fig.8, were conducted by D. Schwen.
Table 2. It should be noted that the bubble population used here corresponds to a burnup of 20 MWd/kgU.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_b$</td>
<td>Bubble density</td>
<td>$7.0 \times 10^{-4} \text{ nm}^3$</td>
</tr>
<tr>
<td>$r_b$</td>
<td>Bubble radius</td>
<td>1 nm</td>
</tr>
<tr>
<td>$\rho_{\text{Xe}}$</td>
<td>Xe density in bubbles</td>
<td>20 atoms/nm$^3$ (4.2 g/cm$^3$)</td>
</tr>
<tr>
<td>$F$</td>
<td>Fission-rate density</td>
<td>$10^{-8} \text{ nm}^3 \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

Table 2. Properties of the intragranular bubble population used in the calculations, provided by ref. [1].

The new TRIM code creates a set of non-overlapping bubbles in a $100 \times 100 \times 100 \text{ nm}^3$ volume with periodic boundary conditions. The identity of the primary knock-on atoms (PKA), and the energies of these recoils, were randomly sampled from the known mass and energy distribution of $^{235}\text{U}$ fission fragments [22], as shown in Fig. 4. The locations of the fission events and directions of the fission fragments were chosen randomly. The BCM software follows every cascade event produced by each fission fragment until all atoms have fallen below a given threshold energy, 100 eV in the present case. Every energy transfer to a Xe atom is recorded, thus generating a recoil energy histogram for Xe atoms, as shown in Fig. 5.

In order to verify the re-solution results from MC simulation, MD simulations will be employed within a selected recoil energy window. All Xe recoils that receive an energy of more than 200 eV and less than 12 keV will be used as input data for MD simulations (solid blue curve), and their recoil event number will be treated as weight factor for MD simulation results to yield a full Xenon atom displacement histogram. This selected recoil energy window will
introduce negligible error, because the high energy side (>12keV) contains only about 2% of all Xe recoils, while the selected energy window contains more than 50% of all Xe recoils.

Fig. 4. (a) Mass distribution of $^{235}$U fission fragments; (b) energy distribution for 4 typical $^{235}$U fission fragments: $^{92}$Kr, $^{94}$Sr, $^{140}$Xe, $^{141}$Ba. Both are provided by ref [22].
Fig. 5. Spectrum of Xe recoil energies obtained from the MC simulation (solid pink curve). The solid blue curve sums up all events in which the Xe atom receives an energy greater than 200eV but less than 12keV from either an O or a U recoil or from a Xe recoil with an energy larger than 12keV. These are the events that are treated by the MD simulation. The dashed blue curve is secondary Xe recoils inside a bubble. The solid red curve sums up all Xe recoils outside the aforementioned energy window. The high energy side contains about 2% of all Xe recoils, while the low energy end contains less than 50% of all Xe recoils.
3.3 MD Simulations

3.3.1 Interatomic potential

The LAMMPS code [23] was employed for the MD simulations using the Particle-Particle Particle-Mesh (PPPM) method for treating the long-ranged coulomb interactions between the oxygen and uranium atoms. The non-coulombic pair interactions and their first derivative were tabulated with a smooth cut-off up to 1.04 nm. Periodic boundary conditions were used for all simulation runs [19].

The large simulation cells required in this work dictated the choice of a simple rigid-ion potential rather than a more complex core-shell potential. For the U-U, U-O, and O-O interactions, I used the Morelon potential [17], which was developed primarily for the simulation of displacement cascades in UO₂ lattices and builds on work by Sindzingre [25] and Karakasidis [26]. Based on a recent review paper by Govers et al. [24], the Morelon potential reproduces the lattice parameter across a broad temperature range. Although it under-estimates the heat capacity by about a factor of two, among comparable potentials it comes closest to the experimental data. The potential also reproduces the melting of the oxygen sublattice (Bredig transition [27]) at 2000 K. The isothermal bulk modulus of UO₂ is well reproduced for temperatures above 1600 K. All of my simulations were carried out at a matrix temperature of 1600 K, which is a typical fuel element centerline temperature under normal operating conditions. Govers [24] report an over prediction of the melting temperature of UO₂ by 300 – 400 K. My own tests, however, put the melting point at about 3300 K, which is only ≈ 150 K above the accepted value of the melting point, 3150 K.
The charges on the uranium and oxygen atoms are taken to be fixed, but fractional (i.e. non-integer). In addition to the coulomb contribution, the U-O interaction contains a Born-Meyer-Huggins covalent bonding contribution and the O-O interaction contains a piece-wise patched function connecting a Born-Mayer part, two polynomials and \(1/r_{ij}^6\) long-range tail (\(r_{ij}\) being the interatomic distance). The U-U interaction is assumed to be dominated by the strong electrostatic repulsion and is therefore taken to be purely coulombic. The fixed ionic charges are expected to enhance the recrystallization to the fluorite structure, the drive for local charge neutrality entails the local preservation of the UO_2 stoichiometry [19].

