On plasma-material interaction in magnetic fusion devices

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Introduction. Tritium retention in the material of the first wall is one of the main issues for future fusion reactors (e.g. see Ref. 1). Therefore, it is important to understand the physics of retention caused by trapping of hydrogenic species in imperfections of material lattices (e.g. vacancies, impurities, grain boundaries, etc.) as well as outgassing of hydrogenic species from the wall surface. Here we present the results of our studies of just two issues related to tritium retention: Transport of hydrogen species in co-deposits and Molecular Dynamic (MD) simulations of H desorption from W surface.

Transport of hydrogen species in co-deposits. Usually modelling of hydrogen in material is performed with 1D reaction-diffusion equations (which take into account hydrogen diffusion and trapping-detrapping processes) and some boundary conditions at the surfaces. In most cases only two-three traps with different trapping energy are considered. However, in fusion devices majority of retained hydrogen is accumulated in a co-deposited material [1-3]. Such material may have traps characterized by a large variety of trapping energies. In this case a more appropriate way for the description of hydrogen transport could be based on a continuum kinetic model of the population of traps over activation energy (broadband distribution), E, assuming that de-trapping energy spectrum, $P_E(\varepsilon)$, is known (here $\varepsilon = E/T$, T is the wall temperature) [4]. For the case of a broadband trap distribution the transport of a trace particle can be analyzed with the theory of random walk on a lattice with varying waiting time, τ, given by the probability function, $P_\tau(\tau)$, (e.g. see Ref. 5). This probability function can be expressed in terms of $P_E(\varepsilon)$ as follows $P_\tau(\tau) = \int_0^\infty \left\{ f(\tau/\tau_E)/\tau_E \right\} P_E(\varepsilon) d\varepsilon$, where $\tau_E = \tau_0 \exp(\varepsilon)$, τ_0 is the normalization constant, and the function $f(\tau/\tau_E)$ describes the contribution to the waiting time distribution from one kind of traps with the energy $E: P_\tau(\tau, E) = f(\tau/\tau_E)/\tau_E)$. For $P_E(\varepsilon) = \alpha \exp(-\alpha\varepsilon)$ we find $P_\tau(\tau \to \infty) \propto \tau^{-(1+\alpha)}$ [4], which for $0 < \alpha < 1$ and the simple cubic lattice with size ℓ, corresponds to the sub-diffusion process [5] resulting in a power-law time dependence of the outgassing flux: $\Gamma_H(t) \propto t^{-(1-\alpha/2)}$. Recalling recent results on the outgassing dynamics in JET and Tor Supra showing $\Gamma_H(t) \propto t^{-0.7}$ [2, 3], we can conclude that within our approach these experimental results can be explained with exponential trapping spectrum for $\alpha = 0.6$ [4]. In more general nonlinear case, where some traps can be occupied, we need to consider kinetic equations describing both free and trapped hydrogen

$$\partial n_{fr}/\partial t = D\nabla^2 n_{fr} - \int d\varepsilon \left\{ K_{tr} n_{fr} (\varphi - f) - \nu_d(\varepsilon) f \right\}, \tag{1}$$

$$\partial f/\partial t = K_{tr} n_{fr} (\varphi - f) - \nu_d(\varepsilon) f, \tag{2}$$

where $\varphi(\varepsilon)$ is the distribution function of traps over trapping energy so that the trap's density can be expressed as $N_{tr} = \int \varphi(\varepsilon) d\varepsilon$; $f(\varepsilon, \vec{r}, t)$ is the distribution function of the population of these traps with hydrogen so that the density of trapped hydrogen is $n_{tr}(\vec{r}, t) = \int f(\varepsilon, \vec{r}, t) d\varepsilon$; D and $n_{fr}(\vec{r}, t)$ are the diffusion coefficient and the density of free hydrogen; K_{tr} and $\nu_d(\varepsilon) = \hat{\nu}_d \exp(-\varepsilon)$ are correspondingly the rate constant and frequency of hydrogen trapping and de-trapping processes (here $\hat{\nu}_d$ is the normalization constant and we assume that K_{tr}

does not depend on ε). We notice that Eq. (1) can be substituted with the equation describing the balance of total hydrogen density, $N_H = n_{fr} + n_{tr}$:

