H Diffusion and Segregation at the W/Cu Interface

Based on DFT calculations

Y. Silva-Solis [1] and **Y. Ferro [1]**

WP PWIE 2022 Reporting Meeting

(1) Aix-Marseille University, France

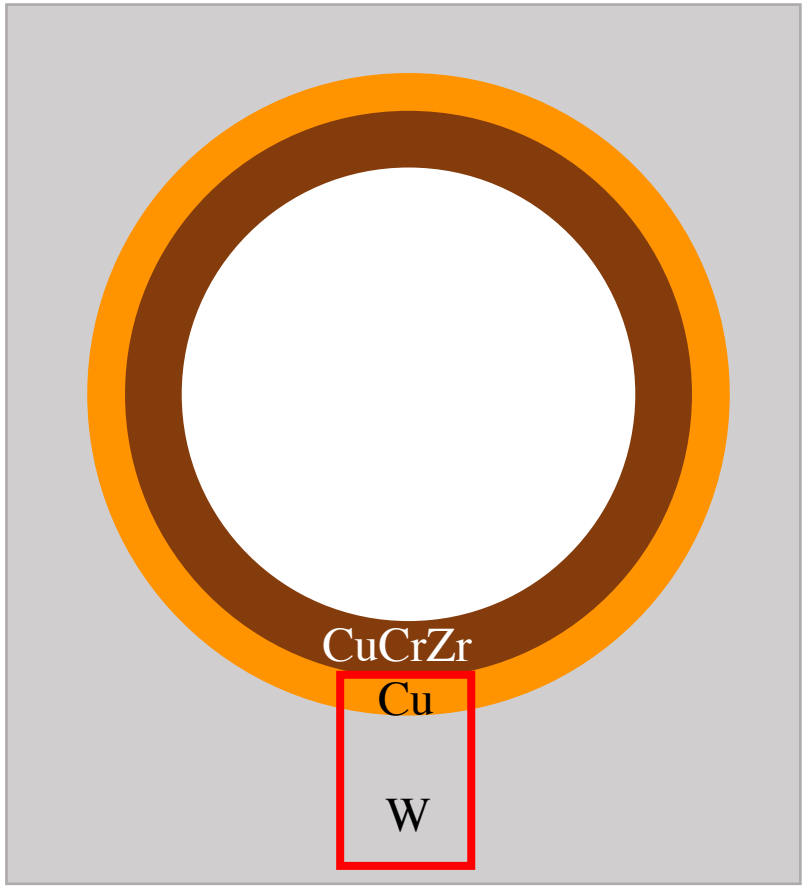
Outline

1 – The basic tools

2 – Past activities in WP PWIE (for understanding)

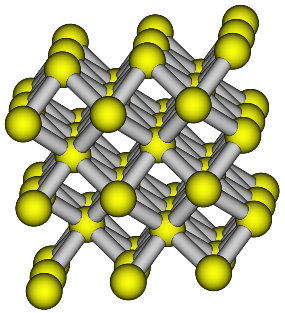
3 – This year activity: H at the W/Cu interface

4 – Conclusion and Perspectives



1. Basic Tools

Density Functional Theory



Atomic Scale

Accurate

Energies: binding, solution, formation of (point) defects …

Statistic Thermodynamics

Potential of the macroscopic system

$$G(T, p, n_1, n_2, \dots, n_N) = \sum_j n_j . g_j(T) - T . S^{conf}(T)$$

Kinetic model : Rate-Equations

MHIMS E. A. Hodille
CEA Cadarache

J. Denis
Aix-Marseille Univ.
EUROfusion Researcher Grant

DWE

Out of Equilibrium …

Macroscopic system → Bulk, surface, interface …

Determine the behavior of → Various solute, defects, adsorbants, etc …

At Thermal Equilibrium

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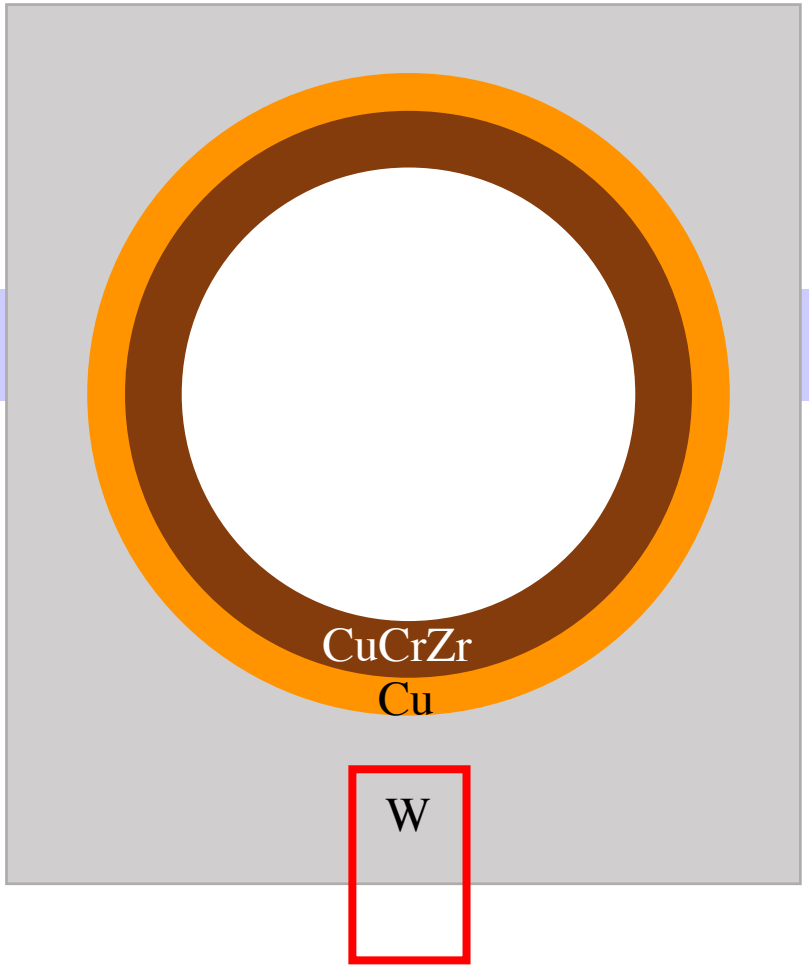


2 – Modeling Surface Properties

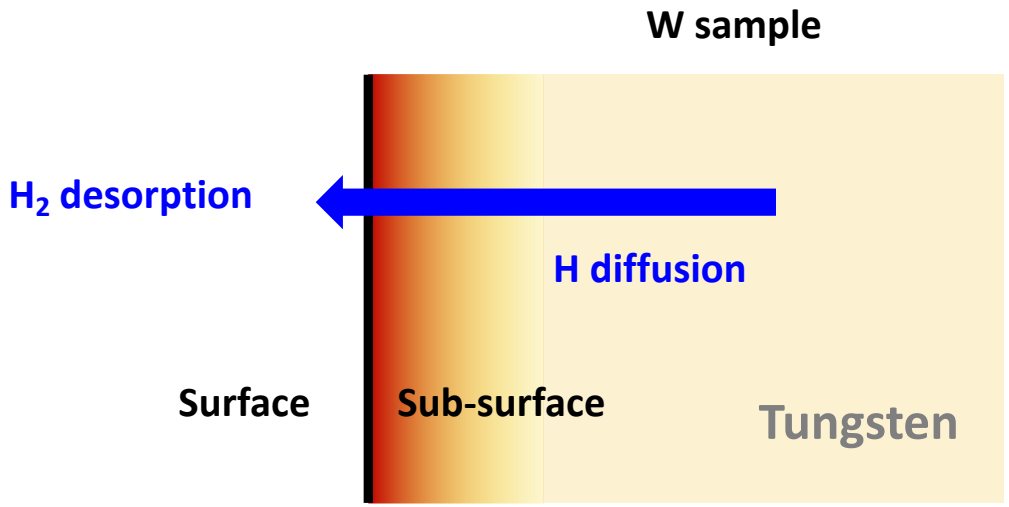
Experimental modelling of H material interaction in Labs

- Thermal Desorption Spectroscopy (TDS)

  Understanding requires Rate-Equation modellings

  What's the effect of the surface?

