Karlsruhe Institute of Technology

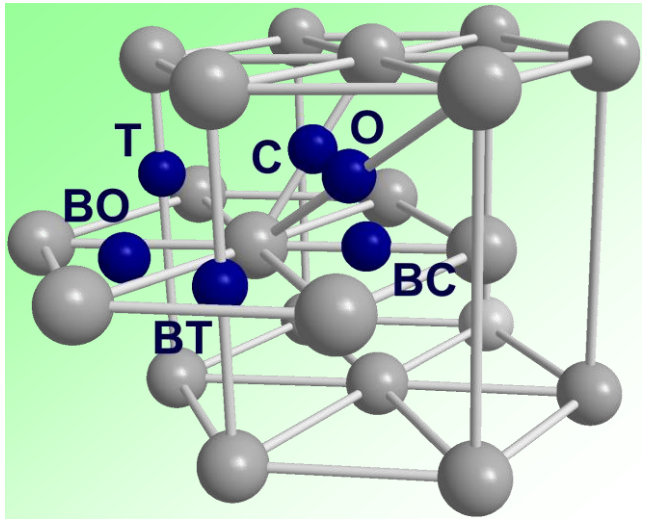
Int. Workshop on Models & Data for Plasma-Material Interaction in Fusion Devices

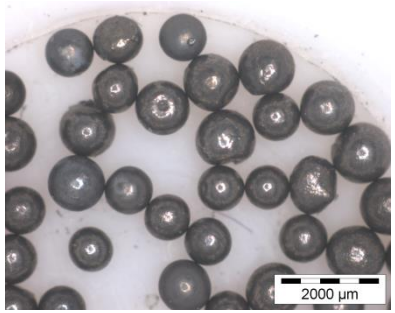
Aix*Marseille université

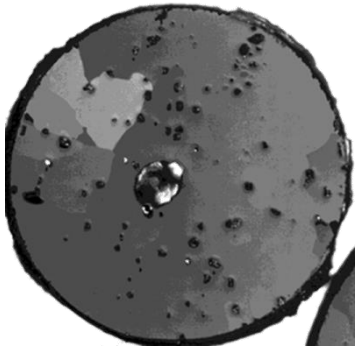
Modelling of Hydrogen Interactions with Beryllium Surfaces in Fusion Reactor

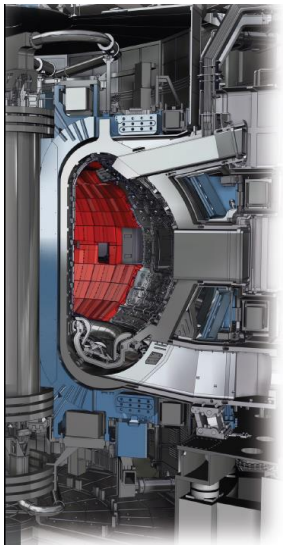
P. Vladimirov, D. Bachurin, Ch. Stihl

INSTITUTE OF APPLIED MATERIALS (IAM-AWP), Atomistic Modeling and Validation Group,
Department of Metallic Alloys









Outline

- Beryllium in Fusion Reactor
  - Be as plasma facing material
  - Be in T-breeding pebble bed
- Simulation method
- Adsorption and desorption
  - H_2 dissociative adsorption on (0001)Be
  - Hydrogen surface adsorption sites
  - H_2 adsorption on precovered surface
  - Hydrogen interaction on Be surface
  - Hydrogen absorption in bulk
  - Hydrogen associative desorption
- Surface energy modification
  - Clean surface energies
  - Surface energy with hydrogen
  - Faceting of H-covered bubble
- Conclusions

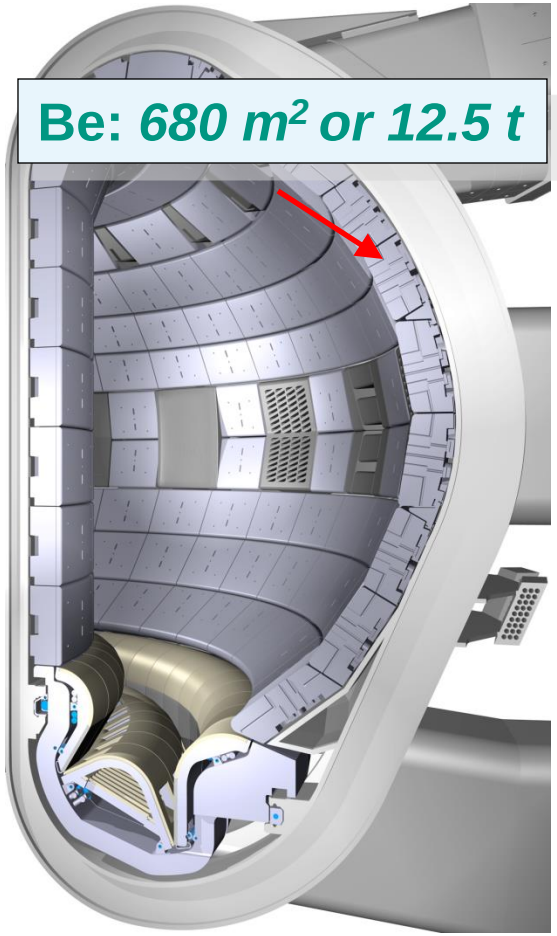
Outline

- Beryllium in Fusion Reactor
  - Be as plasma facing material
  - Be in T-breeding pebble bed
- Simulation method
- Adsorption and desorption
  - H_2 dissociative adsorption on (0001)Be
  - Hydrogen surface adsorption sites
  - H_2 adsorption on precovered surface
  - Hydrogen interaction on Be surface
  - Hydrogen absorption in bulk
  - Hydrogen associative desorption
- Surface energy modification
  - Clean surface energies
  - Surface energy with hydrogen
  - Faceting of H-covered bubble
- Conclusions

Outline

- Beryllium in Fusion Reactor
  - Be as plasma facing material
  - Be in T-breeding pebble bed
- Simulation method
- Adsorption and desorption
  - H_2 dissociative adsorption on (0001)Be
  - Hydrogen surface adsorption sites
  - H_2 adsorption on precovered surface
  - Hydrogen interaction on Be surface
  - Hydrogen absorption in bulk
  - Hydrogen associative desorption
- Surface energy modification
  - Clean surface energies
  - Surface energy with hydrogen
  - Faceting of H-covered bubble
- Conclusions

Beryllium in fusion reactor

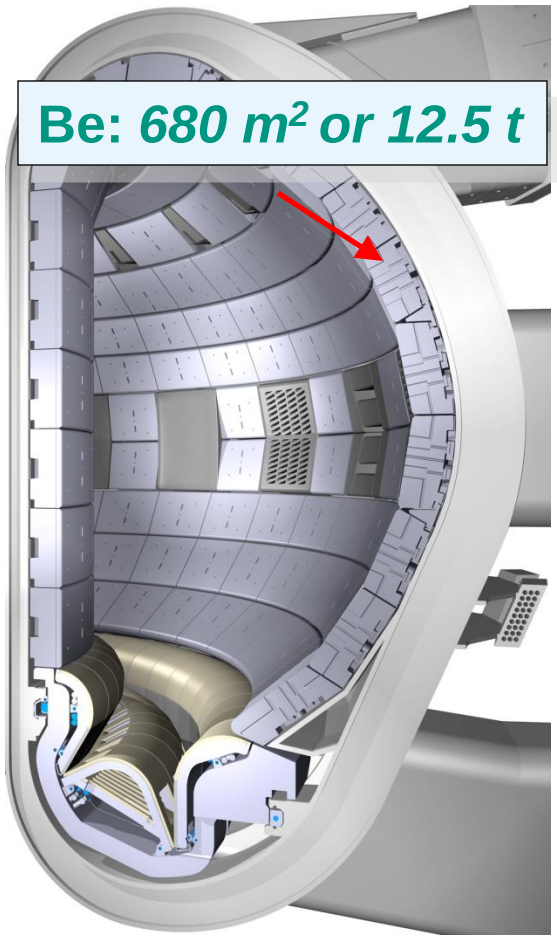


ITER Torus
cross-section

K.Ioki et al. Nucl.Fusion **41**(3) 2001 265-275

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)

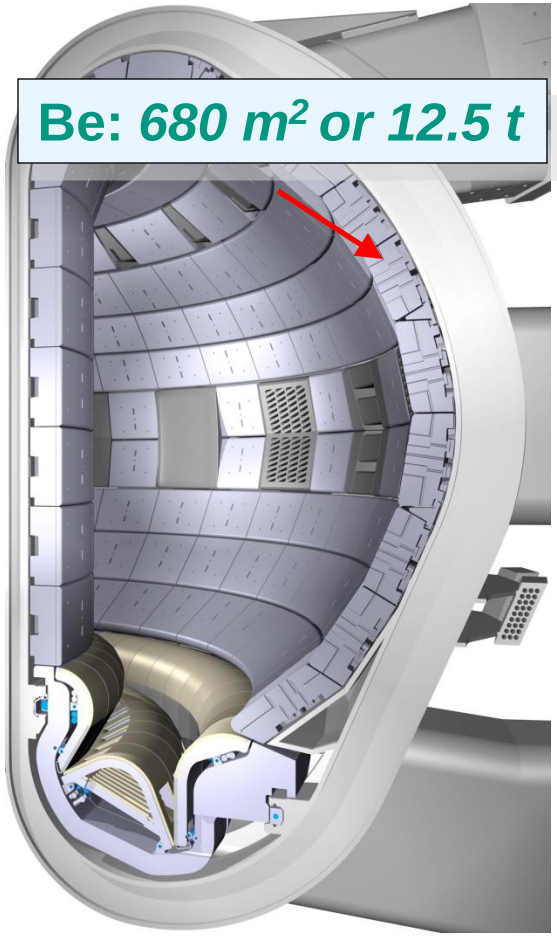


ITER Torus cross-section

K.Ioki et al. Nucl.Fusion **41**(3) 2001 265-275

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)
- Hydrogen isotopes and impurities are implanted into Be first wall tiles

