Molecular dynamics study of fission gas bubble nucleation in UO_2

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Abstract

Molecular dynamics (MD) simulations are used to study helium and xenon gas bubble nucleation in UO_2 . For helium bubbles, the pressure release mechanism is by creating defects on the oxygen sublattice. Helium atoms diffuse away from the bubbles into nearby bulk UO_2 , thus forming a diffuse interface. For xenon bubbles, over-pressurized bubbles containing xenon can displace uranium atoms, which tend to aggregate around the xenon bubble as a pressure release mechanism. MD simulations of xenon atoms in pre-existing voids suggest that xenon atoms and the replaced uranium atoms occur in a 1:1 ratio, although kinetic factors may reduce that ratio depending on availability of xenon atoms and vacancies around the bubble. Finally, MD simulations suggest that for small bubbles (1-5 xenon atoms), the xenon bubble nucleus at UO_2 grain-boundaries has much lower formation energy compared to that of bubbles of similar sizes in the bulk. However, when the xenon bubble grows into larger sizes, this energy difference is reduced.

I. INTRODUCTION

The volatile fission products in nuclear fuels such as uranium dioxide (UO_2) have low solubilities and tend to precipitate into bubbles, contributing to the swelling and ultimately failure of the fuels¹. Understanding of the fission gas bubble nucleation mechanism in UO_2 fuel is thus technologically important. At the very early stage of gas bubble nucleation in the oxide fuel, the small bubble size also poses a challenge for experiments, making it difficult to characterize the physical processes involved. Modeling and simulation studies at the atomistic scale could provide important insights, complementary to experimental efforts. The atomistic level results can also inform higher scale (*e.g.*, mesoscale) models for prediction of fuel performance.

Xenon (Xe) is the dominant volatile fission product^{2,3}, which in UO_2 forms Xe bubbles, and may also be released from the bulk. Several molecular dynamics (MD) studies of Xe bubble behavior in UO_2 have been carried out⁴⁻⁷. Moore *et al.*⁴ found that the Xe atom cluster forms from individual Xe atoms occupying Schottky sites, facilitated by a supersaturation of Schottky vacancies in UO_2 . Tian *et al.*⁵ carried out constant pressure MD simulations of a single Xe bubble in UO_2 to estimate the bubble pressure and radius at different Xe concentrations in bulk UO_2 . Recent work by Murphy *et al.*⁶ studied the free energies of Xe from point defects to small bubbles in UO_2 . Finally, Jelea *et al.* also studied the behavior of Xe bubbles in UO_2 and their influence on its swelling. In this paper, using the Basak type of empirical potential⁸, MD simulations are carried out to study the Xe and helium (He) bubble nucleation in UO_2 . Even though He concentrations are small in nuclear fuels, He has a much higher mobility than Xe in UO_2 , thus offering the opportunity to study migration in a much more effective way using MD simulations. Second, a comparative study of the He and Xe behavior in oxide fuel is also of interest. Earlier, Parfitt and Grimes carried out MD studies of radiation enhanced He resolution in UO_2 ⁹.

This paper is organized as follows. First, the methodology is introduced. Then simulations of bubble nucleation in bulk UO_2 , or homogeneous nucleation, are reported, followed by simulations of heterogeneous nucleation at grain-boundaries (GBs) in UO_2 . Finally, we conclude with a summary.

II. METHODS

The Basak potential⁸ is used to describe U-U, U-O interactions in UO_2 . The Basak potential is comprised of a Buckingham term plus a Morse term. This potential was shown to be one of the better potentials for describing UO_2 , especially for defect properties^{10,11}. For the Xe- UO_2 interaction, the parameters fitted by Geng *et al.*¹⁴ are used. The Basak-Geng potential was also used in our earlier studies of the transport mechanism for transient migration of Xe, diffusion prefactors of Xe in UO_2 ^{11,12}, and the Basak potential was used in our earlier study of thermal conductivity of UO_2 ¹³. For the He- UO_2 interaction, the parameters fitted by Grimes *et al.*¹⁵ are used. We employ the parallel MD code LAMMPS¹⁶ for the simulations, and the particle-particle particle-mesh solver (pppm) as implemented in LAMMPS is used to compute the long-range Coulombic interactions.

