

Behaviour of Tungsten in Fusion Environment Damages by Hydrogen

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Abstract: *The analysis of the interaction of hydrogen and their isotopes with tungsten is important, since this material is a strong candidate to form the first wall of fusion reactors for both magnetic and inertial confinement, and these atoms have a very sensitive (desired and unwanted) interaction with it. For this purpose, we study the effects and electronic state densities of atomic hydrogen in pure tungsten, in order to analyze some important properties such as the density of states of the system. Focusing on this application, this work is a preliminary study of the behavior of atoms of hydrogen on a surface of tungsten. We use a program simulation based on the DFT (density functional theory) implemented in the Jellium Code, in order to obtain the adsorption energy and the density of states of the systems, as well as some properties derived from them.*

Keywords: Hydrogen, Tungsten, Fusion

1. Introduction

In terms of energy, for the sustainable development of the nuclear option, there is currently worldwide renewed interest in new reactors and in the research and technological development of the fuel cycle. In this framework, the next generations of reactors are under evaluation. The new reactor concepts are characterized by greater efficiency and better use of nuclear fuel, with the minimization of nuclear waste. This approach means that a new and in-depth analysis of the structural materials with radiation resistance will have to be introduced more accurately than the current ones [1]. To achieve high performance parameters, continuous research and testing of materials is necessary. Hence the need to study the design and optimization of alloys and composite materials that present properties suitable for the latest generation reactors, including fusion ones.

This work is oriented to the study of properties of materials for its probable use in advanced technologies in fusion reactors. The actual issues to achieve those performances are some materials like composites (SiC), oxides dispersed steels (ODS) or Ferritic-Martensitic (FM) that could be chosen to constitute the walls and the divertor of the fusion reactor [1-3]. Those materials are radiation resistant, but have some other difficulties.

Eventually, tungsten (W) was chosen to build the plasma-facing components. This is the pure metal with the highest melting point (3422 °C), the highest tensile strength and the lowest coefficient of thermal expansion. That is why it is an adequate material to face the high pressure and high temperature conditions in fusion reactor. Furthermore, due to its 5d electrons, there are strong covalent bonds between atoms [4].

Thus, the divertor and the first wall of the reactor of the ITER project will be in tungsten. This part of the reactor must withstand high heat flux and bombardment by particles

escaping the plasma. This project, to update the fusion reactor of ITER projects, is named WEST [5].

In this work, we focus in the study of the interaction of hydrogen with tungsten through computational analysis. Firstly, we are going to study some properties of atomic hydrogen embedded in tungsten. This is very useful because during the process, huge quantities of hydrogen is ejected due to the fusion reaction $D(T,n)\alpha$. Hydrogen impurities are the most preponderant part of damages in fusion reactor. In this study, we won't take into account nuclear process like neutron capture and others. We only focus on the interaction between hydrogen and tungsten. We will find some important quantities such as the volume of solution of hydrogen in a tungsten material, the heat of this solution and the phase shift of the wave function of the system, used to calculate the density of states in the material. Then, we add the pressure and temperature contribution to the Jellium model. This part is quite considerable since it will lead our model to the real conditions of a fusion reactor (high pressure and high temperature).

2. Theoretical Frame

One of the most useful quantities of characterising metal-hydrogen systems is their electronic density. This is fundamental for determining properties such as volume of dissolution of hydrogen, heat of solution, activation energies, diffusion properties, values of chemical potential, among others.

2.1 Modelling approach

The model used to obtain the electronic density is the so called Jellium model, based on Density Functional Theory [6].

The Jellium model considers a background as the equivalent of the nucleus of the atoms and the core electrons, fixed and uniformly distributed. The valence electrons are embedded

in this positive background, and are represented by a uniform electron gas. Thus the electronic neutrality condition remains due to that the density of valence electrons is equal to the density of positive charges, which is equal to the initial atom density [7].

In particular, we use the DJELLY code, which is based in the jellium model and uses finite elements method. This code is a very useful simulation because the output data give direct information about: the distance to the impurity R, the screen charge density, the valence density and the integrated screen charge density.