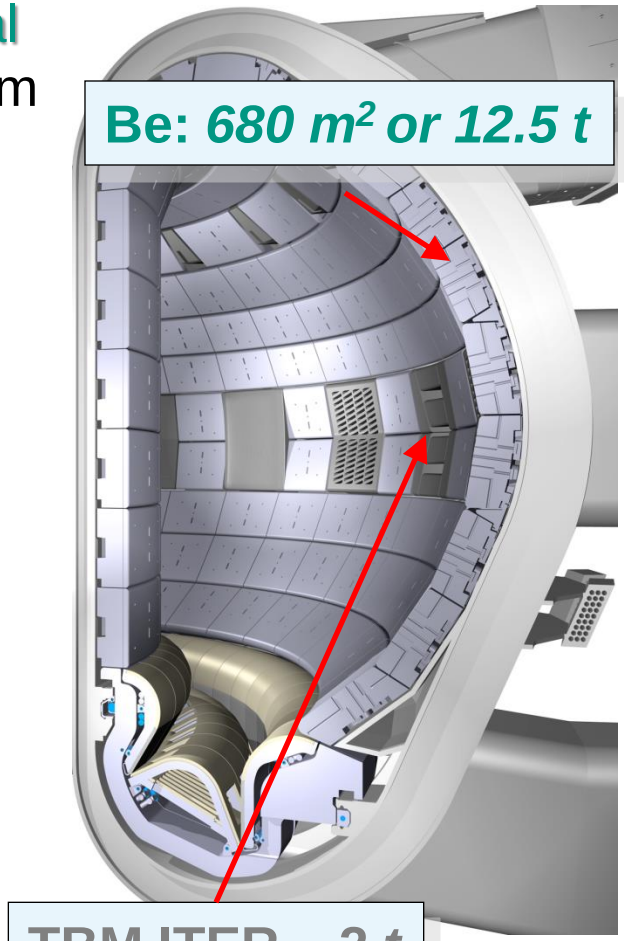


ITER Torus cross-section

K.Ioki et al. Nucl.Fusion **41**(3) 2001 265-275

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)
- Hydrogen isotopes and impurities are implanted into Be first wall tiles

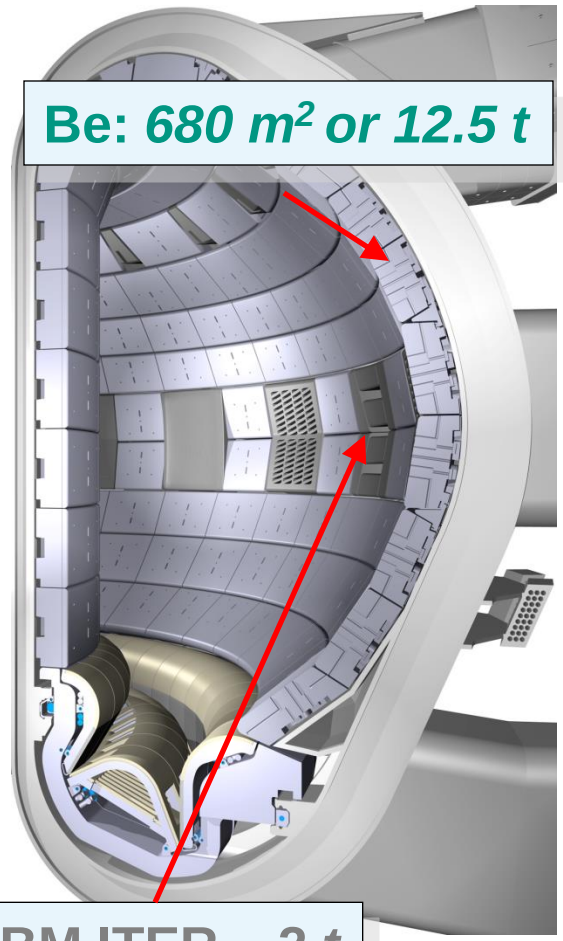


ITER Torus cross-section

K.Ioki et al. Nucl.Fusion 41(3) 2001 265-275

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)
- Hydrogen isotopes and impurities are implanted into Be first wall tiles
- He and T are produced in Be under neutron irradiation

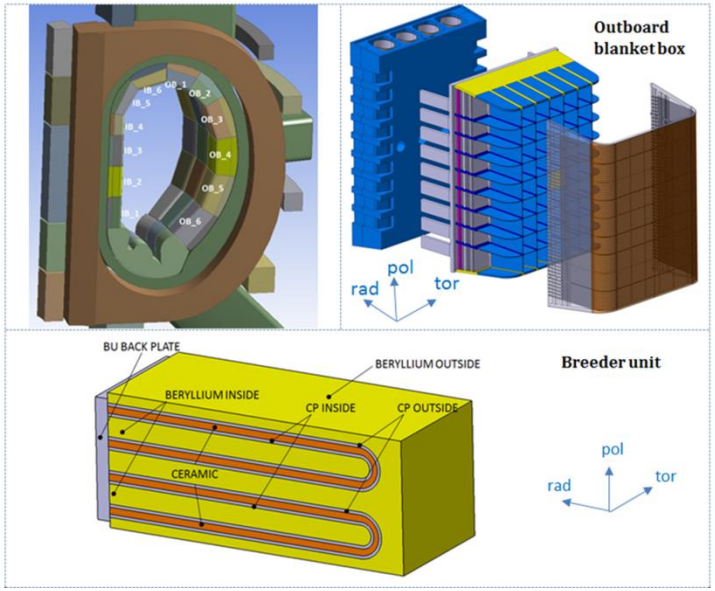


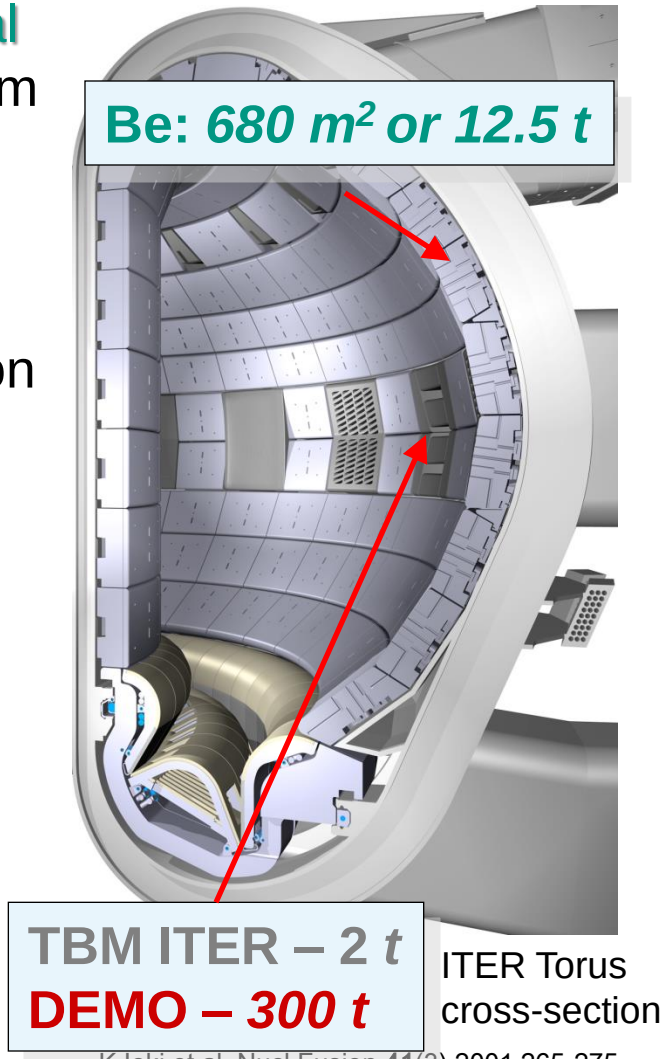
ITER Torus cross-section

K.Ioki et al. Nucl.Fusion 41(3) 2001 265-275

Beryllium in fusion reactor

- Be is considered as plasma facing material and as effective neutron multiplier for tritium breeding blanket (HCPB)
- Hydrogen isotopes and impurities are implanted into Be first wall tiles
- He and T are produced in Be under neutron irradiation

