



Article Effects of Point Defects on the Stable Occupation, Diffusion and Nucleation of Xe and Kr in UO₂

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Abstract: Xe and Kr gases produced during the use of uranium dioxide (UO₂)-fuelled reactors can easily form bubbles, resulting in fuel swelling or performance degradation. Therefore, it is important to understand the influence of point defects on the behaviour of Xe and Kr gases in UO₂. In this work, the effects of point defects on the behavioural characteristics of Xe/Kr clusters in UO₂ have been systematically studied using molecular dynamics. The results show that Xe and Kr clusters occupy vacancies as nucleation points by squeezing U atoms out of the lattice, and the existence of vacancies makes the clusters more stable. The diffusion of interstitial Xe/Kr atoms and clusters in UO₂ is also investigated. It is found that the activation energy is ~2 eV and that the diffusion of the interstitial atoms is very difficult. Xe and Kr bubbles form at high temperatures. The more interstitial Xe/Kr atoms or vacancies in the system, the easier the clusters form.

Keywords: UO2; Xe; Kr; occupation; diffusion; nucleation; molecular dynamics

1. Introduction

With the increasing consumption of energy on Earth, the development of nuclear energy has attracted considerable research attention from all walks of life. Nuclear fission is a critical way to generate clean energy, and uranium dioxide (UO₂) is the standard nuclear fuel used in pressurised water reactors [1]. Fission gases, such as Xe and Kr, are among the essential fission products in UO₂ fuel, which can exacerbate the fuel swelling, thereby leading to the interaction between the fuel and the cladding [2–6]. As the fission products deposit energy in the surrounding material, point defects that control the microstructural evolution of the fuel occur. The point defects that survive the initial damage from irradiation in nuclear fuel form extended defects, such as vacancy clusters, dislocation loops, and voids [7]. Numerous experimental and modeling studies have been conducted to improve the understanding of the behaviour of Xe and Kr gases [7–14].

Among all volatile fission products, Xe and Kr have the highest concentration and are mainly studied herein. Previous literature mainly focused on stable configurations with a constant Xe-vacancy ratio; for example, Moore et al. [15] found that clusters of Xe atoms are formed by single Xe atoms occupying Schottky positions, which is caused by the supersaturation of Schottky vacancies in UO_2 . Due to the complexity of the behavioural characteristics of UO_2 fuel materials and Xe bubbles, it is difficult to determine the behavioural mechanism of Xe gases. Consequently, several separation effect experiments have been proposed to simplify complex material systems by describing the physical processes of one or more fission gases to elucidate the underlying behavioural mechanisms. Thus, Zhang et al. [16] briefly explained the mechanism of UO_2 by simulating molybdenum.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). They simulated the stable configuration of Mo by adding Xe atoms and found that Mo was most stable when the Xe-to-vacancy ratio was unity. This study compares the stable occupation of Xe/Kr clusters in perfect and varying defect-containing systems.

The diffusion of the Xe atoms in bulk UO_2 or Xe-vacancy clusters formed by Xe atoms in Schottky vacancies has been studied in previous literature, and even the self-diffusion behaviour of U and O in UO_2 has been studied [17–19]. Yun et al. [20] have investigated the vacancy-assisted diffusion of Xe in UO_{2} , and calculated the incorporation, binding, and migration energies. They found that the tri-vacancy is a significant diffusion pathway of Xe in UO₂. Lawrence [21] discussed the uncertainty in fission gas diffusion coefficients as a function of temperature. Higher activation energies in computing diffusion are usually compensated by higher pre-exponential factors [22]. The diffusion of cations in UO_2 and other related compounds is very slow, at $<10^{15}$ or $<10^{17}$ cm²/s [23,24], even at high temperatures from 1800 to 2000 K, which is one of the highest temperatures achieved in crystal correlation experiments. One of the most commonly used models in fuel performance codes was published by Massih and Forsberg [25–27]. Turnbull et al. [7] analysed this model and other models, and then computed the bulk fission gas diffusion rates, which capture both intrinsic and radiation-enhanced diffusion. This model divides the diffusivity into three regimes. Davies et al. [28] experimentally studied the diffusivity of UO₂ at high temperatures (D_1 , T > 1650 K) and concluded that its activation energy (E_a) and pre-exponential factor (D_0) were 3.04 eV and 7.6 \times 10⁻¹⁰ m²/s, respectively. This study provides significant guidance for the subsequent diffusion studies of UO_2 by many researchers [29–31]. The in-pile diffusion coefficient of UO_2 is close to the intrinsic diffusion coefficient, so it is considered that the radiation-enhanced diffusion coefficient has high uncertainty [32]. However, due to the complex diffusion of Xe at interstitial sites, the diffusion of interstitial clusters has not presently been well described. Therefore, it is necessary to explore the diffusion behaviour of Xe/Kr clusters at octahedral interstitial sites in UO₂ and to explain the relationship between the interstitial and vacancy diffusion mechanisms.

