He migration and bubble formation in Ga stabilised δ-Pu

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Abstract

The migration and formation of He into bubbles in Ga stabilised δ-Pu has been investigated using molecular dynamics simulation. Formation energy calculations indicate that isolated He interstitial atoms are unfavourable and that it is preferential for He to reside as a substitutional atom at the expense of producing a Pu self-interstitial. Migration energy barrier calculations and on-the-fly kinetic Monte Carlo simulations support this result establishing that an interstitial He atom soon becomes substitutional, after which migration is unlikely unless assisted by local vacancies. He-vacancy cluster formation energies show that as the void size increases, a He:vacancy ratio up to 2:1 becomes energetically favourable over isolated He substitutional atoms and vacancies.

1. Introduction

The build up of inert gases due to irradiation is a significant problem common to all nuclear materials, in particular nuclear fuels. The low solubility of the gas atoms in the surrounding matrix and the inherent presence of vacancies due to radiation damage promotes the formation of bubbles, typically at nucleation centres such as grain boundaries [1–3]. This can lead to macroscopic swelling which impacts the structural integrity of the host material. In addition, the build up of bubbles at surfaces can result in gas release which accelerates surface degradation and impacts the performance of fuels and cladding materials [4–6].

Of the inert gas species produced in the nuclear fuel cycle, helium is the most abundant and contributes significantly to the radiation induced aging of Pu and its alloys. The continual alpha decay events not only produce primary damage from collision cascades initiated by recoiled lattice atoms, but also inject He far from the cascade core. In contrast to the well understood collision cascade mechanics, the processes of He migration, clustering and eventual bubble formation are lesser known. More complex events such as the effect of residual damage on bubble formation or the interaction of pre-existing bubbles with a cascade remain unexplained.

In this work, calculations of the migration pathways of He in Ga stabilised Pu are investigated to determine the atomistic mechanisms responsible for initial bubble formation. Energy barriers for a range of interstitial to substitutional transitions are presented involving isolated He and local vacancies. These calculations are complemented by kinetic Monte Carlo simulations of He migration. The formation energies of a range of bubble sizes and densities are also computed to determine the most energetically favourable bubble configuration.

2. Background

Amongst the first investigations into the presence of inert gas atoms in metals was carried out by Rimmer and Cottrell [1]. Using a theoretical approach, the work estimated energies of solution in Copper concluding that Ar, Kr and Xe would reside substitutionally. It was also noted that the calculated interstitial energies were large enough to make ejection of a lattice atom to form a copper interstitial and a substitutional gas atom favourable. Calculations incorporating He and Ne suggested that occupying substitutional sites was only favourable when the gas atom was placed into a pre-existing vacancy. Otherwise these species should remain interstitial.

Early models of inert gas bubble formation, swelling and release were proposed by Greenwood et al. [7,8] and Barnes [9]. The main mechanism for bubble growth was reportedly due to the diffusion of vacancies created during irradiation. Swelling was attributed to the presence of larger bubble sizes and as such could be minimised by ensuring bubbles were nucleated within a fine spacing. The solution of gas bubbles by irradiation was also studied and was indicated to be unlikely by either direct interaction with a fission track or indirectly through a thermal spike.

Much of the early work concerning inert gases in nuclear materials considered uranium [7,10,11] and uranium dioxide [12–14] fuels. The experiments of Hudson [10] irradiated samples of U at temperatures between 400 and 700 °C. Volume measurements post irradiation indicated minimal swelling, a result attributed to
an even distribution of gas bubbles which supports the previous model of Barnes. The work concluded that higher burnups (>0.2%) are required to produce any significant swelling.

The works of Nelson [13] and Whapham [14] examined the balance of the induced kinetic solubility of bubbles and irradiation enhanced diffusion of gas atoms in UO₂. This study highlighted the complex nature of bubble nucleation and growth, as the continual fission events aid formation through increasing diffusivity yet restrict growth by breaking up gas-atom clusters. Temperature was also found to effect the nucleation of bubbles, as at high temperature thermal diffusion in addition to irradiation enhanced diffusion aids bubble formation.