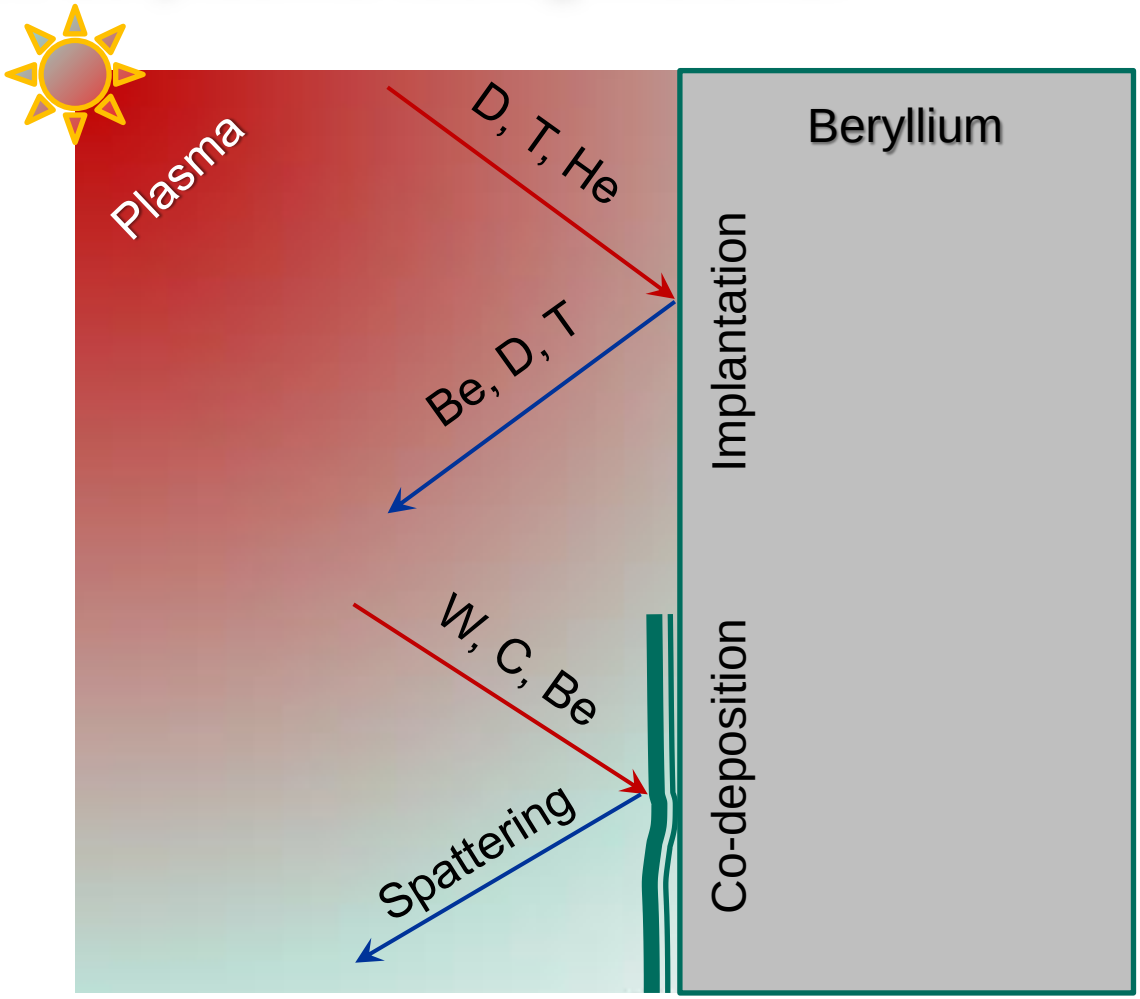




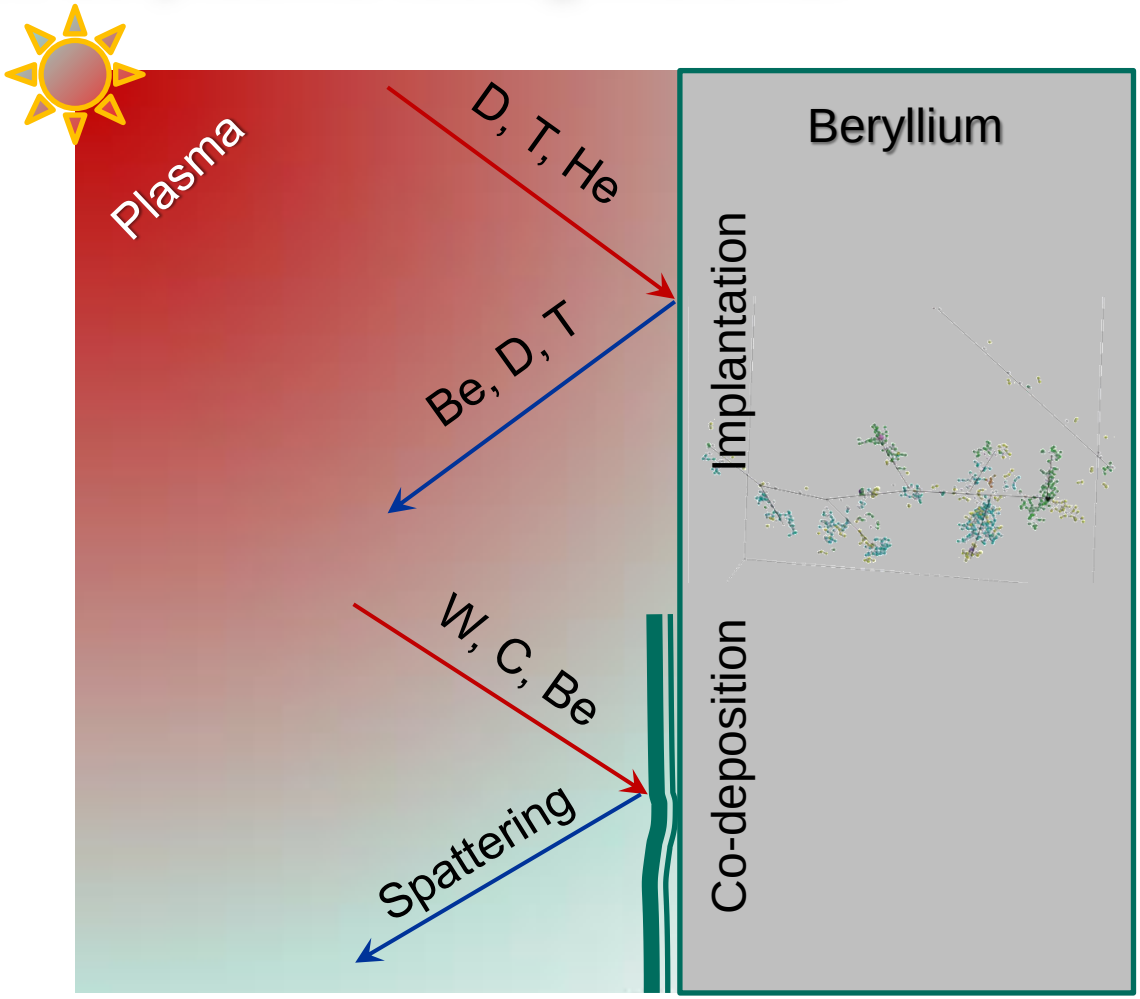
ITER Torus cross-section

K.Ioki et al. Nucl.Fusion 41(3) 2001 265-275

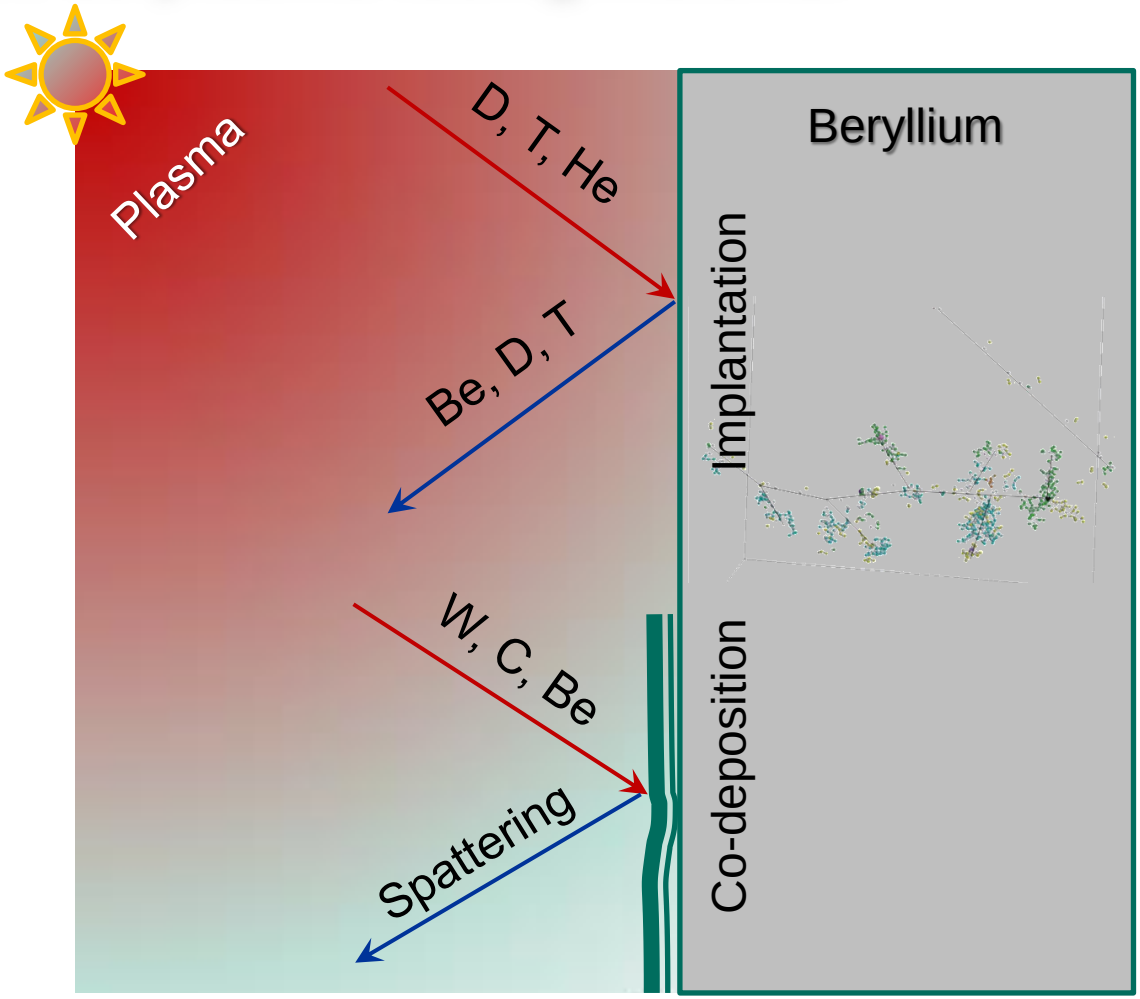
Be as plasma facing material



Be as plasma facing material



Be as plasma facing material



$E_n \geq 2.7$ MeV:

