Molecular dynamics simulation of collective behaviour of Xe in UO_2*

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This paper performs atomic simulations of the nucleation and growth of Xe bubble in UO_2 at 1600 K. The bubble growth was simulated up to the bubble containing 50 Xe atoms. The Xe atoms were added directly to the bubble one by one, followed by a relaxation of the system for several picoseconds. The simulations estimated the bubble pressure and radius at different Xe concentrations. The results indicate that the bubble pressure drops with the increasing Xe/U and bubble size at low Xe concentration, while the pressure will increase with the Xe/U ratio at high Xe concentration. The swelling of the system associated with the bubble growth was also obtained. Finally, the recovery of the damaged structure was investigated.

Keywords: uranium dioxide, molecular dynamics, bubble growth, swelling
PACC: 7115Q, 2890

1. Introduction

As a standard nuclear fuel in a pressurized water reactor, uranium dioxide (UO_2) is generally fabricated by pressing powder into green pellets, which are sintered and then assembled into fuel rods.[1] Until now, many studies have been undertaken about the behaviour of this material under irradiation. On the other hand, as one of the major fission products, the behaviour of Xe in uranium dioxide has also been a focus of considerable experimental and theoretical attention.[2] Fission gas atoms generated in UO_2 lattice have a strong tendency to precipitate into intra- and intergranular bubbles due to their low solubility.[3] At higher burnups, larger amounts of Xe atoms diffuse into the bubbles, causing the bubbles to overpressurize. Driven by the excess pressure, the flux of vacancies flows into the bubbles and eventually causes fuel swelling, which is one of the most important cladstraining mechanisms at high burnups.[3] Although there have been numerous previous theoretical and experimental studies of xenon in uranium dioxide in the past, the fundamental understanding of the mechanism of xenon bubble growth is incomplete, especially the information of the early stage of the rare gas bubble growth in UO_2, which is urgently needed.

Experimental capabilities for investigating intragranular rare gas bubbles under dynamic conditions are extremely limited. It is the goal of computer simulations to compensate for this shortcoming in current experimental capabilities to obtain the numerical approximation of microstructural changes taking place in nuclear materials. Computer simulations are capable of studying interactions of fission gas with nuclear fuels and, atomistic simulation method, such as molecular dynamics (MD) simulation,[4,5] is a power method, which allows one to study the growth of fission gas bubble in UO_2 on the microscopic level.

In this paper, we attempt to obtain some useful information of the growth of a xenon bubble at an early stage by using atomistic computer simulations. As far as we know, there are still few studies on the nucleation and growth of fission product bubbles in UO_2 using MD simulation although this method has been successfully applied in the simulation of He bubbles in metal. The major emphasis of this study is the nucleation and growth of the Xe bubble in UO_2 and the bubble pressure and swelling associated with the bubble growth.

2. Simulation methods

2.1. Interatomic potential function

The MD simulations require a description of the interactions between atoms. We separate the inter-

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atomic potential of this ionic solid into a Coulombic part, which represents the interaction between point charges, and a short-range interaction. For UO_2, the potential by Morelon *et al.*[6] was employed. This rigid-ion potential was developed primarily for the simulation of displacement cascades in UO_2 lattices.[7,8] For the calculation of the Coulombic interaction energy, the uranium and oxygen atoms were both assumed fixed, but fractional charges. The comparatively long range Coulombic energy was computed via Ewald's[9] summation. Dealing with short-range energy, the U–O interaction contains a Born–Meyer–Huggins (BMH) covalent bonding contribution and the short-range U–U interaction is neglected due to that the U–U distances are always so large that the results are unaffected by short-range potential.[6]

Additionally, the interaction of O–O is in the Jackson *et al.*[10] model, which connects a Born–Mayer part, two polynomials and $1/r_{ij}^{-6}$ long range tail (where r_{ij} is the interatomic distance).[6,11] Recently, Schwen *et al.* employed this rigid-ion potential to simulate the re-solution of Xe fission gas bubbles in UO_2 and interesting results have been obtained.[11]

The interatomic potentials for Xe–U and Xe–O interactions were taken from a recent work by Geng *et al.*[12] The Xe–U pair is of the Born–Meyer form, which follows Jackson's adoption.[13] A Lennard–Jones (LJ) model was employed for describing the Xe–O interaction. For the Xe–Xe, we chose the exponential-six potential[14] taken from the work by Oh *et al.*[15] This potential can produce reasonable pressure–volume–temperature data for Xe.

