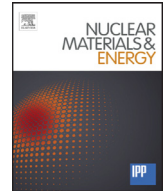




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Multiscale modelling of hydrogen behaviour on beryllium (0001) surface

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ABSTRACT

Beryllium is proposed to be a neutron multiplier and plasma facing material in future fusion devices. Therefore, it is crucial to acquire an understanding of the microscopic mechanisms of tritium accumulation and release as a result of transmutation processes that Be undergoes under neutron irradiation. A multiscale simulation of ad- and desorption of hydrogen isotopes on the beryllium (0001) surface is developed. It consists of ab initio calculations of certain H adsorption configurations, a suitable cluster expansion approximating the energies of arbitrary configurations, and a kinetic Monte Carlo method for dynamic simulations of adsorption and desorption. The processes implemented in the kinetic Monte Carlo simulation are deduced from further ab initio calculations comprising both, static relaxation as well as molecular dynamics runs. The simulation is used to reproduce experimental data and the results are compared and discussed. Based on the observed results, proposals for a refined model are made.

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1. Introduction

Future fusion devices like ITER and DEMO are proposed to deploy beryllium as a plasma facing material for the first wall [1] and neutron multiplier in tritium breeding blankets [1–3]. Within the helium cooled pebble bed blanket (HCPB), lithium ceramics are used as the actual tritium breeding material while beryllium acts as a neutron multiplier, thus providing for a self-sustained tritium fuel cycle. As the fusion plasma emits highly energetic neutrons, beryllium undergoes transmutation reactions generating considerable amounts of helium and tritium [4] as a result. With the accumulation of these reaction products, gas filled bubbles emerge [5] as tritium and helium are captured by vacancies which coalesce. These processes also lead to considerable degradation of material properties [6]. The inner surfaces of gas filled bubbles as well as the outer surfaces of plasma facing Be tiles imply a pronounced importance of the interactions of hydrogen isotopes with beryllium surfaces, which will ultimately need to include interactions of (pre)adsorbed hydrogen. Regarding safety concerns, assessment of the radioactive tritium inventory trapped inside beryllium pebbles and the handling of radioactive beryllium waste after the end-of-life of the blanket are very important for the actual oper-

ation of a fusion reactor. Therefore, it is crucial to acquire a thorough understanding of the microscopic mechanisms of tritium retention and release, naturally including a faithful representation of mechanisms at surfaces.

Therefore, numerous experimental and theoretical studies have been conducted to gain insight into the governing mechanisms of tritium retention and release.

Typical experiments consist of exposing beryllium samples to hydrogen isotope gases [7–9], hydrogen isotope ion implantation beams [10–15], or neutron irradiation [5,6], all of which resulting in the accumulation of hydrogen isotopes within the beryllium samples. Subsequently, an array of experimental techniques like low-energy ion scattering (LEIS) [13], X-ray photoelectron spectroscopy (XPS) [13], low-energy electron diffraction (LEED) [9], high-resolution electron-energy-loss spectroscopy (HREELS) [9], nuclear reaction analysis (NRA) [9], transmission electron microscopy (TEM) investigations [10], and/or temperature programmed desorption (TPD) spectroscopy [7,8,12–14] are routinely applied to either directly track the hydrogen isotope behaviour within the samples or deduce it from the data taken. Especially TPD spectra, which aim to establish a mapping from desorption rate peak temperatures to activation energies and therefore atomic scale desorption processes, leave a wide field of possible, competing explanations for several similar features.

Typical theoretical studies are usually based on ab initio, i.e. density function theory (DFT) calculations. There are numerous

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publications relevant to beryllium surfaces and their interactions with hydrogen, see e.g. [16,17] and [18–21], respectively. For the (0001) beryllium surface, there is a rather well established consensus of hydrogen atomically adsorbing at two stable sites for low hydrogen concentrations on the surface. These sites are named the fcc and hcp adsorption sites, with the latter one being energetically more favourable. Here, we adopt the notion of a coverage relative to those adsorption sites, i.e. a coverage of 1.0 corresponds to all fcc and hcp adsorption sites being occupied. Significantly more uncertainty is attributed to regimes of higher coverages. The two-fold coordinated bridge sites right between the fcc and hcp adsorption sites becoming stable adsorption sites at a coverage of 0.5 is a rather well established finding our calculations agree with. Some publications suggest these bridge sites are available in addition to hcp and fcc sites, e.g. [22]. At those coverages, the energetical hierarchy of fcc and hcp adsorption sites is reversed and the bridge site is now the new groundstate adsorption site. However, our calculations also indicate the bridge site replaces the fcc and hcp adsorption sites instead of becoming available for adsorption in addition.

Based on ab initio calculations performed by us, a multiscale modelling approach to hydrogen ad- and desorption deploying our own atomic kinetic Monte Carlo (kMC) code was developed. The goal of this work is to establish the overall validity of our approach by reproducing aspects of actual experiments. To this end, we focus on modelling of atomic deuterium exposure experiments undertaken by Lossev and Kueppers [7,8].