Helium bubble nucleation and growth in aged PuGa alloys was investigated by Wheeler and Bayer using dilatometry [15]. During isothermal treatment, the evolution of the alloy was categorised into four distinct stages. After initial periods of lattice contraction due to defect recombination, a final stage of linear expansion was observed and was attributed to the formation of He bubbles. Such bubbles were on the micron-scale and clearly visible by optical microscope. The mechanism for He migration and bubble formation was suggested to be vacancy driven.

Advances in experimental techniques with the capability to probe the atomic scale have proven useful for the study of defects produced by radiation damage. One such technique; positron annihilation spectroscopy (PAS), was used by Asoka-Kumar to examine voids in Pu [16]. Combining the experimental lifetimes with theoretical calculations by Sterne and Pask [17], nanometre size voids were found to be in fact He bubbles containing around 2–3 He atoms per vacancy. This was later supported by the transmission electron microscopy observations carried out by Schwartz et al. [18].

Calculations of activation and binding energies of He atoms and clusters in fcc copper were reported by Wilson et al. [19] Using interatomic potentials, this atomistic approach established that isolated interstitial He atoms were loosely bound up to a cluster of five atoms. However, the inclusion of a single vacancy increased this binding energy to around 0.86 eV for a six atom cluster and was suggested as a precursor for bubble formation.

The impact of vacancies on He bubble formation was also investigated by Grimes et al. for UO₂ by means of formation and migration energy calculations [20]. A significant reduction in the activation energy for He interstitial migration was reported for mechanisms involving vacancies. As the barrier for lone He interstitial migration (3.8 eV) was found to be much higher than that for vacancy assisted migration (0.3 eV), the mechanism for He diffusion and bubble formation was deemed to be vacancy assisted.

In the development of the Modified Embedded Atom Method (MEAM) Baskes et al. [21,22] and Valone et al. [23] parameterised potentials for the Pu–Ga–He system. The ability to simulate the fcc δ-phase of Ga-stabilised Pu along with suitable He pair interactions allowed studies into He bubble stability. Simulations suggested an equilibrium He-to-vacancy ratio of 2:1 in 5 at.% Ga-stabilised Pu, which supported the earlier experimental results [16–18]. The MEAM was also employed in the work of Dremov et al. which carried out MD simulations of isolated He interstitials in pure Pu [24]. Simulations indicated the tendency of the He interstitials to become substitutional, creating mobile Pu interstitials which readily diffuse away. An alternative EAM potential was developed by Ao et al. and was used to study Helium-vacancy clusters in pure Pu [25,26]. Calculations of binding energies for a range of cluster sizes and densities suggested the trapping of He in vaccines is likely, providing nucleation centres for bubble formation.

3. Methodology

All calculations employ the Modified Embedded Atom Method (MEAM) [27,21,28] with parameters taken from the work of Valone et al. [23]. The MEAM has been utilised in the precursors to this work where defect production and migration were investigated in both pure Pu and Ga stabilised Pu [29–31]. The form of the MEAM potential is given by:

$$E_i = F_i(p) + \frac{1}{2} \sum_j \phi(r_{ij})$$  \hspace{1cm} (1)

where $F_i(p)$ represents the embedding energy of atom i, which is deduced from the specific geometry of the local environment and $\phi(r_{ij})$ is a pair potential with contributions summed from all neighbours j.

To gather good statistics, a large number of PuGa configurations were considered. Each lattice contains 5% Ga, a typical concentration falling in the middle of the δ-phase stability range. Each lattice is created to ensure no first nearest neighbour (1NN) Ga–Ga bonds, as found experimentally by Faure et al. [32] and supported by simulation [22,30].

To examine the initial stages of bubble growth and to gain some understanding of the overall formation energy of He-vacancy clusters, a large number of small cluster sizes were constructed and relaxed using the conjugate gradient method. To enable the simulation of the complete size range of clusters from a single He substitutional up to a He₀V₂₀ cluster, the process was distributed over several hundred cpus. At higher He concentrations care had to be taken to ensure the additional He atoms were placed within the boundary of the cluster yet reasonably spaced between other He atoms. As well as a large number of cluster configurations, each was tested in 25 different PuGa arrangements to ensure statistically significant results.