The Xe-U potential has the Born-Meyer form, while the Xe-Xe and Xe-O interactions are modeled using Lennard-Jones potentials, the parameterization for all three interactions is taken from a recent work by Geng et al. [28]. All interactions are splined to the universal ZBL potential for short ranges. High energy scattering kinematics is determined by the ZBL parts of the interaction potential [19].

### 3.3.2 MD Simulation configuration

Several Xe recoil energies within the 200 eV – 12 keV window were chosen for simulation (200 eV, 400 eV, 1000 eV, 1500 eV, 2 keV, 4 keV, and 10 keV), and a cubic volume containing a UO_2 lattice was created for each energy. The overall size of the simulation box was chosen such that the recoil energy does not exceed 1/20 eV per atom, thus preventing unrealistic heating of the cell. A spherical void was created in the UO_2 lattice by stoichiometrically removing atoms, and thereby preserving the overall charge neutrality of the system. The void was filled with a close-packed Xe lattice, and the system was relaxed at 1600 K for 70 – 125 ps. After relaxation
the Xe gas density in the bubble was determined to be about 3.4 g/cm³ with bubble diameter of 2 nm, which is in good agreement with reported experimental densities [29]. The bubbles remain compact and spheroidal, no Xe atoms were observed leaving the bubble during annealing.

For each cascade, a Xe atom inside the bubble was randomly selected and assigned the predetermined kinetic energy, by sampling from the distribution in Fig. 5, with a random direction. Out of the entire displacement cascade produced by the fission fragment only the subcascades created by the Xe recoils inside fission gas bubbles are simulated. The omission of high energy displacements produced in the UO₂ lattice by the fission fragment allows both the choice of longer simulation time steps due to a lower maximum velocity in the simulation volume as well as the use of a smaller simulation volume, reducing the computational cost per simulated displacement cascade initiated by Xe recoils. This omission of lattice recoils has negligible effect on the outcome.

My MD simulation scheme neglects any possible displacement events that bring lattice material into the gas bubbles. Uranium and oxygen atoms knocked into the Xe bubbles are expected to quickly move to the bubble walls due to coulomb attraction by the inhomogeneously distributed charge. The rates of such atom knock-in’s are comparable to the rates of atoms being knocked-out, which helps to keep the intra-bubble pressure in balance. Knock-ins of re-dissolved Xe atoms are not considered due to their negligible probability. My approach also neglects overlapping displacement events either from two successive fission fragments or from subcascades of a single fission fragment. The time between successive fission fragment cascades in real fuel in operation is sufficiently long to restore local thermal equilibrium, while the time
difference between nearby events in the same displacement cascade is short enough so that the lattice is not much disturbed during flight of the recoiling Xe atom. The Xe atoms thus recoil into a virtually undisturbed surrounding lattice.

3.4 Results and Discussions

3.4.1 Displacement histogram of recoil Xe atom

A set of 400 recoil events per energy was simulated, and the final distribution of all Xe atom distances around the bubble center was recorded. Wrap around due to the periodic boundary conditions and the finite simulation volume was encountered in roughly 10% of all simulation runs; it was accounted for by unfolding the full trajectory data for the Xe atoms. No events where the knocked-out atom crossed the simulation volume boundary and re-entered the bubble were observed. Fig. 6 shows for various energies the histogram of Xe atom displacement distances, measured from the centers of their bubbles of origin. The probability of re-dissolving a Xe atom decays faster than exponentially with re-solution distance. The high Xe intensities at short distances from the bubble center are explained by the onset of the Xe bubble surface.
Fig. 6. Histogram of displacement lengths of Xe atoms from the centers of their bubbles of origin, compiled from a library of MD simulations for various Xe recoil energies.