$$\partial N_H / \partial t = D\nabla^2 n_{fr}. \tag{3}$$

We will consider Eq. (1-3) under the following assumptions: i) we will assume that $\varphi(\varepsilon) = \alpha N_{tr} \exp(-\alpha\varepsilon)$, where $\alpha < 1$ is an adjustable parameter; ii) density of free hydrogen is smaller than the trapped one, $N_H \approx n_{fr} >> n_{tr}$, since the opposite case is trivial, see Eq. (3); iii) hydrogen density is much smaller than the density of traps, $N_H < N_{tr}$; iv) trap density is relatively small, so that $\nu_{tr} \equiv K_{tr} N_{tr} < \hat{\nu}_d$; v) scale length of hydrogen density variation, Δ, and, therefore, effective diffusion time of free hydrogen, $\tau_\Delta \sim \Delta^2 / D$, are large enough so that re-trapping of free hydrogen is vital for the hydrogen dynamics $\nu_{tr}\tau_\Delta > 1$, in opposite case hydrogen flux will be simply determined by the de-trapping process of initial distribution of trapped hydrogen. If we ignore the impact of free hydrogen diffusion, than the system (1, 2) will approach with time the equilibrium relation between free and trapped hydrogen densities for equilibrium condition, $(n_{fr})_{eq}$ and $(n_{tr})_{eq}$, as well as the condition ensuring inequality $N_H \approx (n_{tr})_{eq} >> (n_{fr})_{eq}$

$$(n_{tr})_{eq} / N_{tr} = \{\pi\alpha / \sin(\pi\alpha)\}(\nu_{tr}/\hat{\nu}_d)^\alpha \left((n_{fr})_{eq} / N_{tr}\right)^\alpha, \; N_H / N_{tr} < (\nu_{tr}/\hat{\nu}_d)^{\alpha/(1-\alpha)} < 1, \tag{4}$$

From Eq. (2) we find a formal general solution for the distribution function

$$f = f_0 \exp\{-(K_{tr}\eta(t) - \nu_d t)\} + \int_0^t dt' \varphi K_{tr} \frac{d\eta(t')}{dt'} \exp\{-[K_{tr}(\eta(t) - \eta(t')) - \nu_d(t - t')]\}, \tag{5}$$

where $\eta(t) = \int_0^t n_{fr}(t')dt'$ and $f_0(\varepsilon, \vec{r}) \equiv f(\varepsilon, \vec{r}, t = 0)$. And from Eq. 5, being interested in the transport of hydrogen on the time scale much longer than $\hat{\nu}_d^{-1}$, we find

$$\frac{n_{tr}}{N_{tr}} \exp\{K_{tr}\eta(t)\}\hat{\nu}_d^\alpha = \Gamma(1+\alpha) \int_0^t \frac{dt'}{(t-t')^\alpha} \frac{d}{dt'} \exp\{K_{tr}\eta(t')\} \equiv \frac{\pi\alpha}{\sin(\pi\alpha)} \frac{\partial^\alpha}{\partial t^\alpha} \exp\{K_{tr}\eta(t)\}. \tag{6}$$

However, in so general representation Eq. (6) is actually intractable. Therefore, next we will consider some limiting cases, which allow both significant simplification of hydrogen transport equation and answering some practical questions. First we notice that for the case where the hydrogen density is rather small, so that $K_{tr} n_{fr} \delta t < 1$, where δt is the characteristic time of the variation of free hydrogen density, Eq. (6) can be simplified and assuming $n_{tr} > n_{fr}$ finally gives

$$\frac{\partial^\alpha N_H}{\partial t^\alpha} = \frac{\sin(\pi\alpha)}{\pi\alpha} \frac{D\hat{\nu}_d^\alpha}{\nu_{tr}} \nabla^2 N_H. \tag{7}$$

The applicability limit of Eq. (7) set by inequality $K_{tr} n_{fr} \delta t < 1$ for hydrogen transport in a sample with characteristic scale length, Δ, can be evaluated by noticing that Eq. (3) gives the following estimate $n_{tr} / \delta t \sim n_{fr} / \tau_\Delta$. Estimating δt from the sub-diffusion equation (7) we find $\delta t \equiv \tau_{SD}(\tau_\Delta) \sim \hat{\nu}_d^{-1}(\nu_{tr}\tau_\Delta)^{1/\alpha}$, and, therefore, Eq. (7) can be used for the case where

$$N_H / N_{tr} < (\nu_{tr}\tau_\Delta)^{-1} < (\nu_{tr}/\hat{\nu}_d)^{\alpha/(1-\alpha)} < 1. \tag{8}$$