To understand the energy cost of forming each bubble configuration the formation energy needs to be defined. If we take this as the energy required to form a bubble from isolated vacancies and He substitutional atoms, then the resultant formation energy of a HeₐVₙ cluster is given by:

$$E_{f}^{He/V} = E_a + (m-n)E_V - nE_{He} - N_{Pu}E_{Pu}^{bulk} - N_{Ga}E_{Ga}^{bulk},$$  \hspace{1cm} (2)

where $E_a$ represents the energy of the lattice containing the bubble, $E_V$ is the formation energy of a vacancy and $E_{He}$, $E_{Pu}^{bulk}$, $E_{Ga}^{bulk}$, where $K = Pu$, Ga or He, is the number of atoms multiplied by the bulk energy per atom. It is clear that the result of this equation will depend greatly on the bulk energy per atom of He rather than the values for Pu and Ga. The definition of $E_{He}^{bulk}$ is taken as:

$$E_{He}^{bulk} = E_{He}^{sub} - N_{Pu}E_{Pu}^{sub} - N_{Ga}E_{Ga}^{sub},$$  \hspace{1cm} (3)

where $E_{He}^{sub}$ is the energy of a reference lattice containing a substitutional He and $E_{Pu}^{sub}$, $E_{Ga}^{sub}$, where $K = Pu$ or Ga, is the product of the number of atoms and energy per atom of each specie in the reference lattice. The inclusion of the $(m-n)$ $E_V$ term in Eq. 2 is important due to balance the number of vacancies when the He:V ratio is not 1:1. This idea is illustrated in Fig. 1.

Transition energy barriers are calculated using the Climbing Nudged Elastic Band (CNEB) method [33,34], with initial and final states manually created to study the He migration transitions of interest. All transitions concerning interstitial lattice atoms are considered to involve Pu atoms due to the high formation and migration energies of Ga atoms reported previously [31]. As with the formation energy calculations, it is important to sample different PuGa environments. Therefore, each transition was calculated using between 50 and 100 PuGa lattice configurations.

To study the pathways of He migration, on-the-fly kinetic Monte Carlo (OTF-KMC) simulations were carried out using the methodology outlined by Vernon et al. [35]. Transitions states are determined using the Relaxation and Translation (RAT) method [36] which is augmented by the CNEB method to accurately resolve the energy barrier. These simulations only require an initial He configuration,
with each transition state discovered during run time. Each step involves finding 40 unique transitions with the successful transition chosen based on the rate calculated from the Arrhenius equation:

\[ k_i = A_i e^{-\frac{E_i^b}{k_B T}} \]  

(4)

where \( k_i \), \( A_i \) and \( E_i^b \) are the rate, rate prefactor and the energy barrier for transition \( i \) respectively, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. A fixed rate prefactor of \( 10^{13} \) s\(^{-1}\) was employed with the simulation temperature at 300 K.

### 4. Results

Here we present results from the formation energy and migration barrier calculations involving both interstitial and substitutional He. In addition, the impact of vacancies on He migration is also demonstrated. A summary of the transitions and the associated energy barriers can be found Table 2. The final set of results in this section report the formation energies of He-vacancy clusters up to \( \text{He}_{40}V_{20} \).

#### 4.1. Helium substitutional and interstitial formation energies

To determine if an isolated He atom would reside substitutionally or as an interstitial the energy cost of each arrangement was calculated. These energies are shown in Table 1 and are given relative to the corresponding relaxed PuGa fcc lattice. Calculations suggest that within the MEAM model, He will reside substitutionally, even at the cost of creating a Pu interstitial. Although somewhat counter intuitive, this was also noted by the developers of the MEAM and is due to both the hardness of the Pu–He and Ga–He interactions at the distances around the He interstitial and the relatively low formation energy of the Pu self-interstitial [23]. The large errors reported in Table 1 relate to differences in the local environments produced by sampling across the 50 PuGa lattice arrangements.