There are two main nucleation mechanisms of fission gases, such as homogeneous and heterogeneous nucleation [33]. Transmission electron microscopy (TEM) images of UO₂–irradiated bubbles show that they are characterised by their high density and small, almost uniform bubble size. Nelson [34] predicted that the nucleation density of bubbles was almost independent of irradiation temperature and fission rate. Evans [35] observed bubbles in Kr- and Xe-irradiated UO₂ using TEM and found that the threshold temperature for bubble nucleation was in the range of 350 °C–500 °C. Michel et al. [36] found subnanometer Xe bubbles in polycrystalline UO₂ under low flux irradiation at 600 °C. Previous studies focused on the vital role of temperature and irradiation dose in the nucleation and growth of bubbles in UO₂, but there are few studies on defect concentration. Hence, studying the formation of Xe/Kr clusters in systems with different defect concentrations is important for subsequent nucleation studies.

Thus, the influence of defects in materials on Xe/Kr gas clusters is worth further investigation. Therefore, it is crucial to investigate the effect of point defects on Xe/Kr clusters in UO_2 to understand the evolution of fuels.

2. Simulation Method

2.1. Interatomic Potential

The interatomic interaction potentials of UO₂ have been widely reported previously. Among them, the potentials reported by Basak et al. [37], Morelon et al. [38], and Cooper et al. [39] are more commonly used. For the further addition of fission gas, Xe, based on UO₂, and UO₂–Xe interatomic interaction potentials have been mainly developed by Geng et al. [40], Chartier et al. [41], Thompson et al. [42], and Cooper et al. [43]. For the UO₂–Kr system, only one interatomic interaction potential developed by Cooper et al. [43] can be presently used. These UO₂–Xe and UO₂–Kr potentials use the Xe and Kr potentials proposed by Tang and Toennies [44].

Herein, the UO₂ potential reported by Cooper et al. [39] is adopted to describe the U–U, U–O, and O–O interactions. This potential reproduces a range of thermophysical properties, such as the lattice parameter, bulk modulus, enthalpy, and specific heat at temperatures between 300 and 3000 K, as well as some defect properties in UO₂. In addition, this potential's bulk modulus and elastic constant are more accurate and in accordance with experimental values [45]. The Xe–Xe interaction is described by the Tang–Toennies potential [44]. Further, the interactions of Xe–U and Xe–O have been described by Thompson et al. [42], and are very flexible and can be applied to a wide variety of potential forms and materials systems, including metals and EAM potentials. For the UO₂–Kr system, the interaction potential developed by Cooper et al. [43] is adopted.

2.2. MD Simulation Setup

An MD simulation programme, LAMMPS (7Aug19 version) [46], is employed herein for all simulations. Images of atomic configurations were produced with the visualisation tool OVITO (3.5.0 version, Darmstadt, Germany) [46]. The Wigner–Seitz (W–S) cell method determined the type and position of the interstitial atoms or vacancies [47,48]. The time step was set as 0.001 ps for all MD simulations. The temperature was controlled via a Nose/Hoover temperature thermostat, and the periodic boundary condition was used. For static relaxation, the energy minimisation was performed, and the minimisation algorithm was set as the conjugate gradient method (cg). The specific simulation processes for different behaviours differ, and the details of the different simulations are described as follows.

2.2.1. Stable Occupation of Xe/Kr Cluster in UO₂-Containing Point Defects

In addition to studying the stable occupation of Xe(Kr) clusters in defect-free bulk UO₂, the influence of different defects in UO₂ on the stable occupation of Xe(Kr) clusters was studied, such as U, O, UO double, Schottky, and double Schottky vacancies. A cubic box of 25 $a_0 \times 25 a_0 \times 25 a_0$ (a_0 is the lattice constant of the UO₂ fluorite structure at 0 K) containing 187,500 atoms was used. MD simulation was performed after generating each configuration to equilibrate the system. After energy minimisation, the first atom was introduced into the system. The site with the lowest energy formation was searched through energy minimisation again to determine the stable site of the first atom. Afterwards, the second atom was introduced around the first atom, and the process was repeated to obtain a stable space for the two atoms. Further, the same process was performed until stable positions for six atoms were found successfully.

