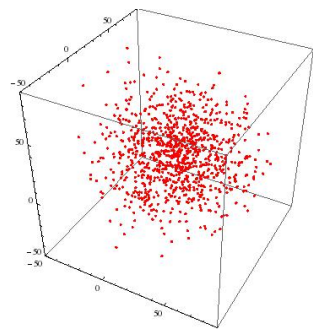
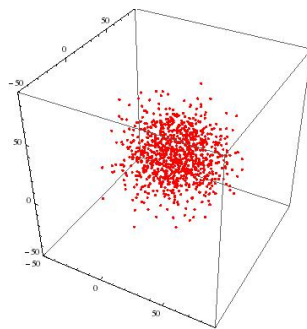
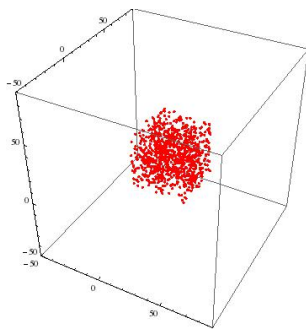


# Modelling diffusion processes of deuterium in tungsten

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## **Abstract**

The diffusion processes in tungsten are simulated by using Monte Carlo methods. Measurements of deuterium retention in tungsten are compared to theory. The influence of traps on deuterium retention is investigated. While simulating the atomic structure of tungsten takes a lot of calculation time, a method is introduced that is able to extend the total time that is simulated to weeks. To reach these timescales, the simple diffusion process is treated different than trapping and detrapping. The influence of traps on diffusion processes is demonstrated. Namely, if trap influence is neglected the observed retention behaviour cannot be recreated. Deep traps with trap energies around 1.2 eV keep deuterium trapped for large timescales at room temperature and they have a large effect on diffusion processes. However, it is very unlikely that they fully account for the observed behaviour of deuterium retention. Shallow traps with trap energies around 0.7 eV are shown to slow down diffusion, predicting behaviour that is in accordance with measurements.

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# 1 Introduction

Nuclear fusion power is a promising solution for the global energy problem. However, developing a fusion power station is a very challenging task. One of the key issues in making an efficient fusion power station is the development of plasma facing components. There are many different designs of nuclear fusion reactors. One of the designs is the so-called tokamak reactor, where plasma rotates inside a vacuum due to magnetic fields. In tokamak fusion reactors there are locations where the plasma reaches the walls of the reactor, such that heat and waste can be extracted from the plasma. ITER is a tokamak fusion reactor that is currently being built and it will have a divertor area where plasma will reach the walls. Little materials are capable of withstanding the conditions in the divertor, because of the high heat and particle fluxes of the plasma inside the divertor area. Tungsten is one of the materials that is being investigated to become wall material in future devices and it will be used in ITER. Tungsten is chosen because it retains little deuterium and tritium compared to other materials [1] and it has a very high melting point. The temperatures in the divertor are only a fraction of the temperatures in the core plasma where fusion will occur, but they are still very high. Before tungsten can be used, it is important to understand the processes that occur inside the material during the full time of operation in a fusion device. Linear plasma generators are used to simulate the conditions inside the divertor area and to expose materials to fluxes and temperatures similar to those in a fusion device.

The hydrogen isotopes deuterium and tritium will be used as fuel for fusion reactions, so these substances will be present in plasmas facing the wall materials. Because tritium is a radioactive material, there are safety limits on the total amount that is allowed to be inside a machine. When plasma touches tungsten in a divertor, deuterium and tritium will be implanted into tungsten and they will diffuse through the tungsten material. Parts of deuterium and tritium can be retained in the material after exposure to plasma. Tritium is needed for the fusion reaction, so it is undesirable that a large part of the amount that is allowed to be in the machine is retained inside the walls of the divertor. The diffusion processes of hydrogen in tungsten are not fully understood and they have to be investigated, so that the interaction between tungsten and hydrogen plasma can be explained and possibly manipulated.

Around the world, research is being carried out into the properties of tungsten as material for plasma facing components (PFCs) in fusion devices. At FOM institute DIFFER, two linear plasma generators called Magnum-PSI and Pilot-PSI are used to study the reaction of materials to plasma exposure. These machines simulate the conditions in the divertor area and they are unique in their capability of reaching high plasma fluxes. One of the things investigated is the amount of deuterium that is retained in tungsten after exposure to a deuterium plasma. Tritium is never used because of its radioactivity, but when compensated for the mass difference it is believed to behave exactly like deuterium. Tungsten contains natural defects. These defects can act as a trap for deuterium particles that diffuse through the material. Traps influence the diffusion of deuterium in several ways. Deuterium atoms have to overcome an energy barrier to move out of a trap. The height of this energy barrier

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is called the trap energy. The higher the trap energy, the lower the probability that a particle will leave the trap. So depending on the trap energy, traps influence diffusion in different ways. The exact way in which traps influence diffusion should be investigated.

Previous experiments on Pilot-PSI showed that the amount of deuterium that is retained inside tungsten decreases slowly. Five tungsten samples were exposed to deuterium plasma for 200 s. The total amount of deuterium retained was measured using Thermal Desorption Spectroscopy (TDS). This was done 2 hours, 1 day, 1 week, 1 month and 3 months after exposure. The retention of deuterium was shown to decrease in time. In the first days, there is rapid decrease, while the decrease seems to stagnate after more than a week. The decrease is explained by diffusion of deuterium out of the tungsten material. It will be released from the material when it reaches the surface. The concentration of traps that is present in tungsten could be small relative to the concentration of deuterium, such that traps do not influence diffusion at all. It could also be that these traps would just keep a base level of deuterium trapped forever, while the remaining particles can move through the material freely, uninfluenced by the traps. The aim of this research is to investigate diffusion processes and to find a possible explanation for the observed decrease of retention in time.

The three dimensional lattice structure of tungsten is known and the way in which deuterium atoms can move through this structure can be modelled in three dimensions. The diffusion process can be predicted very precise in this way, but the number of iterations that has to be taken to model one second of diffusion is enormous. One time step will have an order of magnitude around  $10^{-13}$  s, while the observed decrease occurs at timescales with an order of magnitude around  $10^6$  s. Even using methods to reduce the number of iterations, atomic models can only be used to simulate diffusion processes that occur at small timescales with an order of magnitude up to  $10^{-3}$  s. The probability that a free deuterium particle finds a trap in a certain period of time is an example of a diffusion process that occurs at small timescales. However, the atomic model has to be abandoned when the decrease in deuterium retention is simulated. Therefore a one dimensional model is used to simulate diffusion processes on larger timescales. Actual diffusion through the material is averaged using the diffusion constant, while processes like trapping and detrapping are still treated as processes that occur at atomic level. This is sufficient to extend the timescales of the simulations. This program will give the distribution of deuterium in tungsten and can predict how the amount of deuterium decreases in time. The timescales that can be simulated reach up to  $10^6$  s, depending on the exact simulations. These predictions can be compared to measurements, leading to a better understanding of the diffusion processes. Some quantities are varied to investigate how they affect the course of deuterium retention. Examples are the trap configuration and the influx of particles during exposure.

## 2 Theory

### 2.1 Lattice structure of tungsten

Tungsten has a body-centred cubic (bcc) lattice structure [2]. The structure can be described by using cubic unit cells, which are depicted in figure 2.1. The lattice is divided into unit cells stacked onto each other. Points on the outside borders of a unit cell are shared by multiple unit cells. Each tungsten atom at one of the vertices of the cube is shared by eight unit cells, while the tungsten atom at the centre of the cube is only shared by this one unit cell. This means that in a bcc lattice there are two atoms for each unit cell. Tungsten atoms are relatively large compared to deuterium atoms. Tungsten has atomic number 74 while deuterium has atomic number 1, which gives an indication that there is a size difference between their electron clouds. Because of this difference in size, deuterium atoms can move between the tungsten atoms. Deuterium atoms need to overcome potential energy barriers in the material to move through it. In a bcc lattice there are special points where there is extra space, called octahedral and tetrahedral interstitial sites [3]. When atoms are imagined to be spheres, the interstitial sites are the voids that are left between the spheres when they are stacked. A more neat way of seeing this is that these interstitial sites are the locations of local minima in the potential energy of deuterium in a tungsten lattice. In a bcc lattice, interstitial sites are located in the centres of asymmetrical tetrahedra and octahedra, where the atoms are located at the vertices of these polyhedra. For each tungsten atom, there are six tetrahedral and three octahedral interstitial sites. They are depicted in figure 2.1. Setting the origin at a certain tungsten atom, the positions of the tetrahedral interstitial sites are given by

$$\begin{aligned}
 & a \begin{pmatrix} n_1 \\ n_2 + \frac{1}{2} \\ n_3 + \frac{1}{4} \end{pmatrix} & a \begin{pmatrix} n_1 \\ n_2 + \frac{1}{4} \\ n_3 + \frac{1}{2} \end{pmatrix} & a \begin{pmatrix} n_1 \\ n_2 + \frac{3}{4} \\ n_3 + \frac{1}{2} \end{pmatrix} & a \begin{pmatrix} n_1 \\ n_2 + \frac{1}{2} \\ n_3 + \frac{3}{4} \end{pmatrix} \\
 & a \begin{pmatrix} n_1 + \frac{1}{2} \\ n_2 \\ n_3 + \frac{1}{4} \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{1}{4} \\ n_2 \\ n_3 + \frac{1}{2} \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{3}{4} \\ n_2 \\ n_3 + \frac{1}{2} \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{1}{2} \\ n_2 \\ n_3 + \frac{3}{4} \end{pmatrix} \\
 & a \begin{pmatrix} n_1 + \frac{1}{4} \\ n_2 + \frac{1}{2} \\ n_3 \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{1}{2} \\ n_2 + \frac{1}{4} \\ n_3 \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{1}{2} \\ n_2 + \frac{3}{4} \\ n_3 \end{pmatrix} & a \begin{pmatrix} n_1 + \frac{3}{4} \\ n_2 + \frac{1}{2} \\ n_3 \end{pmatrix}
 \end{aligned} \tag{2.1}$$

Here  $n_1$ ,  $n_2$  and  $n_3$  are integers. They represent the translational symmetry of the lattice. Figure 2.1 shows the locations of the tetrahedral interstitial voids. The length of the edge of the cube is called the cell parameter ( $a$ ) and is equal to 316.52 pm [2]. The tetrahedral sites are all positioned on the outer surfaces of the cube and at distances from each other one quarter of  $a$  in one direction and one quarter of  $a$  in another direction. In figure 2.2, a tetrahedral site is shown which is located between four atoms.