  Surface models based on DFT results are being included in Rate Equations Model



Atomic scale modelling of surfaces with DFT

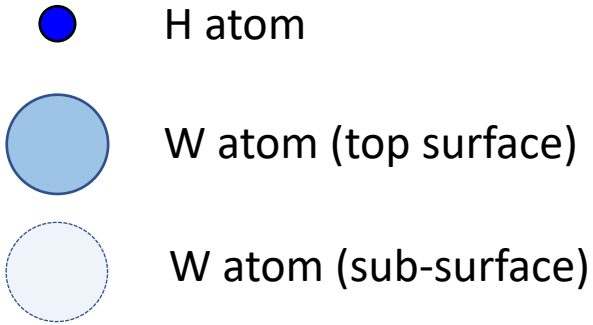
H on W

H + O on W

2 – H on W(110) surface – DFT results

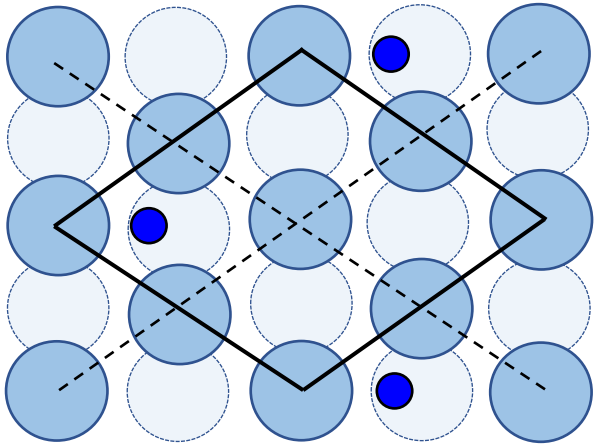
W(110) surface top view

Full energetics of H adsorption determined by DFT

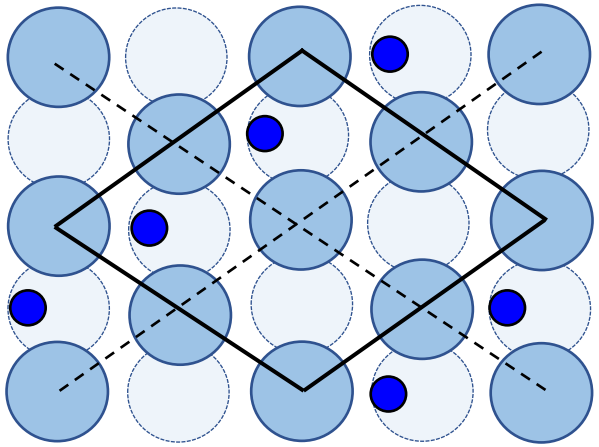


Coverages

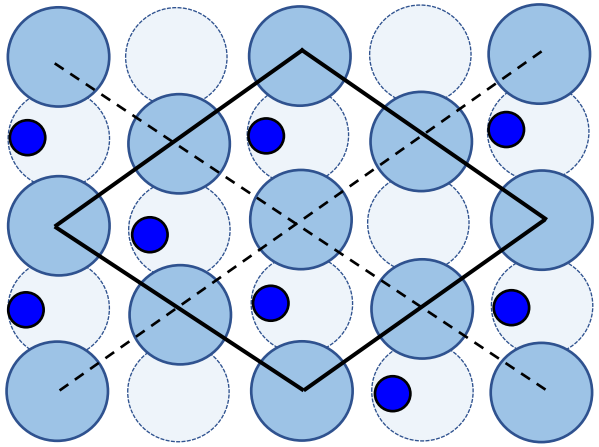
$\theta_H = 0.25$



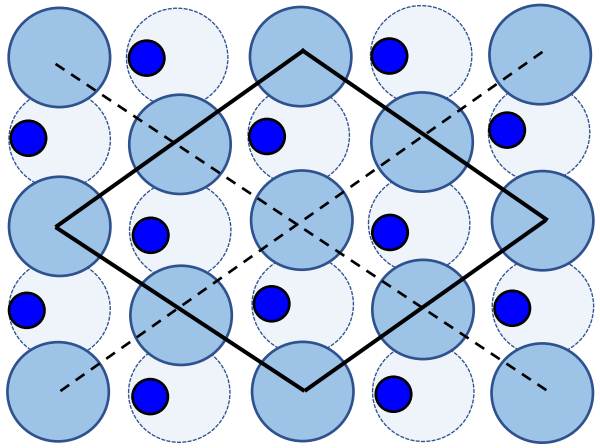
$\theta_H = 0.50$



$\theta_H = 0.75$



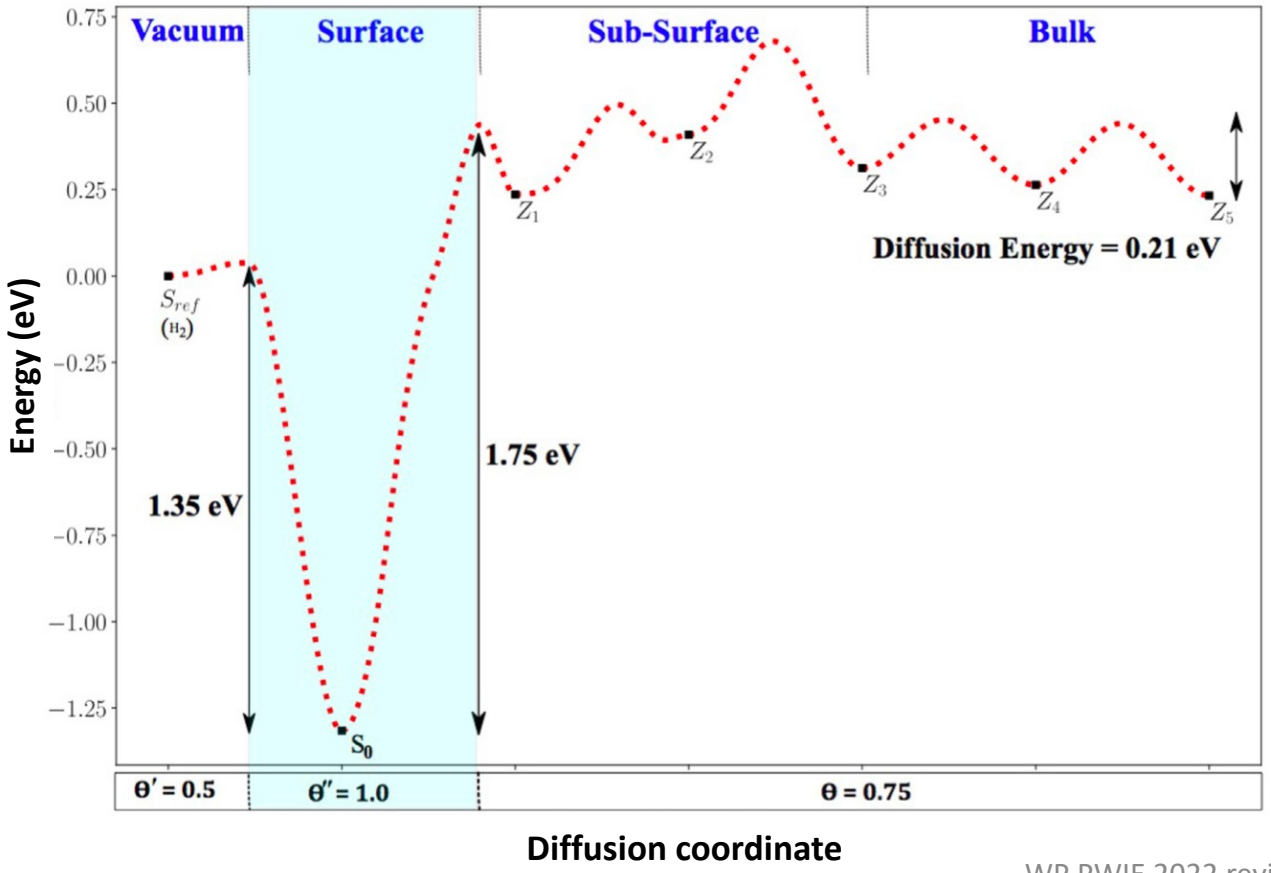
$\theta_H = 1.00$

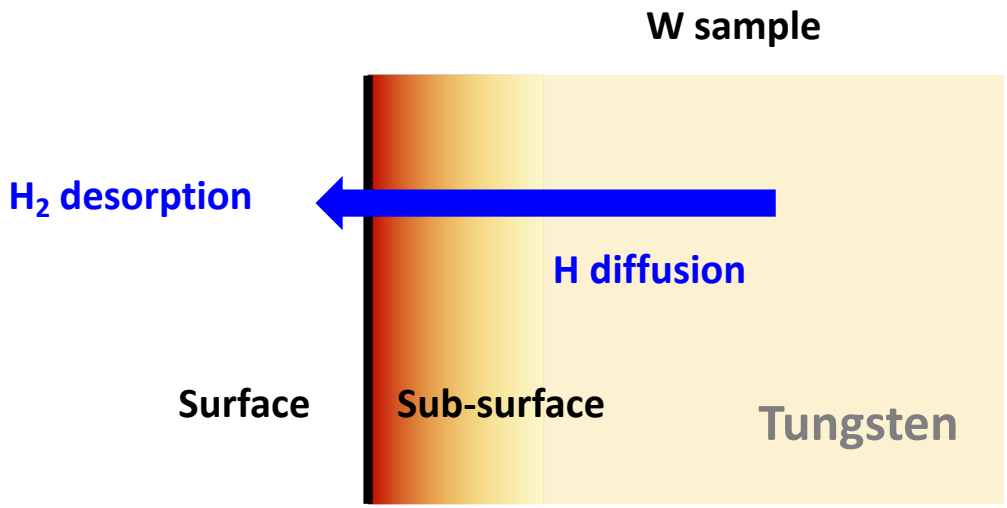


2 – H on W(110) surface – DFT results

Energy profile of hydrogen dissociation and absorption

M. Ajmalghan, Z. A. Piazza, E. Hodille, Y. Ferro* - *Nuclear Fusion 59 (2019) 106022*





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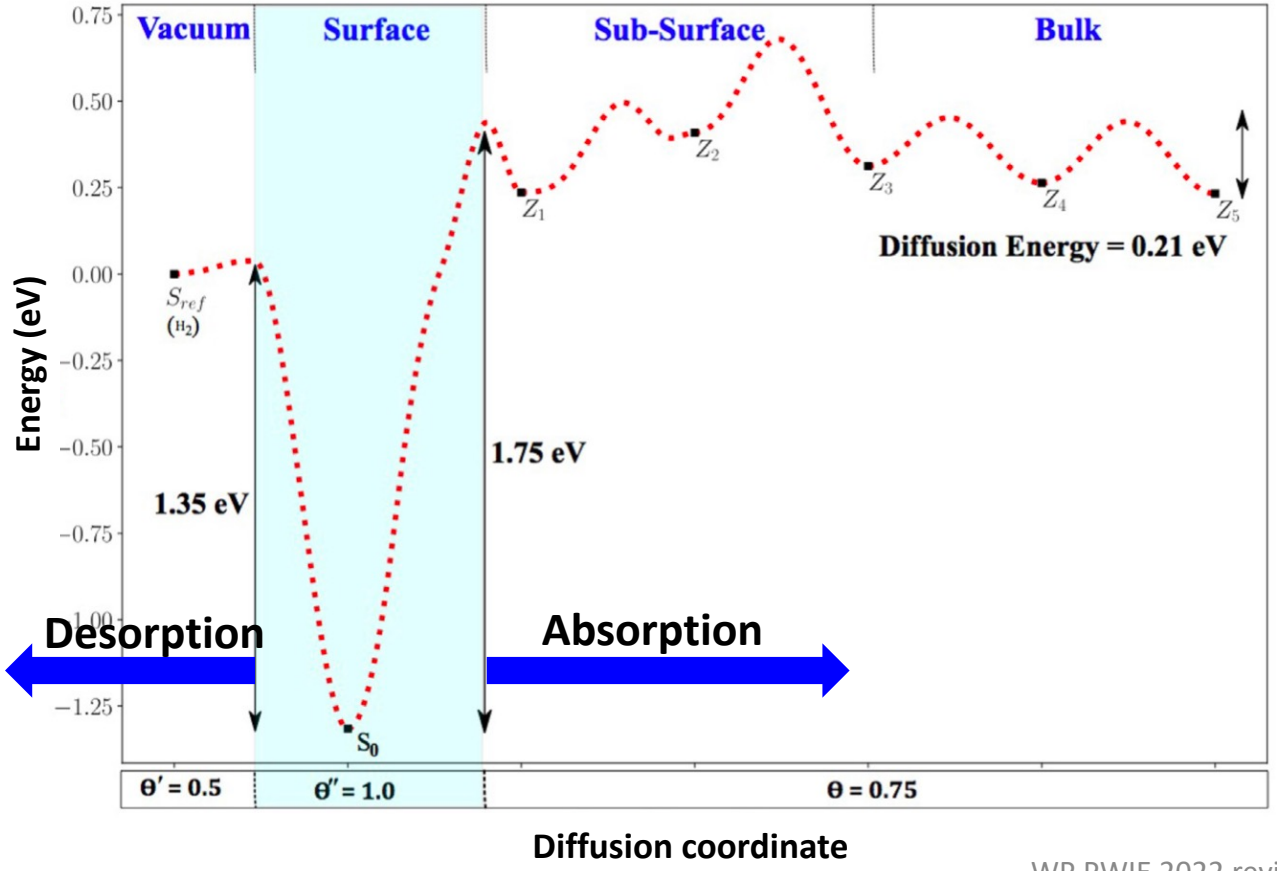
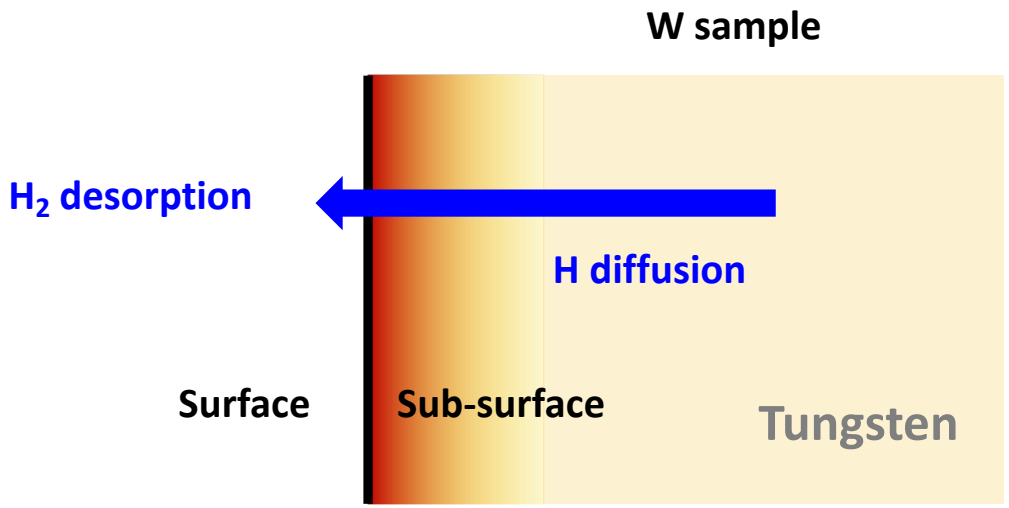