The formation energy of a Xe/Kr cluster in defect-free UO₂ bulk is defined as follows:

$$E_{N \text{ Xe/Kr}}^{f} = E_{N \text{ Xe/Kr}}^{Int} - E^{P} - N E^{\text{Xe/Kr}}$$
(1)

where $E_{N \text{ Xe/Kr}}^{Int}$ is the energy of the UO₂ system containing the Xe (or Kr) cluster, E^{P} is the energy of perfect UO₂, N is the number of Xe (or Kr) atoms, and $E^{\text{Xe/Kr}}$ is the energy of a single-isolated Xe (or Kr) atom (this value is zero for the interatomic potential under consideration).

The formation energy of a Xe/Kr cluster in defective UO₂ is defined as

$$E_{N \text{ Xe/Kr}}^{f} = E_{N \text{ Xe/Kr}}^{Int} - E_{VD}^{m} - NE^{Xe/Kr}$$
⁽²⁾

where $E_{N \text{ Xe/Kr}}^{Int}$ is the total energy of the system with the Xe (or Kr) cluster added on VD (represent different vacancy-type defects), E_{VD}^{m} is the total energy of systems containing the VD, *m* is the number of vacancies for VD, N is the number of Xe (or Kr) atoms, and $E^{\text{Xe/Kr}}$ is the energy of a single-isolated Xe (or Kr) atom.

The binding energy of an additional X (X = Xe or Kr) atom to a VD-X cluster in UO_2 is defined as follows:

$$E^{b}(X + VD - X cluster) = E^{f}(X) + E^{f}(VD - X cluster) - E^{f}(X + VD - X cluster)$$
(3)

where $E^{\dagger}(X)$ is the formation energy of a Xe (or a Kr) atom located on the most stable interstitial site in bulk UO₂.

2.2.2. Diffusion of Xe/Kr Cluster in UO₂

Generally, diffusion in solids occurs with point defects [18]. The point defect concentration is thermally activated, and it increases as the temperature increases. Migration is also a thermally activated process, accelerated by an increasing temperatures. Hence, the diffusion coefficients and diffusion energy barriers of small Xe and Kr clusters (number of atoms < 6) in UO₂ are calculated by the mean square displacement (MSD) method, which can intuitively reflect the strength of the self-diffusion ability of particles. A box of 10 $a_0 \times 10 a_0 \times 10 a_0$ (a_0 is the lattice constant of the UO₂ fluorite structure at different temperatures from 1800 to 2300 K) containing 12,000 atoms was used. The total simulation time is up to 5 ns, with a timestep of 1 fs.

The Arrhenius's equation can express the temperature dependence of the diffusivity,

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{4}$$

where *D* is the diffusion coefficient, E_a is the diffusion barrier, *T* is the temperature, D_0 is a pre-diffusion factor, and k_B is the Boltzmann constant. Taking the logarithms of both sides of the above equation give

$$\ln D = \ln D_0 - \frac{E_a}{k_B T} \tag{5}$$

Therefore, if the ln *D* at different simulated temperatures is obtained, E_a can be obtained by linear fitting, whereas the diffusion coefficient *D* at different temperatures can be obtained by the MSD method:

$$D_T = \frac{(MSD)_T}{2dt} = \frac{\langle \Delta r(t)_T^2 \rangle}{2dt}$$
(6)

In the simulation process, a long simulation time and short coordinate position output intervals are used to obtain the atomic coordinate information. The results are obtained by averaging the MSD trajectory segmentation severally.

2.2.3. Nucleation of Xe/Kr Cluster in UO₂-Containing Point Defects

MD simulation was performed to simulate the nucleation process of Xe bubbles. Five systems with sizes of $10 a_0 \times 10 a_0 \times 10 a_0$ (a_0 is the lattice constant of UO₂ fluorite structure at the temperature of 2500 K) were studied, which are mainly perfect bulk without defects, with 1% vacancies concentration, with 2% vacancies concentration, with 1% interstitial concentration, and with 2% interstitial concentration. Then, 2% and 5% concentration of Xe/Kr atoms were added to the different systems, and the Xe/Kr atoms were randomly and uniformly located at octahedral interstitial sites. The specific simulation process is as follows.