2.2. MD simulation procedure

The LAMMPS code[16] was employed for all the simulations. The simulations were performed at constant temperature and constant external pressure using a Nose/Hoover temperature thermostat[17] and Nose/Hoover pressure barostat.[18,19] These techniques allow the simulations to be performed in the normal pressure and temperature (NPT) ensemble. All of the simulations were carried out at zero pressure and a matrix temperature of 1600K, which is a typical fuel element centreline temperature under normal operating conditions.[11] A time step of 0.001 ps was used in all the MD runs.

In the current work, Xe atoms were added directly to the bubble, that is, the way we used in present work to simulate the bubble growth is to add Xe atoms regularly to the bubble and let the system evolve.

3. Simulation results

3.1. Single Xe atom and Xe dimer

Firstly perfect crystalline UO_2 was simulated using a 6×6×6 supercell of the fluorite structure as the starting configuration. When the system reached thermodynamic equilibrium after relaxing the system at given temperature and pressure, the first xenon atom was randomly introduced into the simulation box and let the system evolve for 30 ps.

We found that after diffusion for a very short time in the UO_2 matrix, the single Xe atom ejected one uranium atom from the face centre lattice and trapped in the uranium vacancy. Additionally, an adjacent oxygen vacancy was found as shown in Fig. 1.

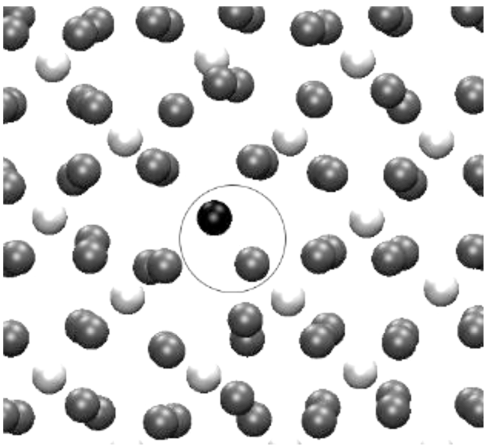


Fig. 1. The single Xe atom trapped in the divacancy. Uranium ions are plotted in white, oxygen in grey and xenon in black.

The single Xe atom was actually incorporated at a divacancy (a uranium vacancy adjacent an oxygen vacancy). The uranium ion substituted Xe atom did not escape this site for additional 20 ps. Yun *et al.*[20] have investigated carefully the stability of Xe in UO_2 through *ab intio* calculations. Their results show that if the thermal creation energy of a vacancy and the incorporation energy are both considered, the majority site of Xe may be a divacancy with the lowest value for the sum of incorporation and vacancy formation energy. Additionally, the calculations suggest that it will be very difficult for Xe to escape from the divacancy due to the high incorporation energy. Parfitt and Grimes also obtained a result that the divacancy is a favourite trapped site for Xe in the MD simulation.[21] These previous results indicate that our simulation is reliable.

When the second Xe atom is added to the system about one lattice distance away from the first one, followed by evolution for 25 ps, a Xe dimer was observed, as presented in Fig. 2.