With this programme code, we can determinate important quantities of the system such as volume of solution, heats of solution, adsorption, interaction and activation energies, chemical potential and stopping power of charged particles, among others.

2.2 Description of the quantities in Jellium model

In order to obtain electronic density, the Wigner-Seitz radius r_s is theoretically defined as:

$$n_0 = V/N = 1/4 \ 3\pi r_s^3 \quad (1)$$

With n_0 the electron of valence density (considered as constant), N the number of electrons, V the volume of the considered material and r_s is the radius of a sphere whose volume is equal to the mean volume per atom in a solid [8]

For metals, the main contributions to the electronic density are the s and p shells electrons, and eventually d shells.

For a non-interacting system, it is defined as:

$$r_s = (3M4\pi\rho Na)^{1/3} \quad (2)$$

with molar mass M , ρ mass density and Na Avogadro number.

Thus, using Jellium model, dealing with density or r_s is strictly the same because in this model, r_s is the radius of the sphere that an electron occupies in the jellium. In this way, the jellium is represented by a uniform electron gas in which each electron is separated from its neighbours a distance $2r_s$. Adding an external charged particle in the material, the charge density abruptly changes. The electronic density is now:

$$n(r) = n_0 + \Delta n(r) \quad (3)$$

with n_0 the initial atomic density and $\Delta n(r)$ the charge density variation induced by the embedded impurity (external charged particle) [7]

An important quantity of the system is the embedding energy in the material. Defining:

$$E = E_f - E_j \quad (4)$$

with E_f the energy of the system Jellium + Impurity and E_j the energy of the pure Jellium

Defining E_{at} the energy of the isolate impurity (it means before embedding), if:

$$E_f - E_j > E_{at} \quad (5)$$

The embedding process is exothermic: the impurity is more bound in the Jellium than in the void.

So, we define the embedding energy as:

$$E_{emb} = E - E_{at} \quad (6)$$

That gives the character of the process.

Finally, observing the piling electronic charge response around the impurity, we see oscillations around it. Those are called Friedel oscillations that are the quantum mechanical analogy to electric charge screening. This phenomenon is well known and has observable consequences whenever a defect is embedded in a metal [8].

3. Results

In our case, the hydrogenic impurity will be generally embedded in the tetrahedral vacancies in the tungsten bcc lattice. However, due to its important mobility, hydrogen atoms diffuse very well through the crystallographic lattice. The atomic number Z of the embedded charge is $Z = 1$, because this is the atomic number of an atom with one proton (hydrogen, deuterium and tritium).

For the value of r_s (or n_0) as input, we select that developed in a previous work [9], that relates r_s with the bulk modulus B of the metal due to that B is a measure of the compression of the electron gas density in the interstitial positions. This method is interesting because we base our theoretical tool r_s on experimental value (from B) and that is a more realistic procedure than using a theoretical value from different models.

The bulk modulus is linked to the energy of each particle of the system as:

$$B = 1/12\pi r_s [\partial^2 \epsilon / \partial r_s^2 - (2/r_s) \partial \epsilon / \partial r_s] \quad (7)$$

The energy ϵ is the sum of the kinetic ϵ_{kin} ($\epsilon = (3/5) \alpha^2 r_s^2$), exchange ϵ_x ($\epsilon = - (3/2)\pi r_s$) and correlation ϵ_c ($\epsilon = \epsilon(rs)$). α is $(4/9\pi)^{1/3}$. The correlation energy is always negative and depends on the value of r_s , going from $0.1\epsilon_x$ to $0.5\epsilon_x$.

Thus, the bulk modulus becomes:

$$B = B_{kin} + B_x + B_c \quad (8)$$

For a good fitting results, and to have a semiempirical parametrization for $r_s > 1$, it becomes:

$$B = B_{kin} + (1/r_s)(B_x + B_c) \quad (9)$$

And finally, the relation between r_s and B is:

$$r_s = (\alpha^{-1} - \pi^{-1}(1+\epsilon)/2\pi\alpha B)^{1/5} \quad (10)$$

With ϵ the contribution factor of the correlation energy (between 0.1 and 0.5).

The equation (10) is a parameterization of r_s against the experimental bulk modulus B , providing a semi empirical definition of r_s or, equivalently, the electronic density n_0 .