2. Simulation methods

Our multiscale modelling approach is based on ab initio calculations carried out using the Vienna Ab initio Simulation Package (VASP) [23,24] in terms of static energy minimization and microcanonical first principles molecular dynamics runs. The projector augmented wave (PAW) potentials as shipped with VASP [25,26] are used for beryllium and hydrogen, modelling beryllium with two valence electrons. For molecular dynamics runs, the atomic mass in the H potential was changed to that of deuterium mass (2.014) via the POMASS-tag in the POTCAR file. The exchange-correlation energy is approximated by the generalized gradient approximation (GGA) according to Perdew and Wang [27]. Moreover, a Fermi broadening as proposed by Methfessel and Paxton [28], a smearing width of 0.2 eV, and a cutoff energy of ENCUT = 450 eV were deployed. The bulk lattice constants $a = b = 2.263$ Å and $c = 3.569$ Å were calculated using these parameters. Throughout all calculations, the k-point grid sampling is done on a gamma centred grid not less dense than $31 \times 31 \times 1$ for a surface simulation cell with lateral lengths of only one unit cell as this has been explicitly confirmed to yield well converged total energies. Total energy convergence with significantly more dense k-point grids was occasionally ensured for laterally larger simulation cells with different lateral geometries, though. All surface simulation cells include a vacuum gap of more than 18.5 Å after full relaxation in order to get rid of unintentional interactions due to periodic boundary conditions.

Utilizing ab initio calculation results in subsequent stages of the multiscale simulation chain requires a high quality parametrization of total energies. For discrete systems, a state of the art parametrization is given by the cluster expansion (CE) formalism [29]. This expansion systematically expands total energies E for arbitrary parent lattice occupations $\vec{\sigma} = (\sigma_1, \dots, \sigma_N)$ denoted by spin variables σ_i on N sites according to

$$E(\vec{\sigma}) = \sum_{\alpha \in A} m_{\alpha} J_{\alpha} \langle \prod_{i \in \alpha'} \sigma_i \rangle, \quad (1)$$

with summation over clusters α symmetrically inequivalent and averaging over clusters α' symmetrically equivalent to α under

parent lattice spacegroup operations. To that end, effective cluster interaction (ECI) energies J_{α} need to be found for a considered set of clusters A , associating each cluster α to an energy contribution via multiplicities m_{α} and the occupation dependent correlation $\langle \prod_{i \in \alpha'} \sigma_i \rangle_{\alpha'}$.

The adsorption layer can be taken as a substitutional alloy composed of hydrogen (H) and vacancies Vac. In this alloy, the two species reside in the fcc and hcp sites which compose the two dimensional parent lattices. That way, the problem is mapped to finding a cluster expansion for a substitutional alloy and the MIT Ab initio Phase Stability (MAPS) code can be used. MAPS searches for a cluster expansion truncation in an iterative manner. At each iteration, MAPS starts by choosing an optimal truncation as indicated by a minimal leave-one-out cross validation (CV) score. The set of trial truncations at this step is limited by a physically plausible heuristic based on the complexity (number of sites) and size (largest pair distance) of the clusters. Subsequently, MAPS proposes a new configuration to include in the training set on the grounds of the best truncation so far. This new configuration either corresponds to a newly predicted ground state or results in the most reduction of the variance component in the least square fit prediction error. If a truncation fails to reproduce the ground state hull, the relative weight of the offending configurations is increased and an iterative refitting scheme is applied.

For the purpose considered in this work, the actual input energies for MAPS are given by

$$E(\vec{\sigma}) = E_{\text{ads},\sigma} = E_{\text{total}} - n_{\text{uc}} E_{\text{uc}} - n_{\text{H}} \frac{E_{\text{H}_2}}{2}, \quad (2)$$

with the total energy of the considered configuration as provided by VASP E_{total} , the size of the simulation cell in multiples of surface unit cell n_{uc} , the total energy of the clean surface unit cell E_{uc} , the number of adsorbed H atoms n_{H} , and the total energy of the H₂ molecule $E_{\text{H}_2} = -6.719$ eV. Small changes within the MAPS code enable an automated adoption of all cluster expansions obtained by MAPS in our own kMC code which is described at the end of this chapter.

To obtain estimates of typical barriers for dissociative adsorption processes, microcanonical molecular dynamics runs were carried out. The setup of those runs generally consist of a D₂ projectile and a fully relaxed Be slab at 0 K. The initial velocities of the ions in the molecule result in a suitable center of mass velocity towards a targeted impact point on the slab. The slab itself may be clean or preadsorbed with atomic H in given amounts and configurations. The actual energy barriers ΔV are then derived from utilizing the losses of kinetic energy ΔT in microcanonical ab initio molecular dynamic simulations, in which

$$E_0 = T_0 + V_0 \stackrel{!}{=} T(t) + V(t) = E(t) \quad (3)$$

$$\Rightarrow \Delta V = V(t) - V_0 = T_0 - T(t) = \Delta T \quad (4)$$

holds. Here, E_0 , T_0 , and V_0 denote the initial total, kinetic, and potential energies while $E(t)$, $T(t)$, and $V(t)$ denote the total, kinetic, and potential energies at time t . As a measure of the validity of calculations like that, the drift in total free energy $E_0 - E(t)$ was monitored. Atomic deuterium adsorption was studied using the same technique.

Estimations of the deuterium surface diffusion activation barriers ΔE for jumps between adjacent adsorption sites are calculated by

$$\Delta E = E_{\text{trans}} - E_{\text{init}} \quad (5)$$

with the energy E_{init} from a relaxed initial state, i.e. H adsorbed in a fcc or hcp site, and E_{trans} from a converged dimer calculation carried out by the method as implemented in the VASP transition state theory (VTST) [30] tools patch for VASP. To that

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