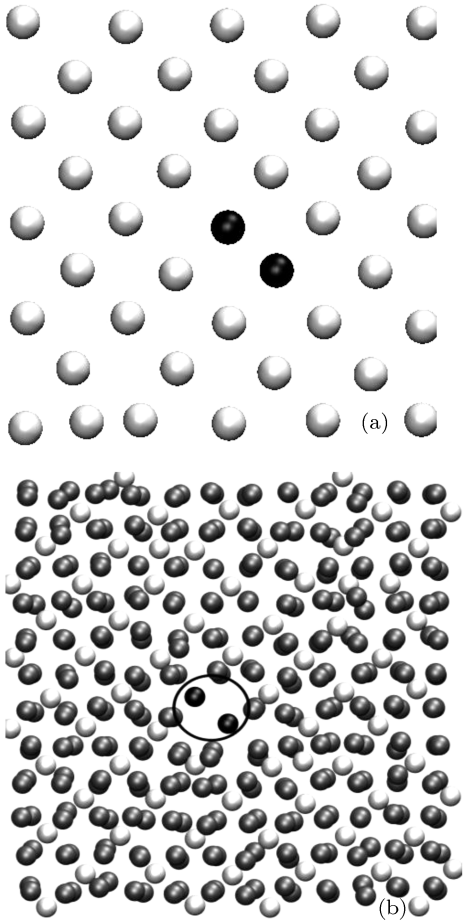


Fig. 2. (a) The dimer of Xe trapped in the nearest two uranium vacancies. (b) Two oxygen ions between the trapped Xe atoms are ejected from former sublattice.

It is found that the dimer bestrides the nearest two uranium vacancies and the two oxygen ions between the Xe atoms are ejected from their former sub-lattices. This conclusion verifies the results of *ab initio* calculations that Xe is more likely to be located at a vacancy cluster than at a single vacancy in UO_2.[20] The dimer acts as a trapping site to trap subsequent Xe atoms randomly in the adjacent region. This phenomenon is similar with the behaviour of He in Titanium.[22]

3.2. Bubble pressure and swelling associated with bubble growth

Similarly, Xe atoms were regularly added to the nearby sites of the former Xe atoms. It was needed several picoseconds for the system to relax from the addition of a single Xe atom. The simulation of the bubble growth was performed till the bubble contained 50 Xe atoms. Since the attractive interaction between Xe atoms is so small, the aggregation of the rare gas atoms attributes to the uranium and oxygen near the bubble which have a strong tendency to recover the former fluorite structure. Figure 3 presents a slice of the bubble containing 40 Xe atoms.

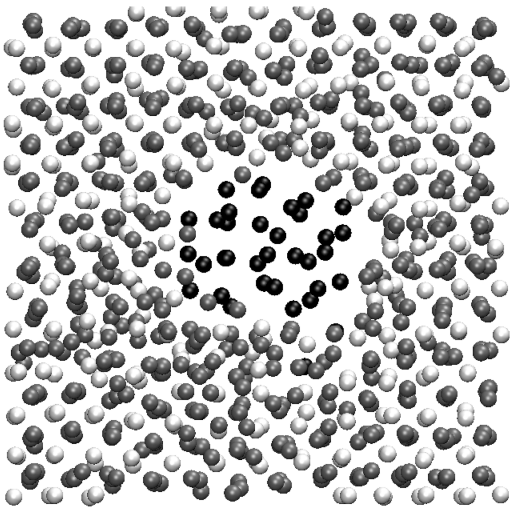


Fig. 3. Snapshot of the slice of Xe bubble in UO_2 matrix containing 40 Xe atoms. Uranium ions are plotted in white, oxygen in grey and xenon in black.

Figure 3 shows that large amounts of defects exist in the surroundings of the bubble, additionally; there is an interface between the bubble and uranium dioxide. During our simulation time, no Xe atoms moved into the surrounding matrix of UO_2. Recently, the studies of fission gas bubble resolution into UO_2 have been performed.[11,21,23] The minimum energies for Xe and Kr to be resolved into UO_2 have been predicted.

For the simulations considered here we have estimated the internal gas pressure. It is reported that the bubbles may be in states far from equilibrium and the smallest bubbles have a very high pressure which results in the densities comparable to that of solid xenon, for the larger bubbles the densities and pressure will be relatively lower.[21] The pressure of internal pressure attributes to both the external stress on UO_2 and surface tension of the bubble void.[21] In the present work, since the number of the Xe atoms in the bubble is too small to give us a good statistical result, the pressure is obtained in simulations of the equivalent density and temperature of free xenon gas. This method was used by Parfitt and Grimes in a previous work.[23] The shape of the bubble is irregular and the exact volume is difficult to obtain. We assume that the bubble exists approximately in a spherical region

with radius R. Such calculation neglects the interface between the bubble and UO_2 and will underestimate the volume of the bubble, so the bubble pressure in our calculations will be slightly higher than the actual value.