Now, we can calculate values of r_s for tungsten: The different values of r_s are given by the contribution factor of the correlation energy. We will take the two extreme values for computing.

$\epsilon_c = 0.1$ this gives $r_{s1} = 2.1395$ a.u.

$\epsilon_c = 0.5$ this gives $r_{s2} = 2.1036$ a.u.

The two input parameters for the program are: the radius of r_s that gives the electron gas density of the involved material, and ISTART, that chooses the electronic potential: ISTART = 0, the program takes the Thomas-Fermi potential. ISTART

= 1, the program reads the potential computed on the last run.

We ran the code taking 24-point Gaussian quadrature for the integration. The radial step size (DR1 in the code) is 0.04. The tolerance on bound state eigenvalues (TOL) is 10^{-6} .

As we can see in figures 1, 2 and 3, the screen charge density is decreasing exponentially and it is observed the Friedel oscillation on charge element and the integrated charge. The graphs come from the computation with r_{s1} and $ISTART = 0$. The tendency is the same for r_{s2} and $ISTART = 1$.

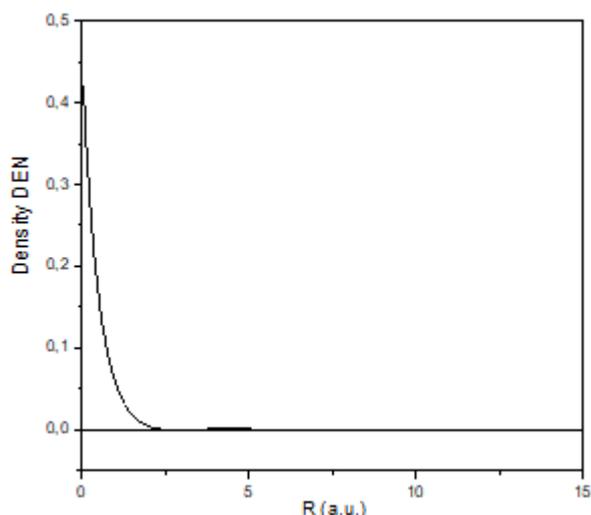


Figure 1: Screen charge density in the W-H system in terms of the distance from the impurity

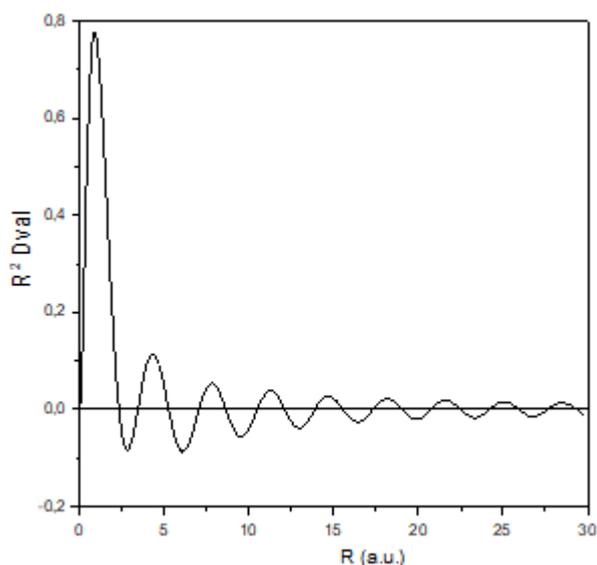


Figure 2: Charge element in the W-H system in terms of the distance of the impurity

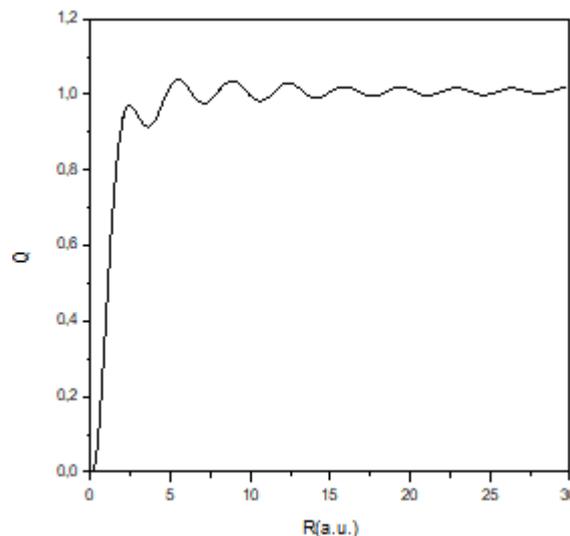


Figure 3: Integrated charge in the W-H system in terms of the distance from the impurity.