### 3.4.2 Probability of Xe atom re-solving from a bubble

The conditions for the loss of a Xe atom from the bubble can be characterized by a threshold energy. Fig. 7 shows as a function of Xe recoil energy the probability for Xe atoms to leave a so-called “radius of influence” of its nascent bubble. Three curves, for radii of influence of 1.5nm, 2.0 nm, and 2.5 nm, are plotted, with the bubble radius being 1nm. The threshold behavior is recognized by the rapid increase in the probability of a Xe atom being removed as the primary recoil energy increases above 300 – 400 eV. This observation is, in fact, in good agreement with the *ad hoc* threshold energy of 300 eV postulated in the homogeneous dissolution model by Nelson [30]. The radius of influence can be estimated by back-diffusion probability.
Disregarding the possible strain fields of the bubbles, the independent sink approximation [31] can be utilized, taking the bubbles as sinks with radius $r_b$ (bubble radius) for the Xe atoms. The probability for a Xe atom to be recaptured by its bubble of origin is given simply by $r_b/r$. The timescale for the recapture to occur depends on the effective diffusion constant, but this is not considered in the present work. Below a distance of $2r_b$ from the center of the bubble of origin, the recapture probability is greater than 50%, and beyond this distance, it asymptotically goes to zero. This suggests choosing the “radius of influence” to be twice the bubble radius, and considering only atoms removed beyond this distance as “removed”. For recoils below 200 eV, virtually no Xe atom leaves a bubble. At recoil energies above 4 keV the number of removed atoms per recoil exceeds unity, signifying the onset of secondary Xe recoils also leaving the bubble.
3.4.3 Xe atom displacement histogram, weighted by recoil energy spectrum

The final step in the dual MC/MD approach is the summation of the Xe atom displacement histograms derived from MD, weighted by the probability densities of the recoil energies, as obtained from MC. Fig. 8 shows a comparison of the weighted summation from MD/MC (solid blue line) and the displacement histogram from the MC simulation alone (solid red line). At small displacement distances, the two curves are quite similar; it is, surprisingly, only at larger
distances that they show significant differences. This means that the local excitation of the cascade plays little role in the re-solution process. I attribute the difference at large distances to channeling in the open fluoride structure. Recoil energies outside of the 200 eV – 12 keV window were not simulated by MD. The dashed pink curve contains the MC long range contribution from the recoils with energies greater than 12 keV, the dotted pink curve contains the MC contribution arising from the recoils with energies below 200 eV; it does not take the threshold energy for atom removal from the bubbles into account.

Fig. 8. Xe atom displacement histograms obtained from both the MC simulation (dash black line) and from the MD simulation as a weighted average of the cascade runs for all Xe recoils in the energy range above 200eV and below 12keV (solid black line). The difference between the MC and MD ranges may be attributed to channeling in the
open fluoride structure. The dashed pink curve contains the MC long range contribution from the >12keV recoils, the dotted grey curve contains the MC contribution from the <200eV recoils, which does not take the threshold energy for atom removal from the bubbles into account.

### 3.4.4 Re-solution parameter \( b_{\text{hom}} \)

Integration of the number of re-dissolved Xe atom plotted in Fig. 8 yields five Xe atoms re-dissolved from bubbles per fission fragment. For a typical fission rate density of \( 10^{-8} \text{ nm}^{-3} \text{s}^{-1} \), and a bubble density of \( 7 \times 10^{-4} \text{ nm}^{-3} \), this re-solution rate results in \( 4 \times 10^{-5} \) fission gas atom knock-outs per bubble per second:

\[
\frac{5 \text{ re-dissolved Xe}}{\text{ff}} \times 2 \times 10^{-8} \frac{\text{nm}^{-3} \cdot \text{s}}{} \times \frac{\text{nm}^{-3}}{7 \times 10^{-4} \text{ bubble}} = 1.4 \times 10^{-4} \frac{\text{Xe(knock-out)}}{\text{bubble} \cdot \text{s}}
\]

Each bubble contains about 79 atoms, yielding a re-solution parameter \( b_{\text{hom}} \) of about:

\[
b_{\text{hom}} = \frac{5 \text{ re-dissolved Xe}}{\text{ff}} \times 2 \times 10^{-8} \frac{\text{nm}^{-3} \cdot \text{s}}{} \times \frac{\text{nm}^{-3}}{7 \times 10^{-4} \text{ bubble}} \times \frac{\text{bubble}}{79 \text{atom}} = 2 \times 10^{-6} \frac{\text{Xe(knock-out)}}{\text{ff} \cdot \text{s}}
\]

This number is a factor of \( \approx 50 \) lower than Nelson’s revised analytical results [2]. This discrepancy is rooted in the Xe recoil energy spectra used for the fission gas displacement calculations (Fig.5). For energies below 10 keV, Nelson’s primary recoil spectrum shows higher intensities, up to a factor of two above the results from my calculations. For the secondary recoil spectrum, Nelson's intensity estimate is greater by a factor of \( \approx 40 \) than my results. It is reasonable to believe that the Monte Carlo BCM calculations, which are based on the experimentally verified ZBL potential, are far more accurate than the previously used analytical approach using coulomb potentials in the hard-sphere approximation. Moreover, the spectrum
averaged recoil distribution for a fission fragment or recoil atom slowing down in the UO₂ is obtained naturally in the MC simulation considering both nuclear as well as electronic stopping, but it can be an additional source of error in analytical calculations. The approach employed here of building a cascade library using MD simulation also takes care of ion channeling, and it provides good accuracy in the low energy region, where continuum binary collision models break down.