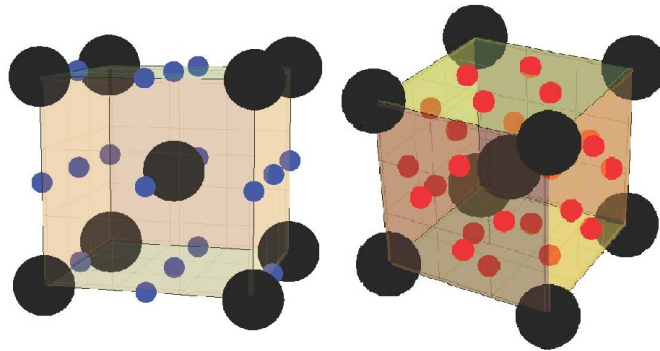


Figure 2.1: Unit cell of bcc lattice. Tungsten atoms are represented by black spheres, octahedral interstitials by blue spheres (left) and tetrahedral interstitials by red spheres (right). Eight tungsten atoms are fixed at the vertices of the cube and one is fixed at the centre of the cube. There are three octahedral sites and six tetrahedral sites per tungsten atom.

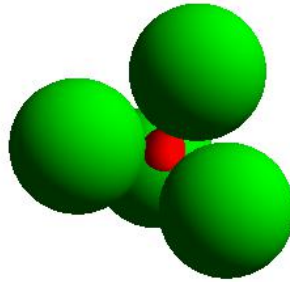


Figure 2.2: Tetrahedral interstitial site. The green spheres indicate the positions of tungsten atoms, the red sphere represents the interstitial void.

Tungsten contains natural defects. These can mostly be classified into dislocations, mono-vacancies and grain boundaries. Mono-vacancies are lattice locations where a tungsten atom is missing. These pointlike defects can act as a trap for deuterium atoms that pass the defect location. The polycrystalline tungsten lattice is build up of grains, which are areas in the lattice where the lattice is orientated in a certain direction. A simplified picture is given in figure 2.3. The lattice has different orientations in different grains, resulting in lines of imperfections along the grain boundaries. Dislocations are also larger imperfections in the lattice. These linelike impurities in tungsten can also act as a trap to passing deuterium atoms. This study will focus on the effects of pointlike defects only.

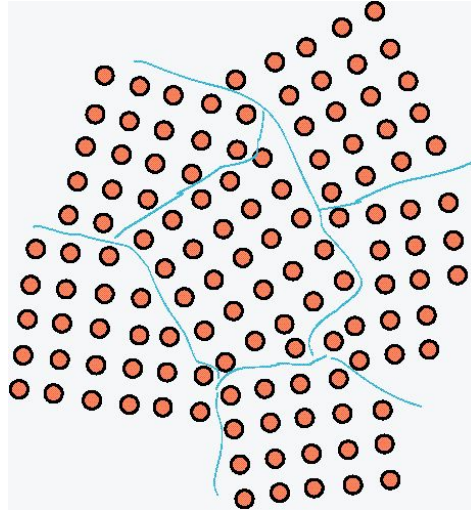


Figure 2.3: Simplified overview of the grain structure in a lattice. The blue lines represent the grain boundaries. Grains are rotated with respect to each other.

## 2.2 Deuterium diffusion through tungsten

Because of the size difference between deuterium and tungsten, deuterium can sit at interstitial sites inside a tungsten lattice. At these interstitial sites, there is a minimum in the potential energy for deuterium atoms. Research has shown that deuterium greatly prefers tetrahedral interstitial sites over octahedral interstitial sites [4] [5]. According to calculations by Heinola et al., the potential energy of deuterium is 0.38 eV higher for an octahedral site than for a tetrahedral site [6]. According to computational calculations by Xu et al., this difference is even larger and around 0.79 eV [7]. Because of this extra potential energy, deuterium atoms will not move to octahedral sites but they will use the tetrahedral interstitial sites.

Deuterium atoms can hop from one tetrahedral site to the other. It is possible that they use several paths through the tungsten lattice. For each path, there is an energy barrier that has to be overcome to hop to a nearest neighbour interstitial site. This barrier can be overcome due to thermal fluctuations. Diffusion is now driven by thermal fluctuations and the movement can be modelled by a discrete process of moving from one tetrahedral site to another. Using a computational method, Johnson et al. have calculated the energy barrier for deuterium over the minimal energy pathway inside tungsten [8]. This was computed to be 0.39 eV for deuterium and 0.38 eV for hydrogen, where previously Frauenfelder measured it to be  $0.39 \pm 0.09$  eV for hydrogen [9]. Using another method, Heinola et al. calculated this energy to be 0.21 eV, but Johnson et al. criticised their method. Xu et al. calculated a value of 0.33 eV for this path [7]. The path goes through one of the faces of the tetrahedron. This means that a deuterium atom moves through the middle of the triangle made up by three tungsten atoms, as seen in figure 2.2. There seems to be a larger space there to move through. In reality a deuterium particle can also use different paths, but these will have higher energy barriers. Xu et al. have calculated the next least energy pathway to have a barrier energy of 0.79 eV [7], which shrinks the probability of using this path enough to neglect it completely. It runs via an octahedral interstitial site, so octahedral sites are not considered any more. The only path that is really taken by deuterium atoms is the one with the smallest energy barrier.



Computational methods give values for the diffusion energy that are close to the measured value, but the measured value is more reliable as it relies less on assumptions. Frauenfelder's data were confirmed by later experiments [10]. A value of 0.4 eV is used in the calculations.

The tetrahedron has four faces, so when a deuterium particle is at a certain site it can move in four directions to other tetrahedral interstitial sites. These sites are all at equal distances away from the initial site. The tetrahedra can have different orientations inside the tungsten lattice, all rotated relative to each other. There are six different orientations of tetrahedral interstitial sites, corresponding to the six tetrahedral sites that are present for each tungsten atom. Each tetrahedral site has four nearest neighbour sites.

Diffusion of deuterium through tungsten is discrete in position, but also time can be seen as discrete. Tungsten atoms vibrate around their lattice positions with a certain typical frequency. These lattice vibrations called phonons are described by the Debye model. The Debye frequency  $\omega_D$  is defined as the maximal frequency at which the lattice vibrates [11]. For tungsten, the Debye frequency is equal to  $4.05 \times 10^{13}$  Hz. The maximal vibrational frequency of tungsten  $\nu_t$  is calculated from this by

$$\nu_t = \frac{\omega_D}{2\pi} \quad (2.2)$$

In the Debye model, the energy levels of the lattice vibrations are taken to be harmonic oscillators. The equation of motion for a classical harmonic oscillator with a spring constant  $k$  and mass  $m$  is

$$\frac{d^2x(t)}{dt^2} = -\frac{k}{m}x(t) = -\omega^2x(t) \quad (2.3)$$

where  $\omega$  is the angular frequency of the oscillator. It follows that the angular frequency is proportional to  $\frac{1}{\sqrt{m}}$  (if  $k$  does not depend on  $m$ , which is not the case here because it is due to electromagnetic interactions). Assuming that deuterium atoms get their vibrational frequency  $\nu_d$  from the lattice vibrations of tungsten and compensating for the mass difference between tungsten and deuterium, equation 2.2 leads to

$$\nu_d = \sqrt{\frac{m_t}{m_d}}\nu_t = \sqrt{\frac{m_t}{m_d}}\frac{\omega_D}{2\pi} \quad (2.4)$$

where  $m_t$  and  $m_d$  are the masses of the tungsten and deuterium atom respectively. This equation predicts a value of  $\nu_d = 6.2 \times 10^{13}$  Hz.

Deuterium that is located inside a potential energy well will try to get out of that well. The attempt frequency  $\Gamma$  represents the number of times that a deuterium atom tries to get out of the well every second. The timescale  $\frac{1}{\Gamma}$  represents the average time that a deuterium particle occupies a single state before it chooses a next state. The attempt frequency is assumed to be general, so the attempt frequency for a deuterium particle at a tetrahedral site will be the same as the frequency at a trap. The way in which the attempt frequency depends on the maximal vibrational frequency of deuterium atoms  $\nu_d$  is rather unclear. At least, the vibrational frequency should be averaged. However, there is a different way to calculate the attempt frequency.