Given the preference of He to reside substitutionally an obvious question arises regarding the kinetics of initial bubble nucleation. Although the energy cost of an isolated He interstitial are significantly larger than that of the substitutional, it is important to consider the energy barrier associated with interstitial and substitutional migration.

#### 4.2. He interstitial transitions

The simplest He interstitial migration mechanisms are direct transitions to neighbouring interstitial sites. These transitions are shown in Fig. 2 and have similar average energy barriers of between 0.4 and 0.7 eV. The lowest barrier was associated with the tetrahedral to tetrahedral transition along the \( \{100\} \) direction with a barrier of \( 0.4 \pm 0.3 \) eV. The octahedral to octahedral interstitial transition along the \( \{110\} \) direction was found to have a marginally higher barrier of \( 0.6 \pm 0.3 \) eV. Of the transitions between interstitial sites, the tetrahedral to octahedral transition down the \( \{111\} \) direction was found to be lowest at \( 0.5 \pm 0.2 \) eV with the octahedral to tetrahedral around \( 0.2 \) eV higher. These values, along with the barriers calculated for all transitions are summarised in Table 2.

#### 4.3. He interstitial to substitutional transitions

Exchange interstitial to substitutional mechanisms were considered initially where the interstitial He replaces a neighbouring Pu lattice atom. Examples of these mechanisms are shown in Fig. 3 for both octahedral and tetrahedral transitions. These migration mechanisms were found to have high energy barriers of between 2.3 and 3 eV with tetrahedral interstitials producing the lowest barriers.

As an alternative to the exchange type transitions, more intuitive linear pathways were considered. The main transitions are shown in Fig. 4 for both the octahedral and tetrahedral interstitials. The energy barriers associated with this type of migration were significantly lower than those reported for the exchange transitions with averages of \( 0.4 \pm 0.2 \) and \( 0.9 \pm 0.4 \) eV for the octahedral and tetrahedral interstitials respectively. Combining these low barriers with the indication that substitutional He is energetically favoured suggests that once He is introduced to the lattice it will soon become substitutional. This is better understood by looking at the distribution of energy barriers for the linear interstitial to substitutional transition along with the reverse barriers, as shown for the octahedral interstitial in Fig. 5. The average reverse barrier, which represents the substitutional to interstitial transition, is on average around 2 eV higher reiterating the unlikelihood of residual interstitial He atoms in isolation. Fig. 5 also indicates that there are instances when the He interstitial to substitutional transition is associated with an energy barrier significantly lower than \( 0.4 \) eV. This most likely relates to the occasions where the He interstitial is created in a Pu-rich region, where the displacement of neighbouring Pu atoms is easier than in Ga-rich regions, as reported previously [31]. This behaviour is in line with Valone et al. [23] and suggests in some cases the transition from He interstitial to substitutional is a barrier-less process.

#### 4.4. Helium substitutional transitions

With the strong indication that isolated He atoms would reside substitutionally, migration although unlikely, may occur through exchanges with other lattice atoms. To investigate this, the energy barriers of substitutional He migration transitions were calculated. The simplest substitutional transition is shown in Fig. 6(a) and

![Fig. 1. Illustration of the definition of \( \text{He}_{40}V_{20} \) cluster formation energy, where He atoms are considered originating from substitutional sites.](image-url)
involves the He atom exchanging with a first nearest neighbour Pu atom. This was found to have an extremely large barrier of around 6 eV. Upon inspection of the transition mechanism, this was found to relate to the significant degree of lattice distortion required to allow for the exchange to take place. To lessen this effect, cooperative transitions involving two (Fig. 6(b)) and three (Fig. 6(c)) lattice atoms were constructed and the barriers determined. The resultant barriers were found to be 4.8 ± 0.4 and 3.8 ± 0.6 eV for the transitions involving two and three lattice atoms respectively. Although the decrease in energy barriers suggest that complex, cooperative transitions are more likely to occur, the overall barrier heights for substitutional migration remain considerably large.