In order to describe regions of high He or Xe concentrations in UO_2 , such as in gas bubbles, the interactions among He or Xe atoms need to be taken into account. For He-He interactions, we use Beck's form¹⁷,

$$V_{ij} = A \exp(-\alpha r - \beta r^6) - \frac{0.869}{(r^2 + a^2)^3} \left(1 + \frac{2.709 + 3a^2}{r^2 + a^2}\right) \quad (1)$$

where A , a , α and β are fitted parameters. The parameter values used¹⁷ are $A = 398.7$ eV, $a = 0.0675$ nm, $\alpha = 43.90$ nm⁻¹, and $\beta = 374.6$ nm⁻⁶. For Xe-Xe interactions, we use Tang and Toennies form¹⁸,

$$V_{ij} = A \exp(-\beta r) - \sum_{2n=6}^{\infty} \left[1 - \sum_{k=0}^{2n} \frac{(br)^k}{k!} \exp(-br)\right] \frac{C_{2n}}{r^{2n}} \quad (2)$$

where A , b , C_{2n} are coefficients. In practice, a summation up to $n = 5$ is used. The parameter values used¹⁸ are $A = 951.8$ eV, $b = 16.81$ nm⁻¹, $C_6 = 0.02859$ eV·nm⁴, $C_8 = 1.281 \times 10^{-4}$ eV·nm⁸, and $C_{10} = 6.198 \times 10^{-5}$ eV·nm¹⁰. This potential was shown to reproduce the effect of pressure on both Xe gas and solid up to 50 GPa reasonably well¹⁹.

We would like to comment on the appropriateness of combining the Basak UO_2 potential with other potentials for He and Xe. The He- UO_2 interaction was originally developed together with the Buckingham UO_2 potential¹⁵. Govers *et al.*²⁰ have studied the transfer of this set of interactions to the Basak potential for UO_2 , by assessing different incorporation energies. A consistent result was obtained, details in Ref. 20. In the original development of He- UO_2 model, there is no He-He interaction. Govers *et al.*²⁰ used a Lennard-Jones potential for the He-He interaction. A more elaborate potential for He-He interaction such as the

Beck's form¹⁷ has been used together with the He- UO_2 potential in the more recent work of Parfitt and Grimes⁹. Our calculations suggest there is negligible effect on the incorporation energies from adding a He-He interaction for the low He concentrations considered. The original Xe- UO_2 interaction developed by Geng *et al.*¹⁴ was consistent with the Basak UO_2 potential. However, the Xe-Xe interaction was expressed in Lennard-Jones form. The Tang and Toennies form¹⁸ is used to replace the Lennard-Jones Xe-Xe interaction due to its excellent description of Xe gas and solid under pressure¹⁹. This replacement also has negligible effect on the incorporation energies for low Xe concentrations. Tang and Toennies¹⁸ also provided He-He interactions in their form. However, we did not evaluate such interaction form in comparison to the Beck's form in this study. In conclusion, our approach to combine potential forms is appropriate.

The microcanonical NVT (constant volume and temperature) ensemble is used for the simulations of He bubbles in UO_2 . The temperature control is performed by the velocity rescaling method as implemented in LAMMPS¹⁶. The same setting is used in the MD simulations of Xe incorporation in pre-existing voids in UO_2 . For simulations of over-pressurized Xe bubble in UO_2 , the Nose-Hoover style NPT (constant pressure and temperature) ensemble is also used to relieve the system pressure. For MD simulations, a time step of 1 fs is used for all cases that do not include any He atoms. Due to small mass of helium atoms, a smaller time step of 0.01 fs is used in these MD simulations. The pressure of fission gas bubble is computed from summation of the diagonal components of atomic stress tensors. It is a local quantity that does not depend on the system size.