$$^9Be(n,2n)^8Be$$

$$^8Be \rightarrow 2\alpha$$

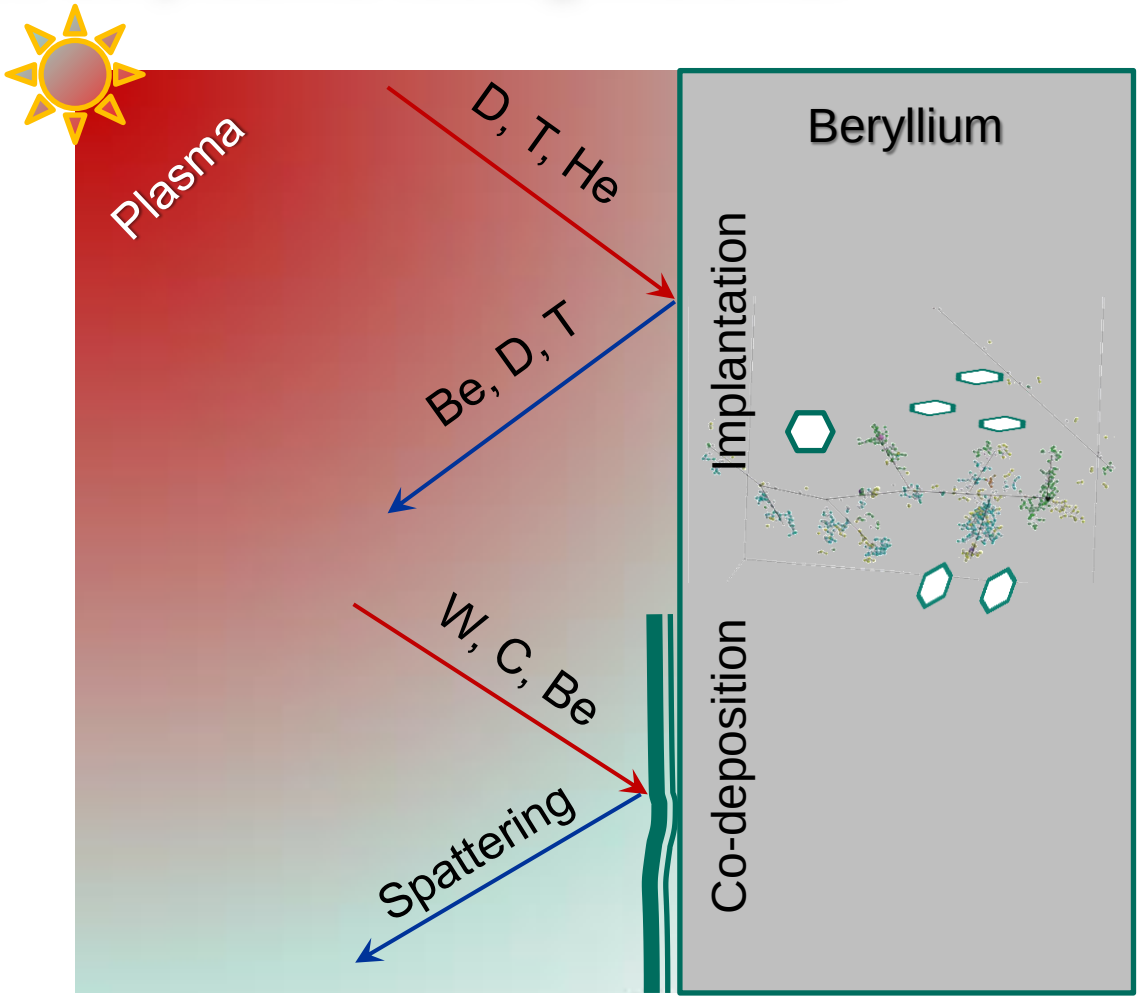
$E_n \geq 0.71$ MeV

$$^9Be(n,\alpha)^6He$$

$$^6He \rightarrow {}^6Li + e^- + \bar{\nu}_e$$

$$^6Li(n,t)\alpha$$

Be as plasma facing material



$E_n \geq 2.7$ MeV:

$$^9Be(n,2n)^8Be$$

$$^8Be \rightarrow 2\alpha$$

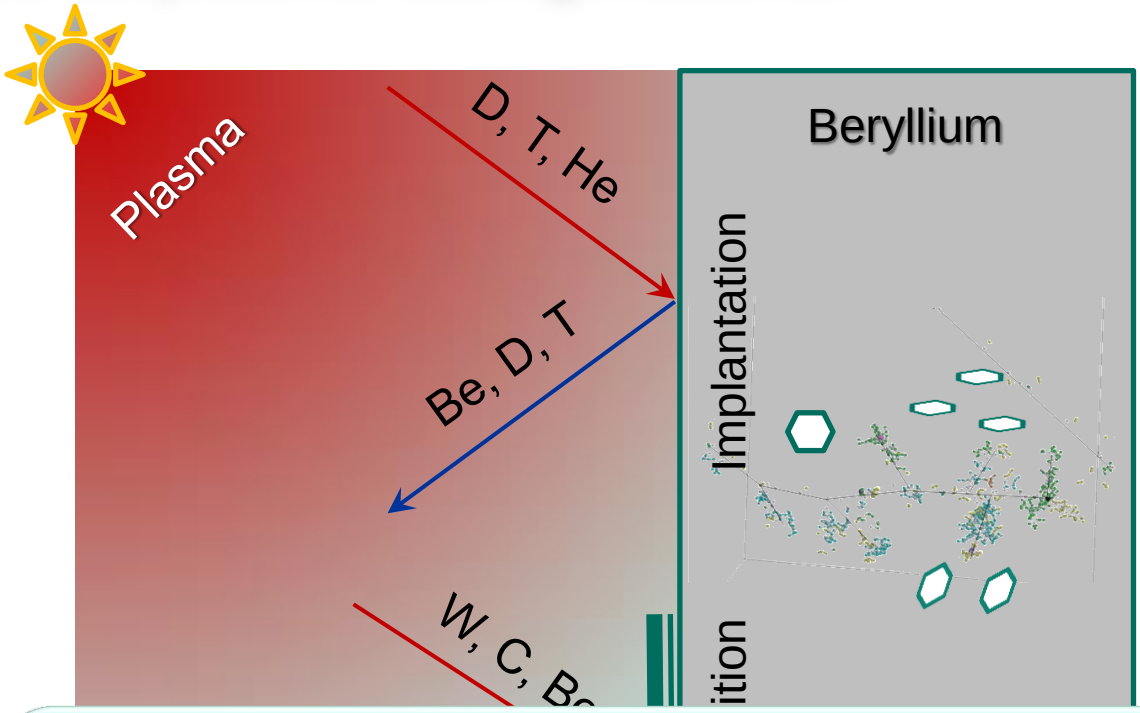
$E_n \geq 0.71$ MeV

$$^9Be(n,\alpha)^6He$$

$$^6He \rightarrow {}^6Li + e^- + \bar{\nu}_e$$

$$^6Li(n,t)\alpha$$

Be as plasma facing material



$E_n \geq 2.7$ MeV:

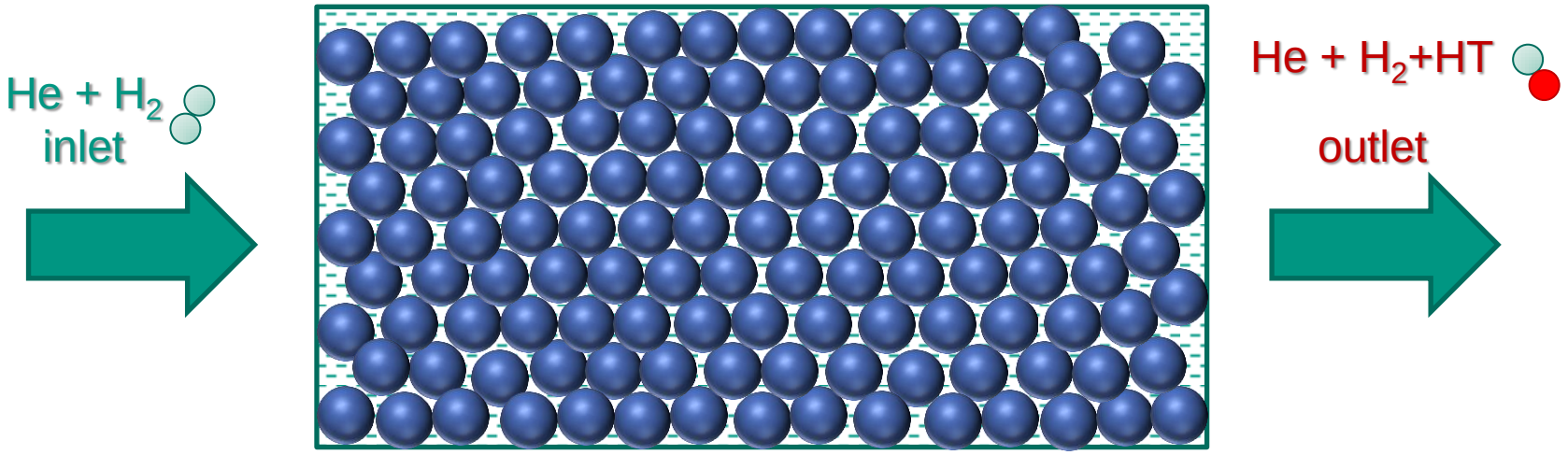
$$^9Be(n,2n)^8Be$$
$$^8Be \rightarrow 2\alpha$$