4.5. He interstitial on-the-fly KMC simulations

To complement the migration barrier calculations and to provide support to the indication that interstitial He formation and migration is unlikely, on-the-fly kinetic Monte Carlo (OTF-KMC) simulations of a lone He interstitial and a He di-interstitial were carried out. The final states of these simulations can be seen in Fig. 7 which shows the pathways atoms displaced more than 0.2 nm. The significant observation from these simulations is the immediate transition of the He interstitial into a lattice site forming a Pu interstitial, in line with the reports of Dremov et al. [24]. The migration of the Pu interstitials away from the He site is relatively rapid and occurs with very low barriers as reported previously [31]. As such, the bulk of the simulation time is spent during the initial He interstitial to substitutional transitions. It should also be noted that migration in both simulations involved solely Pu atoms which is attributed to the high energy barriers associated with removing substitutional Ga atoms [31].

Results from all calculations and simulations involving isolated He atoms suggest interstitial formation and migration is unlikely. With He preferentially residing substitutionally, an option for migration is through the assistance of additional impurities or defects.

Fig. 2. He interstitial migration transitions. (a) Tetrahedral transition with an average barrier of 0.4 ± 0.3 eV. (b) Octahedral transition with an average barrier of 0.6 ± 0.3 eV. (c) Tetrahedral to octahedral transition with an average barrier of 0.5 ± 0.2 eV and a reverse barrier around 0.2 eV higher.

Fig. 3. Exchange mechanisms for the interstitial He to become substitutional. (a) Single octahedral atom exchange with an average barrier of 3.0 ± 0.8 eV. (b) Double octahedral atom exchange with an average barrier of 3.8 ± 0.7 eV. (c) Single tetrahedral atom exchange with an average barrier of 2.3 ± 1.3 eV.

Table 2

Summary of the calculated transition energy barriers for He migration in 5 at.% Ga stabilised Pu. Transition mechanism are shown in Kröger–Vink notation [37] with superscripts denoting additional information regarding the type of defect. For interstitials, tet and oct represent tetrahedral and octahedral locations. For vacancies, superscripts give the positioning in terms of nearest neighbour sites. Labels above the arrows signify the local environment of the transition.

| Transition | Energy barriers (eV) |
|------------|----------------------|
| **He interstitial transitions** | |
| \( \text{He}^{\text{tet}}_{\text{H}} \rightarrow \text{He}^{\text{oct}}_{\text{H}} \) | 0.4 ± 0.3 |
| \( \text{He}^{\text{oct}}_{\text{H}} \rightarrow \text{He}^{\text{tet}}_{\text{H}} \) | 0.6 ± 0.3 |
| \( \text{He}^{\text{oct}}_{\text{H}} \rightarrow \text{He}^{\text{oct}}_{\text{H}} \) | 0.5 ± 0.2 |
| **He interstitial to substitutional transitions** | |
| \( \text{He}^{\text{tet}}_{\text{H}} \rightarrow \text{He}^{\text{oct}}_{\text{Pu}} + \text{Pu}^{\text{oct}}_{\text{i}} \) | 3.0 ± 0.8 |
| \( \text{He}^{\text{oct}}_{\text{H}} \rightarrow \text{He}^{\text{oct}}_{\text{Pu}} + \text{Pu}^{\text{oct}}_{\text{i}} \) | 3.8 ± 0.7 |
| \( \text{He}^{\text{tet}}_{\text{H}} \rightarrow \text{He}^{\text{oct}}_{\text{Pu}} + \text{Pu}^{\text{oct}}_{\text{i}} \) | 0.4 ± 0.2 |
| \( \text{He}^{\text{oct}}_{\text{H}} \rightarrow \text{He}^{\text{tet}}_{\text{Pu}} + \text{Pu}^{\text{oct}}_{\text{i}} \) | 2.3 ± 1.3 |
| \( \text{He}^{\text{tet}}_{\text{H}} \rightarrow \text{He}^{\text{tet}}_{\text{Pu}} + \text{Pu}^{\text{oct}}_{\text{i}} \) | 0.9 ± 0.4 |
| **He substitutional transitions** | |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | –6.0 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 4.8 ± 0.4 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \) | 3.8 ± 0.6 |
| **Vacancy assisted transitions** | |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 0.9 ± 0.3 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 2.9 ± 0.3 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 3.5 ± 0.5 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 1.5 ± 0.4 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 1.3 ± 0.4 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 0.5 ± 0.2 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} + \text{He}^{\text{Pu}}_{\text{C}} \) | 1.5 ± 0.4 |
| \( \text{He}^{\text{Pu}}_{\text{C}} \rightarrow \text{He}^{\text{Pu}}_{\text{C}} \) | 1.5 ± 0.3 |
4.6. Helium-vacancy transitions