$\Gamma$  can be calculated from the diffusion constant. The diffusion constant can be equated as a function of the length of the discrete steps in time and space. First, the mean square displacement of a deuterium particle  $\overrightarrow{r}^2$  is calculated at atomic level. If you take  $N$  trials

to move from one interstitial site to another, then the mean square displacement can be calculated. The different trials are indexed by  $i$  and  $j$ .

$$\langle \vec{r}^2 \rangle = \left\langle \left( \sum_{i=1}^N \vec{r}_i \right) \cdot \left( \sum_{j=1}^N \vec{r}_j \right) \right\rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \vec{r}_i \cdot \vec{r}_j \rangle \quad (2.5)$$

Here the brackets mean that the thermal average is taken. Two different steps are completely uncorrelated. The direction of movement at a certain step  $i$  does not influence the direction of movement at step  $i + 1$ . All probabilities of hopping stay exactly the same. The components of  $\vec{r}_i$  have equal probability to be negative or to be positive, making the average of each component zero. So,  $\langle \vec{r}_i \cdot \vec{r}_j \rangle$  vanishes when  $i \neq j$ . When  $i = j$ , the square of one step is taken. Because we are in three dimensions, the total mean square displacement of one step is given by

$$\langle \vec{r}_i^2 \rangle = \langle r_{x,i}^2 \rangle + \langle r_{y,i}^2 \rangle + \langle r_{z,i}^2 \rangle = 3\langle r_{x,i}^2 \rangle \quad (2.6)$$

where the last step follows from the rotational symmetry of the unit cell. Using that a deuterium particle will spent equal time in all six different orientations of the tetrahedra, the mean square displacement can be calculated. If  $P$  is the probability to move from one tetrahedral site to the other during one time step, the displacement becomes

$$\langle r_{x,i}^2 \rangle = \frac{1}{6} P a^2 \quad (2.7)$$

The factor  $\frac{1}{6}$  comes from the lattice structure of tungsten. It can be calculated using that an atom can move in four directions from one site. Only the x-component of the displacement in each possible event has to be considered, because this can be related to the total mean square displacement by equation 2.6. The calculation of the mean displacement is repeated six times for all possible orientations of the tetrahedral sites, where the contribution from each direction gets a weight of  $\frac{1}{6}$  because there are six rotations of the tetrahedra. This all combined leads to the final factor of  $\frac{1}{6}$ . Summarising, equations 2.6 and 2.7 give

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{cases} 0, & \text{if } i \neq j \\ \frac{1}{2} P a^2, & \text{if } i = j \end{cases} = \frac{1}{2} P a^2 \delta_{ij} \quad (2.8)$$

where  $\delta_{ij}$  is the Kronecker delta. This is plugged into equation 2.5 to give

$$\langle \vec{r}^2 \rangle = \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2} P a^2 \delta_{ij} = \frac{1}{2} N P a^2 = \frac{1}{2} \Gamma t P a^2 \quad (2.9)$$

where the time since the start of the diffusion is called  $t$ . In  $d$  dimensions, the diffusion constant obeys [12]

$$\langle \vec{r}^2 \rangle = 2dDt \quad (2.10)$$

In three dimensions, equations 2.9 and 2.10 lead to

$$D = \frac{1}{12} \Gamma P a^2 \quad (2.11)$$

The probability of moving from one tetrahedral site to another can be calculated using statistical physics. A deuterium atom that is located at a tetrahedral site can stay where it

is or it can move to one of four neighbouring tetrahedral sites. The assumption is made that the atom will jump to another site once the atom has enough thermal energy to overcome the energy barrier that separates the two sites. During one time step, there will be five different states available for the atom. The first state, which is staying at the current site, requires no additional energy. When the atom is situated at the location of the maximum in the energy barrier between two tetrahedral sites, it is said to be at a transition state. There are four of these states and once the atom reaches a transition state it is assumed to move along to the next site. The partition function for a particle in one time step is given by

$$Z = \sum_{\alpha=1}^5 e^{-\beta E_{\alpha}} = 1 + 4e^{-\beta E_m} \quad (2.12)$$

where  $\alpha$  gives the label of each microstate and  $\beta = \frac{1}{k_B T}$  with  $k_B$  the boltzmann factor and  $T$  the temperature.  $E_m$  is the activation energy for mobile diffusion, the height of the energy barrier between two tetrahedral interstitial sites. The probability that a particle will get to a transition state (so move to another tetrahedral site) is

$$P = \frac{1}{Z} e^{-\beta E_m} = \frac{e^{-\beta E_m}}{1 + 4e^{-\beta E_m}} \approx e^{-\beta E_m} \quad (2.13)$$

where the last approximation assumes that  $E_m \gg k_B T$ .  $E_m = 0.4 \text{ eV}$  corresponds to a temperature of  $T \approx 4600 \text{ K}$ , a temperature that is not reached by far in experiments. The combination of equations 2.11 and 2.13 leads to the Arrhenius equation of the diffusion constant.

$$D = \frac{1}{12} \Gamma a^2 e^{-\beta E_m} = D_0 e^{-\beta E_m} \quad (2.14)$$

with

$$D_0 = \frac{1}{12} \Gamma a^2 \quad (2.15)$$

Equation 2.14 is the actual equation to which experimental data were fitted by experimentalists to find the diffusion constant. Their reported value of  $D_0$  can now be used to find the value of  $\Gamma$ .

$$\Gamma = \frac{12D_0}{a^2} \quad (2.16)$$

Frauenfelder fitted the Arrhenius equation to his measurement data of diffusion of hydrogen, finding a value of  $D_0 = 4.1 \times 10^{-7} \text{ m}^2/\text{s}$ . Because deuterium atoms have approximately two times the mass of hydrogen atoms, this value should be divided by the square root of two to get the value of deuterium. Equation 2.16 now gives a value of  $\Gamma = 3.5 \times 10^{13} \text{ Hz}$ . This value is chosen for further calculations, because it directly comes from experimental data. It corresponds well to the maximal vibrational frequency derived earlier.

## 2.3 Deuterium distribution in tungsten

If it is not trapped, deuterium that is retained in tungsten diffuses slowly out of the material. First deuterium diffuses through bulk material towards the surface and then it moves from

the surface into the air. Deuterium particles are assumed not to move back into the material when they reach the surface. The retention of deuterium in tungsten is then fully dependent on bulk diffusion.

Because atoms are very small and macroscopic processes involve great numbers of atoms, diffusion can be seen as a continuous process. In this continuum, particles are replaced by the density  $C(x, t)$ . The diffusion equation in one dimension is given by

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \quad (2.17)$$

During exposure to plasma the concentration of deuterium at the surface of tungsten is constant. At infinity, the concentration should be zero because deuterium cannot reach infinity at finite times. Applying the boundary condition

$$C(0, t) = C_0 \quad (2.18)$$

the solution of equation 2.17 is given by a complementary error function

$$C(x, t) = \frac{C_0}{\sqrt{\pi D t}} \int_x^\infty e^{-\frac{x'^2}{4 D t}} dx' \quad (2.19)$$

The previous derivation is only true when there are no traps present in the material. If there are, diffusion of deuterium is influenced by them and the depth profile will differ from equation 2.19.

Tungsten contains natural traps for deuterium, which are characterised by their trap energy and density [13]. Traps can be divided into two classes depending on their trap energy. If a deuterium atom is expected to leave a trap within an hour after it was trapped at room temperature, it will be called a shallow trap. Otherwise, the trap will be called a deep trap. The border between these classes lies around 1 eV, so deep traps have trap energies higher than 1 eV. The timescales of trapping an atom respond very delicately to the trap energy. For example, a deuterium atom is expected to be released from a 0.8 eV trap in a second, while it takes the atom months to get out of a 1.2 eV trap. The different classes have different influences on diffusion of deuterium.

The shallow traps will have a delaying effect on diffusion. Atoms get trapped and de-trapped rapidly, but they spend more time at a trap site as they would do at a tetrahedral site. This effect depends on the concentration of traps present. If the concentration is high, deuterium atoms will be trapped almost immediately. It should be high with respect to the concentration of deuterium, because deuterium should not saturate the traps. The time that deuterium atoms spend at a trap site should be larger than the time spend in mobile diffusion. In this case, diffusion will look like hopping from one trap site to the other with a certain probability per second. So the effective diffusion constant becomes lower. If the concentration is too low, there will only be occasional trapping of the atoms, so diffusion will be governed by mobile diffusion while a part of the particles is slowed down.

The deep traps have a different effect on the diffusion. If their concentration is high enough, particles that enter an area where an empty trap is present will be absorbed into traps almost immediately. The fast end of the diffusion distribution is taken away from diffusing any further, enlarging the time it takes the edges of the deuterium concentration to reach further distances. Once all traps in an area are filled, they do not influence the diffusion process any more. Deep traps have an obvious effect on retention of deuterium,

because deuterium is stored in the traps for a very long time. This should be visible when deuterium retention is measured in time.

# 3 Simulation

## 3.1 Three dimensional atomic model

If a deuterium atom diffuses through tungsten and a trap is present, there is a probability that the atom becomes trapped. This probability depends on the time the particle is allowed to diffuse. The atomic structure of the tungsten lattice is modelled to calculate this probability. Only the tetrahedral sites have to be considered to simulate the correct movement of deuterium, because deuterium is only allowed to move from one tetrahedral interstitial site to another in pure tungsten. When the deuterium atom meets a tetrahedral site that is located next to a missing tungsten atom, the deuterium atom is believed to be trapped. The lattice structure of tungsten is changed a little in the direct surroundings of a mono-vacancy [14] and this makes that deuterium atoms get trapped when they reach those surroundings.