Lösönen [32] obtains a re-solution parameter of about $5 \times 10^{-4}$ s⁻¹ fission gas knock-outs per fission fragment by fitting his model to experimental bubble size distribution data by Baker [33]. While Lösönen dose not explicitly assume either a homogeneous or heterogeneous re-solution mechanism in his model, and his method of obtaining the re-solution parameter is indirect, it still seems that his re-solution cannot be explained by single fission gas atom knock-outs.
Chapter 4. Heterogeneous Re-solution

4.1 Overview

Typical electronic energy losses \( (dE/dx)_e \) are \( \sim 18 \text{ keV/nm} \) for heavy fission fragments, and \( \sim 22 \text{ keV/nm} \) for light fission fragments [12]. The focus of this part is the local heating arising from the electronic energy loss of these fission fragments, and whether it can cause heterogeneous Xe bubble re-solution. A two-step approach is employed to evaluate thermal spike as a possible re-solution mechanism. First, sputtering simulations are used to determine the e-p coupling constant in the TTM for \( \text{UO}_2 \) by fitting the simulations to experimental data. Then the thermal spikes are simulated as a function of electronic stopping power in sample of \( \text{UO}_2 \) containing Xe bubbles.

The theoretical modeling process of the electronic sputtering yields has three components which are explained in detail in the following sections. Their interplay is a key point of this work. The first component is the use of TTM to calculate the lattice heating around the fission fragment trajectories as a function of time and space. The next component is a MD simulation of a \( \text{UO}_2 \) surface region. It uses the temperature profile obtained from the TTM as the starting conditions at a time when most of the electronic excitations in the track have converted to lattice heating. This time is so short that no significant amount of sputtering could have occurred earlier. Lastly, a comparison of MD sputtering yields with the experimental sputtering data, using different values of \( \lambda \) in the TTM, yields an effective \( \lambda \) value with which the experimental data can be exactly reproduced by MD simulations.

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2 This chapter includes a published paper: M. Huang, D. Schwen, R. S. Averback, J. Nucl. Mater. 399 (2010) 175.
4.2 MD Simulations

4.2.1 Sublimation energy of the Morelon potential

The Morelon potential (discussed in Chapter 3) is used again in MD simulations here. For sputtering calculations, the sublimation energy is a key quantity. My MD test shows that the Morelon potential yields a sublimation energy of 818.7 kJ/mol for UO$_2$, which is higher than the experimental value of 616.4 kJ/mol [12]. To compensate for this error in the sublimation energy, a higher thermal spike peak temperature in MD simulations is needed to obtain the same sputtering yields as the experimental data. Hence a smaller value of $\lambda$ in the TTM calculation, to intensify e-p coupling, will be deduced from my fitting procedure. This will be clarified in what follows.

4.2.2 Sputtering simulations

Simulations of sputtering were performed on samples with (110) surface planes; these are the lowest index charge neutral planes in the UO$_2$ structure. This choice thus avoids excessive surface relaxation due to the fixed charge potential used in the simulations. A large computational box with periodic boundary conditions and dimensions of about 45 nm × 60 nm × 60 nm was filled with a crystal slab with the dimensions of about 15 nm × 60 nm × 60 nm (4,199,040 atoms), resulting in a sample with two free surfaces, as shown in Fig.9. One surface was left unconstrained to allow sputtering. The atoms in the outermost two atomic layers of the other surface were constrained to move only perpendicular to the axis of the spike simulating a semi-infinite crystal below and preventing sputtering at that surface. The total thickness of the sample in the direction of the spike was chosen based on several trial simulations. These showed
that the sputtering yield becomes independent of the sample thickness for thicknesses greater than 15 nm. Atoms were counted as sputtered as soon as they passed a threshold distance from the original sample surface and were not connected to the bulk by a chain of chemical bonds. This enables reliable detection of sputtered atoms, molecules and larger clusters. Two atomic layers at the periodic boundaries of the sample were maintained at 300 K to approximate heat dissipation to a semi-infinite medium. The thermal spikes were initiated as sets of heated coaxial cylindrical shells along the x direction, as next described.