As in previous works, vacancies have been reported to greatly effect the migration of He \[15,20\]. The inherent presence of vacancies due to continual radiation damage suggests vacancy-assisted migration of He may provide a mechanism for bubble formation.

To determine the impact of vacancies on substitutional He, energy barriers associated with transitions of substitutional He to first, second and third nearest neighbour vacancies were calculated. A schematic of these transitions along with the distribution of energy barriers can be found in Fig. 8. The energy barrier corresponding to substitutional He migrating to a first nearest neighbour vacancy (Fig. 8(a)) was found to be 0.94 ± 0.28 eV. Significantly, this is lower than all of the barriers found for the substitutional He to either migrate or become interstitial. From the distribution of energy barriers, it is clear that migration can occur at lower energies at values around 0.5 eV. Importantly, when comparing these barriers with the values reported for first nearest neighbour mono-vacancy hops in pure Pu and 5 at.% Ga-stabilised Pu (1.1 and 1.3 eV respectively) there is a distinct reduction when the migrating atom is He. This suggests a migrating vacancy may become pinned by the substitutional He which proceeds to oscillate between lattice sites. This is inline with the binding energy calculations of Ao et al. that indicated that He atoms are very strongly bound to small vacancy clusters\[26\].

Although the barriers determined for the substitutional He to migrate to a first nearest neighbour vacancy are comparable to mono-vacancy migration, transitions to second and third nearest neighbour vacancies are much higher (Fig. 8(b) and (c)). The average barriers are found to be 2.9 ± 0.3 and 3.5 ± 0.5 eV for the transitions to second and third nearest neighbour vacancies respectively. Significantly, the lowest barriers calculated are also much larger than that of mono-vacancy migration, at around 2–2.5 eV. This suggests that only mono-vacancies that migrate in very close proximity to a substitutional He may become trapped. In addition, this has implications for migration of the substitutional He which will be confined to first nearest neighbour hops and require additional vacancies to migrate.

In addition to considering the barriers relating to the substitutional He migrating into neighbouring vacancies, the barriers associated with the vacancies migrating away from the He atom were also calculated. Transitions were constructed to determine the preference of vacancies to migrate towards or away from the substitutional He between nearest neighbour sites. These transitions can be found in Fig. 9 along with the distribution of energy barriers. Although the distributions are similar, the lowest energy barriers calculated relate to vacancies migrating away from the first nearest neighbour positions. Furthermore, many of these transitions had barriers on par with the barriers for the substitutional He to migrate into the first nearest neighbour vacancy. This

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**Fig. 4.** Linear mechanisms for the interstitial He to become substitutional. (a) Octahedral transition with an energy barrier of 0.4 ± 0.2 eV. (b) Tetrahedral transition with an energy barrier of 0.9 ± 0.4 eV.

**Fig. 5.** Distributions of forward and reverse energy barriers for the He octahedral interstitial to substitutional linear transition as shown in Fig. 4. The average forward barrier of 0.4 ± 0.2 eV is significantly lower than the average reverse barrier of 2.6 ± 0.6 eV.