A periodic trap distribution models the concentration of mono-vacancies in tungsten. This is achieved by replicating a cube of tungsten atoms, where the tetrahedral sites are located at positions given by equation 2.1. The tungsten atom in the middle of this cube is taken from the lattice, making the 24 tetrahedral sites surrounding this location to be marked as trap locations. If a deuterium atom reaches one of these locations, it is said to be trapped and it cannot move any further. The initial distribution of deuterium is calculated by giving all particles random locations in the cube. By applying periodic boundary conditions to the cube, atoms are able to move arbitrary distances. The cubes used consist of  $10 \times 10 \times 10$  or  $30 \times 30 \times 30$  unit cells. Periodic boundary conditions imply the periodic trap concentration. The time steps in the program are given by the attempt frequency  $\Gamma$ . The movement of a particle is calculated for a certain amount of time steps. The program takes one particle at a random location, calculates its movement during a certain time, reports its last position and takes the next particle. No interaction between different deuterium particles is assumed. By repeating this calculation for different periods of time and for many particles at random locations, the probability for one particle to be trapped in a certain period of time is calculated.

The movement of particles through the material is modelled by using the six different orientations of tetrahedral interstitial sites. For each particle the location and the orientation of its site are remembered. A particle can jump in four directions, determined by the orientation of the tetrahedral site. The new location and orientation of the particle are then stored. The program chooses randomly from one of the four possible directions to simulate a jump.

During one time step a particle can move to one of the neighbouring tetrahedral sites or it can stay at its current location. The probability to move in a single time step is very small at room temperature, namely around  $10^{-7}$ . This leads to an enormous amount of calculation steps for the program and therefore extending the calculation time. To decrease the calculation time, the program takes only into account the actual jumps of the particle. This is sufficient for calculating the probability to get trapped if the values are compensated for the probability to make an actual jump. This is only possible if the particles do not interact, which is the case. Using this new approach, the diffusion distance during a certain time should not change. According to equation 2.9, the mean squared distance is given by

$$\langle \vec{r}^2 \rangle = \frac{1}{2}NP a^2 = \frac{1}{2}(4NP)\left(\frac{1}{4}\right)a^2 = \frac{1}{2}N^*\left(\frac{1}{4}\right)a^2 \quad (3.1)$$

where

$$N^* = 4NP \quad (3.2)$$

The new probability to jump to a certain neighbouring site is chosen to be  $\frac{1}{4}$  and because there are four of these sites, the total probability to jump equals one. Because  $P$  is very small, the number of steps that the program should take,  $N^*$ , becomes much smaller than  $N$  and the total calculation time of the program is decreases by a factor around  $10^7$ . Now, the program is able to simulate milliseconds of diffusion.

The program calculates the probability for a particle to get trapped as a function of the number of jumps that a particle has to take and of the trap density in the material. It is assumed to be dependent on the product of these two variables. This assumption will be tested. The program calculates the function only for a certain trap concentration  $\rho_0$ . This function is called  $P_{tr}(N^* \cdot \rho_0)$ . Because the probability is linearly dependent on the trap concentration  $\rho$ , the general function is given by

$$P_{tr}(N^* \cdot \rho) = P_{tr}\left(\left(N^* \cdot \frac{\rho}{\rho_0}\right) \cdot \rho_0\right) = P_{tr}(N' \cdot \rho_0) \quad (3.3)$$

so  $N'$  is the scaled number of steps, depending on the density and on  $N^*$ , given by equation 3.2. Once the program has calculated the probability function for one trap concentration, this function can be adapted for every trap concentration and temperature.

## 3.2 Diffusion simulation at large timescales

Some difficulties arise when the entire diffusion process is modelled at atomic level. The number of calculation steps that a program should take is the main difficulty. Because there are many particles and the attempt frequency is very high, it takes a program a lot of time to calculate the macroscopic behaviour of deuterium diffusion. This is still a large problem after reducing the number of steps using equation 3.2. It is also difficult to simulate a macroscopically large piece of tungsten. To cope with larger timescales, the three dimensional model is abandoned and replaced by a one dimensional model that operates at a more macroscopic level. In this model, the depth of a material is split up into zones with a length in the sub-micrometre range. Processes that occur at atomic level like trapping and diffusion are averaged per zone. The processes that occur in a zone are illustrated in figure 3.1. During one time step in the model, the probability that two of these processes occur should be very small. Then, the occurrence of multiple events in one time step can be neglected.

Because computers cannot handle the actual amount of particles that are present in diffusion processes, each particle in the model represents many particles in reality. Two programs are made using this model. One simulates the exposure of tungsten to a deuterium plasma and is called the exposure program. The other simulates the diffusion process that occurs afterwards when the material is stored at room temperature and this one is called the release program. In the exposure program particles enter the material, while they do not in the release program. These programs can be used to simulate how deuterium retention develops in time. The effects of deep and shallow traps on the diffusion processes can be studied.

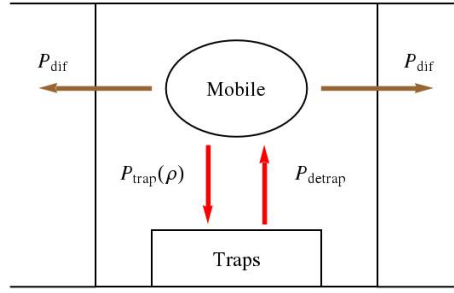


Figure 3.1: Illustration of the different processes that occur in a zone. Deuterium particles can be trapped and detrapped, or they can move to a neighbouring zone. Each process occurs with a certain probability in one time step. The probability to trap depends on the trap concentration  $\rho$ .

In this model, diffusion of a particle is seen as the movement of a particle from one zone to another. The probability to move to a neighbouring zone can be calculated from the diffusion constant. Assuming that this probability is small, such that it is very unlikely that a particle moves two zones in one time step, the mean squared displacement is given by

$$\langle r^2 \rangle = 2NP_{dif}s^2 = 2Dt = 2DNt_s \quad (3.4)$$

where  $P_{dif}$  is the probability to move to a neighbouring zone,  $s$  is the length of a zone,  $N$  is the number of time steps taken and  $t_s$  is the size of one time step. Equation 2.10 is used to relate the diffusion constant to the mean square displacement in one dimension. The equation leads to

$$P_{dif} = \frac{Dt_s}{s^2} \quad (3.5)$$

This equation only holds for small values of  $t_s$ . Another way to calculate the probability of a particle moving to a neighbouring zone would be to place it in the middle of a zone and solve the diffusion equation 2.17. The solution for this situation is given by a Gaussian probability distribution. First deuterium is concentrated at a single point in the middle of a zone and when time continues this concentration collapses into a Gaussian distribution due to diffusion. The probability to find a particle in a neighbouring zone after a while can be derived by integrating the concentration profile over this zone. The profile is illustrated in figure 3.2. When time continues, the Gaussian curve will spread out. If the time step is small enough, the probability to find the particle two zones away from the zone where it started will be small. If it was assumed that during the next time step the particle started in the middle again, a crude approximation would have been made. When a particle diffuses to a neighbouring zone, it is most likely to be at the edge of the zone on the side where it came from. The probability to move back in the next time step is far greater than the probability to move forward. If the particle is assumed to be in the middle of the zone every time, the forward movement would be exaggerated. In equation 3.5 the actual forward movement is by construction always equal to the movement predicted by the diffusion constant. Nothing is assumed about the location of deuterium inside the zone. The size of a time step should be small to ensure that the probability to move two zones in a single time step can be neglected.



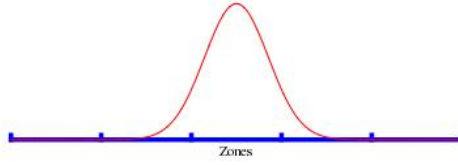


Figure 3.2: Illustration of the probability profile of the location of a particle after it started in the middle of the third zone. The zones are depicted in blue. The probability of finding the particle in the middle zone will be high, the probability of finding it in the outer zones will be very low.

The probability to find a trap can be calculated using equation 3.3. The traps are considered to be able to hold one deuterium atom at a time. If they are able to hold more, this can be compensated by making the trap concentration higher. The probability of a free particle to find a trap depends on the part of the traps in the neighbourhood of the particle that is filled at that instant. This is done in the program by making the probability linearly dependent on the part of the traps that is filled in the zone that the particle is in. It would be netter to use function 3.3, but the linear combination can be done more easily by the program and it will take less time to run.

The movement of particles is now averaged and the atomic processes are abandoned there. But for the other processes, the atomic processes are still considered. The probability to leave a trap in one time step is calculated similar to the probability of moving to a neighbouring tetrahedral site in equation 2.13. The deuterium atom is only allowed to be in or out of the trap, giving two possible states. The probability to stay at a trap site with a trap energy  $E_t$  is given by

$$P_{stay} = \frac{1}{1 + e^{-\beta E_t}} \quad (3.6)$$

The attempt frequency  $\Gamma$  is assumed to be universal and it is given by equation 2.16. If the number of attempts in one time step of the zone programs is  $N$ , the probability to leave a trap is given by

$$P_{detrapp} = 1 - (P_{stay})^N = 1 - (P_{stay})^{\Gamma t_s} = 1 - \left(\frac{1}{1 + e^{-\beta E_t}}\right)^{\frac{12D_0 t_s}{a^2}} \quad (3.7)$$

The probabilities that are used by the program are therefore calculated from the physical quantities with equations 3.3, 3.5 and 3.7. Using a random number generator, the program will decide for each time step what action is taken. The number of traps that is present per zone should also be deduced from the trap concentration. In the exposure program, the flux of particles that is entering the material  $F_{real}$  is modelled by a certain number of particles that enters the first zone per second called  $\gamma$ . Because the number of particles is only a fraction of the real number of particles present in a material, the number of traps per zone  $n$  should be scaled similarly.