$E_n \geq 0.71$ MeV

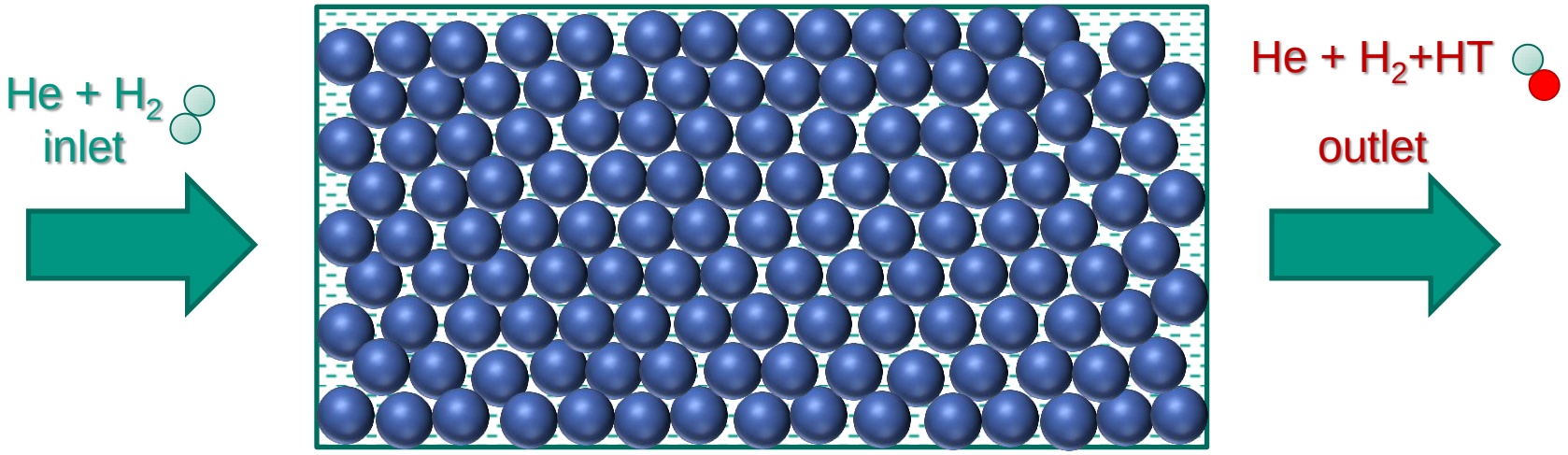
$$^9Be(n,\alpha)^6He$$
$$^6He \rightarrow {}^6Li + e^- + \bar{\nu}_e$$
$$^6Li(n,t)\alpha$$

- Helium and hydrogen isotopes are produced in Be by nuclear transmutations as well as implanted from the hot plasma.
- He and H can be trapped within vacancies and vacancy clusters produced by neutron irradiation and facilitate formation of gas filled bubbles.