After static relaxation of the initial system relaxation of the above configuration with a high temperature, the temperature was raised to 2500 K to accelerate the diffusion of Xe/Kr atoms. Then, the simulation was conducted in the NVT ensemble for 20 ns. Finally, the obtained configuration was subjected to static relaxation to ensure a stable configuration.

3. Results and Discussion

3.1. Stable Occupation of Xe/Kr Cluster in UO₂-Containing Point Defects

By studying the position and energy changes of Xe/Kr atoms in UO_2 , it is found that, after adding Xe/Kr atoms into UO_2 , the Xe/Kr atoms move to the octahedral interstitial sites after structural optimization. Figure 1a shows that, when a Xe atom is randomly inserted into the bulk UO_2 , it moves to the nearest octahedral site. The energy is lowest at the octahedral interstitial site, with a formation energy of 9.79 eV. The phenomenon is the

same for the Kr atom, but, because the Kr atom is smaller than the Xe atom, its formation energy is smaller at 8.45 eV. When two interstitial Xe or two interstitial Kr atoms are added into UO_2 , after relaxation, the energy of the two atoms forming a dimer is the lowest. The formation energies of Xe_2 and Kr_2 are 16.44 and 15.60 eV, respectively. The stable structure of three interstitial atoms is shown as an equilateral triangle. The formation energies of Xe_3 and Kr_3 are 22.49 and 21.53 eV, respectively. After the addition of the fourth Xe atom and complete relaxation (Figure 1b), the positions of the four atoms appear as triangular cones at different octahedral sites. The first lattice U atom is squeezed out of the cluster, and the Xe atoms cluster around the U vacancy. However, the interstitial U atom moves away from the cluster, and the formation energy of Xe₄ is 27.92 eV. The Kr₄ cluster slightly differs from Xe₄. The four Kr atoms are located on different octahedral gaps, forming a planar quadrilateral. However, no interstitial atoms are squeezed out of clusters, and the formation energy of Kr₄ is 27.38 eV. After inserting the fifth atom, the first lattice U atom in the Kr cluster is squeezed out. After adding the sixth atom, the second lattice U atom is squeezed out of the Xe cluster (Figure 1c). The formation energies of Xe₅, Kr₅, Xe₆, and Kr₆ are 32.19, 32.41, 39.79, and 37.21 eV, respectively.



Figure 1. Relaxation configuration diagrams of different UO_2 systems after adding Xe atoms. (**a**–**c**) are 1, 4, and 6 Xe in the defect-free system, respectively; (**d**–**f**) are 1, 3, and 6 Xe in the system containing U vacancies, respectively. (**g**–**i**) are 1, 3, and 6 Xe in the system containing double Schottky vacancies, respectively. The dashed frames are the schematics of the squeezed interstitial atoms. The red, yellow, green, and purple balls represent U atoms, Xe atoms, U vacancies, and U interstitial atoms, respectively. The O atoms are ignored.

Additionally, the stabilities of Xe/Kr atoms in configurations with different defects are compared. As shown in Figure 1d, in the configuration containing a single U vacancy, the addition of one Xe/Kr atom occupies the vacancy. When adding three or six Xe/Kr atoms in this system (Figure 1e,f), the atoms occupy the vacancy and distribute in the octahedral interstitial sites around the vacancy. The configuration of a single O vacancy is consistent with that of a single U vacancy. In the case of the UO double vacancy, one Xe/Kr atom was added to occupy the U vacancy. Two Xe/Kr atoms are evenly distributed into the central

region of the two vacancy centres; when multiple atoms are added, they take the central region as the origin and occupy the surrounding octahedral interstitial sites. Figure 1g–i shows that, when there is a double Schottky vacancy, the Xe/Kr atom moves to the position near the central vacancy region. When more than one atom is present in the box, the Xe/Kr atoms are mainly distributed in the central vacancy region or the surrounding octahedral interstitial sites.

Figure 2 shows that, as the number of Xe/Kr atoms increases, the formation energy of the configuration with various defect types increases gradually. The formation energy of the O vacancy was 5 eV larger than that of the U vacancy on average at each stage. The Xe/Kr atom was more accessible to form in the U vacancy than in the O vacancy. Further, Figure 2 shows that the formation energy of Xe/Kr clusters in the six systems can be divided into three layers. The first layer contains the bulk UO_2 and the system with O vacancy. They are characterized by no U vacancy, and the formation energy difference is very small. The second layer contains U, UO double, and Schottky vacancies, which contain only one U vacancy. The third layer contains double Schottky vacancies, which contain two U vacancies. Additionally, the volume of the U vacancy is much larger than that of the O vacancy, which provides more space for clusters. Thus, the stability of Xe/Kr clusters depends on the number of U vacancies. Figure 3 shows that, as the number of Xe/Kr atoms increases, the binding energy of Xe/Kr and cluster decreases and stabilises. The overall trends of adding Xe or Kr atoms are consistent, and the changes caused by different defects in the system are similar. The double Schottky configuration has a more vital ability to adsorb Xe atoms and weaken. When additional atoms are adsorbed to a certain extent, the adsorption capacities of all defective configurations tend to be the same, which mainly depends on the number of vacancy defects contained in the configurations.