$$\frac{n_{real}}{n_{model}} = \frac{F_{real} \cdot A}{F_{model} \cdot A} = \frac{F_{real} \cdot A}{\gamma} \quad (3.8)$$

Here  $A$  is the area of material where the flux of deuterium is entering. The trap concentration  $\rho$  is given as the part of tungsten lattice locations where a trap is present. Using the

volume density  $\mu$  of tungsten atoms, this gives

$$n_{model} = n_{real} \frac{\gamma}{F_{real} \cdot A} = \rho \cdot \mu \cdot A \cdot s \frac{\gamma}{F_{real} \cdot A} = \frac{\gamma \cdot \rho \cdot \mu \cdot s}{F_{real}} \quad (3.9)$$

In the release program, the number of deuterium particles in the system in the beginning is fixed to be  $M$ , so the number of traps per zone in the model scales with this quantity. Using that the part of the deuterium that remains in the material during exposure is  $\eta_{exp}$  and the total exposure time is  $t_{exp}$ , the number of traps is

$$n_{model} = \frac{M \cdot \rho \cdot \mu \cdot s}{F_{real} \cdot \eta_{exp} \cdot t_{exp}} \quad (3.10)$$

In the exposure program the influx of particles should be simulated. This is done by introducing a particle to the first zone during every time step. The particles can walk through the material and they are able to be trapped and detrapped. When particles reach the surface of the material, they can escape it. The assumption is made that particles leave the material once they reach this surface, so the probability to go out of the material during one time step equals the probability to move one zone, calculated using equation 3.5. Of the particles that enter the material at first remains only a small part, because of the high temperature during exposure. The exposure program calculates this part by comparing the number of particles that has left the material to the total number of particles that was put into the material during the run of the program. The distribution of deuterium in tungsten after a given exposure time is produced. The depth of the distribution, the height of the distribution and the part of the particles that is retained are given as functions of time. The actual samples that are used to be compared to the simulations were exposed for 200 s. The program is able to simulate exposure times of 40 s up to 200 s depending on the trap configuration and properties. If shallow traps are present the time steps should remain small, because the detrapping probability should remain small. The smaller the trap energy of a shallow trap, the smaller the time steps should be and the longer it takes to do calculations. Because deuterium is even detrapped from deep traps at the temperatures of exposure, this gives a similar problem. Shallow traps with energies smaller than 0.7 eV are considered to have no influence during exposure. The time that deuterium spends at these trap sites becomes very small at these temperatures and the trap concentration is also very small, making that these traps may be neglected at high temperatures.

Because the deuterium distribution develops very smoothly in time, the depth and part that is retained can be extrapolated to get the expected distribution after 200 s. The shape of the distribution depends on the properties of the traps and it may be approximated by corresponding functions, like by an error function or by straight lines. Particle locations are then randomly picked from the distribution and these locations are exported to the second program. This program simulates diffusion of deuterium without a source of particles. The initial distribution does not have any information about which particles are trapped and which are not. Deuterium particles that were at deep traps directly after exposure will stay in them, so deep traps are filled first. Then the remaining deuterium particles are put into shallow traps. When the program starts running, particles are allowed to detrap from the shallow traps, making a part of them mobile again. The part that is mobile becomes constant quickly, so there are no crude approximations here. The part of the deuterium that is retained  $\eta_{dif}$  is produced by the program as a function of time and this can be used to determine the expected total deuterium retention  $D_{ret}$ .

$$D_{ret} = \eta_{dif} \cdot \eta_{exp} \cdot F_{real} \cdot t_{exp} \cdot A \quad (3.11)$$

### 3.3 Values of input parameters

The programs require values of various quantities to simulate the diffusion processes. The size of the zones and time steps should be chosen carefully. These values have no physical meaning, but if they are too large some assumptions become invalid and the calculated probabilities become flawed. However, if they are too small the calculation time of the programs will be too large to get a good understanding of the processes at large time scales.

The simulations are performed to compare to actual experiments, so the same conditions should be used in the simulations as in the experiments. The experiments were done previously to calculate the total amount of deuterium that was retained in tungsten after time periods ranging from hours to months.

The tungsten samples are discs with a thickness of 1 mm and a radius of 1.5 cm. The samples were exposed to 200 s of deuterium plasma at an average temperature of approximately 460 K. The peak temperature was around 500 K, but because the models are one dimensional it is not possible to take the temperature differences on the surface of the material into account. An average temperature of the exposure zone is taken to simulate diffusion in the total material. The flux of particles that was presented to the tungsten material during exposure is in the order of magnitude of  $10^{24}$  particles/m<sup>2</sup> · s, but the actual flux that enters the material is much lower and is around  $10^{18}$  particles/m<sup>2</sup> · s. This number is rather uncertain and it is varied as input in the simulations. After exposure, the samples were stored for different periods of time. The temperature is taken to be 295 K to be comparable with room temperature. A small deviation from this value will have small consequences, because it only appears in formulas together with an energy and the values of the energies are all quite uncertain. The area of the exposed material is approximated by a circle with a diameter that is around 1 cm. This value is not needed until the calculation of the deuterium retention, so it is actually used to fit the calculated line to the measurement point that was taken at 24 h after exposure. This point is taken because it has a high value, making the relative uncertainty lower. The point measured after 2 h also has a larger uncertainty, because the exact time after which it was measured might deviate a little from the reported 2 h, implying a large relative uncertainty.

Another value that is needed is the diffusion constant for deuterium diffusion at high temperature. As mentioned before, the value measured by Frauenfelder is used. By equations 2.16 and 3.5 the attempt frequency and diffusion probability are calculated from it, eventually being involved in all probabilities entering the programs. The attempt frequency is only dependent on  $D_0$ . Varying  $D_0$  will also affect the speed of diffusion, but because both the diffusion into the material and the diffusion out of the material are effected, the course of retention in time will not be effected. This is checked using the models. The final physical quantities that enter the model are the trap concentrations and trap energies. Their values are uncertain and these are varied in different runs of the programs.

# 4 Results

## 4.1 Probability to trap

The three dimensional program calculates the probability for a deuterium atom to get trapped after a certain number of steps. The results are given in blue in figure 4.1. These calculations were performed by simulating the tetrahedral sites in a cube of 2000 tungsten atoms and a single trap, representing a trap density  $\rho_0 = 5 \cdot 10^{-4}$ . To check if the function in equation 3.3 is indeed proportional to the product of  $N^*$  and  $\rho$ , the program was run using a cube of 54000 tungsten atoms with one trap, representing a trap concentration of  $\rho = 1.8 \cdot 10^{-5}$ . The values of  $N^*$  are compensated by taking the product with the ratio of the two trap concentrations. The results of these calculations are shown in red. The two graphs are very similar, indicating that the scaling was correct. In the range of trap concentrations that are physically relevant, equation 3.3 is a very good approximation.

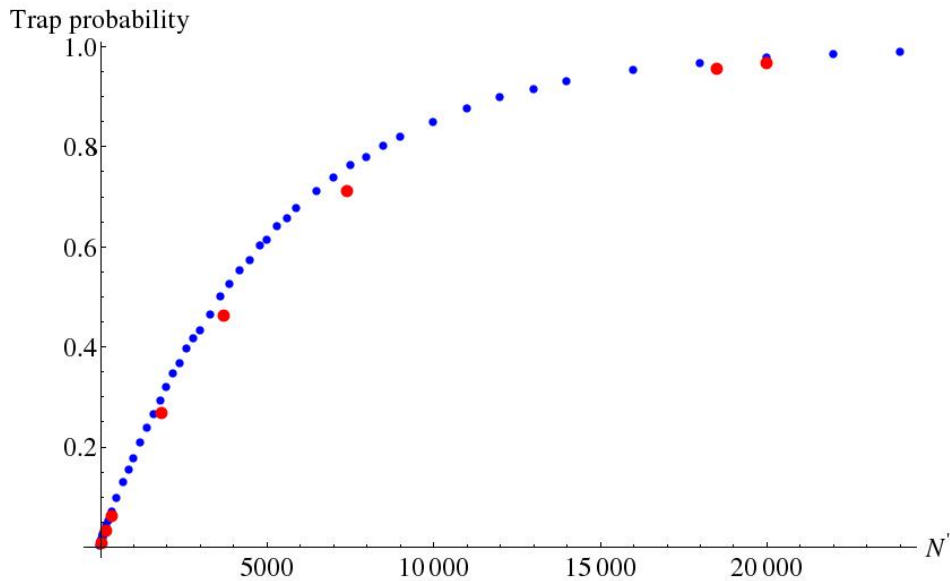


Figure 4.1: The blue points give the probability that a deuterium atom gets trapped after a scaled number of jumps  $N'$ . This calculation was done for a trap density of  $5 \cdot 10^{-4}$ . The red dots give the same calculation with a trap density of  $1.8 \cdot 10^{-5}$  which scales the number of steps.