The TTM calculations show that the heat transfer from the electronic system to the lattice in UO₂ occurs on a timescale of $10^{-14}$ to $10^{-13}$ s (discussed in Chapter 2.3), and therefore before the onset of any possible phase transitions. The initial radial temperature profile to be used in the MD simulations could therefore be calculated using the TTM without taking into account the enthalpies of fusion and vaporization. The temperature profile is initialized in MD simulation by creating several coaxial cylindrical shells in the sample (along the x axis) with increasing radius, and rescaling the atomic velocities in each shell. Although this produces a discontinuous step-shaped temperature profile as the starting condition, running this initial state for approximately 1 ps under constant volume and energy (NVE) conditions partitions the energy with other degrees of freedom and smoothes the temperature profile, yielding a temperature distribution in the UO₂ system similar to the TTM calculation. Several tests were made to ensure that the thermal spike temperature profile obtained at the end of NVE stage did indeed agree with the TTM calculation. No sputtering is observed during this relaxation phase. Following this initial relaxation period, the UO₂ sample was evolved at constant pressure for about 10 ps, after which the sputter yield no longer changed. A typical sputtering process is shown in Fig.10, with a thermal spike $(dE/dx)_c =$
47 keV/nm and $\lambda = 3$ nm. To clearly illustrate the molten zone inside the thermal spike, only a thin slice of UO$_2$ is chosen here, thus the sputtering yield shown in the figure is only a small part of the total yield.

Fig. 9. Schematic figure to illustrate the UO$_2$ sample and thermal spike configuration used in sputtering simulation. The dimensions of this large crystal slab are 15 nm $\times$ 60 nm $\times$ 60 nm (4,199,040 atoms). The top surface is left unconstrained to allow sputtering. The atoms in the two atomic layers of the bottom surface (shown as red atoms) are constrained to move only perpendicular to the axis of the spike. The temperature profile of thermal spike is initialized by creating several coaxial cylindrical shells in the sample (shown as red, orange, green, blue cylinders) with increasing radius, and rescaling the atomic velocities in each shell based on the calculation from the TTM model. This produces a discontinuous step-shaped temperature profile as the staring condition.
Fig. 10. Snapshots of a thin slice UO$_2$ sample to represent the sputtering evolution in MD simulation. The thermal spike used here is 47keV/nm, with the e-p constant $\lambda = 3$nm. (a) at $t = 2$ps; (b) at $t = 5$ps; (c) at $t = 8$ps; (d) at $t = 10$ps.
4.2.3 Bubble re-solution simulations

Simulations of Xe bubble resolution were performed using a UO$_2$ sample with a size of 20 × 80 × 80 lattice units with a lattice parameter of 0.546 nm. A single, spherical void was incorporated in the UO$_2$ lattice by stoichiometrically removing U and O atoms, thus preserving the overall charge neutrality of the system. The void was subsequently filled with a close-packed Xe lattice, and the system was relaxed at 300 K for ~100 ps. The density of Xe in the relaxed bubble was \( \approx 4.2 \times 10^3 \) kg/m$^3$ which is in agreement with experimental observations of bubbles of similar size [1]. The resulting Xe bubbles remained compact and spherical during this time, relaxing to a diameter of 2 nm, and without loss of Xe atoms from the bubble. The thermal spike temperatures were then initialized using the same procedure described for the sputtering simulations. The distance of the spike axis from the center of the bubble was varied from 0 nm (spike axis crosses the center of the bubble) to 1 nm (spike axis is tangential to the surface of the bubble), as shown in Fig.11. After equilibrating for \( \approx 1 \) ps under NVE condition, the sample was allowed to evolve for \( \approx 20 \) ps under NPH condition, with a fixed boundary temperature of 300 K.

Fig. 11. Schematic figure to illustrate the positions of “cross” and “tangent” thermal spikes.
4.3 Results and Discussion

4.3.1 Sputtering

Schlutig [16] measured the sputtering yields of UO₂ for several different ions and energies. By comparing these experimental data with my sputtering simulation results, the free parameter $\lambda$ can be determined for my model of UO₂. I chose four stopping powers for the sputtering simulations: $dE/dx = 55.4$ keV/nm, 47.0 keV/nm, 43.0 keV/nm, and 32.8 keV/nm. The sputtering results (blue line) are shown in Fig. 12 as a function of $\lambda$. By comparing the simulation and experimental sets of data in Fig. 13, using only the three highest stopping powers, a value of $\lambda = 3.2$ nm is deduced for my model UO₂ described by the Morelon potential. This value is smaller than the published estimate of $\lambda = 4$ nm [10]. The smaller value of $\lambda$ is expected since higher thermal spike temperatures are needed to compensate for the higher sublimation energy of my model for UO₂ (818.7 kJ/mol), as compared to the experimental value of 616.4 kJ/mol. The Sigmund model of thermal spike sputtering is then used to illustrate this point.