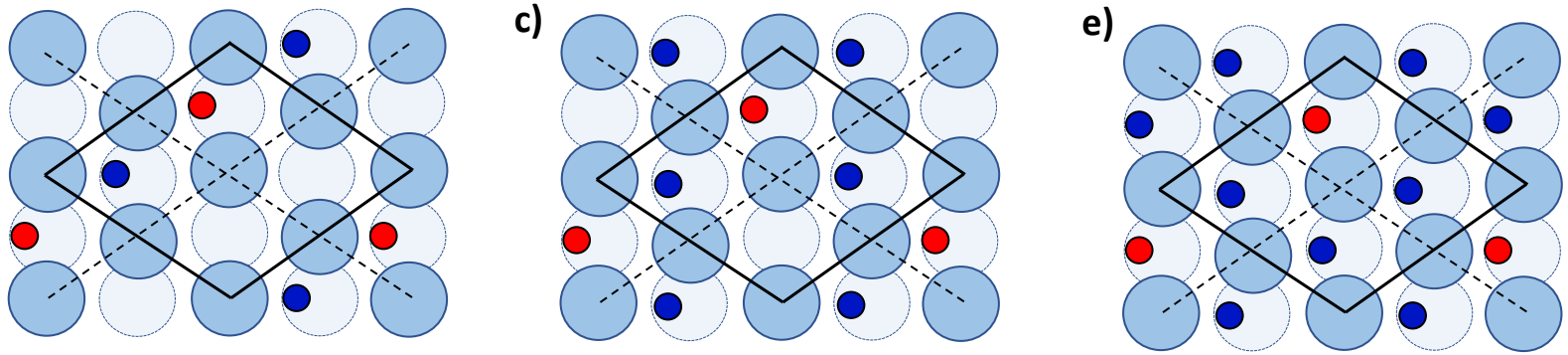
Absorption and Desorption
Strongly dependent on the surface coverage

2 – H and O on W(110) surface – DFT results

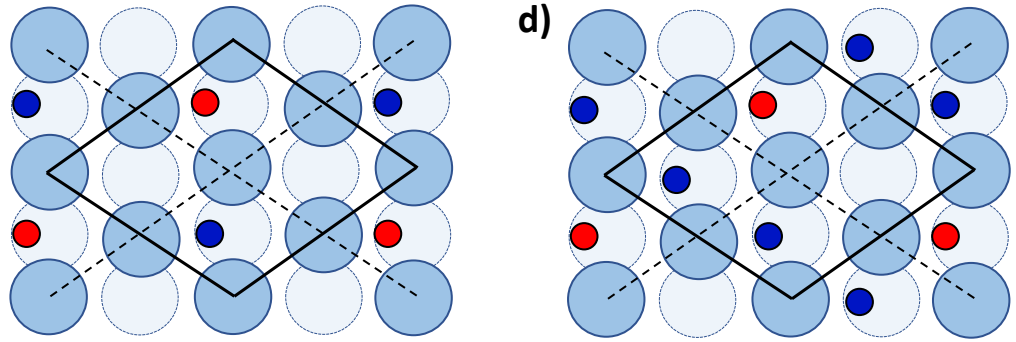
Coverages

$\theta_H = 0.25$ $\theta_H = 0.50$ $\theta_H = 0.75$

a) c) e)



b) d)



W(110) surface top view

Full energetics of H adsorption determined by DFT

H atom

O atom

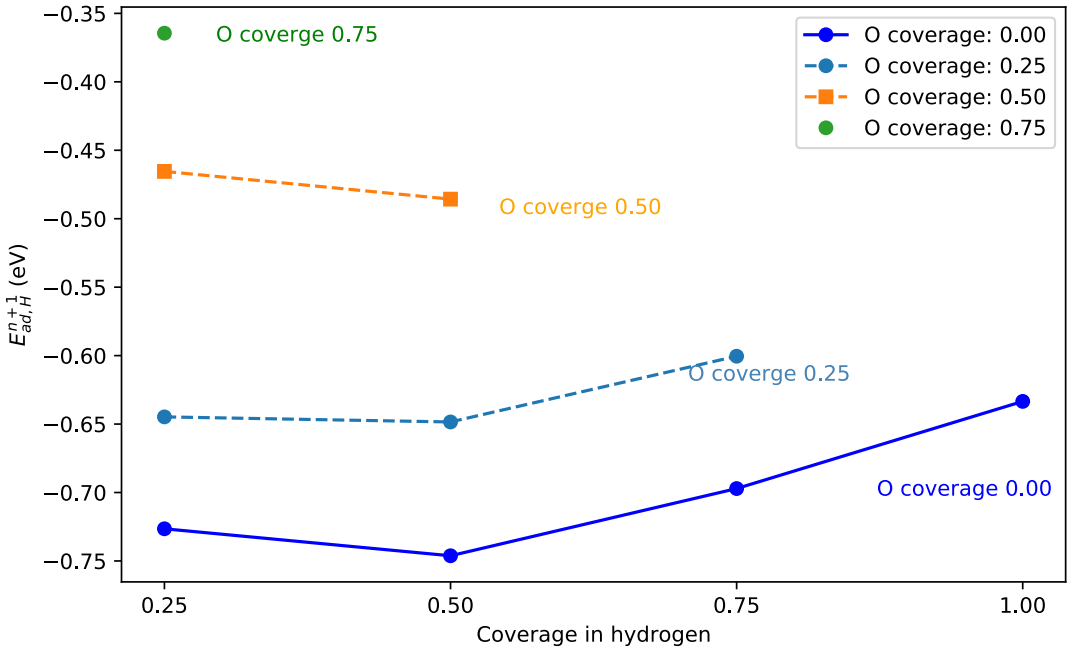
W atom (top surface)

W atom (sub-surface)

Saturation corresponds to $\theta_H + \theta_O = 1.00$

2 – H and O on W(110) surface – DFT results

Hydrogen adsorption on W(110) - The energetics



O weakens adsorption energy for H on W(110)

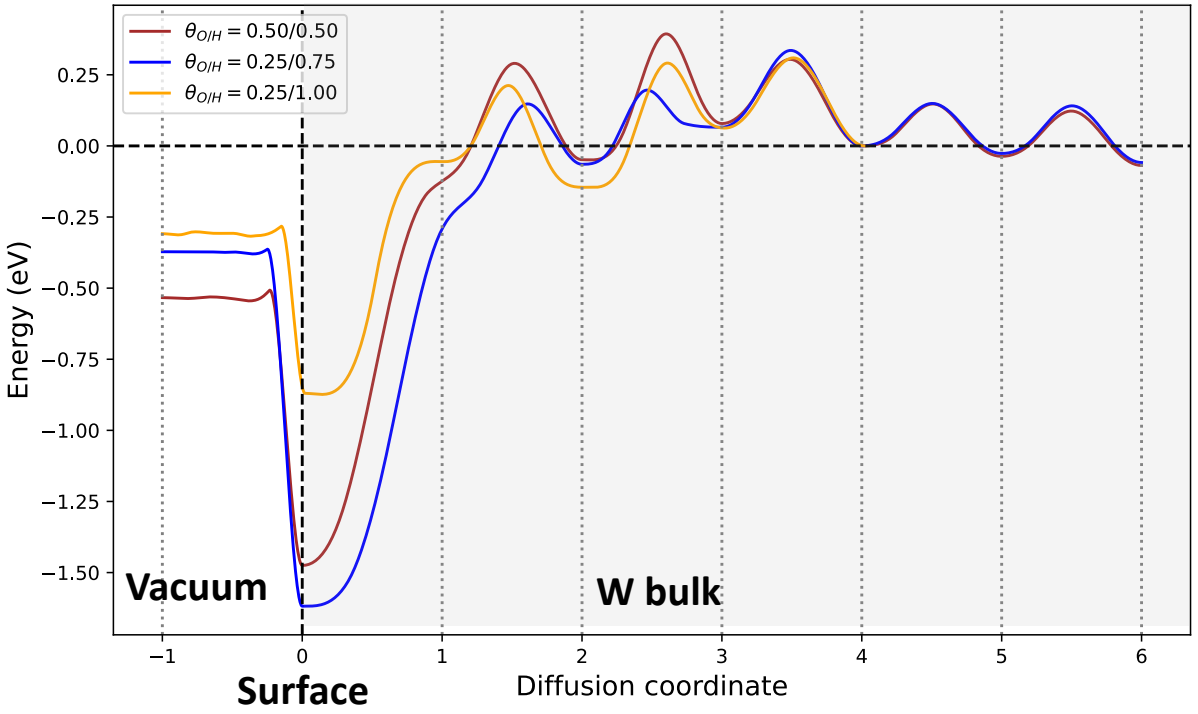
O limits the amount of H adsorption on W(110)

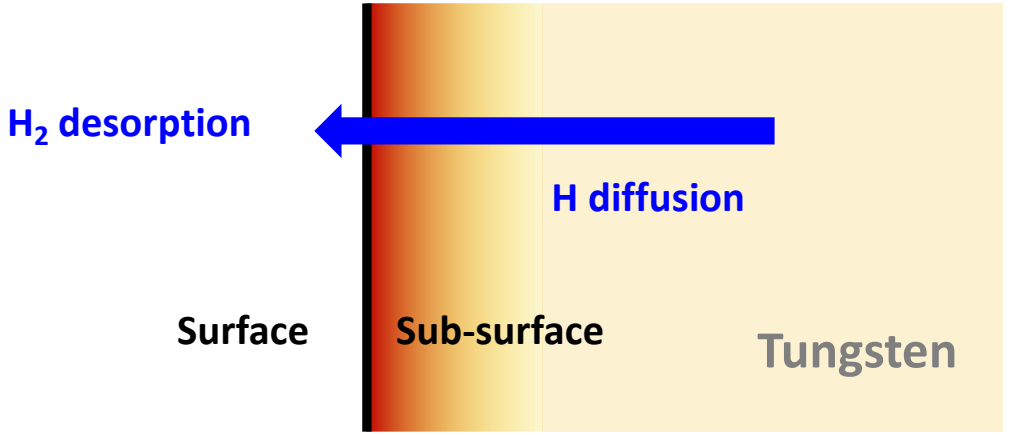
Consistent with experimental observations indicating that no H adsorbs above $\theta_O = 0.35$

What about H migration across the oxide layer ?