3.1 Calculation of volume of solution of hydrogen in tungsten

The volume of solution of hydrogen, vH , is important because it is a measure of the expansion that produces a hydrogenic impurity in the lattice [10, 11].

In the Jellium model, this quantity is:

$$vH = S/3B \tag{11}$$

with $S = 4\pi n_0 \int_0^\infty dR(1-Q(R, n_0))$, $0 \leq R < \infty$

With these quantities, we calculate vH , the volume of solution of hydrogen in tungsten:

Table 1: Volume of solution of hydrogen in tungsten

r_{s1} Istart=0	r_{s1} Istart=1	r_{s2} Istart=0	r_{s2} Istart=1
vH [a.u.] 1.46E+01	vH [a.u.] 1.17E+01	vH [a.u.] 1.44E+01	vH [a.u.] 1.19E+01
vH [\AA^3] 2.1805	vH [\AA^3] 2.2291	vH [\AA^3] 2.1510	vH [\AA^3] 2.2488

From ref [10] we have the empirical rule $vH = 2.9 \pm 0.3 \text{\AA}^3$ / atom for transition metals.

Till now, there is no experimental data of vH in tungsten. So, according with our model, we estimate our value as 2.5\AA^3 . This value is coherent with the boundary conditions of the system (Friedel sum rule and cusp condition [8]).

3.2 Phase shifts

The phase shift of a wave function gives information about the probability electronic density. It is very useful to compute the electronic Density of State of the system (DOS) [12, 13].

The DJellium code gives the variation of the phase shifts as:

$$\partial del(l, k) = \delta \delta(l, k) / \partial k \tag{12}$$

With $\delta(l, k)$ the phase shift of the wave function of the system, l the angular momentum and k the wave vector.

The code gives $\partial \text{del}(l,k)$ from $k = 0$ to $k = k_F$, being k_F the Fermi wave vector, maximum value that can have in the solid. The total contribution is:

$$\text{total}(k) = (2/\pi) \sum_{l=0,1,\dots,7} (2l+1) \partial \text{del}(l,k); \quad (13)$$

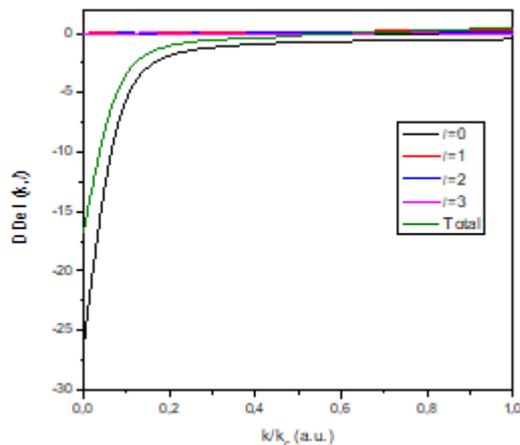


Figure 4: $\partial \text{del}(l,k)$ for $l = 0$ to $l = 3$ and the total as a function of k/k_F for $r_{s2} = 0.5$ and Thomas Fermi potential.

In Figures 4 we show each contribution correspond to $l=0, 1, 2, 3$ and the total. We see that the largest contribution to the total variation is with $l = 0$. Thus, for this system, it is enough to take into account the contribution of phase shifts with the orbital quantum number $l = 0$.

3.3 Heat of solution

Finally, the other important thermodynamic property of hydrogen atom into tungsten is the heat of solution, or enthalpy (at infinite dilution).