## 4.2 Retention dependence on diffusion constant

The exponential prefactor  $D_0$  is rather uncertain [9]. The diffusion constant prefactor  $D_0$  is varied in simulations of diffusion in tungsten without traps. The sensitivity of the retention

on  $D_0$  is checked this way. The effect of different values of  $D_0$  on deuterium retention is given in figure 4.2. To simulate the exposure, a complementary error function is used that extends according to the diffusion constant used. For all three simulations the diffusion energies are equal to 0.4 eV. The exposure temperature is set to be 500 K, the storage temperature is 300 K. The zones are 1  $\mu\text{m}$  in size and time steps of 1 s are taken to model the large time scales. The number of particles that is used varies, such that the program is able to calculate it in reasonable timescales. Up to  $1 \cdot 10^5$  particles are used for the small timescales, where only  $3 \cdot 10^3$  particles are used for the large timescales. This is done to have large accuracy when calculating the part of the particles that is retained in the material. The values for the part that is retained are normalised to match measurement results. The graph shows that there is hardly any influence of  $D_0$  at first. When  $D_0$  becomes higher, particles move deeper into the material during exposure and afterwards they move faster out of the material, compensating for the larger depth. The points start to differ for the last simulated point. The simulation with the highest value of  $D_0$  has the lowest retention value there. This is entirely due to the fact that deuterium reached the back surface of the material. For  $D_0 = 5 \cdot 10^{-8} \text{ m}^2/\text{s}$  the back is not reached yet, while for the other simulations the back has been reached. The values of the diffusion constant that are used do not correspond to any physically relevant values. Although the actual movement does not depend on it, the values of  $D_0$  still have influence on the probability to detrapp, because the attempt frequency  $\Gamma$  is calculated from  $D_0$ .

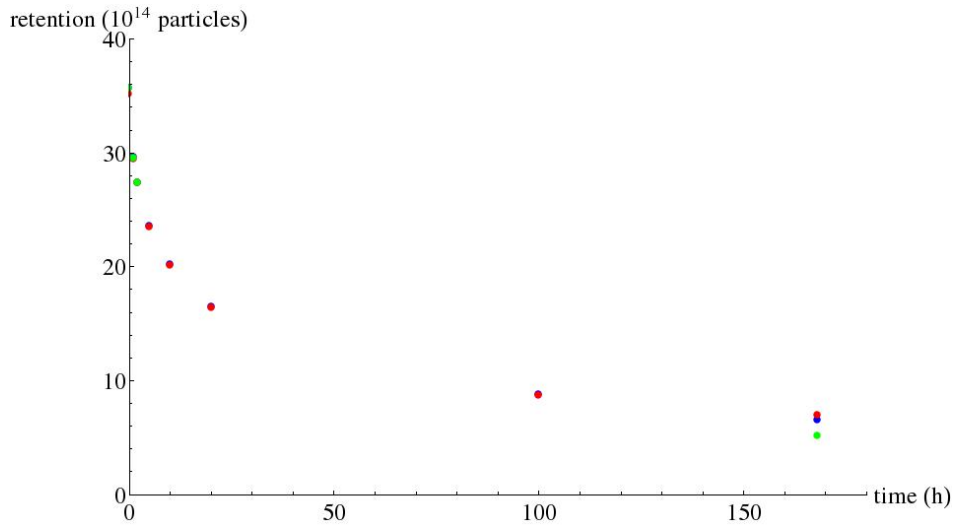


Figure 4.2: Deuterium retention against time since exposure for different values of  $D_0$ . The different lines represent the simulations for  $D_0 = 5 \cdot 10^{-8} \text{ m}^2/\text{s}$  in red,  $D_0 = 4.1 \cdot 10^{-7} \text{ m}^2/\text{s}$  in blue and  $D_0 = 1 \cdot 10^{-6} \text{ m}^2/\text{s}$  in green.

### 4.3 Depth profile of deuterium in tungsten

The depth profile of deuterium in tungsten after 40 s of plasma exposure is calculated by the exposure program for tungsten without any traps. This represents a case where traps have no influence on diffusion processes. The length of the zones is  $10^{-7} \text{ m}$  from now on. For  $D_0 = \frac{4.1}{\sqrt{2}} \cdot 10^{-7} \text{ m}^2/\text{s}$  and  $E_m = 0.4 \text{ eV}$  the profile can also be calculated using equation 2.19.

Normalising this distribution such that it represents one particle when integrated over the entire material, it is given by

$$n(x, t) = \frac{n_{tot}}{\sqrt{Dt}} \cdot 10^{-7} \int_x^{\infty} e^{-\frac{(x' \cdot 10^{-7})^2}{4Dt}} dx' \quad (4.1)$$

where  $n_{tot}$  equals the total amount of particles in the material and the factor  $10^{-7}$  makes that  $x$  equals the number of zones.  $n(x, t)$  gives the number of particles per zone. In the program there are 20044 particles present in the material after 40s of exposure. Together with equation 4.1 this leads to an expected depth profile, which is plotted in blue in figure 4.3. The red points give the depth profile that was calculated by the program. The two methods clearly agree, which means that the diffusion process is calculated well. Using an exposure time of 200s and the extrapolated value of the part of deuterium that was retained during exposure, equation 4.1 can be used to give the initial distribution of deuterium directly after exposure.

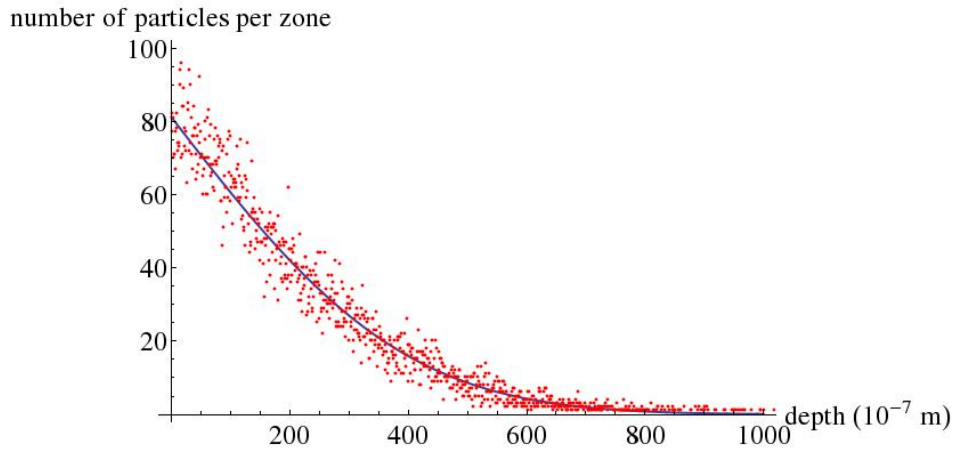


Figure 4.3: The depth profile of deuterium in tungsten after 40s of plasma exposure. No traps are present in the material. In red, the number of particles per zone that is calculated by the program is given. In blue, the expected distribution is plotted.

The release program calculated the diffusion process of deuterium after exposure. Figures 4.4 and 4.5 give a view of the progress of the depth profile. The error function that gives the initial distribution is also plotted as a reference. The particles that are located near the surface of the material swiftly move out of the tungsten. The distribution then broadens, while the peak shifts further into the material. The number of particles decreases during the entire time.

The depth profile of deuterium in tungsten becomes very different when there are traps available. An example is given in figure 4.6. This shows the depth profile during exposure in tungsten with a combination of deep and shallow traps. Deep traps tend to make a horizontal base value in the distribution that extends to a certain depth. The particles in shallow traps and the mobile particles are on top of this base line and they can be distributed in various ways, resembling the concave line of the complementary error function for small trap energies and becoming more convex for larger trap energies. Most particles will be located at shallow traps, because they spend much time at these sites. Only a small part of the deuterium is

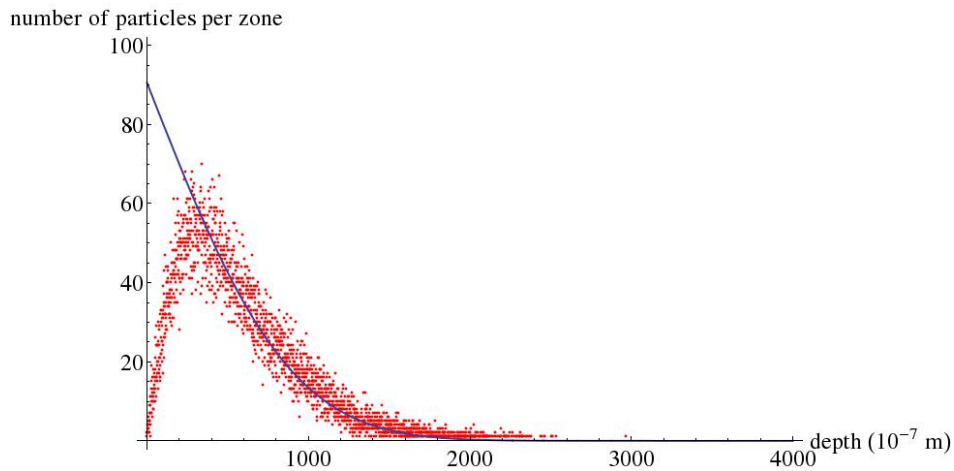


Figure 4.4: The depth profile of deuterium in tungsten 1 h after plasma exposure in tungsten without traps in red. The blue line gives the initial distribution directly after exposure.