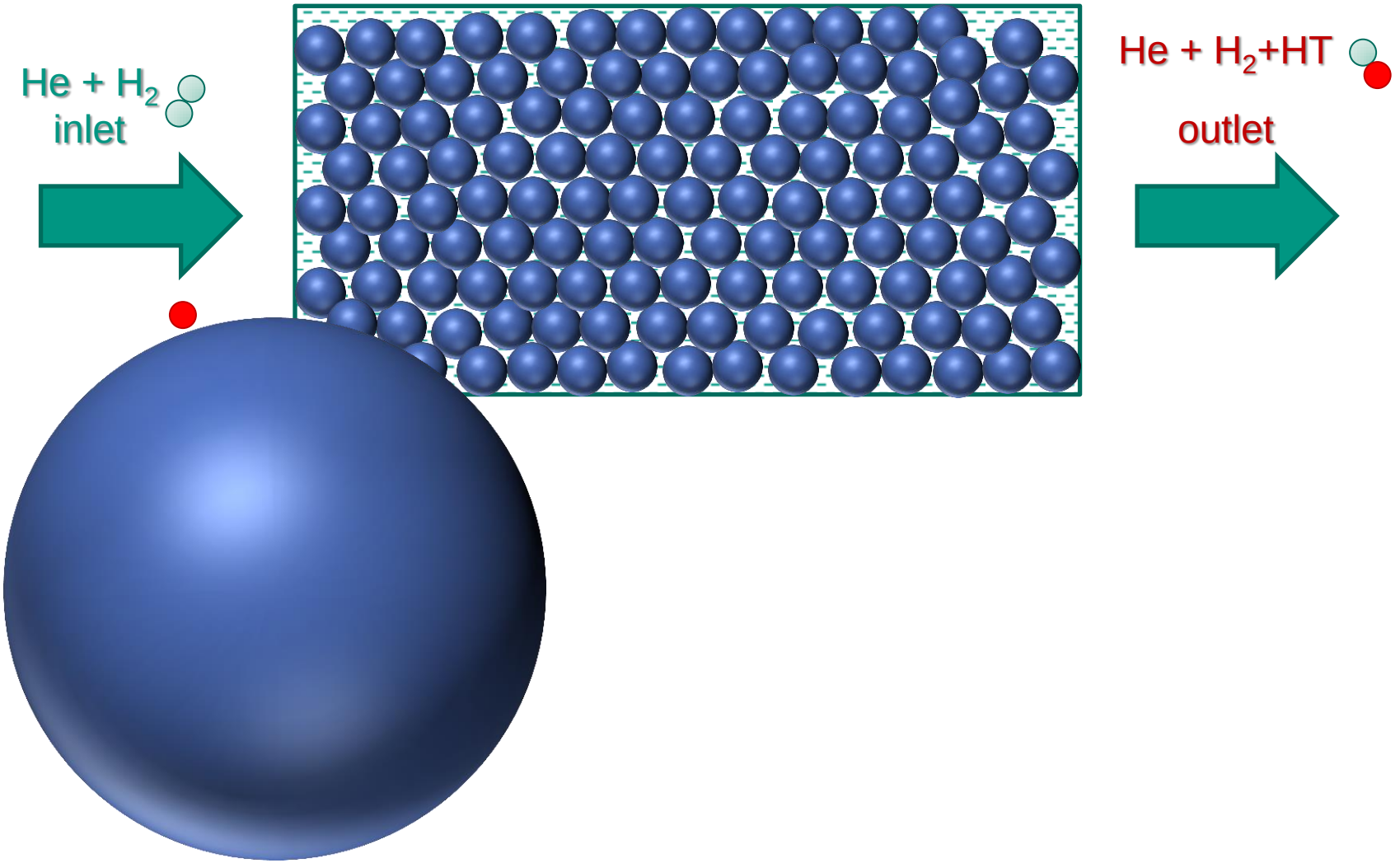
Be Pebble Bed of T-breeding Blanket



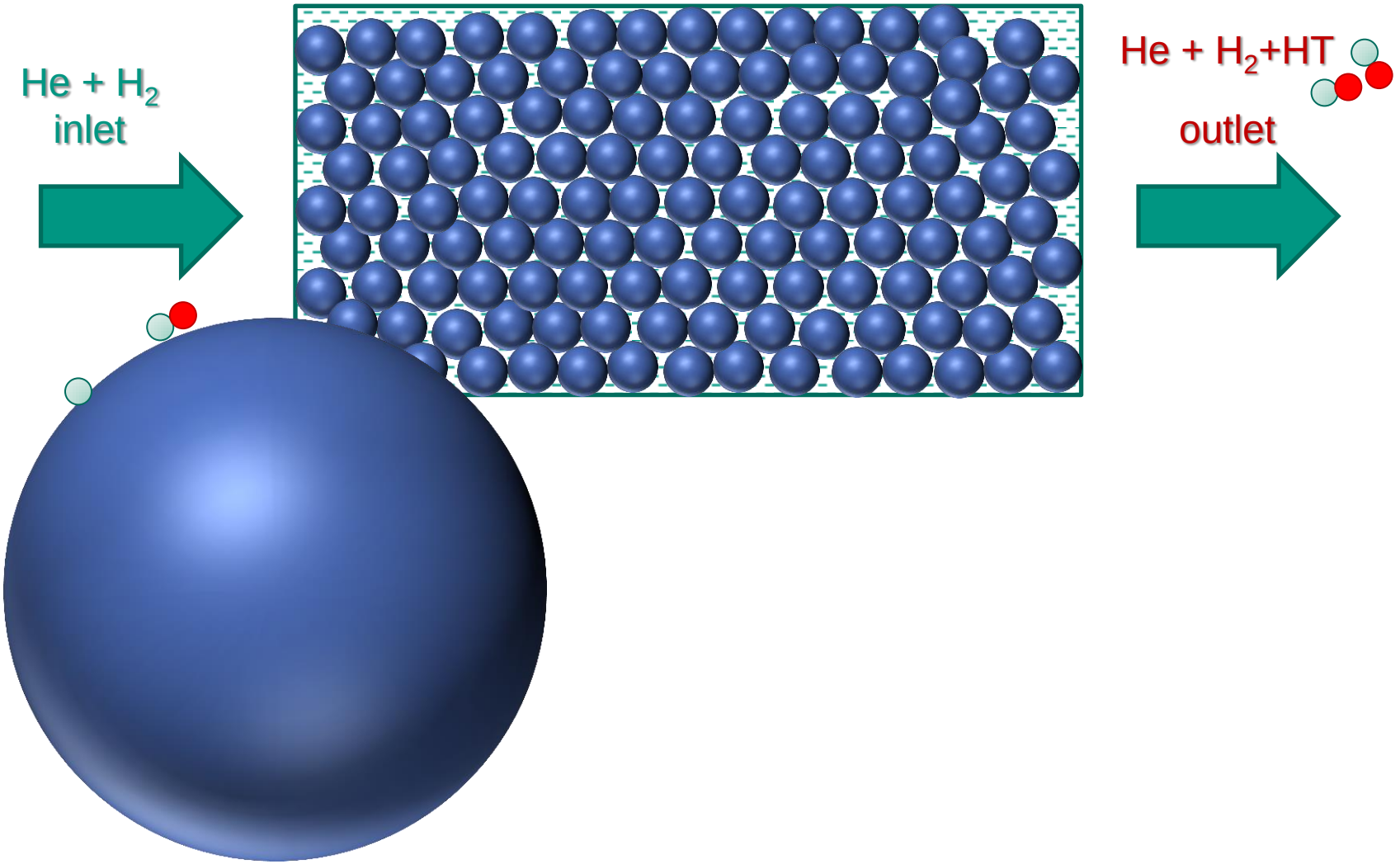
Be Pebble Bed of T-breeding Blanket



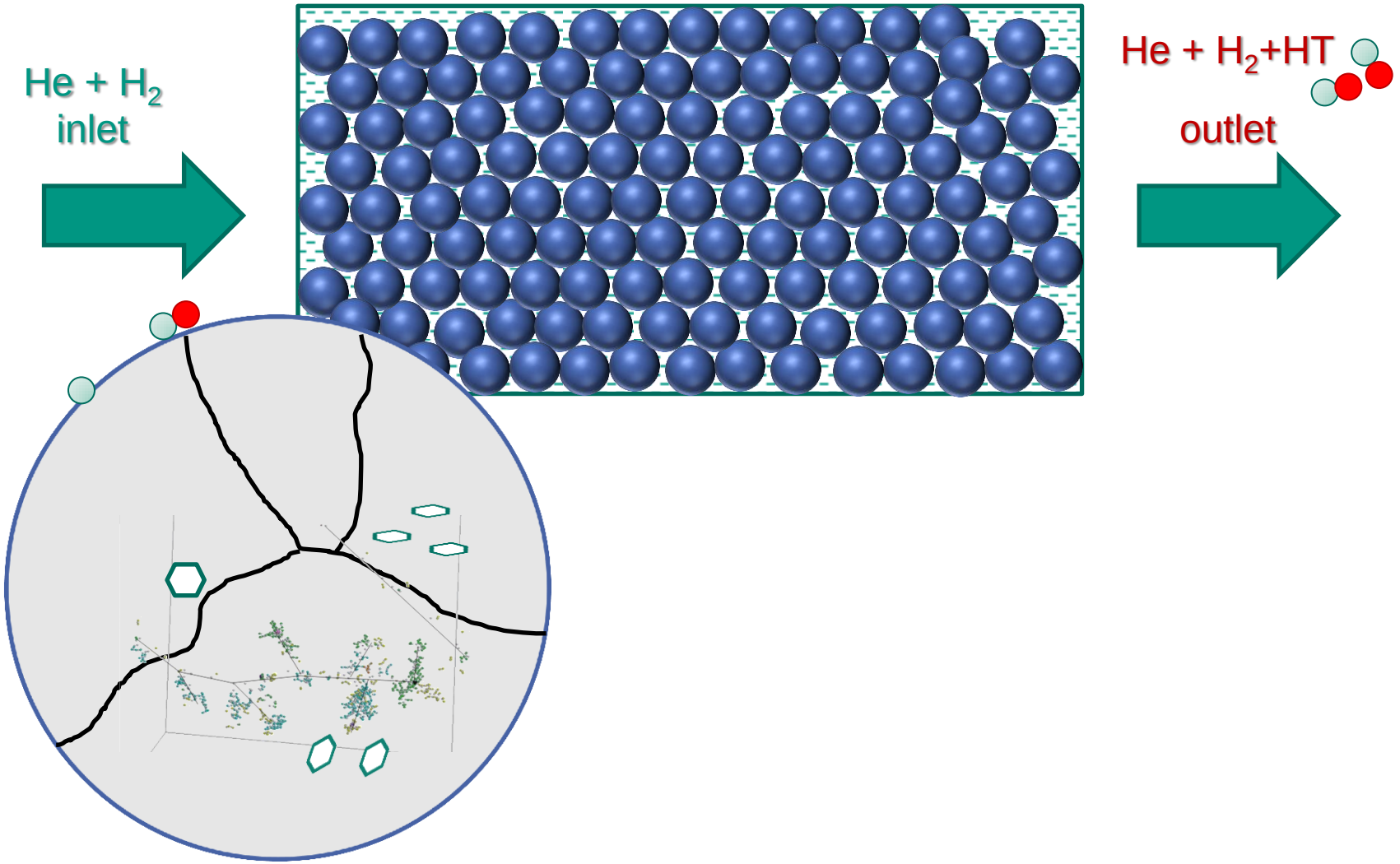
Be Pebble Bed of T-breeding Blanket



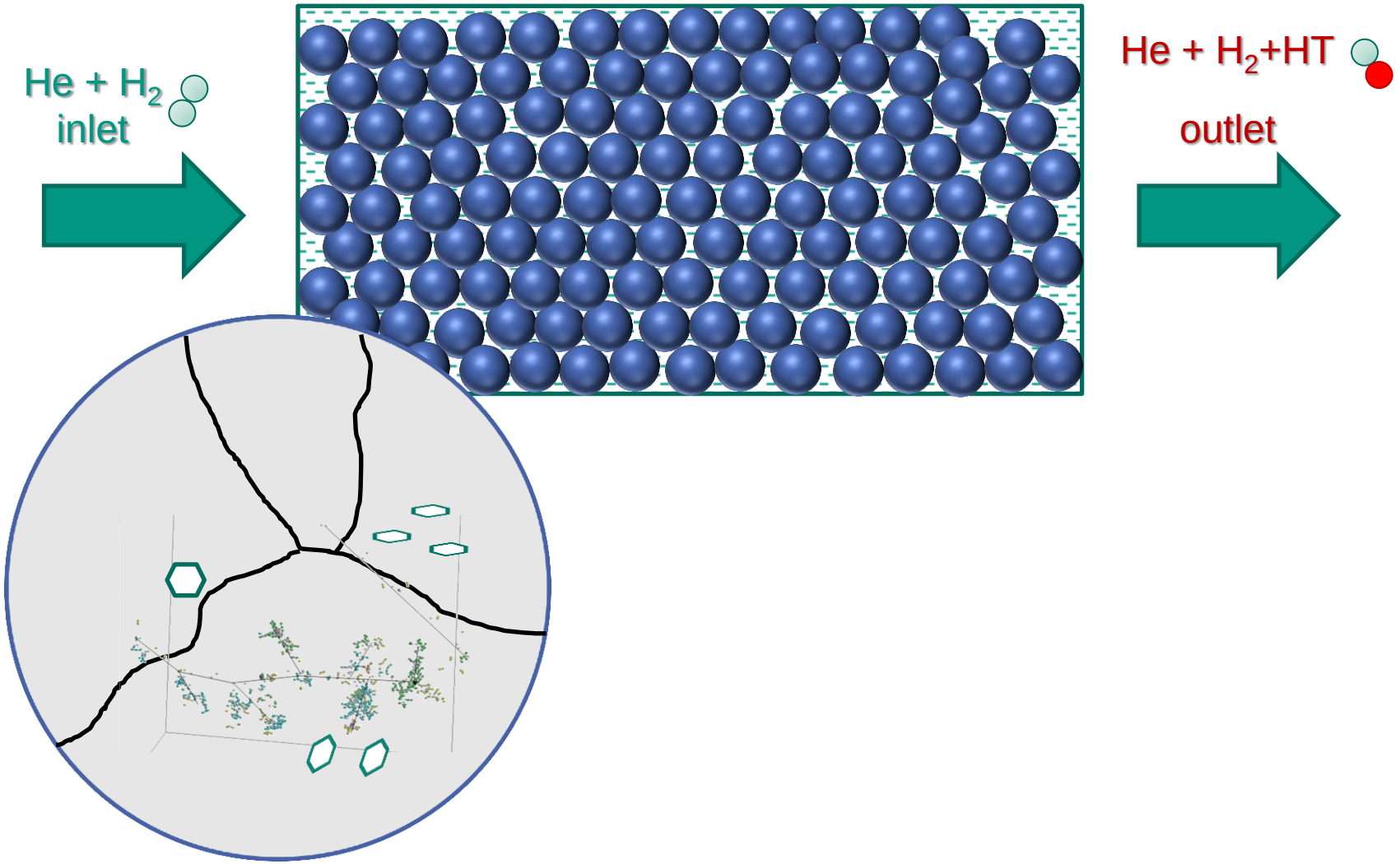
Be Pebble Bed of T-breeding Blanket



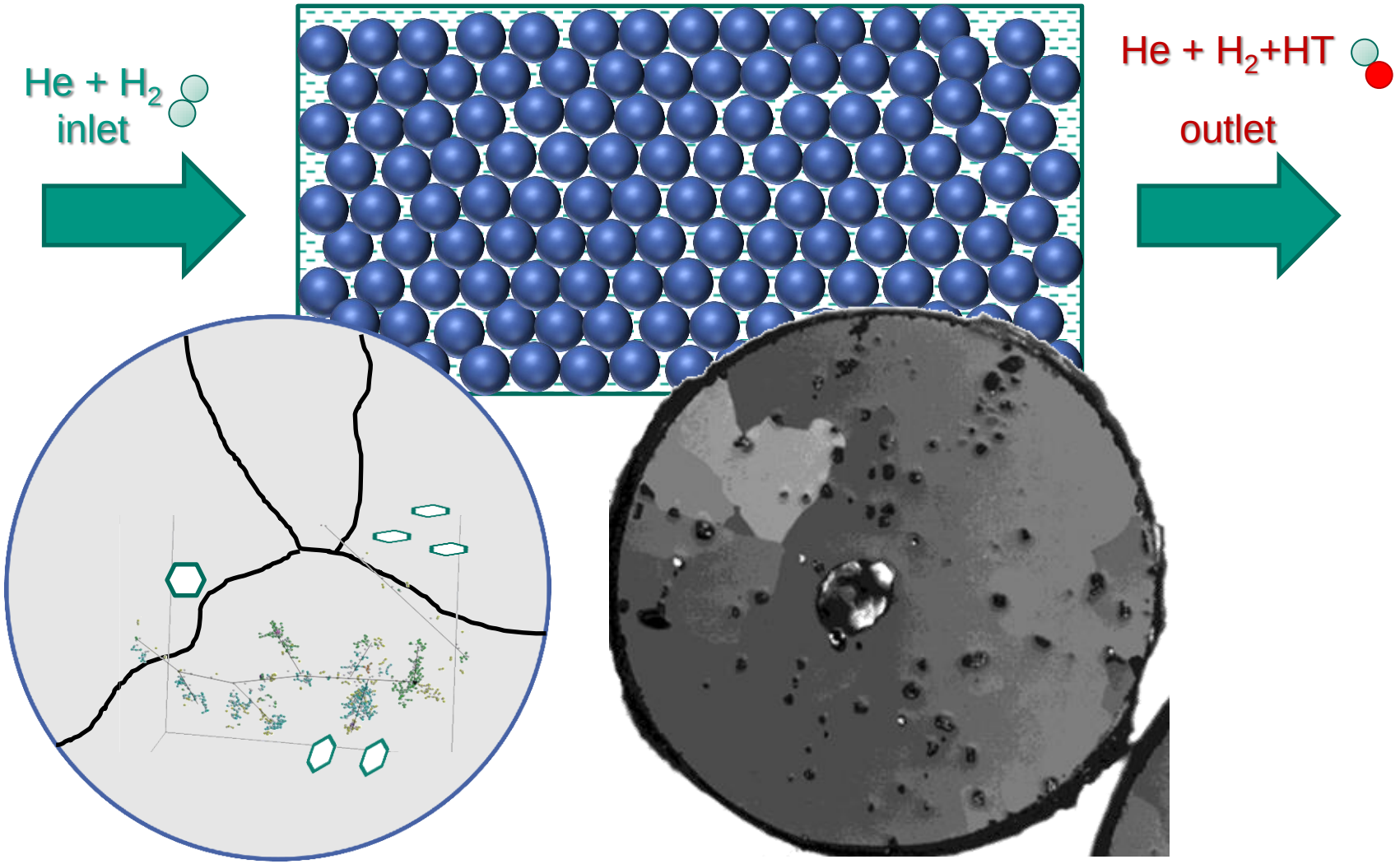
Be Pebble Bed of T-breeding Blanket



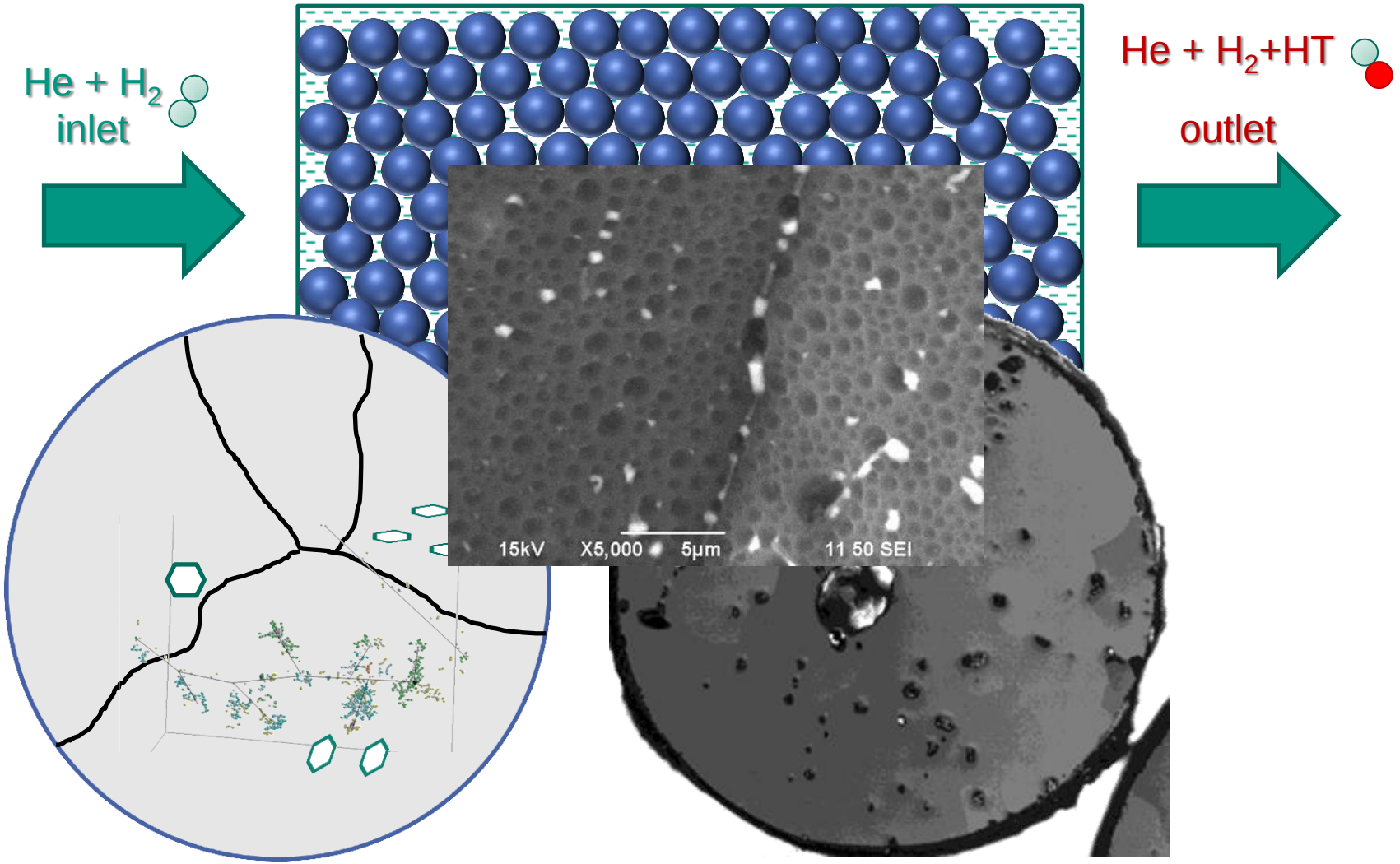
Be T-breeding Pebble Bed



Be T-breeding Pebble Bed



Be T-breeding Pebble Bed



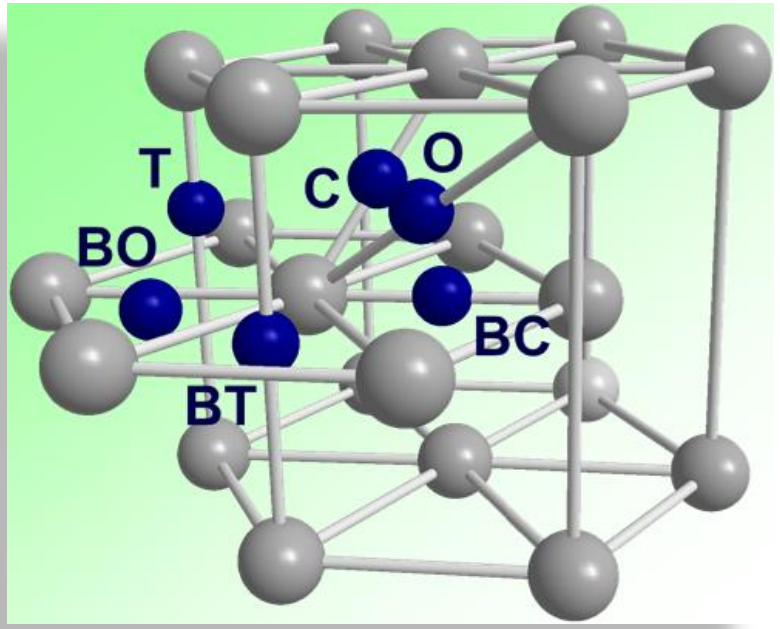
Simulation methods

Density Functional Theory *(ab initio)*