The DJELLIUM code gives the Fermi Energy E_F and the energy of the centre of the lowest conduction band of the host metal E_S , in such a way that [14]:

$$\Delta E = E_F - E_S \quad (14)$$

If the Jellium model were exact, $\Delta H_{\text{JELLIUM}} = \Delta E_{\text{JELLIUM}}$, but this is not. Thus, we must refine the latest equation, as a first approximation, as:

$$\Delta H_{\text{JELLIUM}} = \alpha \Delta E_{\text{JELLIUM}} + \beta \quad (15)$$

Furthermore, with the experimental values ΔH_{EXP} and ΔE_{EXP} , due to thermodynamics laws, we can approximate:

$$\Delta H_{\text{EXP}} / \Delta E_{\text{EXP}} = \alpha + \varepsilon \cong \alpha \quad (16)$$

Fixing $\Delta H_{\text{JELLIUM}}$ to ΔH_{EXP} we obtain:

$$\Delta E_{\text{JELLIUM}} = 0.875 \text{ a.u.}, \quad r_s = 2.1395 \text{ a.u.}$$

$$\Delta E_{\text{JELLIUM}} = 0.907 \text{ a.u.}, \quad r_s = 2.1036 \text{ a.u.}$$

From [10.]: $\Delta H_{\text{EXPERIMENTAL}} = 0.0397 \text{ a.u.}$, for $\varepsilon = 0.1$ and $\Delta E_{\text{EXPERIMENTAL}} = 0.191 \text{ a.u.}$, for $\varepsilon = 0.15$, we obtain :

For $\varepsilon = 0.1$:

$$\Delta H_{\text{JELLIUM}} = 0.208 \left| \Delta E_{\text{JELLIUM}} \right| - 0.142$$

For $\varepsilon = 0.5$:

$$\Delta H_{\text{JELLIUM}} = 0.208 \left| \Delta E_{\text{JELLIUM}} \right| - 0.149$$

Notice that we take $\left| \Delta E_{\text{JELLIUM}} \right|$ and no $\Delta E_{\text{JELLIUM}}$ due to the potential reference ($\Delta E = E_F - E_S$ or $\Delta E = E_S - E_F$).

$$\text{For } \varepsilon = 0.1, \Delta H_{\text{JELLIUM}} = 0.04 \text{ a.u.} \quad (17.a)$$

$$\text{For } \varepsilon = 0.5, \Delta H_{\text{JELLIUM}} = 0.034 \text{ a.u.} \quad (17.b)$$

Those theoretical values coincide with the experimental ones [10].

4. Jellium model with pressure and temperature dependences

Until now, we use the Jellium model for describing a hydrogen atom embedded in a tungsten material without considering temperature and pressure. However, this study does not really fit the genuine conditions of a fusion reactor. Those reactors bring the materials to extreme conditions. The temperature of work is between 100 million and 200 million degrees Celsius. In order to approximate the system to a more realistic regime we must add pressure and temperature dependences in our model.

4.1 Pressure contribution

It is necessary to find a relation (or equation of states) for solids for extended P-V-T conditions. One theory, the Murnaghan equation of states, is particularly remarkable [15]. It is based on the assumption of a bulk modulus linear with pressure. That was experimentally demonstrated at low and intermediate pressure. This theory sets down the derivative of the bulk modulus respective to pressure:

$$n = \partial B / \partial P \Big|_T \quad (18)$$

From [16]:

$$n = -r_s / 3B (\partial B / \partial r_s) \quad (19)$$

Using the equation (10) to get B in terms of r_s , we obtain n constant and equal to 5/3. This result is agree with Murnaghan equation because it made the assumption that the bulk modulus is linear with the pressure. However, the experimental value of n taken in the literature [11] is 4.5 (our theoretical result gives 30% of the experimental value).

It must be consider that the volume of the system can be written as $V = 43\pi r_s N$, with N number of electrons in tungsten. Eventually, we remind that this model is for low and intermediate pressures, and in a fusion reactor pressure is enormously high. Thus the 70% to get the experimental value should come from the temperature contribution. In addition to that, several researches have been made to take into account the temperature dependence of n. All the results suggest that $\partial n / \partial T$ is always positive. So it is reasonable that the value of n of our model (taken at zero temperature) is lower that the value of n of the experiments (with a given value of T and P).