Figure 2. The formation energy (eV) of (**a**) Xe clusters and (**b**) Kr clusters in UO₂ with and without defects as a function of the number of Xe or Kr atoms in the formed cluster.



Figure 3. The binding energy (eV) of (**a**) an additional Xe atom and (**b**) an additional Kr atom to a cluster as a function of the number of Xe or Kr atoms in the formed cluster.

3.2. Diffusion of Xe/Kr Cluster in UO₂

Based on empirical potential calculations, the diffusivity of Xe/Kr clusters in bulk UO₂ has been calculated. Since the first U interstitial atom was excited by adding four Xe atoms or five Kr atoms to the bulk UO₂, we studied the Xe/Kr clusters with less than four atoms. Xe usually diffuses due to a vacancy-assisted mechanism. The diffusion of Xe at U, O, UO, one U, two O vacancies, and vacancy clusters (comprising two U vacancies and zero, one, or two O vacancies) has been studied in most studies. Earlier studies concluded that Xe atoms occupied trap sites that contained at least one uranium vacancy and, in many cases, one or two additional oxygen vacancies [49,50]. The conclusion showed that triple vacancy was the main diffusion pathway of Xe in UO_2 . Previous DFT data [51-53] have shown the activation energies of Xe from 2.87 to 3.95 eV and prediffusion factors from 5×10^{-4} m²/s to 2.9×10^{-12} m²/s. Due to experimental factors, Lawrence et al. [21] found that the diffusion coefficients between different studies have many orders of magnitude. Herein, the interstitial diffusion mechanism of Xe/Kr was investigated. The simulation estimated the diffusion barrier of Xe atoms as 2.11 eV and the pre-diffusion factor index as 1.8×10^{-5} m²/s at temperatures between 1800 and 2300 K, and the simulation estimated the diffusion barrier of Kr atoms as 2.31 eV and the prediffusion factor index as 0.12×10^{-3} m²/s. Tables 1 and 2 show the detailed data of the Xe/Kr atom and clusters. Torres et al. [54] calculated the migration energies of Xe/Kr in bulk UO₂ by a direct mechanism, and the results were 4.09 and 4.72 eV, respectively.

Table 1. Diffusion energy barrier and diffusion prefactor of small interstitial Xe clusters in UO₂.

Number of Xe	Diffusion Energy Barrier (eV)	Diffusion Prefactor (m ² /s)
Xe ₁	2.11	$1.8 imes 10^{-5}$
Xe ₂	2.15	$0.35 imes10^{-5}$
Xe ₃	2.07	$0.25 imes 10^{-5}$

Table 2. Diffusion energy barrier and diffusion prefactor of small interstitial Kr clusters in UO2.

Number of Kr	Diffusion energy Barrier (eV)	Diffusion Prefactor (m ² /s)
Kr ₁	2.31	$0.12 imes 10^{-3}$
Kr ₂	1.89	$0.20 imes 10^{-5}$
Kr ₃	1.95	$0.12 imes 10^{-5}$

The activation energy of the Xe cluster was ~2 eV, and the diffusion coefficient can be seen in Figure 4, which shows the diffusion coefficient for Xe and Kr clusters in bulk UO_2 . Figure 4 illustrates the difficulty of cluster diffusion. It is consistent with the data proposed by Davies et al., indicating that clusters are not easy to diffuse. By analysing the movement of the atoms during migration, we find that, when studying the diffusion of individual atoms, evidently, individual atoms are fast and have a wide range of motion. When studying clusters with two atoms, the atoms move mainly by the rotating bypass method. In the diffusion process, atom A was stapled at random, and then atom B rotated around atom A to find a stable position, and then spread over continuously. When there were three atoms in a cluster, a small cluster was formed with one of the atoms pinned together, and the remaining atoms rotated slightly, causing the whole cluster to move and spread out. These trajectories suggested that the diffusion of interstitial clusters is more complicated and may require more complex conditions. In fact, there are little data on experimental interstitial diffusion.