Fig. 13 shows the sputtering yields obtained using the Sigmund model as given by Eq. (7) for each $\lambda$ (the red solid lines). A sublimation energy of 818.7 kJ/mol was assumed in this model, i.e., the value given by the Morelon potential. Notably, the calculated sputtering yields are 2 orders of magnitude smaller than the MD results. A similar discrepancy between Eq. (7) and MD simulations was reported in earlier published results for other materials [6, 18]. The trend in sputtering yields as a function of $\lambda$, however, is well reproduced.
Fig. 12. Sputtering yields obtained from MD simulations and Sigmund model calculations plotted as a function of the e-p coupling constant in $\lambda$ in the two temperature model. The red lines (● symbols) represent Sigmund model with cohesive energy of UO$_2$ from Morelon potential, X eV [17]; black lines (■) - Sigmund model with actual cohesive energy of UO$_2$, Y eV; blue line (▲) MD simulation model with Morelon potential, showing agreement with experimental data for $\lambda = 3.2$ nm; green line (▼) MD yield scaled by the ratio of the Sigmund model yields (see text), showing agreement with the experimental data for $\lambda = 4$ nm.
Next I changed the sublimation energy in the TTM/Sigmund model from 818.7 kJ/mol to 616.4 kJ/mol, to obtain the analytical sputtering yields for real UO$_2$ (black dash lines in Fig. 12). As expected, the decreased sublimation energy results in higher sputtering yields. By then scaling the MD results for my model UO$_2$, using the ratio of these two analytical yields, the green dashed line is obtained, which is argued as an approximation of the sputtering yields for real UO$_2$ in MD. Comparison of these corrected values with the experimental data for UO$_2$ then yields $\lambda = 4.0$ nm. This result now agrees very well with the value of $\lambda$ suggested in previous work [10]. This exercise illustrates two important factors: that for a very reasonable value of $\lambda$, (i) the experimental sputtering yields can be reproduced by my MD model and (ii) sputtering from
swift ions can be explained entirely by thermal spike behavior, no other mechanism need be invoked.

One detail in the experiments that the MD model fails to reproduce is the gradual decrease in sputtering yields at electronic stopping powers, below ≈ 32.8 keV/nm, see Fig. 13. The Sigmund model calculations also fail to show this gradual decrease. I can presently only speculate about the cause of this discrepancy, but I attribute it to the different surface structures employed in the experiment as compared to the MD simulations. The polycrystalline UO₂ samples used in the experiment are likely to contain some fraction of high sputter yield surface orientations, defects, and possibly a non-stoichiometric surface layer. At low energies, these effects are likely to result in a base-line sputter yield which changes slowly with the thermal spike energy. At high energies, however, the surface structure becomes less significant as more of the sputtered atoms come from sub-surface regions of the sample and cratering starts to occur.

Finally I comment on the implicit assumption used in scaling my MD data according to the Sigmund model, viz. that the emission of sputtered atoms is a consequence of independent sublimation events and that collective behavior is not important. As a simple check, I analyzed the cluster-size distribution of sputtered atoms in my MD runs for the highest two stopping power cases, as shown in Fig.14. Clusters larger than four formula units represent only ~ 15% of the total sputtering yield for any of the simulated stopping powers with λ = 3 nm, and 0% with λ = 4 nm (recall that the correct value of λ for my UO₂ potential is 3.2 nm). The majority of the sputtered clusters are thus single UO₂ molecules.
Fig. 14. Cluster-size distribution of sputtered atoms in MD simulation for different electronic stopping powers and different $\lambda$: (a) 55.4 keV/nm; (b) 47 keV/nm.
4.3.2 Bubble re-solution

MD simulation of bubble re-solution was calculated in UO$_2$ using the value, $\lambda = 3.2$ nm, which gave the best agreement between the experimental data and the MD sputtering yields using the Morelon potential. For each stopping power, two geometries were considered (as shown in Fig.11): (1) the axis of the thermal spike cylinder passing through the center of the bubble (center), and (2) the axis of thermal spike passing tangentially along the outer bubble radius. Two events for each condition were run. Unlike simulations of recoil re-solution, two events provide sufficient statistics for thermal spike mechanisms. The results are compiled in Table 3. The main results are that (i) Xe can indeed be re-dissolved in the matrix due to the thermal spike and (ii) the number of Xe atoms re-dissolved increases with increasing electronic stopping power. The number of re-dissolved gas atoms, moreover, is somewhat smaller for the center of the thermal spike located at the periphery of the bubble than at the center of the bubble. For the lowest fission fragment energy tested, 32.8 keV/nm, no re-solution is observed in either geometry. Thus, no Xe atom re-solution can be expected for fission fragments in UO$_2$, regardless of the distance between trajectory of the fission fragment and the bubble center, since the electronic stopping powers of fission fragments do not exceed $\approx$22 keV/nm in UO$_2$ [12]. I will return to this important point, below.