- VASP 4.6 / VASP 5.2
- Generalized Gradient Approximation (GGA)
- Pseudopotentials:
  - Plain Augmented Waves (PAW)
- Gamma centered Monkhorst-Pack k-point grid ≥ 13x13x13
- Energy cutoff = 450 eV

***Ab initio* Molecular Dynamics (VASP)**

- Time step 0.3 fs
- Run duration ~3000-4000 steps (~1 ps)
- Simulation cell size: 4x4x2 = 64 atoms
- Temperature: 200-1000 K
- k-point grid: 7x7x7
- Energy cutoff 250 eV

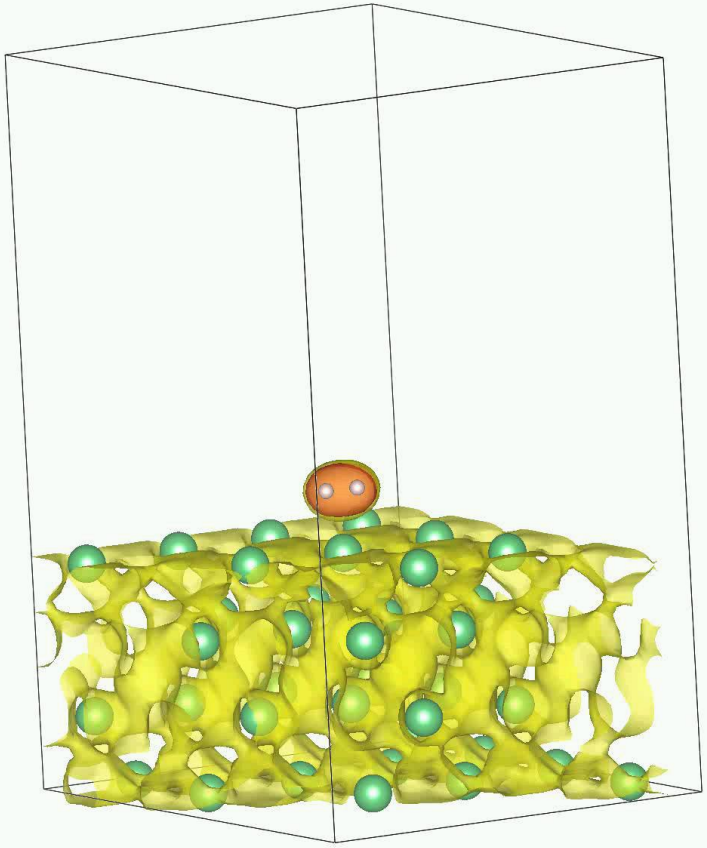


G.Kresse, J.Hafner, Phys. Rev. B (1993) 47, 558; ibid. (1994) 49, 14251;
G.Kresse, J.Furthmüller, Comput. Mat. Sci. (1996) 6, 15;
G.Kresse and J.Furthmüller, Phys. Rev. B (1996) 54, 11169