Figure 4 presents a plot of the bubble pressure and radius as a function of the Xe/U ratio. The bubble pressure is initially quite high and then drops with increasing Xe concentration and bubble size till the number of the Xe atom reaches 35. When there are more Xe atoms in the bubble, the pressure will increase with the increasing Xe atoms number, which is similar to that of He in metal.[24] It is shown that the bubble pressure have a value of several GPa when the bubble radius is between 6.5 and 7.5 Å (1Å=0.1 nm), when the radius is larger, slightly higher pressure is expected to be obtained. Our results are in reasonable agreement with experimental observation[25] although the calculation method overestimates the bubble pressure.

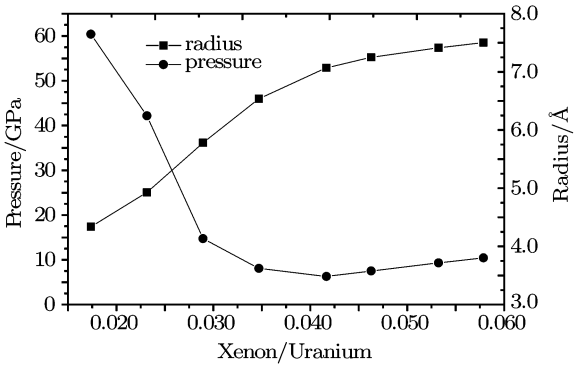


Fig. 4. The Xe bubble pressure and radius as a function of the Xenon to Uranium (Xe/U).

We estimated the density of the bubble, which might be overestimated due to the imprecise calculation of bubble volume. For the bubble radius from 7.07 to 7.50 Å, the density is between 5.16 and 6.16 g/cm^3, which can compare with the experimental value of 3.8–6.0 g/cm^3 for larger bubble radius.

It is noticed that the radius of the bubble increases rapidly with the increasing Xe/U ratio at low Xe concentration and, the rate of radius increases slowly down at high Xe/U ratio. This is in accord with the decreasing bubble pressure at low Xe/U ratio and increasing bubble pressure when Xe concentration is high.

The equation of state of the fission gas is basic foundation for investigating the fission gas behaviour. Using the exponential-six potential mentioned above, we obtained the pressure of Xe gas as a function of molar volume at 1600 K. The simulation was performed in normal volume and temperature (NVT) ensemble. We made initially an 8×8×8 fcc-Xe model with 2048 atoms. The system was allowed to relax and equilibrium for 10 ps. Following the equilibrium, the next 20 ps runs were used to get statistical analysis of the pressure of the simulated system. The results of the MD simulation are presented in Fig. 5 with the data from literatures for comparison. We find that our results are in perfect agreement with the MD results by Oh *et al.*[15] The data of Kaplun's equation[26] and Ronchi[27] match the simulations results up to 210 and 730 MPa respectively. In the low pressure range, all the equations of state converge to ideal gas law due to that the van der Waals force could be neglected.[17] The agreement between our results and the data from literatures suggests again that the estimate of the bubble pressure in our MD simulations is reasonable.

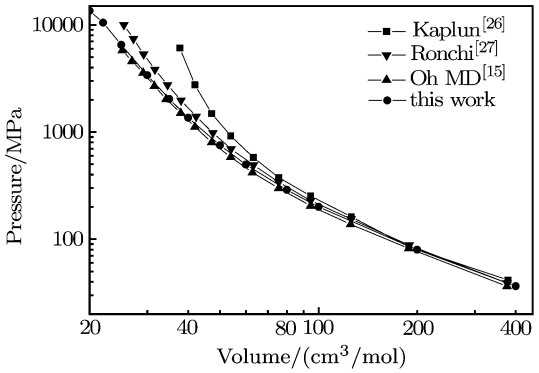


Fig. 5. Pressure of Xe gas as a function of molar volume at 1600 K.

