Bubbles in $\gamma$-uranium: atomistic simulation of surface self-diffusion

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Abstract. Mechanistic models of nuclear fuels require development of multi-scale models that provides the necessary microscopic parameters that are usually cannot be determined experimentally. In this work we present the results of atomistic calculations of the surface diffusivity for nanometer bubbles in $\gamma$-uranium that is used as a parameter in the rate-theory approach describing bubble diffusion. The unexpected features of surface diffusion are revealed and the accuracy of the rate-theory approach is estimated.

1. Introduction

Fast breeder reactors development is one of the perspective ways to future nuclear energy production. As a fuel for such reactors, metallic compounds of uranium are considered, for example, uranium alloys with molybdenum or zirconium. The description of the fuel mechanic and thermodynamic properties changes during its burn-up is important for both efficiency and safety of the projected reactors. Mechanistic approaches based on the fundamental knowledge about the processes occurring in nuclear materials can replace empirical methods. This work is devoted to one aspect of such mechanistic description, namely, to the rate theory description of bubble diffusion.

Fission products behaviour is one of the essential points in a complex approach to the nuclear fuel properties examination. Models for this process are developed in IBRAE RAS within the MFPR code [1,2], which includes a mechanistic description of the physical processes affecting the fission products release. The code contains a wide range of the microscopic parameters defining defect structure, thermal, mechanical and chemical properties of the fuel material. These parameters can be found via supercomputer atomistic modelling [3]. Such an approach appears to be especially valuable for metallic fuels due to the lack of experimental data for them.

Diffusivity of the bubbles in the crystal lattice is one of the key parameters influencing the fission products release velocity, porosity and swelling of the material. In present work diffusivity is calculated via the classical atomistic modelling for the bcc lattice of the $\gamma$-uranium.
was chosen for the study as a prototype of the U-Mo compound with the same bcc lattice structure.

Two methods are implemented in this work. Firstly, the diffusivity is derived from the uranium self-diffusion characteristics using theoretical considerations. Secondly, the diffusivity is computed from the trajectories of bubbles movement. The comparison of two methods allows to estimate the accuracy of the theory and its range of applicability.

The mechanism of bubble diffusion is connected with volume and surface self-diffusion of lattice atoms. While the volume self-diffusion in $\gamma$-uranium is considered in the literature [4], the surface self-diffusion is poorly studied, mostly for fcc crystals and simple cases [5,6], so it is the main focus of the present work.

2. Theory

If the diffusion is normal, the mean squared displacement (MSD) of an object is linear in time [7]:

$$\langle \Delta r^2 \rangle = 2 N D t,$$

where $D$ is the diffusion coefficient and $N$ is the dimension of a system. If the process is ergodic, the time averaged MSD and the ensemble averaged MSD are equivalent.

The motion of a bubble through a solid is described by the surface and volume mechanisms of self-diffusion [8]. In this work the spherical bubbles without internal gas are considered, so their diffusion coefficient is equal to

$$D_{\text{sub}}(R, T) = D_{\text{vol}} \frac{3\Omega}{2\pi R^3} + D_{\text{surf}} \frac{3\Omega^{4/3}}{4R^4},$$

where $D_{\text{vol}}$ and $D_{\text{surf}}$ are the volume and surface diffusion coefficients, $T$ is temperature and $\Omega$ is atomic volume. The volume mechanism is dominant at low temperature and the surface mechanism is the main one at high temperature [9]. We do not consider radiation-enhanced diffusion, therefore, the volume self-diffusion can be calculated from the diffusion of point defects that are vacancies and interstitials:

$$D_{\text{vol}} = C_{\text{vac}} D_{\text{vac}} + C_{\text{int}} D_{\text{int}}.$$  \hspace{1cm} (3)

The concentration of defects and their diffusion coefficient are both described by the Arrhenius equations [10]:

$$C_{\text{vac/int}} = \exp \left( -\frac{E_{\text{form/vac/int}}}{kT} \right),$$

$$D_{\text{vac/int}} = D_{\text{vac/int}}^0 \exp \left( -\frac{E_{\text{migr/vac/int}}}{kT} \right),$$

where $D_{\text{vac/int}}^0$ is the pre-exponential factor, $E_{\text{form}}$ and $E_{\text{migr}}$ are the energies of formation and migration, $\text{vac}$ and $\text{int}$ subscripts correspond to vacancy and interstitial.