III. RESULTS

A. He bubbles in UO_2

For He bubble nucleation in UO_2 simulations, a computational supercell of bulk UO_2 using $6 \times 6 \times 6$ cubic unit cells (2592 atoms for stoichiometric UO_2) with a lattice constant of 0.5454 nm, is first constructed. He atoms are then introduced into a pre-existing Schottky vacancy (consisting of 1 U vacancy and two O vacancies bound together) in the supercell in a one-by-one fashion. There are three types of Schottky trivacancy defects, with two V_O aligned as nearest neighbors in $[100]$ directions (V_{Sch1}), or with two V_O aligned as

next nearest neighbors in $[110]$ directions (V_{Sch2}), or a linear orientation of the O-U-O vacancies along $[111]$ directions (V_{Sch3}). V_{Sch1} has the highest formation energy among the three Schottky defects, 6.3 eV while V_{Sch2} and V_{Sch3} have formation energies close to each other, 5.3 and 5.1 eV respectively. This energetic ordering is in good agreement with density functional theory (DFT) calculations applying the DFT+ U methodology^{21–23}. Recent MD simulations also suggested V_{Sch2} is the most frequently observed of the three types of Schottky defects formed during displacement cascades²⁴. These considerations led to the choice of V_{Sch2} as the Schottky trivacancy defect in this study. After each He atom is introduced, the simulation supercell is ramped up to 1000 K, subjected to MD run for 5 ps and then cooled down to 10 K for 0.1 ps before the final relaxation.

In Fig. 1a, the He bubble pressure calculated from the atomic stress tensors is plotted as a function of the total number of the He atoms in the bubble. The He pressure gradually builds up as more He atoms are introduced. However, at a certain size (~ 20 He atoms), the He pressure is saturated due to a pressure release mechanism. As seen in Fig. 1b, during MD simulations, the uranium sublattice is stable with excess He gas atoms while oxygen interstitials are created, with severe distortions in the oxygen sublattice. As the He bubble is built up with more He atoms, some of the He atoms are pushed away from the gas bubble, facilitated by creation of oxygen defects. This results in a “diffuse” interface between He bubble and the surrounding UO_2 lattice.

Such a pressure-driven process results in pressure release for the over-pressurized He gas bubble. Two implications arise from these results: a) The possibility of diffuse interface for over-pressurized bubbles; b) Due to pressure release, the maximum pressure of He gas is limited to a pressure value that can disrupt the oxygen lattice to create defects, thus facilitating the He atoms to “escape” from the bubble.

Recently, MD studies of over-pressurized He bubble in Fe suggested the bubble growth mechanism via emission of self-interstitial atoms (SIA), and interstitial type dislocation loops^{25–29}. The He bubble growth mechanism in UO_2 is very different from that in Fe, since bonds in oxides are much stiffer and stronger than those in metals making the emission of uranium SIA type defects in oxides not possible.

B. Xe bubbles in UO_2

1. Xe incorporation in pre-existing voids in UO_2

Xe atoms have a much larger atomic size than that of He. Grimes and Catlow³⁰ using Buckingham type empirical potentials, presented a comprehensive model of Xe trap sites as a function of stoichiometry and charge state. Our earlier DFT + U calculations^{21,31} confirm that, under thermodynamic equilibrium, Xe can exist in either V_U (U vacancy), V_{UO} (divacancy), or V_{UO_2} (Schottky vacancy) site depending on the $\text{UO}_{2\pm x}$ stoichiometry. However, for stoichiometric UO_2 , the energy difference between Xe in a V_{UO} or a V_{UO_2} site is very small. When a Xe atom occupies a Schottky vacancy site the system does not need to accommodate any changes in charge state, since both the defect and Xe atom are charge neutral. If the Xe atom instead occupies a U^{4+} vacant site, a change of charge state would be required. In that case, charge accumulation will occur in the Xe bubble, which is less likely to happen. For this reason, we assume that Xe atoms occupy Schottky vacancy sites. It is possible that the bubble may deviate from molecular units at interfaces, which is not considered in our simulations.

A small void is constructed in a supercell of bulk UO_2 containing $11 \times 11 \times 11$ cubic unit cells (15972 atoms without defects) with 13 Schottky vacancy sites. The Xe atoms are then introduced into the void in a sequential way. After each Xe atom is introduced, the simulation supercell is ramped up to 1000 K, then under MD run for 2 ps and then cooled down to 10 K.