When there were 50 Xe atoms in the system, the radial distribution function was computed. The result is shown in Fig. 6. It is clearly presented that the Xe

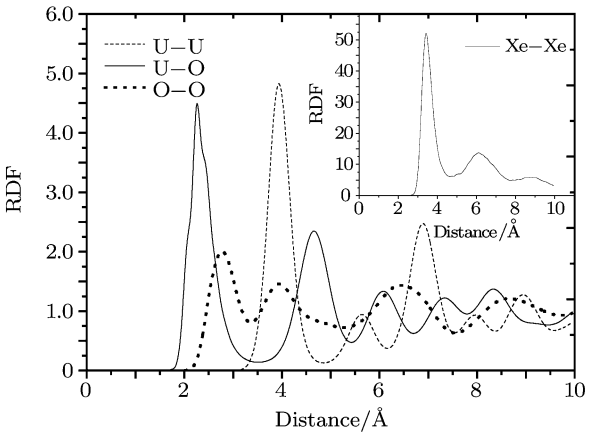


Fig. 6. Radial distribution function (RDF) of UO_2 containing 50 Xe atoms at 1600 K.

atoms are in a liquid state while UO_2 is in a perfect solid state. This indicates that the behaviour of Xe

atoms in UO_2 is similar to the system with a hard-sphere liquid in solid. This conclusion is in agreement with the result obtained by Geng *et al.*[12]

The swelling associated with the bubble growth is presented in Fig. 7 as a function of Xe/U ratio. The swelling is defined as $S = (V - V_0)/V_0$, where V_0 is the initial volume of the system without Xe atoms and the V is the volume of the system containing Xe bubble.

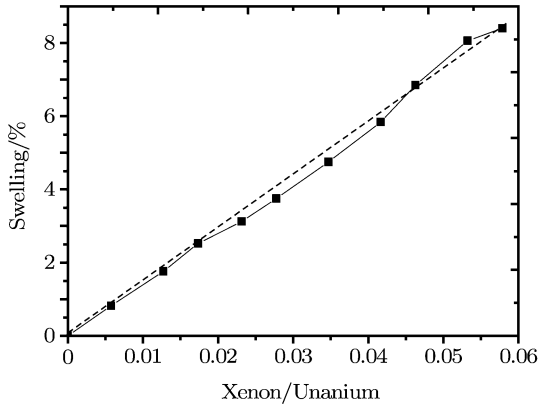


Fig. 7. The computed swelling of the UO_2 due to the growth of the Xe bubble as a function of the xenon to uranium ratio. The dashed line is an accessorial linear line.

We can note that the swelling follows approximately a linear relationship but has a rapid growth trend with the Xe/U ratio at low Xe concentration. At higher Xe concentration, the rate of growth of the swelling will slow down with the Xe/U ratio. This is understandable, initially, the volume of the bubble increases rapidly with the Xe concentration, which is shown in Fig. 4, resulting in the rapid growth of the swelling. Accordingly, the slower growth of the swelling is due to the low grow rate of the bubble volume at higher Xe concentration. Here, the effect of the defects surrounding the bubble is neglected.

3.3. Recovery of the damaged structure

It would be very interesting to study the recovery of the damaged structure of UO_2 after Xe atoms are moved out the simulation box. We found that the damaged structure did not recover completely after a system relaxation for 50 ps at 1600 K. Figure 8 gives us the slice of the system before and after relaxation respectively. We can see that although the damaged system recovers significantly, there are still many defects after 50 ps's relaxation. Many vacancies and interstitials of the oxygen and uranium atoms are observed. Figure 9 compares the layer structure along (0 0 1) direction of both the oxygen and uranium before and after the relaxation of the system without the Xe atoms. This figure of the layer structure reflects again the UO_2's solid state, additionally; it clearly shows that there is still one layer which does not recover to former structure. There may be a further recovery if simulate the system for a longer time, but it must be pointed out that the temperature for the simulation is too low to provide enough kinetic energy to overcome recrystallization barriers.[12] Except for a longer simulation time, a higher temperature is needed to completely recover the damaged system.