It is difficult to distinguish elementary stages of surface self-diffusion, therefore, a single activation energy is used in the corresponding Arrhenius law:

$$D_{\text{surf}} = D_{\text{surf}}^0 \exp \left( -\frac{E_{\text{act/surf}}}{kT} \right).$$

The equation (2) is derived for spherical bubbles in the continuum approximation. The consideration of the diffusion process at the atomistic scale can be useful to determine the limits of applicability of this formula and to find possible corrections that take into account crystal lattice effects.
3. Molecular dynamics model

Large time-scale simulations (at least several nanoseconds) are required to calculate the self-diffusion and atoms and diffusion of bubbles in a solid. Such calculations are currently impossible with ab initio density functional theory models. Therefore, we used molecular dynamics with a classical interatomic potential. Several potentials have been created for uranium: embedded atom model (EAM) [11], different modified embedded atom models (MEAM) [12–14] and angular-dependent potential (ADP) [15].

In this work, we use the EAM potential, as it provides accurate description of the phonon spectrum of α and γ phases of uranium [16,17]. Also, this potential is less computationally demanding than the MEAM and ADP models.

In all calculations of γ-U a cubic box with periodic boundary conditions and zero pressure is used. Bubbles are created by removing atoms in a spherical region of a given radius.

At the beginning of the simulation the temperature is fixed for 200 ps with the Langevin thermostat. Then the simulation in the NVE ensemble is performed.

The detection of defects in the lattice is done using the Winger-Seitz algorithm. If the two atoms are found in the same Winger-Seitz cell of the ideal lattice, then this cell is counted as an interstitial site. Similarly, if there are no atoms in the Winger-Seitz cell, it is counted as the vacancy site.

4. Surface self-diffusion

The calculation of the self-diffusion coefficient along the surface of a bubble is difficult. According to the classical theory [8], the surface is determined as a monoatomic layer at the open boundary of the solid phase. However, this definition does not take into account the structure of the crystal lattice, the coefficient of the self-diffusion may depend on the orientation of the surface. Therefore, it is necessary to know the structure of the surface of a bubble to correctly describe the surface self-diffusion from an atomistic point of view.

The modeling of the bubbles with a radius from 26 to 90 Å is performed to check this effects:

1. To create a bubble, all atoms inside a sphere of a given radius are removed. At least 5 atomic layers between the surface of the bubble and the boundary of the simulation box remain.

2. To check the proper equilibration of the system during molecular dynamics calculation, different parameters are considered: the visual form of the bubble, the surface area, the number of point defects in the bulk. All these parameters become constant after 5-10 ns, the exact equilibration time depends on the radius of the bubble.

It is found that the spherical bubble transforms into a polyhedron with [100] and [110] surfaces after equilibration, as shown in figure 1. The relative fraction of the [100] surfaces is almost zero for small bubbles with \( R < 20 \) Å, and increases with increasing size of the bubble.

Due to this faceted shape of the bubbles, the self-diffusion coefficients along the [100] and [110] surfaces is calculated, as well as total self-diffusion coefficient along the surface of the bubble.

The MSD of surface atoms is calculated as a function of time. The averaging was done both by ensemble and time.

The assignment of the atoms to the surface layer was done with Voronoy tessellation. The volume of each cell \( V_{\text{vor}} \) is calculated and only cells with large volume are considered. For the atomic volume of 21.44 Å³ the threshold value \( V_{\text{vor}} > 26 \) Å³ distinguishes with good accuracy the atoms in the bulk from the atom at the surface. The example of such separation is shown in fig. 2 on the left side.
Figure 1. The averaged positions of atoms in the surface layer of the bubble with a radius of 50Å. Left: at the beginning of the simulation. Right: after 10 ns.

It is found that MSD is not linear in time, but it is a curve with a decreasing derivative (see fig. 2 on the right). The coefficient of self-diffusion along the surface was determined through the limit of derivative at $t \to 0$:

$$D_{\text{surf}} = \frac{1}{4} \lim_{\Delta t \to 0} \frac{\langle \Delta r^2 \rangle}{\Delta t}.$$  \hspace{1cm} (7)

As the exact form of the function $\langle \Delta r^2 \rangle(t)$ is unknown, the calculation is done via the following method. The time interval from 2.5 to 250 ps was divided into short 5 ps sections. The slope of the curve is calculated at each section with different approximations and the limit at $t = 0$ is determined. Different methods of approximation allow to estimate the resulting error, which is about 15%.