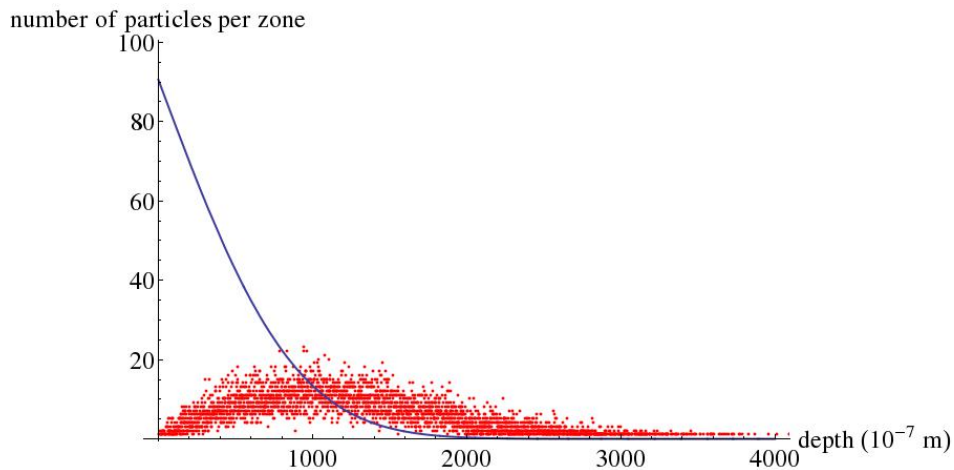


Figure 4.5: The depth profile of deuterium in tungsten 24 h after plasma exposure in tungsten without traps in red. The blue line gives the initial distribution directly after exposure.

mobile. In figure 4.6, the red line gives the total amount of deuterium that is in the material per zone. It is convex in contrast to the complementary error function, which is concave. Deuterium has clearly diffused less far compared to the exposure of material without traps. This is mostly due to the shallow traps, which slow down diffusion.

The development of the depth profile with multiple kinds of traps is shown in figures 4.7 and 4.8. The decrease of the deuterium concentration near the surface of tungsten is rather slow, compared to the decrease seen in figure 4.4. Almost no mobile deuterium is present, so the red line gives the deuterium in shallow traps plus deep traps, while the green line only gives particles in deep traps. The lack of mobile deuterium both during exposure and afterwards is due to the rather high trap energy 0.9 eV of the shallow traps.

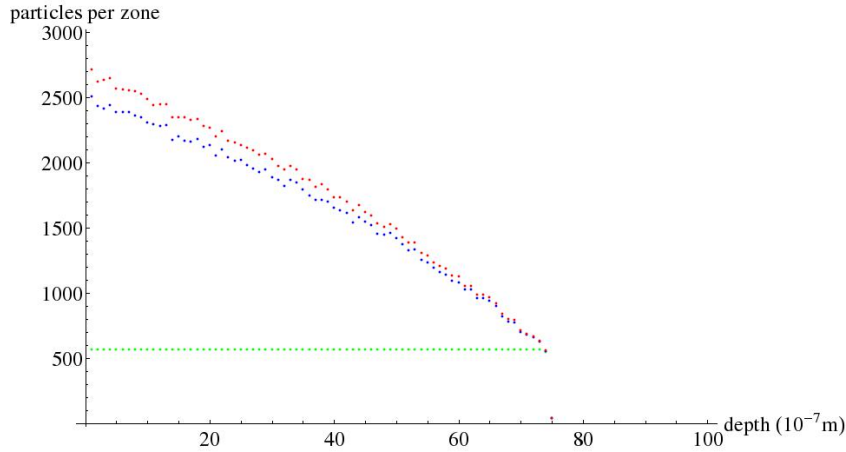


Figure 4.6: The depth profile of deuterium in tungsten after 40s of plasma exposure in tungsten with 0.9eV, density  $1 \cdot 10^{-4}$  and 1.3eV, density  $9 \cdot 10^{-6}$  traps. The green points give the number of particles per zone that are trapped in deep traps, the blue line gives the number of particles in deep and shallow traps and the red line gives all particles. The difference between the red and the blue line gives the number of mobile particles.

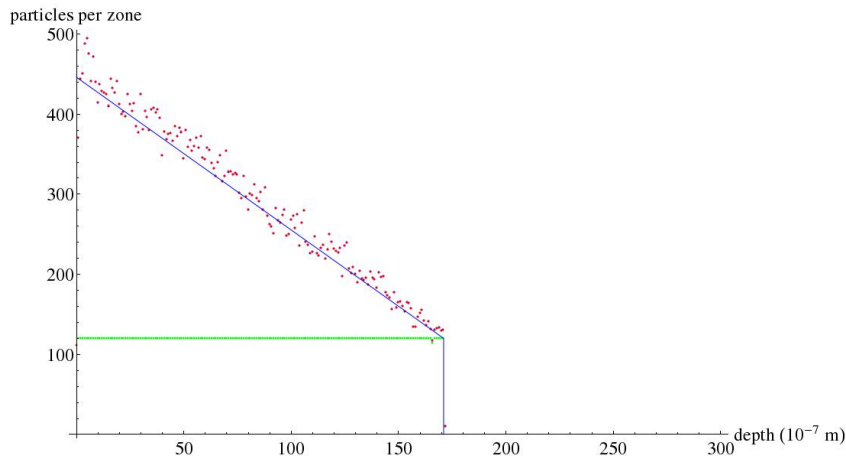


Figure 4.7: The depth profile of deuterium in tungsten 1 h after plasma exposure in tungsten with multiple kinds of traps in red. The green points give only the particles that are in deep traps. Practically no mobile deuterium is present, all deuterium is trapped in deep or shallow traps. The blue line gives the initial distribution directly after exposure that was given to the release program.

#### 4.4 Time dependence of deuterium retention

The results of the retention measurements are shown as blue points in figures 4.9 and 4.10. Retention decreases quite fast at first, but seems to stabilise. The course of deuterium retention in time should be explained. It was simulated for various trap configurations. The values of the variables for some different simulations are given in table 4.1.



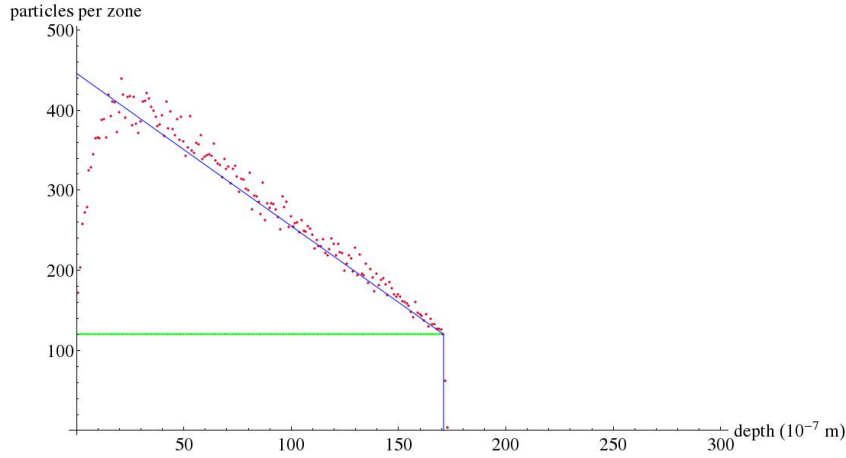


Figure 4.8: The depth profile of deuterium in tungsten 72 h after plasma exposure in tungsten with multiple kinds of traps in red. The blue line gives the initial distribution directly after exposure. Because the shallow traps greatly reduce the speed of diffusion, the profile has changed little in three days.

	No traps	Shallow traps	Combination	Deep traps
Deep trap energy (eV)	–	–	1.3	1.2
Deep trap at. dens.	–	–	$5 \cdot 10^{-5}$	$5 \cdot 1^{-6}$
Shallow trap energy (eV)	–	0.6	0.75	–
Shallow trap at. dens.	–	$1 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	–
Retained in exposure	0.2%	3.3%	0.7%	0.7%
Influx ( $\text{m}^{-2}\text{s}^{-1}$ )	$6.3 \cdot 10^{19}$	$1.2 \cdot 10^{19}$	$1.2 \cdot 10^{19}$	$1 \cdot 10^{19}$
Radius exp. area (cm)	0.85	0.735	0.7	0.977

Table 4.1: The values of different parameters for the different simulations. The "No traps" simulation corresponds to the red line in figure 4.10, "Shallow traps" to the green line, "Combination" to the orange line and "Deep traps" to the purple line.

For tungsten without traps the expected retention of deuterium is plotted in figure 4.9. The figure shows that deuterium retention decreases rapidly at first, after which it keeps decreasing more steadily. A week after exposure, the simulated retention decreases faster than measurements indicate. The initial decrease is far greater than observed in actual experiments, which can be seen better in the red line figure 4.10. The simulated distribution then keeps decreasing too fast, making retention after several months much lower than observed. The uncertainty in the measured points was estimated by looking at the variance of three different measurements of the total retention one month after exposure. The same relative uncertainty of approximately 16% was then applied to all five measurement points.

In this case, the values of the influx and the exposed area are both chosen to fit the measured point 24 h after exposure. The values are rather high, because the amount of deuterium that is retained is really low. This is partly due to the large part of deuterium that leaves tungsten during exposure. Only 0.2% of the atoms that is implanted during 200 s

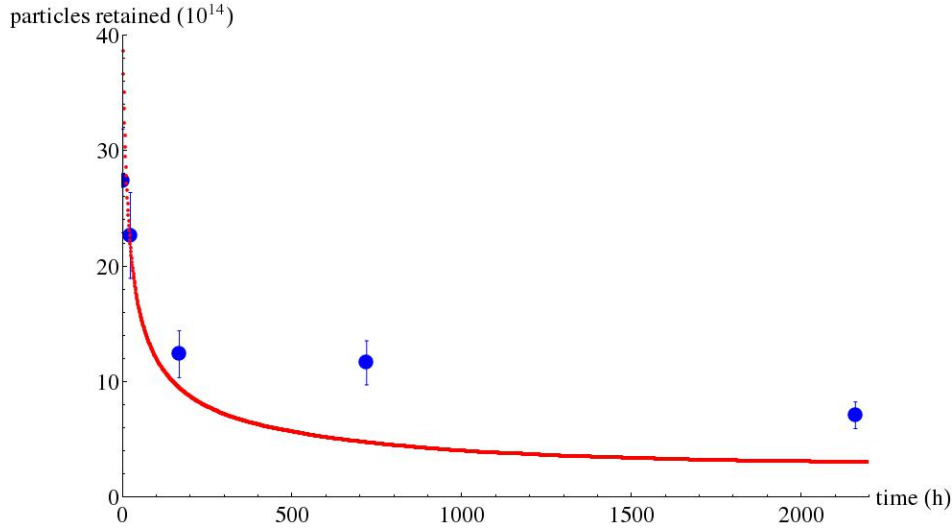


Figure 4.9: The expected (red points) and measured (blue points) deuterium retention in tungsten as a function of time. The expected value was fitted to the measured value at  $t = 24$  h. The simulated retention seems to decrease too fast, being too low for the three latter measurement points.

remains in the material during exposure.