The binding energy of the Xe atom to the void is defined as,

$$E_{Xe}^{bind} = E(n) - E(n-1) - E_{Xe}^{atom} \quad (3)$$

where $E(n)$ and $E(n-1)$ are the total energies of the simulation supercell containing n and $n-1$ Xe atoms in the void, and E_{Xe}^{atom} is the isolated Xe atom energy which equals to zero in our calculations due to the nature of empirical potential. In Fig. 2, the calculated binding energy of the Xe atom is shown as a function of the number of Xe atoms in the void. Interestingly, when the number of Xe atoms goes beyond the number of Schottky vacancies in the void (13 in this case), the binding energy of Xe atoms increases significantly, which brings the binding energy to values about 5 eV higher than the binding energy for Xe in a single Schottky vacancy site³² in UO_2 . This implies that it is energetically less favorable to

incorporate additional Xe. This transition is less obvious in terms of the bubble pressure, which is also plotted in Fig. 2.

To check if this phenomenon is a special case, a separate set of MD simulations employing a void in UO_2 containing 19 Schottky vacancy sites are carried out. In Fig. 2, the binding energy as a function of the number of Xe atoms is shown, which validates the finding established in the smaller void case.

This energy transition indicates that a ratio of about 1:1 in terms of Xe atoms and the replaced U atoms in the void is reasonable for Xe bubbles in UO_2 , from a thermodynamic perspective. In real fuels, kinetics could also play a role influencing the Xe/U ratios, depending on the availability of Xe atoms and vacancies around the bubble. This assumes that Schottky sites are available. From Fig. 2, since the binding energies for a Xe atom in the bubbles are always less than that of a Xe interstitial, it is energetically preferable for Xe interstitials to be absorbed by the bubbles.

To further check if equal partitioned of Xe and U (Xe/U ratio = 1) may be metastable or not, the simulation supercell containing 13 Xe atoms is ramped up to 2500 K, and under a much longer MD run of 0.2 ns. No further structural transition is detected that would allow pressure release from the Xe bubble.

2. *Xe bubble growth in UO_2*

Having determined the preferred Xe/U ratio, Xe bubble growth in bulk UO_2 is studied. The algorithm to grow the Xe bubble is based on the energy minimization criteria. The entropy associated with the Xe bubble is not calculated. The simulation starts with a $6 \times 6 \times 6$ supercell of cubic UO_2 . First, a Xe atom occupying a trivacancy site is introduced and then relaxed. Then all the neighboring U atoms near the existing Xe bubble nucleus, up to the second nearest neighbors, are considered for removal. For each U atom considered, two O atoms should be removed to create a Schottky vacancy. We investigate every combination of O-O pairs up to second nearest neighbors. A Xe atom is then introduced into the new Schottky vacancy site and MD simulations are carried out for each possible Xe configuration. From all the possible Schottky vacancy sites that may be replaced by a Xe atom, the lowest energy configuration of Xe occupying a Schottky vacancy site is chosen. After the replacement of a Schottky vacancy by the Xe atom, the above procedure is repeated which

results in Xe bubble growth.

In Fig. 3, the formation energy and pressure of the Xe bubbles are shown as a function of the bubble size. The formation energy of the bubble is defined as,

$$E^f(n) = [E_{bubble}(n) - E_{bulk} + nE_{coh} - nE_{Xe}^{atom}]/n \quad (4)$$

where $E_{bubble}(n)$ is the total energy of simulation supercell containing n Xe atoms in the bubble; E_{bulk} is the total energy of the supercell without the bubble; E_{coh} is the cohesive energy of UO_2 ; E_{Xe}^{atom} is the isolated Xe atom energy which is again set to zero. As the Xe bubble increases in size, the formation energy of the bubble decreases, approaching a saturation limit when the bubble size is between 40 and 50 Xe atoms, with the bubble diameter in the range of 1-2 nm. This suggests that for smaller size bubbles, the growth of the bubble is advantageous due to the gain in total energy (smaller formation energy) while as the bubble grows to a certain size, such energetic advantage is gradually reduced. This can be understood from the reduction of the fraction of surface atoms in the bubble. The pressure of Xe bubbles also saturates at ~ 14 GPa. Experimentally, the measured Xe bubble pressure in UO_2 is estimated to be in the range of 1.6 -15 GPa³³. **Our MD result of the bubble pressure 14 GPa** is in the upper end of this range. More recently, Garcia *et al.*³⁴ estimated that the Xe bubble pressure to be in the range of 2 - 5 GPa, somewhat lower than our MD result. The difference could be attributed to that Xe/U ratio in the Xe bubble being less than 1 in the experimental condition of Ref. 34.