Figure 4. The diffusion coefficient for (**a**) Xe and (**b**) Kr clusters in bulk UO₂. The lines are linear Arrhenius fits.

3.3. Nucleation of Xe/Kr Cluster in UO₂-Containing Point Defects

Here, the Xe/Kr atoms cluster together at high temperatures. A similar phenomenon occurred while studying Mo. Zhang et al. [16] studied the clustering process of Xe atoms dispersed in Mo at high temperatures. They observed the formation of Xe bubbles when the concentration of Xe atoms exceeded the threshold concentration value. In this paper, we studied randomly distributed Xe/Kr atoms at octahedral interspaces in UO₂. Figure 5 shows that, as the relaxation progresses to 5 ns, small Xe clusters form, and then the tiny clusters gradually grow larger by absorbing extra Xe atoms. The clusters are more evident and are larger, almost stable clusters at relaxation to 10 ns. To ensure the stability of clusters, we observed the clustering phenomenon until 20 ns, which was almost not very different from that at 10 ns. The simulation results were consistent with the growth model proposed by Turnbull [55]. The bubbles were heterogeneously nucleated in the wake of fission fragments. They grew by collecting gas by atomic diffusion for a time controlled by a resolution process.



Figure 5. System evolution of Xe clusters at different times at 2500 K (the yellow balls represent Xe atoms, the red circles mark the clusters); (**a**) 0 ns, (**b**) 5 ns, (**c**) 10 ns, (**d**) 20 ns.

In the system with the same defect concentration, the number of clusters formed increases as the interstitial Xe/Kr atomic concentration increases. Figure 6 shows that the number and size of clusters in the system with 5% interstitial Xe atoms added significantly exceeded those with 2% interstitial Xe atoms. The former are more likely to form larger clusters, with a considerable number of clusters over 50 atoms or even over 100 atoms in size. In comparison, the latter are mainly distributed in 2 to 50 atoms.

When there are equal interstitial atom concentrations, the system with more vacancies is more likely to form larger clusters. Similarly, the more interstitial atoms prearranged in the system, the more difficult it is for the Xe/Kr atoms to aggregate during relaxation. The system mainly forms many small clusters ranging in size from 2 to 10 atoms.

The W–S cell method was used to analyse the defect results of the five systems. Three systems were selected for a detailed demonstration, namely the defect-free system (bulk), the system with 1% vacancy concentration (1% vac), and the system with 2% vacancy concentration (2% vac). Figure 7 shows the final distribution of Xe atoms at 5% concentration and the distribution of vacancy atoms and interstitial atoms after defect analysis, respectively. The Xe/Kr atom cluster region overlaps with the position of the vacancy position by squeezing out the atoms on the original lattice, which is consistent with the analysis of the stable occupation above. The Xe/Kr atoms squeeze out U atoms to form vacancies, and interstitial atoms moved away from clusters. In addition, Xe/vac is ~1.



Figure 6. The cluster sizes distribution of (a) 2% Xe, (b) 5% Xe, (c) 2% Kr, and (d) 5% Kr in different systems, respectively. The pink, light blue, dark blue, green and red bars are the systems with 2% interstitial concentration, with 1% interstitial concentration, perfect bulk without defects, with 1% vacancies concentration, respectively.



Figure 7. Xe clusters distribution and defects distribution at 5% concentration of Xe atoms in different systems. The green, red, and yellow balls represent the lattice U vacancies, U interstitials, and Xe atoms.

4. Conclusions

In this paper, molecular dynamics simulations were used to study the stable occupancy of Xe/Kr clusters in defect-free configurations and configurations with five different defects. The results show that the system was energetically favourable when Xe/Kr clusters were trapped by vacancies, especially U vacancies, because they can provide a larger space, and the complex of Xe/Kr and vacancies were more stable. The diffusion of Xe/Kr atoms and small clusters at octahedral interstitial sites in bulk UO₂ was also studied. The diffusion of Xe/Kr atoms in bulk UO₂ was relatively complex. The activation energy of Xe/Kr small clusters is ~2 eV, and the Xe/Kr clusters are difficult to diffuse. The nucleation of Xe/Kr in systems containing different defect concentrations was also investigated. At 2500 K, the Xe/Kr atoms dispersed in the system gather into clusters after a 20 ns relaxation. A comparison of the different systems revealed that the vacancy-containing system is more likely to form large clusters than a system containing interstitial atoms.

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