2 – H and O on W(110) surface – DFT results

Hydrogen on O pre-adsorbed W(110)





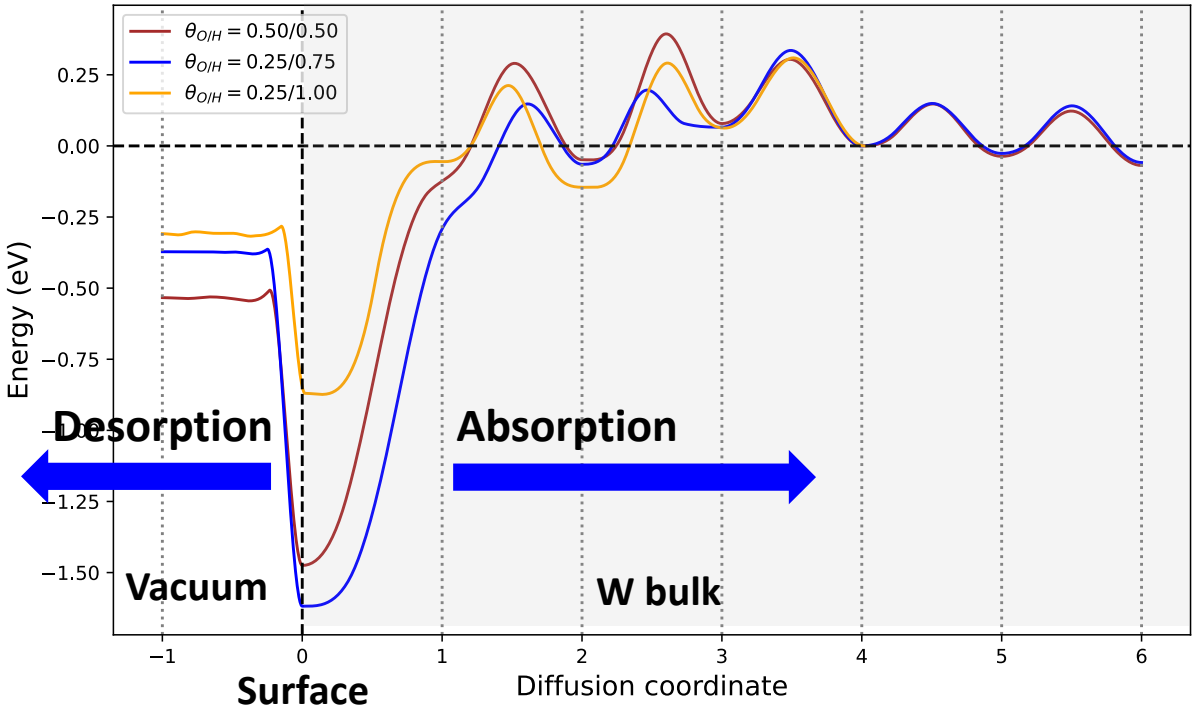
O weakens adsorption energy for H on W(110)

O limits the amount of H adsorption on W(110)

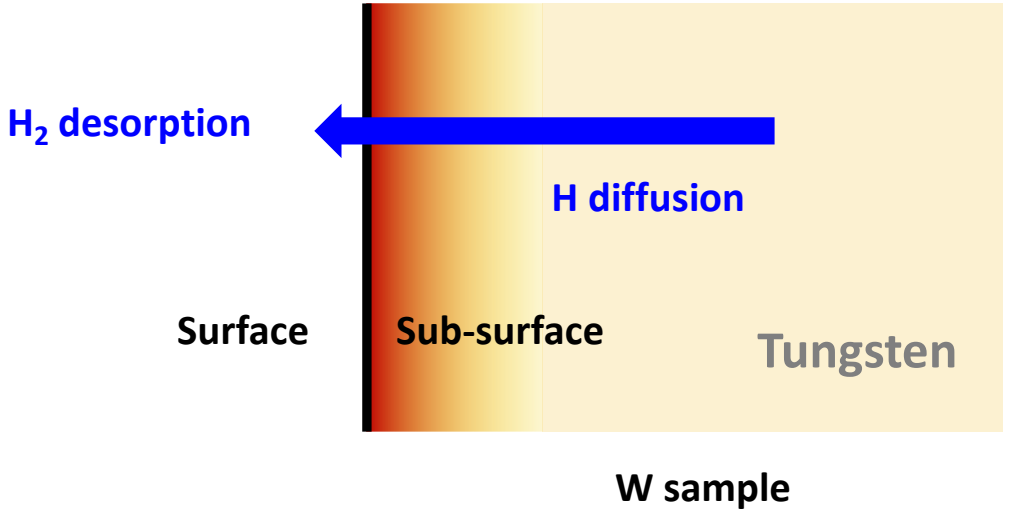
Exp. Obs. *Dunand et al. NF 62 (2022) 054002*

2 – H and O on W(110) surface – DFT results

Hydrogen on O pre-adsorbed W(110)



Under revision – submitted to Nuclear Fusion



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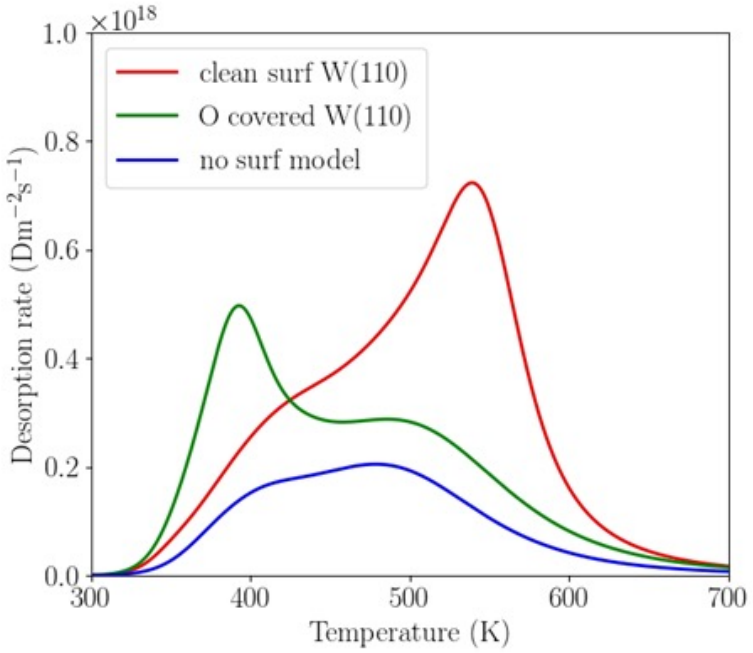
Exp. Obs. *Dunand et al. NF 62 (2022) 054002*

Absorption and Desorption
Strongly dependent on the surface coverage

2 – H and O on W(110) surface - Kinetic model

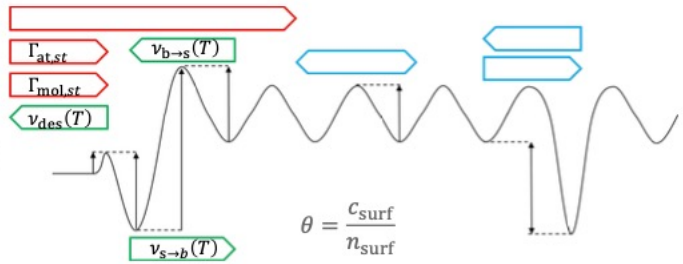
TDS spectra modelling with / without surface mechanisms



Courtesy from E.A. Hodille (CEA)

GOVERNING EQUATIONS

Boundary conditions



- If the surface limits uptake/desorption:
  Concentration of adsorbed H c_{surf} (m^{-2})
  Concentration of mobile H $c_{m,0}$ (m^{-3})

Originally described in: Pick and Sonnenberg, JNM (1985)

Implented in MHIMS: Hodille et al., NF 57 (2017)

$$\frac{dc_{surf}}{dt} = \Gamma_{at,st}(1-\theta) + 2\Gamma_{mol,st}(1-\theta)^2 - \sigma_{abs}\Gamma_{at}\theta - 2\nu_{des}c_{surf}^2 - \nu_{s\to b}c_{surf} + \nu_{b\to s}c_m(1-\theta)$$

$$\frac{\lambda dc_{m,0}}{dt} = -\nu_{b\to s}c_m(1-\theta) + \nu_{s\to b}c_{surf} - D(T)\left(\frac{\partial c_m}{\partial x}\right)_0$$

- If the surface does not limit the uptake/desorption:

  Sievert law:
  $c_m(x=0) = S(T)\sqrt{p_{H_2}}$ with $S(T)$ the solubility of H in the material ($m^{-3}Pa^{-1/2}$)

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Yosvany Silva-Solis PhD's work

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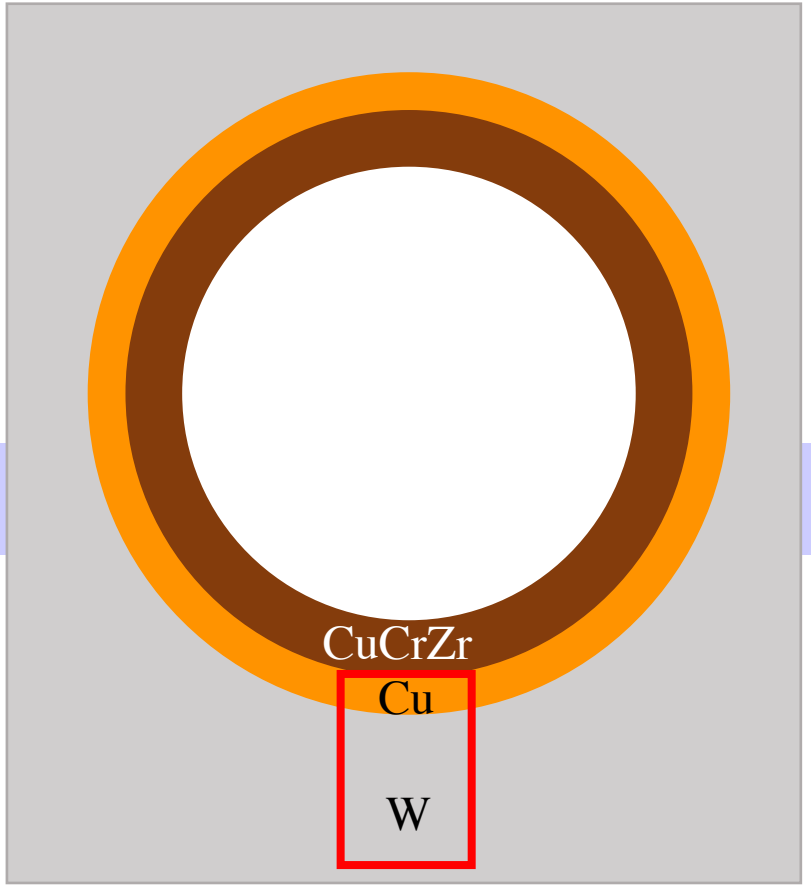
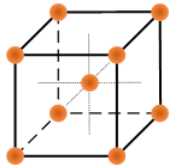
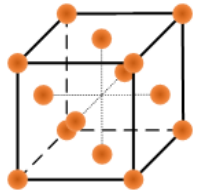


3 – Model of a W/Cu interface

Different crystallin networks for W and Cu

Table 1. Cu unit cells created for E_{cut} and k convergence study.

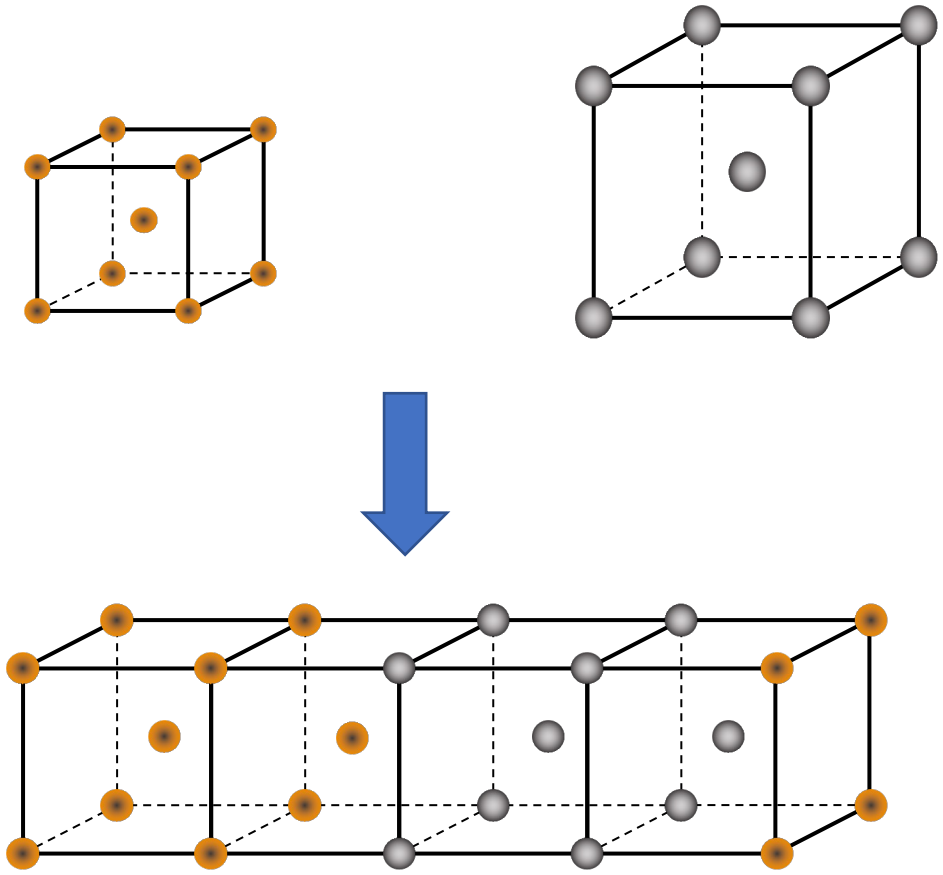
	Structure	UC (unit cell)
W and Cu	*bcc* (body cubic center)	
Cu	*fcc* (face cubic center)	

3 – Model of a W/Cu interface

How to match both Cu and W networks ?