Table 3. Number (and percentages) of re-dissolved Xe atoms from bubbles containing 79 Xe atoms. Results are given for different electronic stopping power values and two different thermal spike positions, through the center of the bubbles and tangentially along the surface of the bubbles. Each data point is averaged from two MD runs.

<table>
<thead>
<tr>
<th>Se (keV/nm)</th>
<th>No. of re-dissolved Xe atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>center</td>
</tr>
<tr>
<td>55.4</td>
<td>11.5 (14.6%)</td>
</tr>
<tr>
<td>47.0</td>
<td>5 (6.3%)</td>
</tr>
<tr>
<td>32.8</td>
<td>0 (0%)</td>
</tr>
<tr>
<td></td>
<td>tangentially</td>
</tr>
<tr>
<td>55.4</td>
<td>9.5 (12.0%)</td>
</tr>
<tr>
<td>47.0</td>
<td>2.5 (3.2%)</td>
</tr>
<tr>
<td>32.8</td>
<td>0 (0%)</td>
</tr>
</tbody>
</table>
Fig. 15 shows cross sectional slices through the computational cell during the late stages of the thermal spike, \( t \approx 100 \) ps. Most of the UO\(_2\) lattice has recrystallized. The re-dissolved Xe atoms are frozen at their respective positions, as substitutionals for U atoms. Fig. 16 illustrates a typical process of bubble re-solution as a function of time for the 55.4 keV/nm stopping power case. From consideration of Fig. 16 and Fig. 17, it is seen that all movement of re-dissolved Xe atoms takes place within the first 30 ps of initiating the event. No atoms, moreover, are displaced further than the maximum extent of the molten zone. The displacement of the Xe atoms thus occurs via diffusion within the molten zone surrounding the ion track. This is expected, of course, since the simulations only considered the thermal spike associated with the fission fragment, not the energetic recoil events.
Fig. 15. Snapshots of the cross section of UO$_2$ + Xe bubble samples: Xe (large blue spheres), U (medium green spheres), and O (small red spheres). Location of the spike indicated in the inserts. (a) U ion, 55.4 keV/nm, at 116.02 ps, thermal spike axis passing through the bubble center; (b) U ion, 55.4 keV/nm, at 118.84 ps, thermal spike axis is tangent to the bubble surface; (c) U ion: 47.0 keV/nm, at 95.12 ps, the thermal axis passing through the bubble center; (d) U ion, 47.0 keV/nm, at 100.98 ps, thermal spike axis is tangent to the bubble surface. In the high stopping power sample the bubble cavity increases in size and numerous dislocations can be observed around the bubble.
Fig. 16. Snapshots of the bubble re-solution process for 55.4 keV/nm stopping power case. The direction of thermal spike is perpendicular to the thin slice of UO$_2$ + Xe bubble sample, and the thermal spike axis passes through the bubble center. (a) $t = 0$ ps; (b) $t = 0.4$ ps, the molten zone created by the thermal spike starts to grow; (c) $t = 10$ ps, the molten zone reaches its maximum extent, and several Xe atoms are re-dissolved via diffusion within the molten zone; (d) $t = 120$ ps, the UO$_2$ lattice has recrystallized.
Fig. 17. The solid black curve shows the square root of the mean square relative displacement (MSRD) of only the re-dissolved Xe atoms for the 55.4 keV/nm stopping power case as a function of time. The radius of the molten zone is indicated by the dashed blue line. The diffusive motion of the re-dissolved Xe atoms saturates at about 30 ps due to falling temperatures in the periphery of the spike. By 80 ps the re-dissolved Xe atoms are frozen in the recrystallized matrix. The solid red line represents the average temperature ($T_{\text{avg}}$) in the center region of the thermal spike ($r < 2.0$ nm).

While the above simulations provide a clear picture of how fission can re-dissolve fission gas bubbles in thermal spikes created by fission fragments, it should be noted that the number of re-dissolved Xe atoms calculated by my model represents a maximum value. This is because the value of $\lambda$ is fixed by using experimental sputtering yields. As I discussed, the effective value of $\lambda$ is lower than what is expected in real UO$_2$, since the sublimation energy deduced from the
Morelon potential for UO$_2$ is larger than the measured value. I used this value in the simulations of bubble re-solution. Unlike sputtering, however, bubble re-solution should not depend directly on sublimation energy, but rather on a quantity more closely related to the heat of fusion since liquid diffusion is involved. The melting temperature of the Morelon potential does reproduce the correct value for real UO$_2$. Consequently, for bubble re-solution, a value closer to to $\lambda = 4.0$ nm which I deduced from scaling the sputtering yields for real UO$_2$, is likely to be more appropriate. Therefore simulations using a value of $\lambda = 4.0$ nm were performed as well and in this case I failed to observe any Xe re-solution for stopping powers less than $\approx 47$ keV/nm. Thus the conclusion is that Xe re-solution induced by thermal spikes is negligible during fission fragment irradiation, is robust and not sensitive to the details of my simulation model.