Simulations were repeated for tungsten with only very shallow traps. The results are shown as the green line in figure 4.10. Due to the high probability to detrapp the shallow traps, the time steps have to be very small, increasing calculation time and limiting the timescale that could be simulated. Retention decreases slower in this case than in the case of mobile diffusion, but it still decreases rather fast.

Also tungsten with a combination of deep and shallow traps was simulated. The orange line in figure 4.10 gives the deuterium retention in this case. The line decreases a lot slower than the line of mobile diffusion does. It also decreases slower than the measured deuterium retention. Both the trap energies and trap densities of combinations of deep and shallow traps can be varied a lot, giving many different possibilities that could be investigated. It seems that adding shallow traps with a trap energy that is higher than 0.6 eV but lower than 0.75 eV would slow diffusion down enough to match the data.

Finally diffusion was simulated through tungsten with only deep traps. The course of retention in time is given by the purple line in figure 4.10. During exposure a large part of deuterium is trapped, but there is also a part that is mobile. After exposure, all traps in the material are filled up to a certain depth. There is still some mobile deuterium in the tungsten, which moves out of the material swiftly. There is also a small part that moves deeper into the material and is trapped there. This part is only small, because the largest part of the mobile deuterium is located near the surface. The decrease of deuterium retention in the beginning is comparable with the measured decrease. A day after exposure all deuterium is trapped and will not leave the material for long times. The decrease of retention stops, which is not observed in measurements. Even after months the amount of deuterium should still decrease. The trap concentration that was simulated here was rather low, which can be seen in table 4.1.

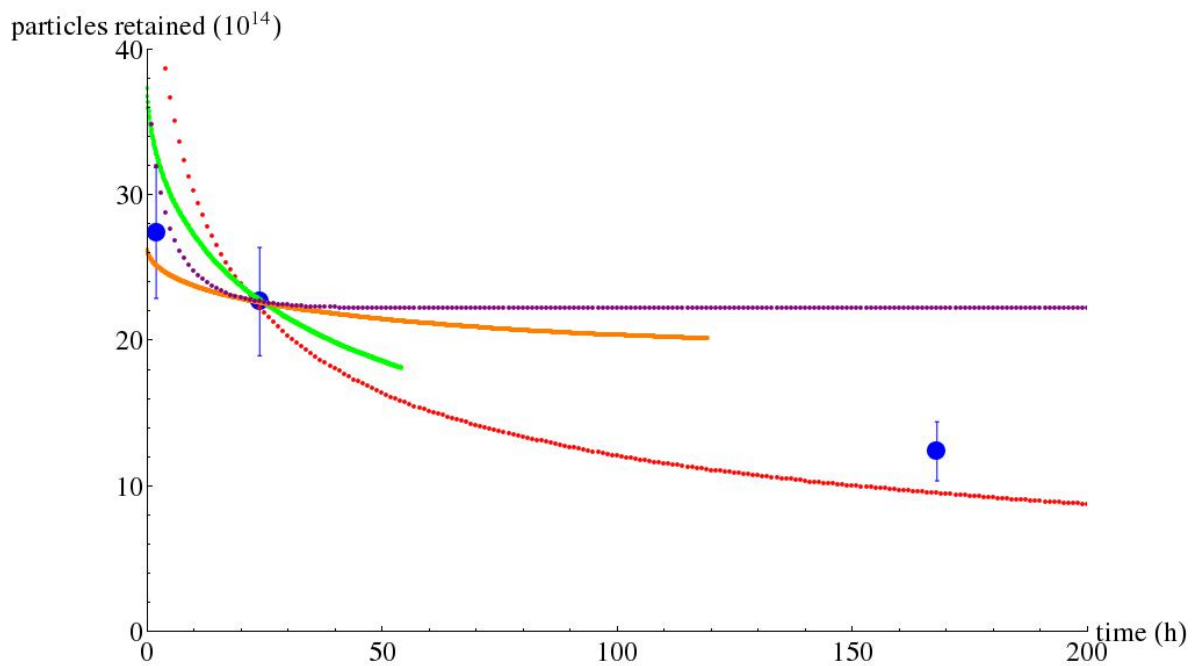


Figure 4.10: Deuterium retention in tungsten as a function of time as a result of measurements (blue points) and various simulations. The simulated values are all fitted to the measured value at  $t = 24$  h. Tungsten with no traps (red), 0.6 eV traps (green), 1.3 eV and 0.75 eV traps (orange) and 1.2 eV traps (purple).

## 5 Discussion

The actual deuterium retention has been measured for different samples after different periods of time. The measurements were only done five times for very different periods of time after exposure, making it hard to check how reliable the measurements were. The uncertainty of each measurement point can be approximated by repeating the measurement several times. This is already done for the measurement of total retention after one month, and the same relative uncertainty is applied to all points. This gives an indication of the uncertainties of all points.

The behaviour of retention occurs at the large timescale of several months. The underlying diffusion processes occur at very small timescales of picoseconds. By averaging the actual movement of the particles, the zone programs can bridge the gap between these timescales. Processes like trapping and detrapping are still considered to be atomic processes, but the programs have no problem with calculating the implications of these processes in days to weeks. The programs are therefore able to simulate deuterium retention for several combinations of traps. First, deuterium retention is shown to be influenced by traps. Only mobile deuterium diffuses too fast and retention would decrease too fast if it was only depending on mobile deuterium. Next, simulating tungsten with deep traps does not give the measured behaviour of deuterium retention. The trap concentration that was used seems low already, but even lower concentrations of deep traps could be tried. They will probably imply a decrease of retention that is too fast. Finally, the exact behaviour of the measurements has not been reproduced yet, but a promising solution is present. Simulations with shallow traps show that they can slow the decrease of retention down. To fully accept this explanation, more simulations should be done.

Other measurements could also improve the understanding of the diffusion processes. TDS measurements give information about the energy and depth at which deuterium is released from tungsten. This might result in finding the energy at which deuterium is stored at the surface. If the surface has little influence on deuterium, the TDS results could aid in finding the trap energies present in the material. Here, values for the trap densities, exposed area and particle influx during exposure are varied a little. However, it could be possible to measure their actual values more directly. If their values are known up to a certain range, it is easier to find the correct values in simulations and some trap combinations could be made impossible.

In the models there is the assumption that tungsten is made up of one crystal with some mono-vacancies in them. This is more complex in reality and grain boundaries and dislocations might have a large impact on deuterium diffusion. The effects that occur at the surface of the material are assumed to be neglectable. It should be checked whether the surface and grain boundaries have a neglectable effect on the deuterium retention.

The zone programs can be extended to two or three dimensions. Two dimensions can be used to calculate the radial dependence of the depth profile, influenced by the radial temperature and particle flux variation. In three dimensions, it might even be possible to simulate grain boundaries. An effect that could occur in grain boundaries is that they act as canals in the material, draining deuterium out of bulk tungsten. With the aid of measurements

and other types of simulations, it should be possible to explain all behaviour of deuterium in tungsten. Adding dimensions to the programs could lead to larger calculation times, but there is a good possibility that the speed of the current programs can be increased. That way, the total calculation will probably be reasonable.

It is also possible to simulate diffusion for more different sets of parameters. Varying only one parameter while keeping all others constant can improve the understanding of the effects of individual parameters. For example, precise values of trap energies that are available in the material could be determined by fitting the results of simulations to measurements.

## 6 Conclusion

The programs are able to simulate diffusion processes at relevant timescales. By simulating several trap energies and densities, comparisons can be made to measurements. These show that the decrease of deuterium retention is definitely not only due to mobile diffusion. Other processes like trapping have a great influence on deuterium retention in tungsten, even in tungsten with natural traps only. Various studies already proved that traps are present in natural tungsten and that they probably influence diffusion. Simulations of deuterium in tungsten without defects shows that it does not explain measurements. It follows that the natural traps can not be neglected and the amount of deuterium that is present in tungsten is very small and is comparable to the number of traps that is present.

A possible explanation for the observed decrease of retention is that the decrease is due to mobile deuterium diffusion, while deep traps are present to leave a part of the deuterium trapped forever. This explanation also seems to have large flaws. The trap density of these deep traps should be very low. Otherwise the number of deuterium atoms that is trapped forever is too high and it will not allow the long term decrease of deuterium retention. But if the trap concentration is that small, mobile deuterium will dominate the total amount of deuterium just after exposure. This will make the decrease of deuterium retention too fast in the first days. However, the uncertainty of the measurements is too high to fully reject this view.

Shallow traps slow diffusion of deuterium in tungsten down. By introducing shallow traps with trap energies around 0.7 eV, the decrease of deuterium retention can be slowed down enough to match the measured initial decrease of retention. The combined effects of deep and shallow traps could be able to explain the full retention behaviour that is observed.

In this study, only pointlike defects are taken into account. Other effects that grain boundaries or dislocations might have, are neglected. Measurements or other simulations should be used to reveal their effect.

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