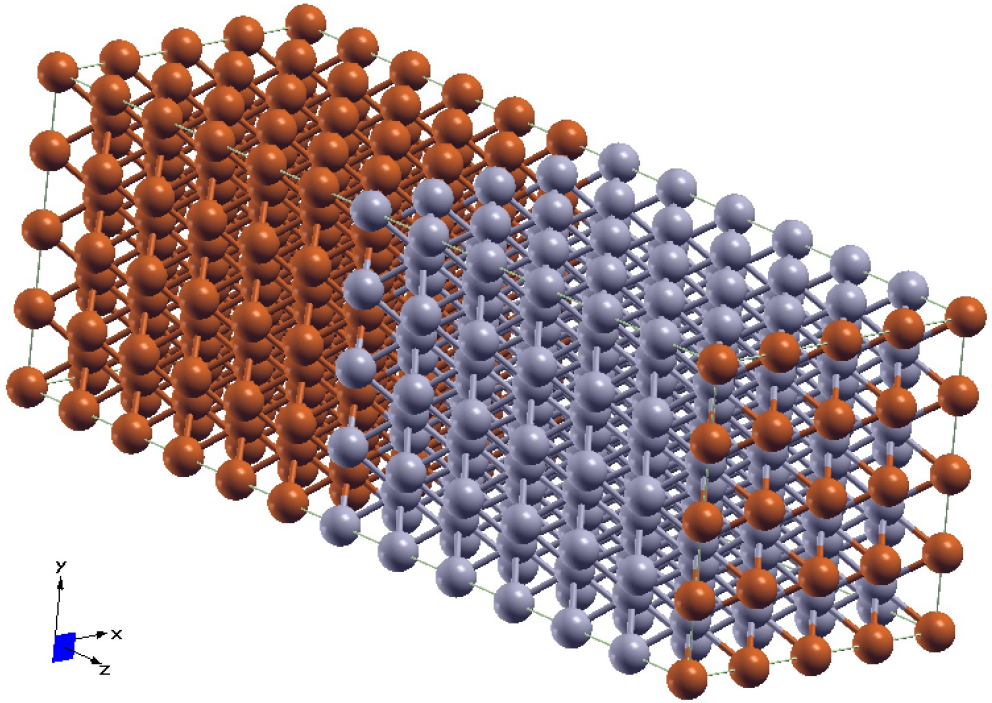
Cu (bcc) or (fcc)

W (bcc)



Both Cu and W networks have different atomic parameters

Distortions



3 – Model of a W/Cu interface

How many layers for a realistic model?

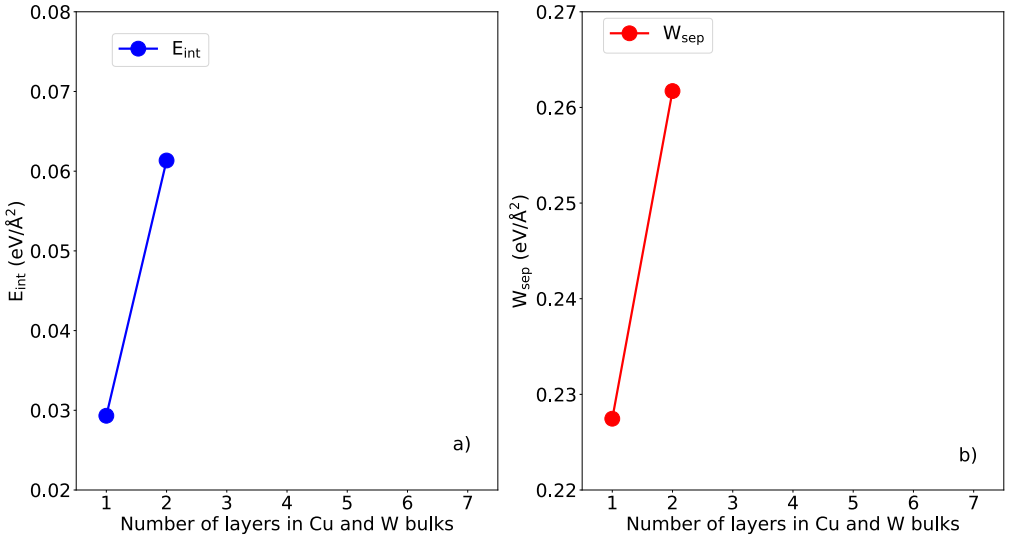


Figure 1. Convergence of E_{int} and W_{sep} changing number of layers in z-direction.

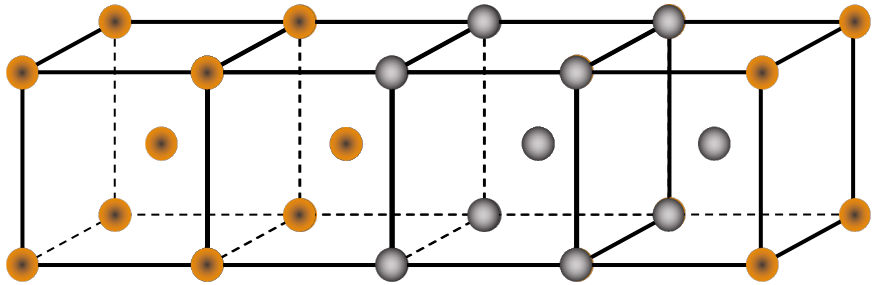
Interface energy:

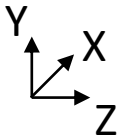
$$E_{int} = \frac{E_{W/Cu} - E_{Cu_b} - E_{W_b}}{2\,A} \quad (1)$$

Work of separation:

$$E_{int} = \frac{E_W + E_{Cu} - E_{W/Cu}}{2\,A} \quad (2)$$

Convergence criterion





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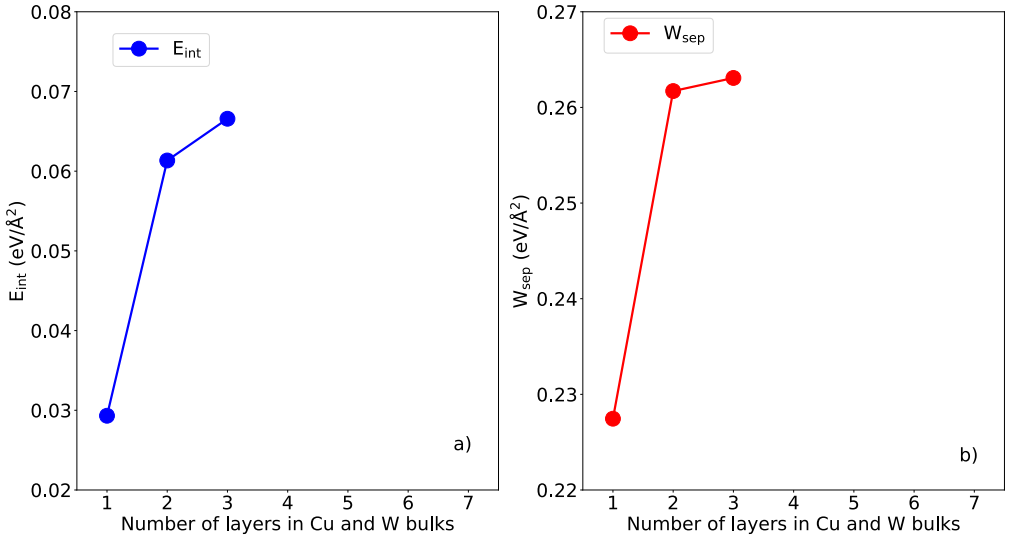

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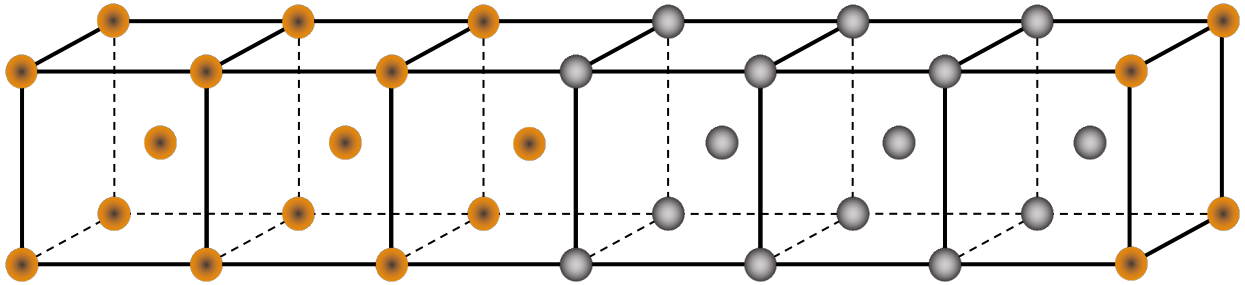

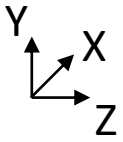

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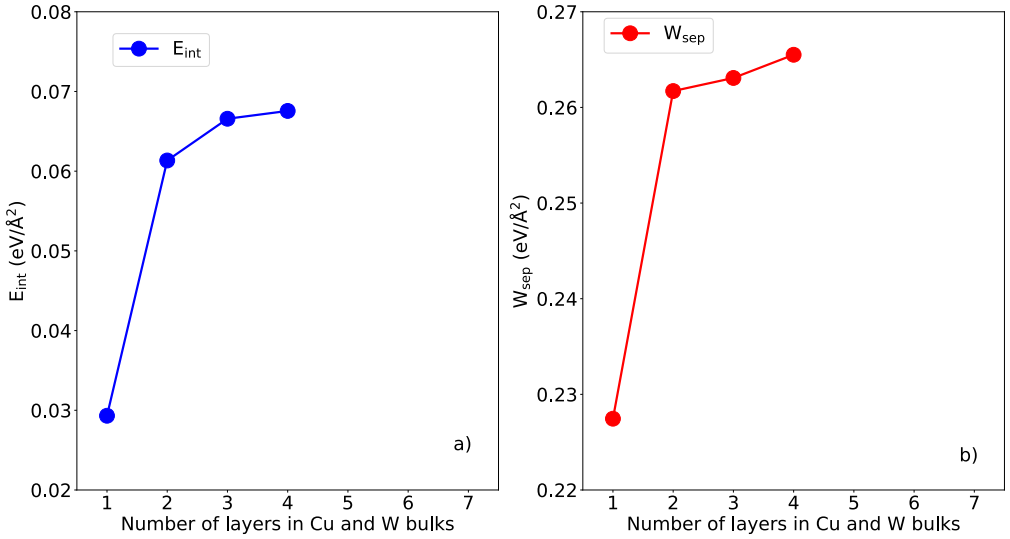