**Fig. 6.** Substitutional He transitions. (a) A single atom replacement transition occurs with a large energy barrier of around 6 eV. (b) An indirect replacement transition involving two lattice atoms is associated with an energy barrier of 4.8 ± 0.4 eV. (c) An indirect replacement mechanism involving three local lattice atoms results in an energy barrier of 3.8 ± 0.6 eV.
suggests there is no significant driving force to attract or pin a mono-vacancy to a substitutional He. Again this effects longer range He migration which, if assisted, must involve additional vacancies.

4.7. He substitutional and di-vacancy transitions

Although calculations suggest that the a lone vacancy does not significantly aid the migration of a local substitutional He atom, mechanisms may be possible using multiple vacancies. To investigate this, transitions were constructed that involved migration of the substitutional He atom to a first nearest neighbour di-vacancy, as in Fig. 10. Barriers were calculated using one of the two symmetrically equivalent transitions of the He atom into one of the nearby vacancies.

The distribution of barriers in Fig. 10 indicates a significant reduction in the barrier heights for substitutional He migration. The average barrier $0.5 \pm 0.2$ eV is lower than that found for migration of the He into a mono-vacancy and also for isolated mono-vacancy migration. The lowest barriers found are around $0.2$ eV which suggests short time scale oscillations of the He atom between the vacancies.

As with the transitions involving the mono-vacancy, the migration of the di-vacancy away from the substitutional He atom was also considered. This involved calculation of the energy barriers for one of the vacancies to migrate from a first to second nearest neighbour position as shown in Fig. 11. In contrast to the energy barriers determined for the mono-vacancy to migrate away (Fig. 9) both the forward and reverse barriers are of similar heights. This is demonstrated by the average barriers, which within error are identical at $1.5 \pm 0.3$ eV. The similarities between the barrier heights may be important in the overall mechanism for substitutional He migration as it allows vacancies to readily migrate to and from the vicinity of the substitutional He atom.

As there are a significant number of possible transitions involving a di-vacancy and a substitutional He atom, manual enumeration of the associated barriers is impractical. For this reason, an OTF-KMC simulation was carried to determine the likely evolution of the di-vacancy and He substitutional. Initial and final snap-shots from the simulation can be found in Fig. 12. During the initial stages of the simulation, the He atom was found to continually cycle between the three possible lattices sites in line with low energy barriers found previously. To encourage different transitions to occur, a rudimentary memory kernel was implemented which logged accepted transitions and denied the occurrence of repetitive transitions. This modification did result in vacancy...
migration, however this involved diffusion of the vacancies away from the He atom and did not produce migration of the He atom itself.

The results from the OTF-KMC simulation do not remove the possibility of vacancy assisted He migration. The mechanism may be complex, requiring concerted or cooperative transitions between the vacancies and the He atom. Simulations suggest that if He diffusion is vacancy assisted in this manner, the time scale for such diffusion would be dependent on the energy barriers associated with vacancy migration. As the migration of a mono-vacancy in Pu is much slower than a lone interstitial [31], point defect annihilation may be more likely than the assistance of He migration. However, the trends found when introducing a second vacancy suggest that additional vacancies may significantly reduce migration barriers and introduce new mechanisms for diffusion.

4.8. He-vacancy cluster formation energies

The importance of the role of vacancies in He migration and the eventual clustering into bubbles leads to question of equilibrium He content and general bubble stability. The work of Valone et al. [23] suggested a He-to-vacancy ratio of around 2:1 was energetically favourable which coincided with experimental reports [16–18]. To investigate this and to determine the energy cost associated with incorporating additional He into a void, formation energies of He-vacancy clusters were calculated. This involved extensive sampling of the He-to-vacancy ratio from 1:1 to 4:1 resulting in cluster sizes from \( \text{He}_2\text{V}_2 \) to \( \text{He}_{80}\text{V}_{20} \).

Resultant formation energies can be found in Fig. 13 which shows the dependency on both He and vacancy content. These values suggest that the formation energy continually decreases up to the 1:1 He:vacancy ratio, suggesting it is favourable for isolated substitutional He atoms to cluster. Clearly, once this clustering occurs the He atoms are no longer substitutional in the exact sense but instead are mobile inside the newly created void.