4.3.3 Heterogeneous re-solution rate

I note that the fall-off of re-solution values as the thermal spike axis shifts from the center to the tangent configuration indicates that the cross section of a fission fragment is no larger than $\approx 5$ nm$^2$. Averaged over the whole decay spectrum, a single fission fragment travels only about 0.5 $\mu$m in the fuel matrix while its stopping power exceeds 15 keV/nm. For typical bubble sizes and number-densities, therefore, each fission fragment interacts with $\approx 1$-5 bubbles. Since I calculated that the number of re-dissolved Xe atoms for a fission fragment in UO$_2$ is zero, the total resolution rate per fission fragment will also be zero. Even using a value of electronic stopping power = 55.4 keV/nm, which is well over twice the actual value of a fission fragment in UO$_2$ ($\approx 22$ keV/nm), the total resolution rate is only $\approx 10$-50 Xe atoms per fission fragment. In Chapter 3, it has been shown that the homogeneous re-solution mechanism yields about five re-dissolved atoms per fission fragment. This value is only somewhat less than that due to
heterogeneous resolution at the unrealistically high stopping power of 55.4 keV/nm. The simulations also demonstrate that the hypothesis that heterogeneous re-solution leads to total bubble destruction is highly unlikely to be true[3, 34, 35]. From these considerations, I conclude that heterogeneous fission gas resolution cannot be a significant contribution to bubble evolution in UO₂ fuels.
Chapter 5. Conclusion

5.1 Summary of Homogeneous Re-solution

The homogeneous re-solution of Xe fission gas bubbles in UO\textsubscript{2} is investigated by combined MC and MD simulations. The key results of this part can be summed as followed:

(1) By using a new 3D-TRIM code, a full spectrum of Xe recoil energy under fission fragment irradiation is obtained.

(2) The probability for Xe atoms to leave their bubbles as a function of Xe recoil energy is obtained by MD simulation. The threshold energy for fission gas atom to escape is about 300 eV.

(3) The full displacement histogram of Xe atom obtained from MC simulations alone and from the weighted summation of MD/MC agree well with each other.

(4) The re-solution parameter $b_{\text{hom}} = 2 \times 10^{-6}$ s$^{-1}$ for homogeneous re-solution calculated from my simulations disagrees considerably from past estimates. It is a factor of one to two orders of magnitude smaller than estimated in previous studies. It is reasonable to believe that MC & MD simulations provide better accuracy than the previous analytical calculations.

5.2 Summary of Heterogeneous Re-solution

I have examined sputtering and heterogeneous bubble re-solution using a hybrid model consisting of the TTM and MD simulations. The key conclusions are:

(1) Comparison of experimental sputtering data with MD simulations yielded an e-p coupling constant of $\lambda = 3.2$ nm in the TTM. This value is lower than expected in real UO\textsubscript{2}, but it is necessary in my model to compensate for the high sublimation energy given by the Morelon
potential. Scaling of my results to the correct sublimation energy using the Sigmund model as a
guide, however, yields a value of $\lambda = 4.0$ nm, which is the value obtained by other means [10].

(2) Xenon bubble re-solution was then simulated for ions having different electronic stopping
powers. Re-solution was observed only for stopping power greater than $\sim 35$ keV/nm. The total
re-solution rate is only $\sim 10$-50 Xe atoms per fission fragment for the extremely high stopping
power (55.4 keV/nm). The number of re-dissolved Xe atom for a typical fission fragment in UO$_2$
($\sim 22$ keV/nm) is zero. Thus the heterogeneous fission gas re-solution cannot be a significant
contribution to bubble evolution.

5.3 Future Plan

In the future, I will focus on experimental work to test the simulation models developed here.
I plan to employ transmission electron microscopy and ion beam analysis to determine how real
Xe bubbles evolve under various irradiation conditions. Since UO$_2$ crystals present many
regulatory issues, I will perform my research on Yttria-stabilized-Zirconia single crystals, which
have the same crystalline structure as Uranium dioxide.
References

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Author’s Biography

Mengqi Huang graduated from Tsinghua University with a Bachelor of Engineering in Engineering Physics in 2006. After college graduation, she entered University of Illinois at Urbana-Champaign to pursue her Master and Ph.D degrees in Nuclear Engineering. Her research project is to study bubble evolution in nuclear materials by both simulations and experiments.