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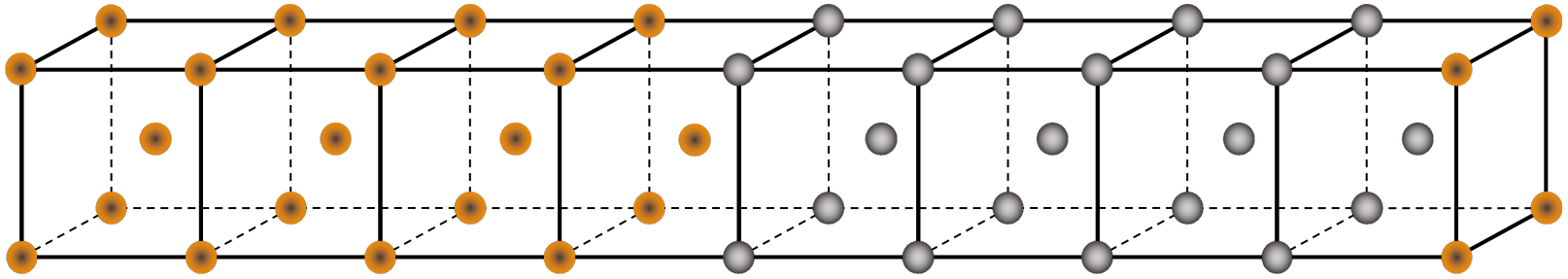

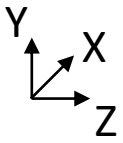

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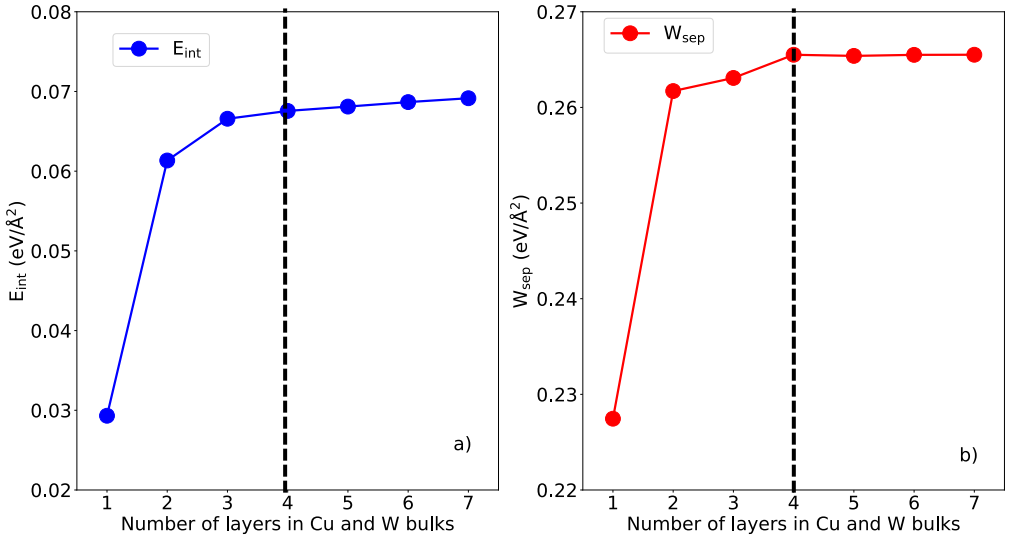

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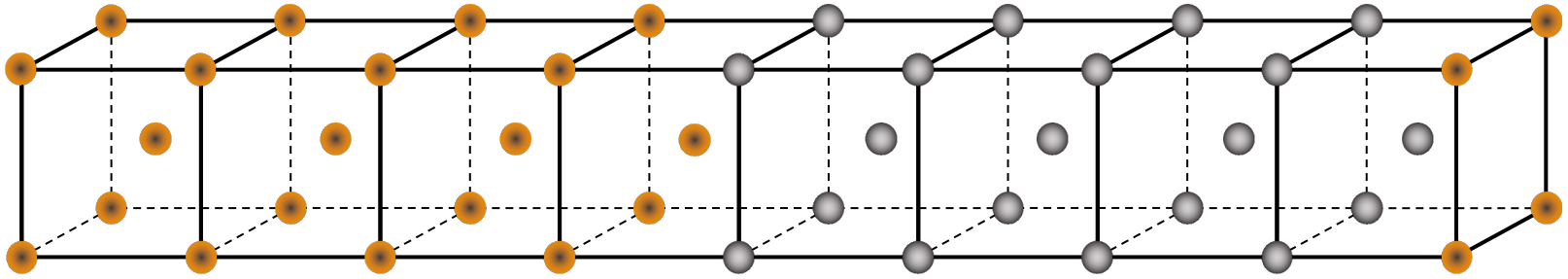
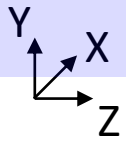
$N_x = N_y = 2.$
$N_z = 8.$



$a = b = 3.16$ Å
$c_{Cu} = 2.53$ Å
$c_W = 3.21$ Å

Converged model



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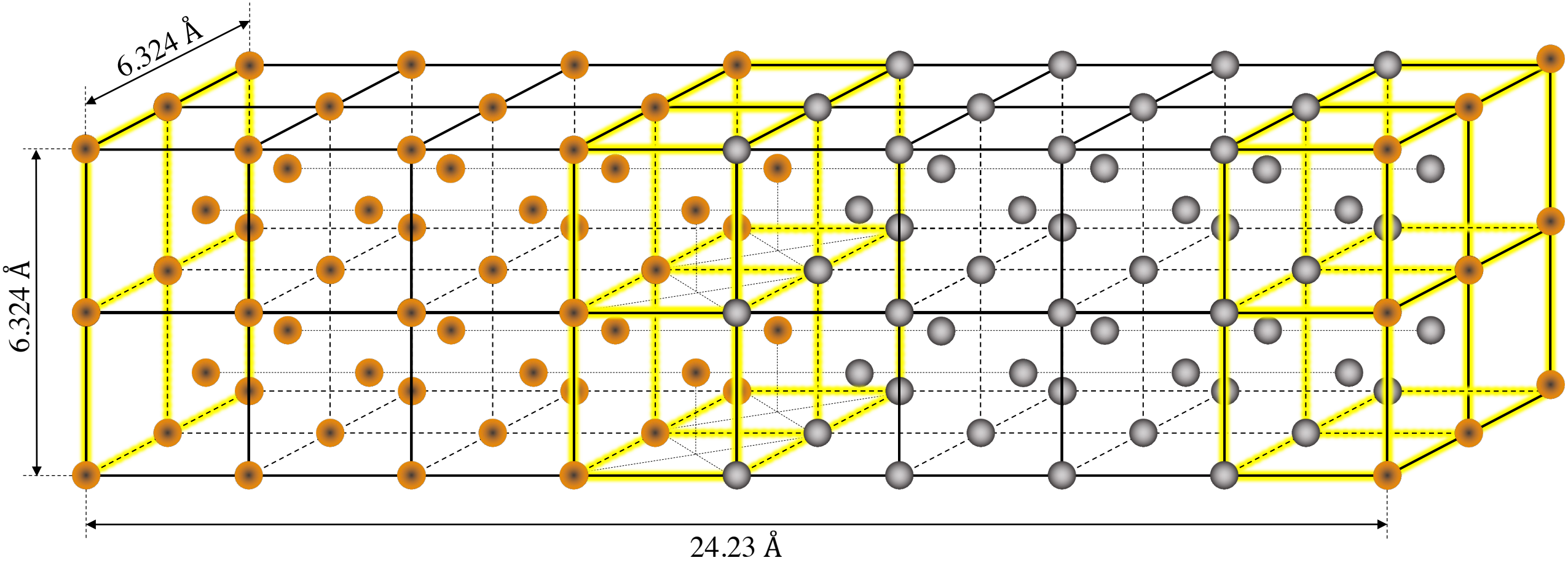


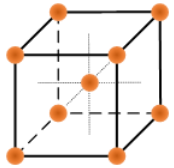
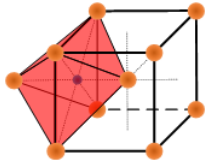
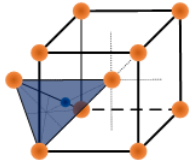
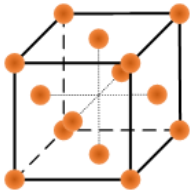
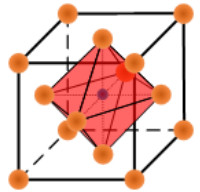
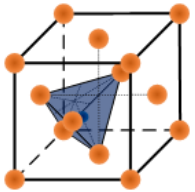
$N_x = N_y = 2$ $N_z = 8$

Converged model

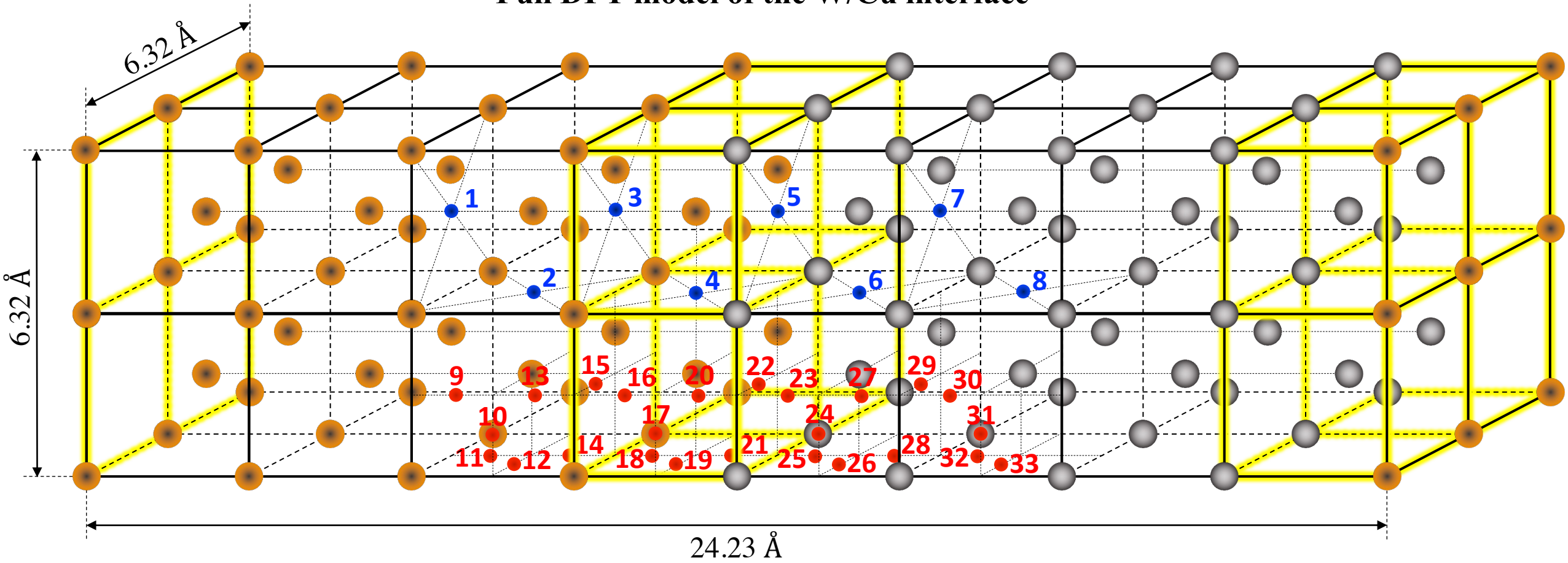
3 – Model of a W/Cu interface

Solution of H in W and Cu

Table 1. Cu unit cells created for E_{cut} and k convergence study.