Figure 2. Left: the surface layer obtained from the Voronoy tessellation for the bubble with the radius of 50 Å. Right: MSD of the surface atoms as a function of time ($R = 50$ Å).
The calculated diffusion coefficients are shown in fig. 3. The diffusion is almost negligible along the flat [110] surface and only [100] surface should be taken into account. It implies also that the average diffusion coefficient along the surface of the bubble has no clear meaning.

The temperature dependencies of the surface diffusion coefficients for the bubbles of different radius and [100] flat surface have almost identical slopes. So we can approximate them with the single activation energy according to equation (6): $E_{\text{surf}} = 0.51 \pm 0.08$ eV.

The dependence of $D_{\text{surf}}$ on $R$ at $T = 1300$ K is shown in fig. 3 on the right. It can be seen that the diffusion coefficient increases with the radius of the bubble. One of the possible explanations is the polyhedral shape of the bubble (fig. 1). The ratio of [100] and [110] surfaces varies with the radius, therefore, the average self-diffusion coefficients are also different.

**Figure 3.** Left: the surface self-diffusion coefficient for different temperatures and bubble radii. Right: the surface self-diffusion coefficient different radii at 1300 K. The flat surface [100] limit is also shown.

5. Bubble diffusion

To validate the equation (2) it is necessary to compare diffusion coefficients from direct simulations $D_{\text{real}}^{\text{bub}}$ and from theory $D_{\text{th}}^{\text{bub}}$. $D_{\text{th}}^{\text{bub}}$ can be obtained with the previously calculated values of $D_{\text{vol}}(T)$ and $D_{\text{surf}}(R, T)$.

As the motion of bubbles becomes slower with the increase of its radius, the direct calculations are performed at $T = 1400$ K for small bubbles only (6 and 10 Å). To find the position of the bubble, the vacancies positions are calculated with respect to the ideal lattice. The center of the bubble is defined as the geometrical center of the vacancies in the bubble.

The value of $D_{\text{vol}}(T)$ is taken from the work of [4], where the same EAM potential was used. $D_{\text{surf}}(R, T)$ was calculated according to equation (6) at 1400 K. The results are shown in table 1. Theoretical values of diffusion coefficient is approximately 3.5 times larger than the value from direct molecular dynamics calculations.

6. Conclusions

It is found that the spherical bubbles with the radii of 2690 Å transform into polyhedra with [100] and [110] surfaces during system equilibration. The diffusion processes are fast on the [100] surface and almost negligible at the [110] surface. The coefficient of the surface self-diffusion increases with increasing radius, as well as the relative area of the [100] surface. The activation
Table 1. The results of direct modelling of the diffusion of the bubbles with the estimate from equation 2.

| $R$, Å | $D^{\text{real}}_{\text{bub}}$, m$^2$/s | $D^{\text{th}}_{\text{bub}}$, m$^2$/s | $\frac{D^{\text{th}}_{\text{bub}}}{D^{\text{real}}_{\text{bub}}}$ |
|--------|---------------------------------|----------------------------|---------------------|
| 6      | $(1.0 \pm 0.2) \times 10^{-12}$ | $(3.8 \pm 2.7) \times 10^{-12}$ | 3.5                 |
| 10     | $(1.2 \pm 0.3) \times 10^{-13}$ | $(7.2 \pm 3.6) \times 10^{-13}$ | 3.6                 |

energy does not depend on the radius of the bubble. We can conclude that the process of self-diffusion along the surface of the bubble is reduced to the diffusion along the [100] surface. In this case, the diffusion of atoms along the entire surface of the bubble is much slower than along the individual facets.

Direct modelling of the small bubble motion shows that the formula (2) overestimates the diffusion coefficient by about 3.5 times. This acceptable level of accuracy shows that the classical theory is applicable indeed for diffusion of nanometer-sized bubbles in the lattice if the dependence of $D_{\text{surf}}$ on $R$ is known. The detailed study of this dependence is a subject of further studies.

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