Furthermore, we tried to get a better approximation to the experimental value using our model and the correlation explain in the part 3.2 dealing with a correlation B(T). However, we have not dependable relation between B(T) and n.

This definition of n (eq. 19) describes the electronic contribution. For p-type and d-type metal, the electronic contribution to n is no more than 30%. To improve this model, we have to add other contributions like the crystallographic lattice or maybe we can change the parameterization of B, adding a new term. Those contributions might be due to the temperature and the pressure of the experiment. Thus, to complete our model, we propose:

$$n = n_0 + \tilde{n}(T, P) \quad (20)$$

with $n_0 = 5/3$.

We use an experimental correlation $\tilde{n}(T)$ found in the reference [17] and also use the perfect gas equation of states. Thus, writing:

$$n = \partial B / \partial P = (\partial B / \partial T) (\partial T / \partial P) \quad (21)$$

$\partial B / \partial T$ is known due to the experimental correlation of [10], and $\partial T / \partial P$ is computed from the perfect gas equation of states ($\partial T / \partial P = V/nR = M/dR$, with M the molar mass, d the density of tungsten, R the constant of perfect gas). With this approximation, we improve the value, (40%), but we are far from the experimental ones due to the symmetry of the system was broken.

4.2 Temperature contribution

In reference [18], we obtain a correlation between the bulk modulus B and the temperature for polycrystalline tungsten. This correlation coincides with experimental available values between 28°C and 1800°C [19]. In fact, these results were obtained from ultrasonic shear and compressional waves experiments, measured with a pulse echo technique, for polycrystalline tungsten at 99.4% dense. Our correlation, for pure dense tungsten (100%, and in Celsius degrees), is: $B(T) = 3.122410^{11} - 1.775510^7 T - 1.33310^3 T^2$ (22)

In figure 5 we observe the bulk modulus decreases with the temperature.

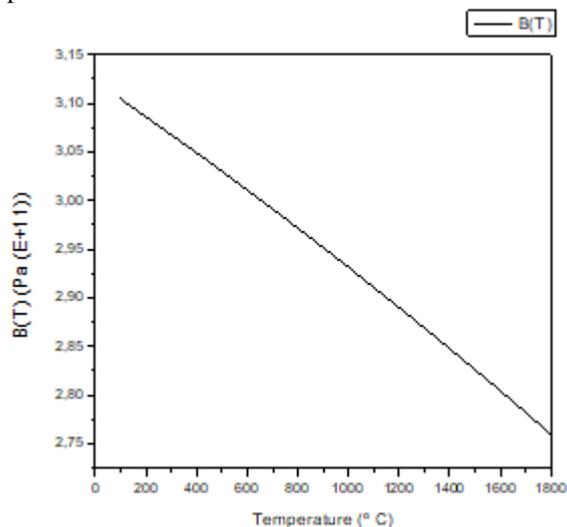


Figure 5: Bulk modulus in terms of temperature

5. Conclusions

In our work, we consider the extended nature of Tungsten-hydrogen interaction, using the effective jellium model, where the metal ion cores are spread in a uniform background. With this model, we take into account the fundamental effects of the electron screening in the conduction band of the material. On the other hand, the effects due to the local environment of the hydrogenic impurity are reasonably well incorporate including exchange and correlation through the local density approximation.

The results obtain with our model are in a very good approximation to the available experimental values of volume of solution and heat of solution of hydrogen in tungsten. Clearly, this approximation is good in the systems that have spherical symmetry. For the density of states this method is not exact, but is simple and general and can be used as long as sufficiently accurate first principles results are not available.

For the application in a fusion reactor, we have to take into account the pressure and temperature at which the system is undergo. In order to introduce these contribution, we applied the non-stabilized jellium model, which requires external parameters, as we indicated through this work.

Taking into account the temperature, we see that in approximately a range of temperature of 1800°C, the bulk modulus varies as a function of second order. This behaviour is the realistic one in a fusion reactor, and we have to take into account this behaviour. Although we have to improve our results with high temperatures, the method used here is useful and gives some accurate results for the complex tungsten-hydrogen system in extreme conditions as is in the first wall of a fusion reactor.

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