Structure	UC (unit cell)	OH (octahedral)	TH (tetrahedral)
W and Cu: *bcc* (body cubic center)			
Cu: *fcc* (face cubic center)			

3 – Model of a W/Cu interface

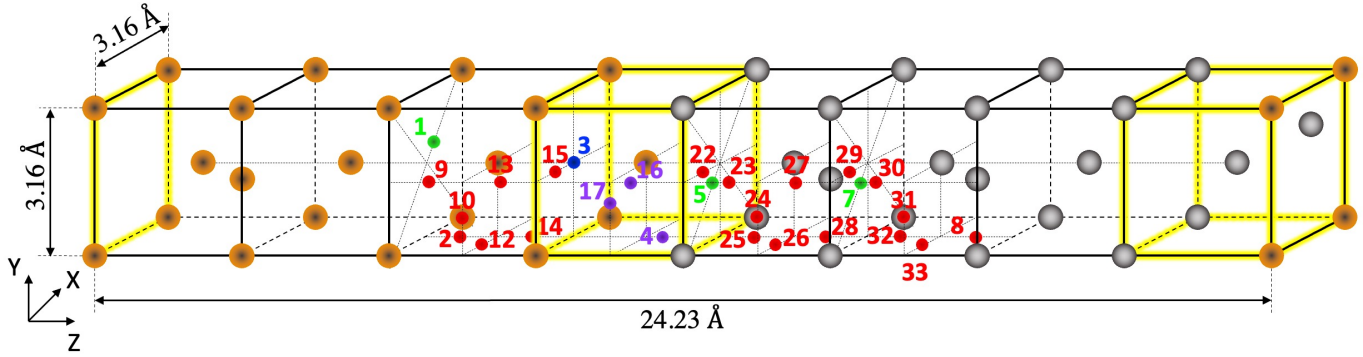


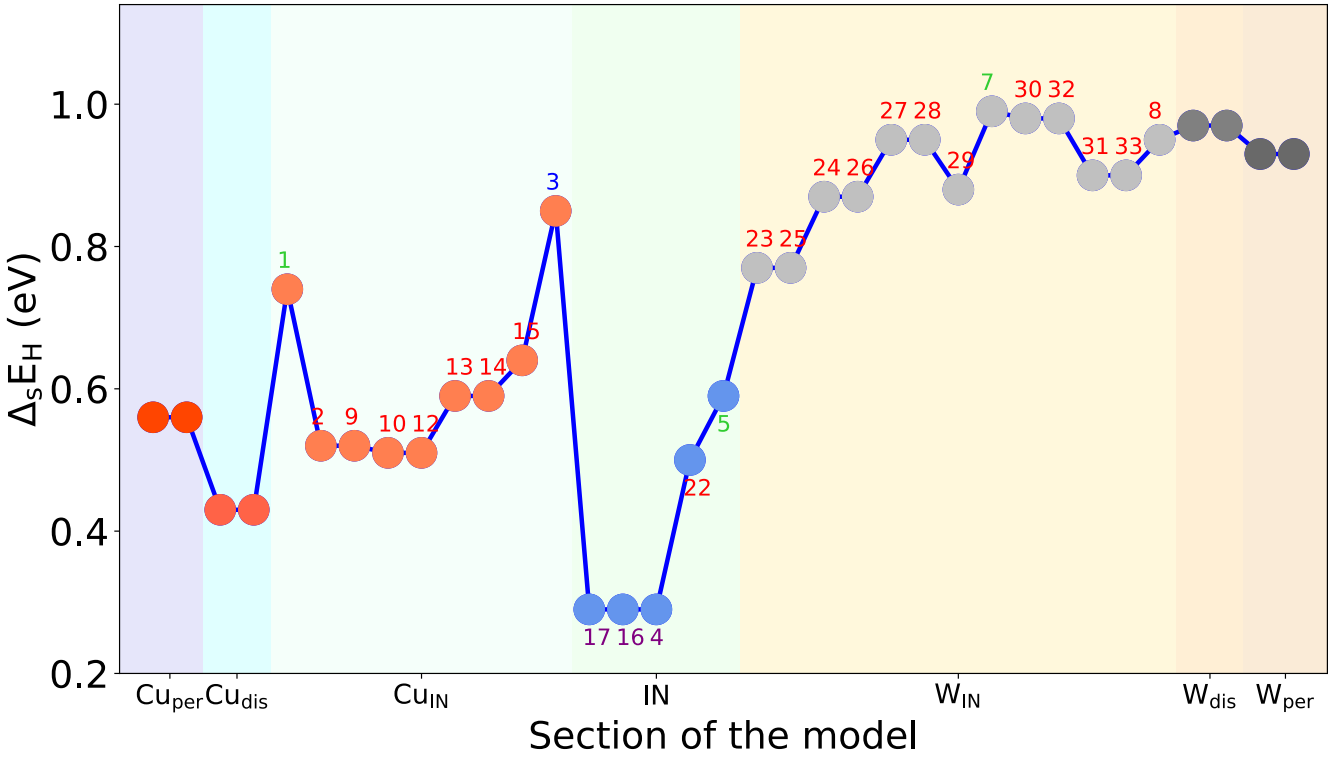
Electronic and phonon calculations for all these points

3 – Model of a W/Cu interface

Energetics of H at the W/Cu interface

2022 deliverable in WP PWIE SPC



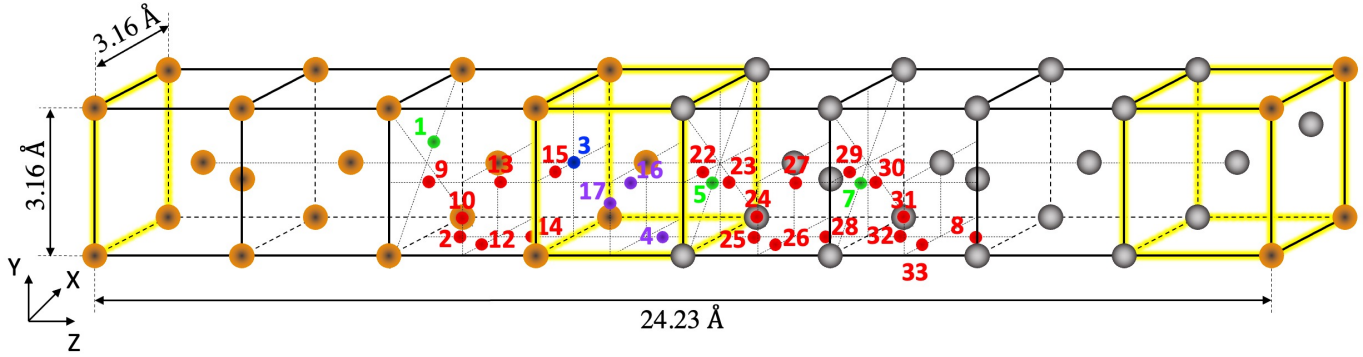


This is not an energy profile

This the energetics of all interstitial stable site for H close and at the interface.