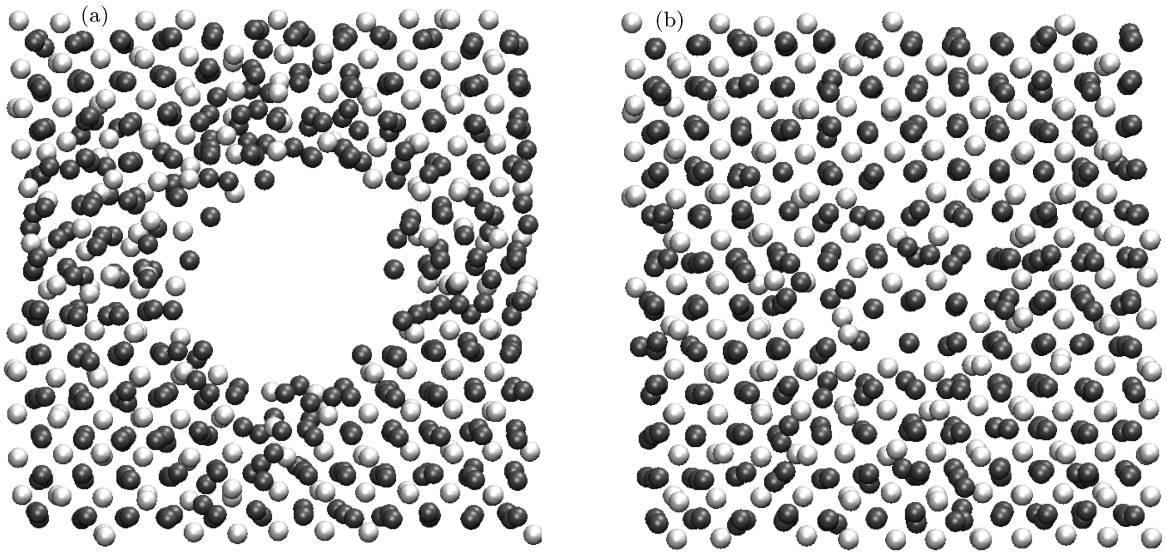


Fig. 8. Snapshots of the slice of the damaged UO_2 structures at 1600 K after Xe was released out: (a) before relaxation and (b) after relaxation for 50 ps. Uranium ions are plotted in white and oxygen in grey.

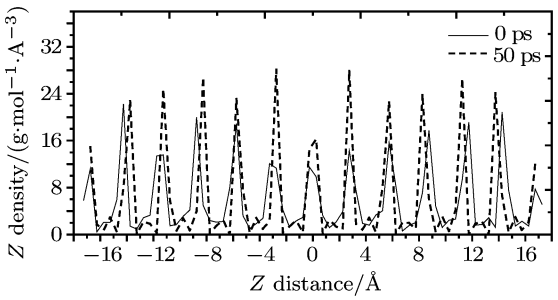


Fig. 9. Recovery of the layer-structure of UO_2 along (0 0 1) direction after Xe atoms are released out from the UO_2 matrix.

4. Conclusion

Using the pair potential model, the growth of Xe bubble in UO_2 matrix was investigated with an MD simulation to obtain the bubble pressure, bubble size and the swelling associated with the bubble growth. Our simulations reveal that the single Xe atom has a strong tendency to be trapped in uranium vacancy, which is in accord with the result of *ab initio* calculations that there is a low incorporation energy of Xe for uranium vacancy. Adding the second Xe atom near the first Xe, a dimer will be formed. We add the Xe atoms to the bubble and let the system evolve. Then the bubble pressure and size is estimated at a different Xe/U ratio. In our simulations, the bubble pressure drops with the increasing Xe/U and bubble size at low Xe concentration, while the pressure will increase with the Xe/U ratio at high Xe concentration. This is similar to the behaviour of He in metal. Additionally, the swelling follows an approximate linear relationship but has a rapid growth trend with the Xe/U ratio at low Xe concentration. At higher Xe concentration, the growth of the swelling will slow down. Finally, the recovery of the damaged structure was studied. It is found that the damaged system did not recover completely at this temperature. For a further recovery, a higher temperature and longer simulation time will be needed.

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