3. Over-pressurized Xe bubble in UO_2

MD simulations are also used to study how the Xe bubble evolves as the bubble is over-pressured with Xe atoms. The intent is to explore the possible mechanism by which the over-pressurized Xe bubble can develop into the equilibrium structure.

We use a $4 \times 4 \times 6$ tetragonal supercell with x in $[110]$, y in $[\bar{1}10]$, and z in $[001]$ directions, containing a total of 2304 atoms. Xe atoms are introduced into a pre-existing single Schottky vacancy site in a sequential way. After each Xe atom is introduced, the supercell is ramped up to 2500 K, under MD run at constant pressure for 20 ps and then cooled down to 100 K, with another constant pressure MD run for 5 ps, followed by structural relaxation using the conjugate gradient algorithm.

In Fig. 4, a snapshot of one such MD event is shown, with 15 Xe atoms introduced at the Schottky vacancy site. The Xe atoms form a compact structure, with nearest neighbors with distances of 0.323 - 0.429 nm. In fact, for a larger simulation supercell and at a higher temperature of 3000 K, a tetrahedron-like Xe bubble structure is developed, with nearest neighbors with distances of 0.352 - 0.421 nm. The wide range of nearest neighbor distances in the Xe bubble clusters suggests that the clusters display a closely packed yet non-solid structure. Such observation is in good agreement with a recent study⁷, which suggested a glassy state for the Xe bubble clusters. The structure of oxygen atoms near the bubble is distorted, and some nearby U atoms are also displaced from their equilibrium positions. Interestingly, these displaced U atoms aggregate around the Xe bubble in a polarized manner. The displaced U atoms form dumbbell interstitials in [100] or [110] directions, or single interstitials. The nearest U-U neighbors in distance ranges from 0.307 nm to $a_0/\sqrt{2}$ (or 0.386 nm, where a_0 is the lattice constant of UO_2 bulk) without any obvious gap in the range.

C. Xe bubble at grain-boundaries in UO_2

As a model for Xe bubbles at GBs in UO_2 , we study a $\Sigma 5$ tilt GB. This boundary was investigated earlier using the Basak potential^{35,36}. The GB supercell is $1.64 \times 1.73 \times 10.43$ nm in size, containing 2160 atoms. A single Xe atom is found to segregate strongly to this GB, by 4.09 eV³⁶ in energy. In the segregation calculations in Ref. 36, the segregation profile was obtained by replacing each U atom with a Xe atom. Calculation of Xe segregation to such a GB when the Xe atom replaces a Schottky vacancy site in UO_2 instead of a U^{4+} vacancy site, shows that the segregation energy is 3.6 eV, in close agreement with previous results.

The collective behavior of Xe segregation to GBs is less straightforward, since Xe atoms in UO_2 tend to aggregate together to form bubbles. When another Xe atom segregates to the GB that already contains one Xe atom, the total energy gained is 4.7 eV for the second Xe atom. In Fig. 5a, the relative energy vs. distance to the GB is plotted. The corresponding lowest energy structure is shown in Fig. 5b. When both Xe atoms segregate to the UO_2 GB and aggregate together, the total segregation energy is about 8.3 eV. When two Xe atoms aggregate together in the bulk only, 4 eV in energy is released. This indicates a stronger thermodynamic driving force for Xe to aggregate at the GB than in the bulk.

Following the algorithm described earlier, the Xe bubble growth at the $\Sigma 5$ tilt GB in UO_2 is also studied. To avoid a significant interaction between the bubbles due to the periodic boundary conditions, a GB supercell in $3.28 \times 3.46 \times 10.43$ nm in size, containing 8640 atoms was used in the simulations. In Fig. 6a, the Xe bubble structure containing 20 Xe atoms is shown. The development of the bubble structure is similar to what was observed in bulk UO_2 . The Xe atoms grow into the bulk-like regions away from the GB plane (where the initial Xe segregation site is located). The shape of the bubble is influenced by several factors, including thermodynamic factors such as the bubble surface energy, Xe bulk energy, and the GB energy, as well as kinetic factors such as Xe diffusion along GB and in UO_2 bulk. The kinetic factors are not captured in current simulations.