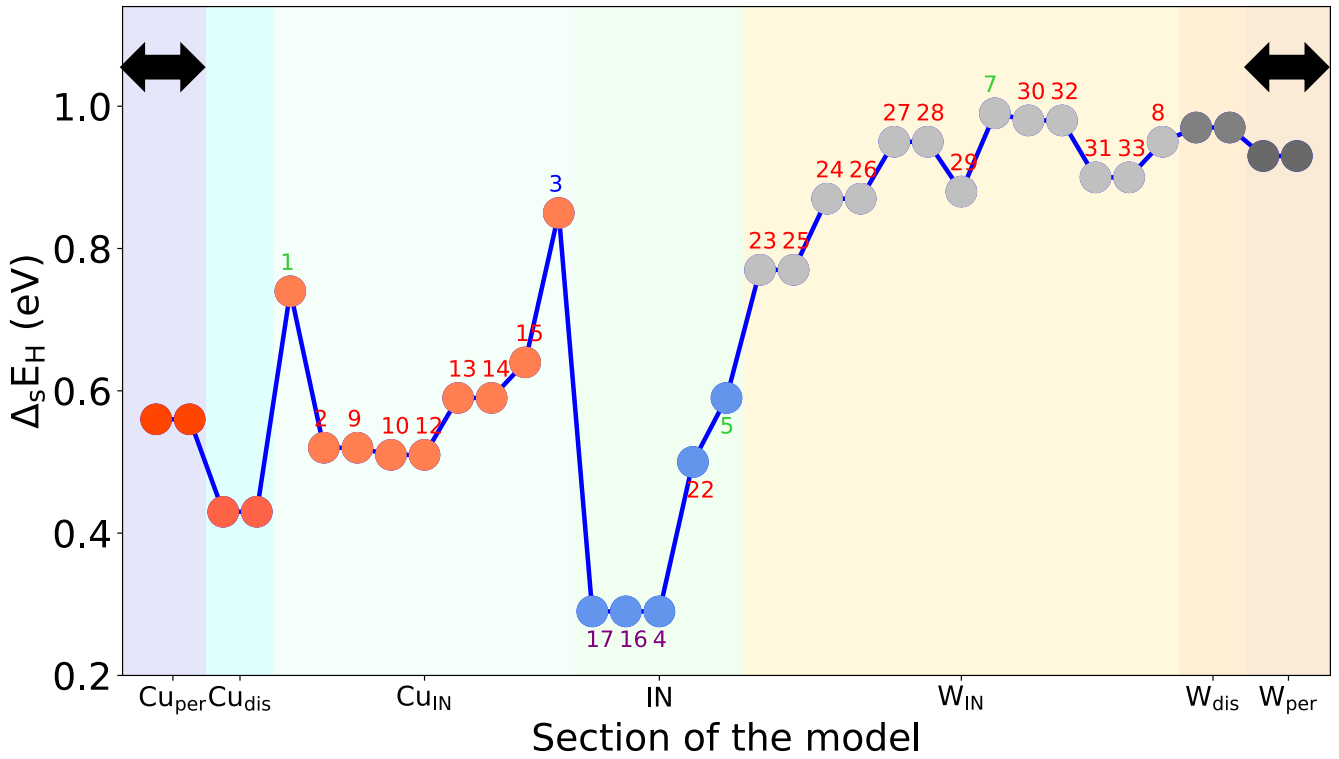
3 – Model of a W/Cu interface

Solution energy of H at the W/Cu interface



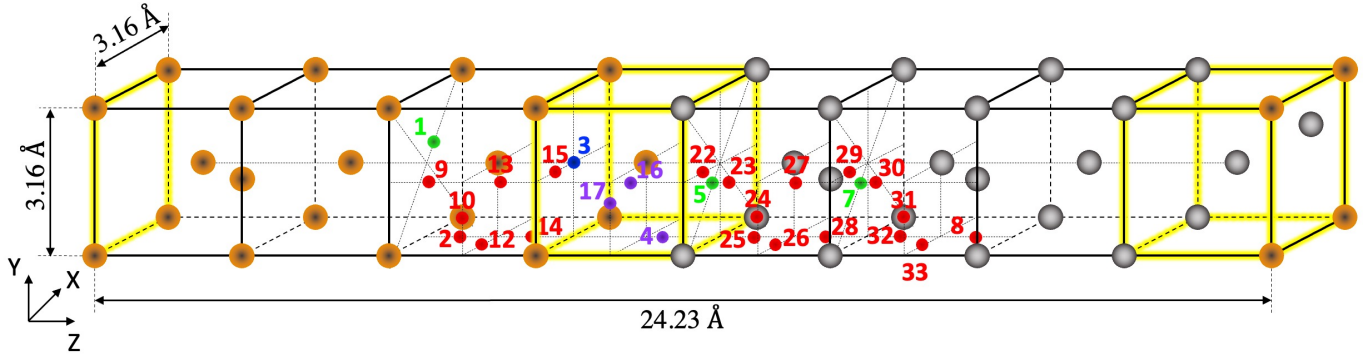
In perfect W and Cu

Higher solubility
in Cu than in W



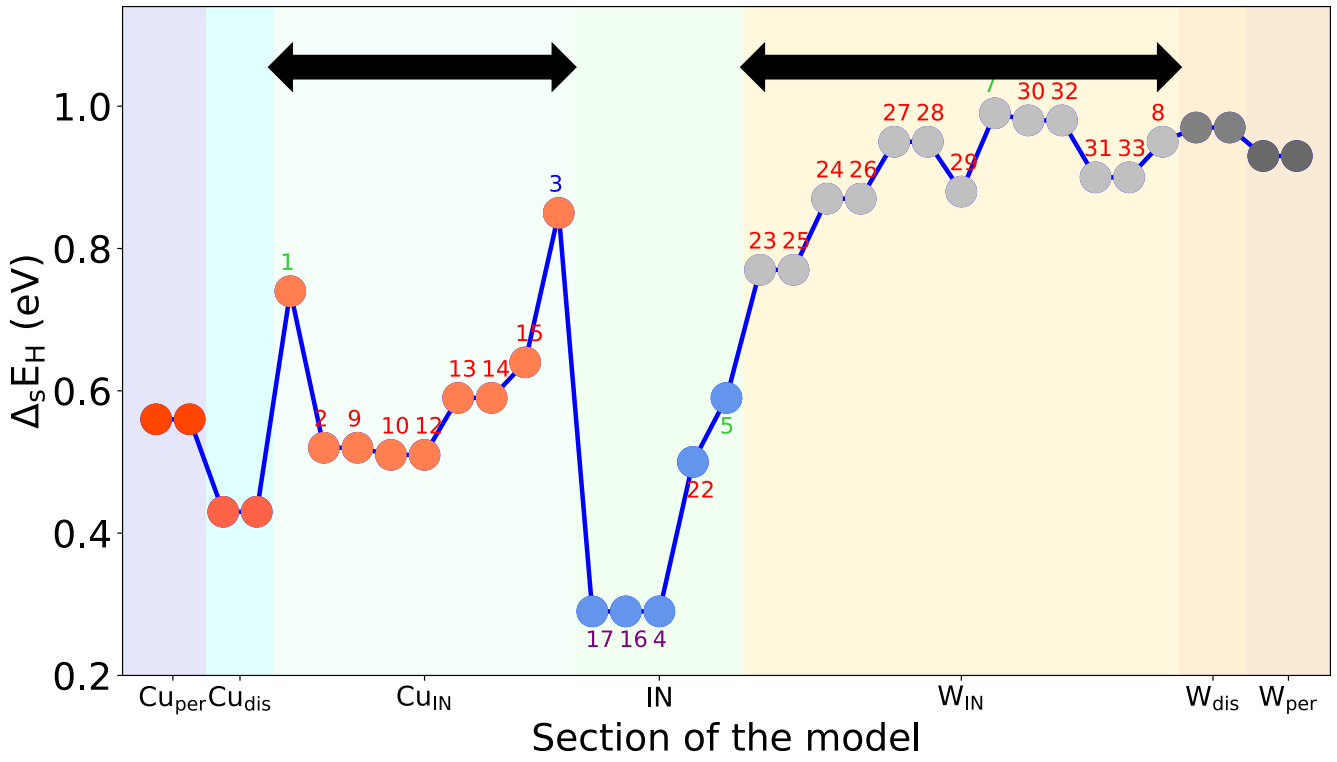
3 – Model of a W/Cu interface

Solution energy of H at the W/Cu interface



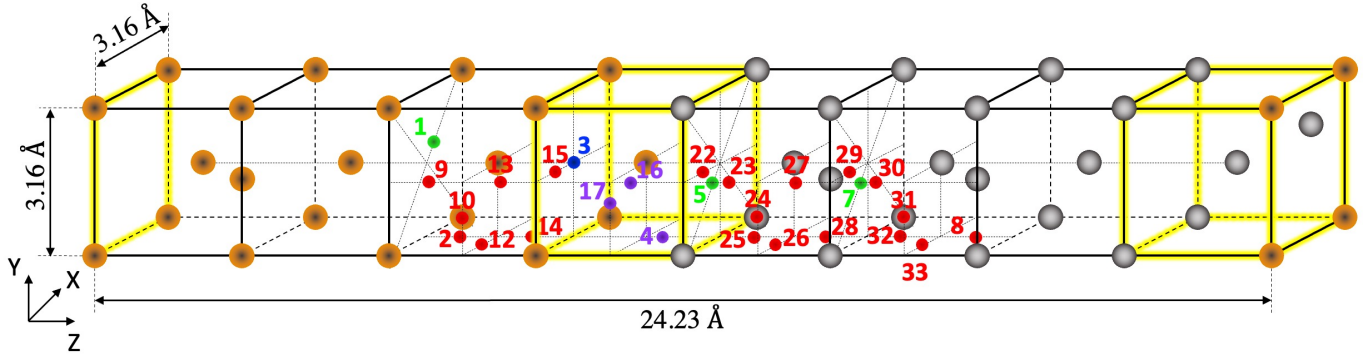
Close to the interface

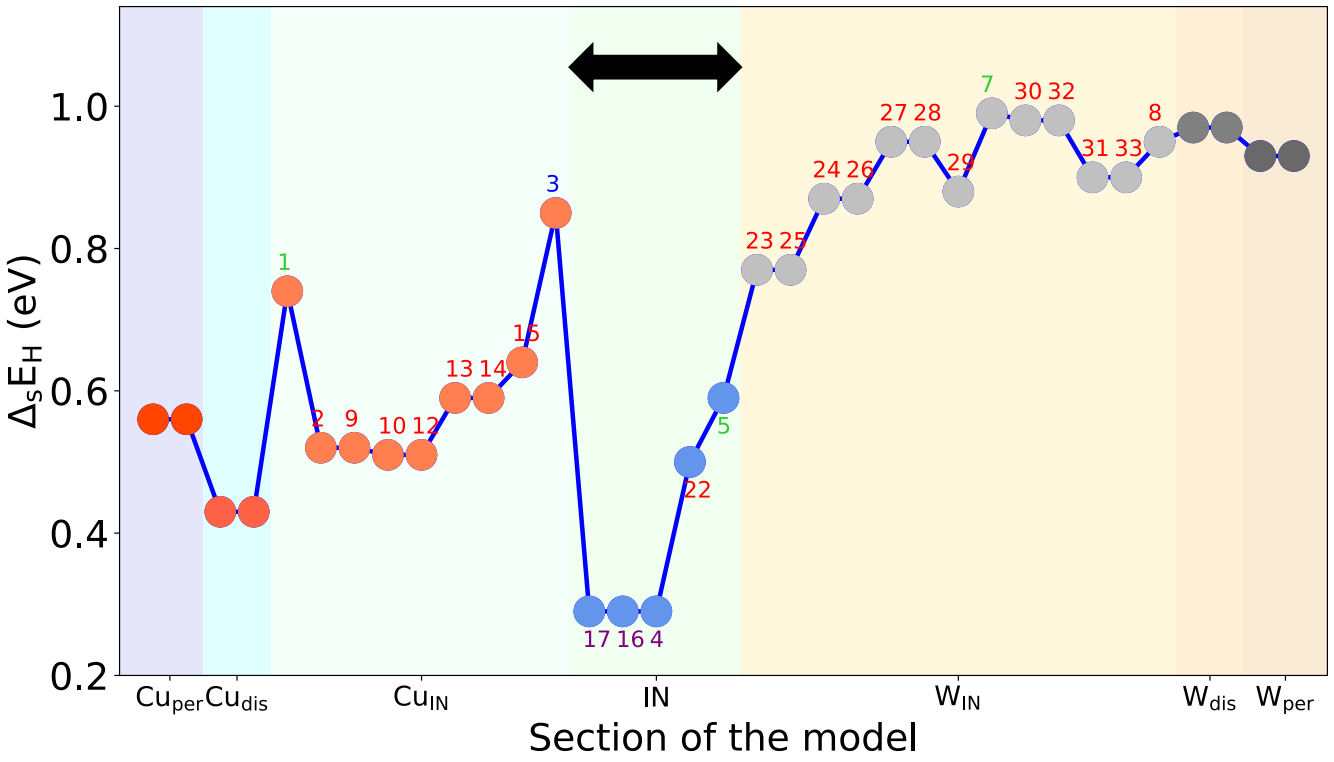
Impact of the distortion on H solub.



3 – Model of a W/Cu interface

Solution energy of H at the W/Cu interface





At the interface

Very High Solubility.

The interface behaves like a sink for HIs

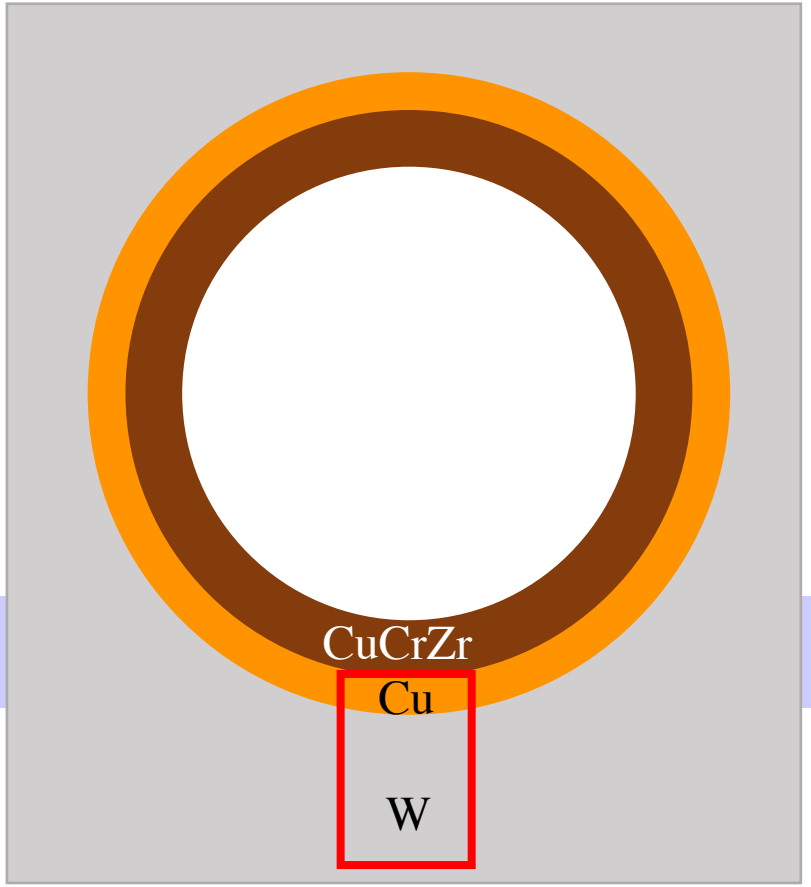
Outline

1 – The basic tools

2 – Past activities in WP PWIE (for understanding)

3 – This year activity: H at the W/Cu interface

4 – Conclusion and Perspective



4 – Conclusion and Perspectives

Conclusion on W/Cu

- A DFT model of the W/Cu interface was built
- Solution energy and vibrational frequencies are being computed **close** and **at** the W/Cu interface
- The interstitial sites and their energetics are determined across the interface

→ The interface acts as a sink for Hydrogen's Isotopes

Perspectives

- Computing the full energy paths joining each interstitial sites
- Providing activation barriers for Rate-Equations modelling of H diffusion at the W/Cu interface
- Effect of H accumulation at the interface

J. Denis (ERG) – PIIM AMU

Y. Silva Solís (PhD) – PIIM AMU

Y. Ferro – PIIM AMU

Collaboration **E.A. Hodille** – CEA Cadarache France

Aix-Marseille Université & CNRS, France