We notice that once inequalities (8) are satisfied we automatically have a strong re-trapping of free hydrogen $\delta t \nu_{tr} > 1$ and can neglect nonlinear term $\propto n_{fr} f$ in the right hand side of Eq. (1, 2) so that we are coming to the case describing a random walk with a power-law waiting time distribution resulting in a sub-diffusion process [4]. Analyzing Eq. (5) for the case $K_{tr} n_{fr} \delta t > 1$ we notice that since $K_{tr}\eta(t) > 1$, we can expand the difference $\eta(t) - \eta(t')$ in the exponent of Eq. (5) and evaluate $d\eta(t')/dt'$ at $t'=t$. As a result, after some algebra, we come to $n_{tr} \approx (n_{tr})_{eq}$ and

$$\partial N_H/\partial t = \alpha D(\hat{v}_d/\nu_{tr})\left(\sin(\pi\alpha)/\pi\alpha\right)^{1/\alpha}\nabla\cdot\left\{\left(N_H/N_{tr}\right)^{(1-\alpha)/\alpha}\nabla N_H\right\}. \qquad (9)$$

In other words, for $K_{tr}n_{fr}\delta t > 1$, the densities n_{tr} and n_{fr} abide by the quasi-steady-state relation (4). This is not surprising, since from Eq. (1, 2) one sees that equilibrium distribution function can only be reached for $K_{tr}n_{fr}\delta t > 1$. It is possible to show that the applicability of Eq. (9) is bounded by the following inequalities

$$(\nu_{tr}\tau_\Delta)^{-1} < N_H/N_{tr} < (\nu_{tr}/\hat{v}_d)^{\alpha/(1-\alpha)} < 1. \qquad (10)$$

Comparing Eq. (8, 10) we find that sub- and nonlinear- diffusion equations (7, 9) are applicable for relatively low and high hydrogen density respectively [6].