In Fig. 6b, the formation energy of Xe bubbles at the tilt GB is plotted as a function of the bubble size and compared to the corresponding results for Xe bubbles in the bulk. At smaller bubble size (1-5 Xe atoms), the Xe bubble nucleus at the GB has much lower formation energy compared to that of similar size bubbles in the bulk. However, when the Xe bubble grows into larger sizes, this energy difference is much reduced. At the size of about 20 Xe atoms (about 1 nm in diameter), the formation energy of Xe bubble approaches that of similar sized bubbles in the bulk. This is due to the fact that as the Xe bubble grows, the majority of Xe atoms in the larger size bubbles are at bulk-like regions away from the GB plane, offering no advantage in the energy compared to that in the bulk.

IV. SUMMARY

MD simulations are used to study He and Xe gas bubble nucleation in bulk UO_2 and at UO_2 GBs. For He bubbles, the pressure release mechanism is by creating defects on the O sublattice. He atoms diffuse away from the bubbles into nearby bulk UO_2 , thus forming a diffuse interface. Due to the larger size of Xe atoms compared to He, over-pressurized bubbles containing Xe atoms can displace U atoms, which tend to aggregate around the Xe bubble, as a pressure release mechanism. MD simulations of Xe atoms in pre-existing voids suggest that Xe atoms and the replaced U atoms occur in a 1:1 ratio, however kinetic factors may reduce that ratio depending on availability of Xe atoms and vacancies around the bubble. For small bubbles (1-5 Xe atoms), the Xe bubble nucleus at GBs has much lower formation energy compared to that of similar size bubbles in the bulk. When the Xe

bubble grows into larger sizes, this energy difference is reduced. At a bubble size of about 20 Xe atoms with 1 nm in diameter, the Xe bubble formation energy approaches that of similar sized bubbles in the bulk.

The low mobility of the U atoms in UO_2 and the many possible arrangements of the O pairs that are associated with a specific U ion in UO_2 add the complexity in the bubble nucleation problem. A combination of Monte-Carlo and MD may provide an improved algorithm.

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³² The binding energy of a Xe atom occupying V_{Sch2} , or 4.9 eV is used. If the Xe atom is in V_{Sch1} or V_{Sch3} site, then the binding energy value will be changed slightly, by -0.1 eV or 0.1 eV respectively.

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FIG. 1: (a) The helium bubble pressure as a function of the total number of helium atoms in the bubble; (b) UO_2 with 39 helium atoms introduced at the Schottky trio vacancy site. Grey atoms: U, red atoms: O, and yellow atoms: helium.

FIG. 2: The Xe atom binding energy as a function of the total number of Xe atoms in pre-existing 13 and 19 Schottky trio voids in bulk UO_2 . The Xe bubble pressure for the 13 Schottky trio void case is also plotted. The DFT value for the binding energy of a Xe interstitial is taken from Ref. 31.

FIG. 3: The formation energy and pressure of Xe bubbles in bulk UO_2 .

FIG. 4: UO_2 with 15 Xe atoms introduced at the trivacancy site. Grey atoms: U, red atoms: O, and blue atoms: Xe. The view is along $[001]$ direction.

FIG. 5: (a) The relative energy vs. distance from the $\Sigma 5$ tilt GB. Due to the periodic nature of the simulation, there are two GBs in the supercell. One Xe atom is assumed to have already segregated to the middle of the second GB. (b) The lowest energy structure of two Xe atoms at the $\Sigma 5$ tilt GB. Grey atoms: U, red atoms: O, and blue atoms: Xe. The view is along the tilt axis $[001]$ direction.

FIG. 6: (a) The Xe bubble structure containing 20 Xe atoms at the $\Sigma 5$ tilt GB. Grey atoms: U, red atoms: O, and blue atoms: Xe. (b) The formation energy of Xe bubbles in bulk UO_2 and at the $\Sigma 5$ tilt GB.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

Figure 6

(a)

Figure 6

(b)