A more significant result from Fig. 13 is that as bubble size increases, He:vacancy ratios much larger than 1:1 can achieve a negative formation energy. This is due to the increase in the number He atoms within the bubble core relative to the number of vacancies.

**Fig. 9.** The distribution of energy barriers for the mono-vacancy to migrate away from the substitutional He atom. (a) Vacancy transition from the first to second nearest neighbour position. (b) Vacancy transition from the first to third nearest neighbour position. Blue and green arrows represent to the forward and reverse transitions and correspond to the colouring in the distributions of energy barriers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 10.** The substitutional He-to-vacancy transition incorporating a local di-vacancy alongside the distribution of the energy barriers found in 100 PuGa configurations.

**Fig. 11.** Transitions involving a di-vacancy local to a substitutional He atom in which one vacancy moves from a first to second nearest neighbour position. The distribution of forward (vacancy migrating away from the He atom) and reverse (vacancy migrating towards the He atom) barriers are also shown.

**Fig. 12.** Snap-shots of an OTF-KMC simulation of a substitutional He atom and local di-vacancy. (a) Initially the He atom oscillated between the vacancies on the nanosecond time scale. (b) The eventual migration of the vacancies away from the cluster resulted in trapping of the He atom on a lattice site. The migration of the vacancies was associated with a significantly longer time scale of the order of seconds and minutes.

**Fig. 13.** The distribution of formation barrier heights for He-vacancy clusters.
interfacial He atoms. As the Pu–He and Ga–He interaction energies are significantly more repulsive than the He–He pair interactions, smaller clusters where the majority of He atoms are at the bubble interface are highly unfavourable. The formation energies calculated for the largest bubble, $\text{He}_V\text{Ga}$, indicate that He:vacancy ratios up to 1:9:1 return negative values. This is in line with the ratio of 2:1 reported elsewhere which is shown as a solid black line in Fig. 13.

To normalise the data in Fig. 13 it is useful to calculate the formation energy per He atom for each cluster. This data is shown in Fig. 14 and is plotted as a function of the number of vacancies. Again, clusters with a 1:1 He:vacancy ratio are associated with the lowest formation energies. However as the number of vacancies in each cluster increases, the formation energy per He atom soon converges to a minimum value of around $-0.5 \text{ eV}$. It may also be suggested that for the larger clusters (>16 vacancies) the formation energy begins to increase, albeit marginally. For higher He concentrations, although clusters are found to have a positive formation energy per He atom, this value steadily decreases as void size increases. For the 3:1 He:vacancy ratio, convergence to around 0.5 eV is observed and there is no indication that larger clusters may give a negative formation energy. However, for clusters containing a 2:1 He:vacancy ratio, a continual decrease in the formation energy per He atom is evident as the number of vacancies increases. Extrapolating the results shown in Figs. 13 and 14 suggests that as void size increases to over 20 vacancies, a 2:1 He:vacancy ratio becomes favourable relative to isolated He substitutional atoms.

5. Conclusions

The formation and migration of He into clusters and bubbles has been investigated by means of atomistic computer simulation. Using the Modified Embedded Atom Method, calculations of formation energies suggest isolated He atoms favour substitutional sites over residing as interstitials. This is compounded by migration energy barrier calculations that suggest the transition of substitutional He to an interstitial site is unlikely. Calculations involving vacancy assisted migration show that local vacancies can induce substitutional He migration, however the exact mechanism of He diffusion remains unknown.

Calculations of the formation energies of larger He-vacancy clusters indicate that the formation of bubbles is preferred over isolated He substitutional atoms. As the number of vacancies in the bubble increases, a He:vacancy ratio of up to 2:1 was found to be energetically favourable. This supports the He density reported experimentally by both positron annihilation spectroscopy [16,17] and transmission electron microscopy [18].

In line with previous studies into the behaviour of He in reactor fuels and other nuclear materials, the role of vacancies is central to mechanisms of He migration and eventual bubble formation. The dependency of He migration on residual vacancies suggests that rates of diffusion and bubble formation will relate to the defect production and recovery mechanisms inherent to a given material.

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