Molecular dynamic (MD) simulations of H migration/desorption on/from W surface. In the context of hydrogen transport and outgassing from the solids, hydrogen desorption from a solid surface is usually described as desorption of hydrogen molecules formed by recombination of adsorbed hydrogen atoms on surface. Hydrogen desorption flux, Γ_H, is then described as a second-order kinetic process $\Gamma_H = K_{rec}n_s^2$, where K_{rec} is hydrogen recombination constant at the surface, which is usually described in Arrhenius's form $K_{rec} = \hat{K}_{rec}\exp(-E_{rec}/T)$, and n_s is hydrogen surface density. We notice that such expression for the outgassing rate implies uncorrelated distribution of hydrogen atoms on the surface. However, experimental data show large discrepancies for both $\hat{K}_{rec}$ and E_{rec} as well as contradictory temperature dependencies [7]. In addition, several binding states for adsorbed hydrogen on tungsten surface were observed in thermodesorption experiments and desorption kinetic order may be different from two [8]. Here we addressing the issue of hydrogen transport on and desorption from tungsten surface with MD simulations including temperature accelerated dynamics (TAD) [9]. In particular, TAD was used in the case of computationally demanding hydrogen transport with W-H Tersoff interatomic potential proposed in [10]. We start with analysis of hydrogen binding energy, $E_b(x,y)$, on tungsten surface (we keep tungsten temperature close to 0K by applying dumping viscous force). We used original W-H Tersoff interatomic potential from [10]. For <100> tungsten surface we found several sites with local maximum of binding energy (see Fig. 1). Three of them have very similar values: $E_b = 2.39\,eV$, at the bridge site (B), $E_b = 2.35\,eV$ at the three-fold hollow site (T), $E_b = 2.4\,eV$ at the orthohedral site (O). In addition to that there are several rather narrow maxima (D) with $E_b \approx 1.9\,eV$. For <110> surface we find $E_b = 1.6\,eV$, $E_b = 2.35\,eV$, and $E_b = 2.4\,eV$ B, T, and O sites correspondingly. These data are in agreement with both binding energy found with LEPS potential for <100> B-site, $E_b = 2.4\,eV$ in [11] and, taking into account experimental uncertainties, experimental values of the activation energy $E_{des} = 2.9\,eV$ for hydrogen desorption as single atom from polycrystalline tungsten [12]. Next we studied hydrogen transport on tungsten surface. TAD simulations with one hydrogen atom on tungsten surface were then used to analyze hydrogen transitions between adsorption sites, and to estimate activation energy of these transitions with the nudged elastic band (NEB) method. For temperatures 500K and 1200K, TAD have been performed on <100> surface, revealing one additional site (T2) with local maximum $E_b = 2.15\,eV$. Activation energy of hydrogen transition between local adsorption sites estimated with NEB method show that the transition $(T) \Rightarrow (B)$ has the highest activation energy ~0.55 eV. Activation energies for other transitions do not exceed 0.35 eV and is particularly weak (below 0.1 eV) for (D)$\Rightarrow$(T2). Transitions between adsorption sites occur only between spatially adjacent states, and hydrogen atoms can thus only migrate from one lattice cell to an adjacent one through (B) sites. It suggests that the diffusion of hydrogen on <100> surface is limited by hydrogen migration from (T) to (B) sites, and that the activation energy for diffusion $E_b \approx 0.55\,\mathrm{eV}$. However, transition barriers between adsorption sites other than (B) sites are lower than barriers for transitions toward (B) sites, and therefore hydrogen atoms will mostly explore sites (T, T2, O, D) before exploring (B) sites. These observations suggest that diffusion process of hydrogen atom on <100> surface might be more complex than diffusion modeled by single hydrogen hop from one lattice cell to another one. But no further quantitative analysis of adsorption sites and diffusion process can be reasonably performed without better validation of the W-H interatomic potential. For instance, existence of (D) sites is questionable regarding their narrowness, and may be due to cut-off effects in interatomic potential. Despite uncertainties in interatomic potential, comparison of adsorption site properties to experimental observations shows that W-H interatomic potential used in MD may still well describe at least main features of adsorption sites on W surfaces, in particular effects of many adsorptions sites in one lattice cell on hydrogen diffusion. Finally, we consider hydrogen molecular desorption from tungsten surfaces. We find that molecular desorption is not well described by the W-H Tersoff interatomic potential proposed in [10] (instead we observe desorption of single hydrogen atoms), and three-body interactions parameters of this potential, which describe effects of tungsten environment on hydrogen recombination, should be adjusted to qualitatively reproduce main features of hydrogen recombination into H_2. For relatively large tungsten surface coverage, ϑ, with hydrogen we observe hydrogen clustering on surface (Fig. 2), which is solely due to nonlinear interactions of an ensemble of hydrogen atoms with tungsten lattice (inter-hydrogen distance exceeds the cut-off radius of H-H interaction). This can explain experimentally observed sudden variations of desorption characteristics as a function of the hydrogen surface coverage [12]. Hydrogen clustering also suggests that kinetic of hydrogen desorption from tungsten surface may be not always second-order.

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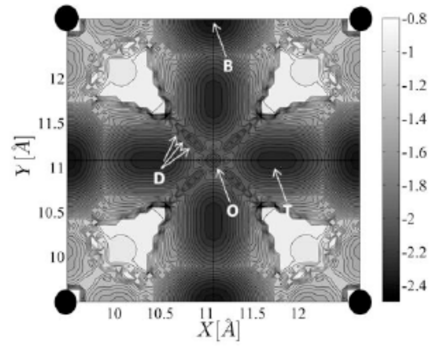

Fig. 1. Hydrogen binding energy $E_b(x,y)$ [eV] on <100> tungsten surface.

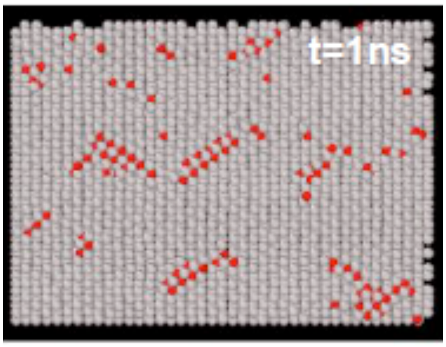

Fig. 2. Hydrogen clusters (red) on <100> tungsten surface, $\vartheta = 0.1$, T=1500 K.