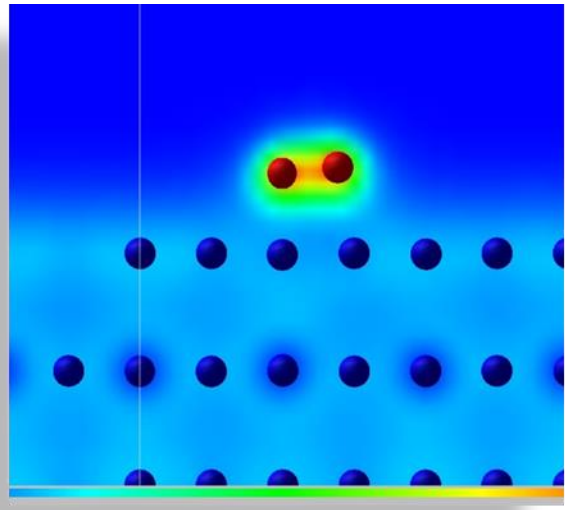
Outline

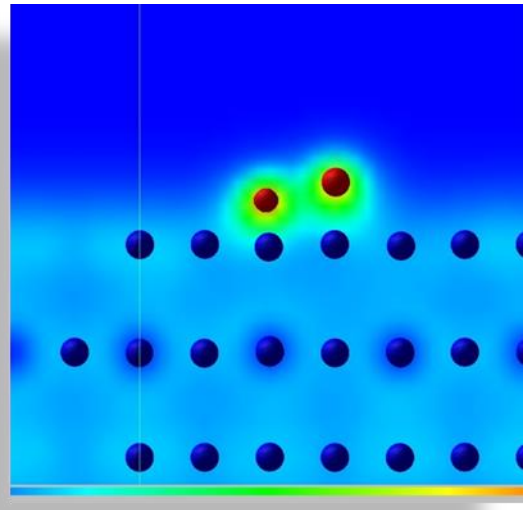
- Beryllium in Fusion Reactor
  - Be as plasma facing material
  - Be in T-breeding pebble bed
- Simulation method
- Adsorption and desorption
  - H_2 dissociative adsorption on (0001)Be
  - Hydrogen surface adsorption sites
  - H_2 adsorption on precovered surface
  - Hydrogen interaction on Be surface
  - Hydrogen absorption in bulk
  - Hydrogen associative desorption
- Surface energy modification
  - Clean surface energies
  - Surface energy with hydrogen
  - Faceting of H-covered bubble
- Conclusions

H_2 dissociative adsorption on (0001)Be

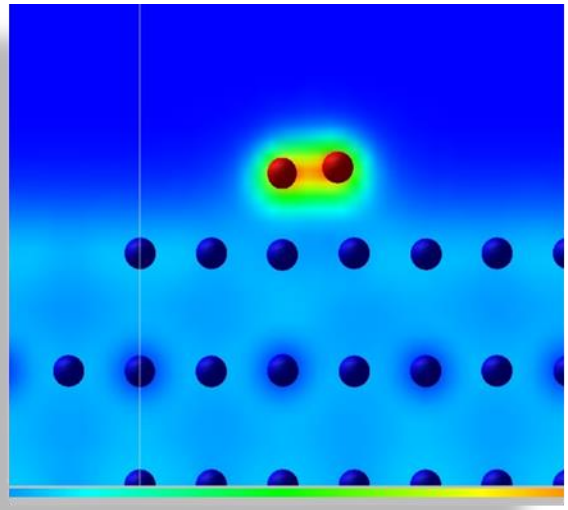


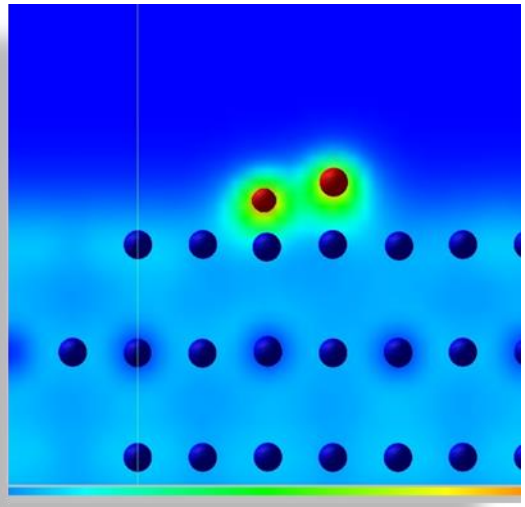
H_2 dissociative adsorption on (0001)Be

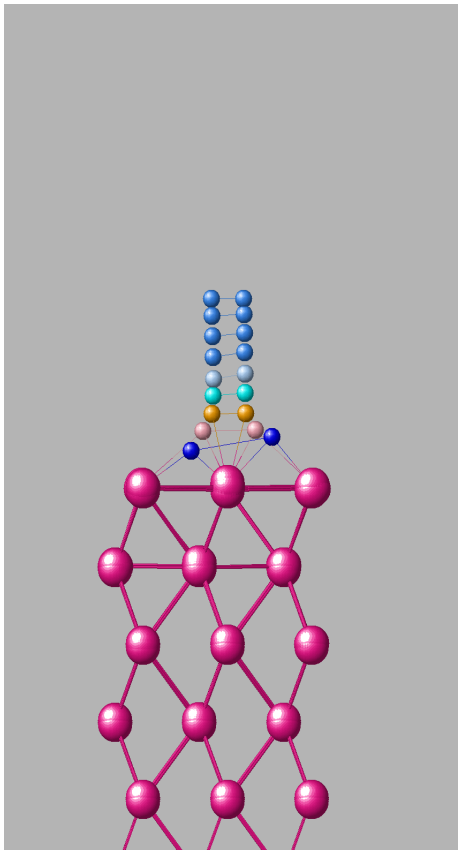




H_2 dissociative adsorption on (0001)Be



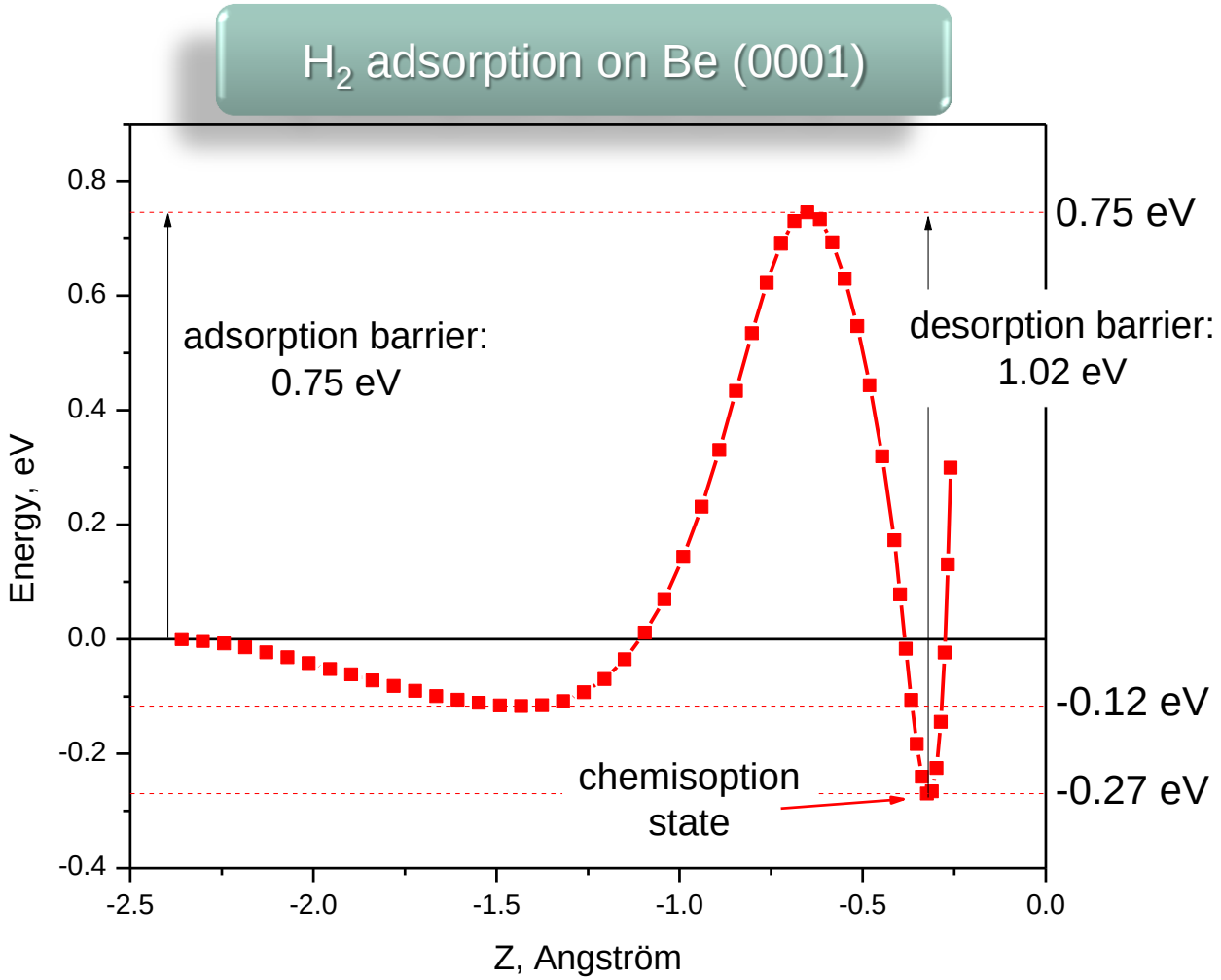




H_2 dissociative adsorption on (0001)Be

Vacuum

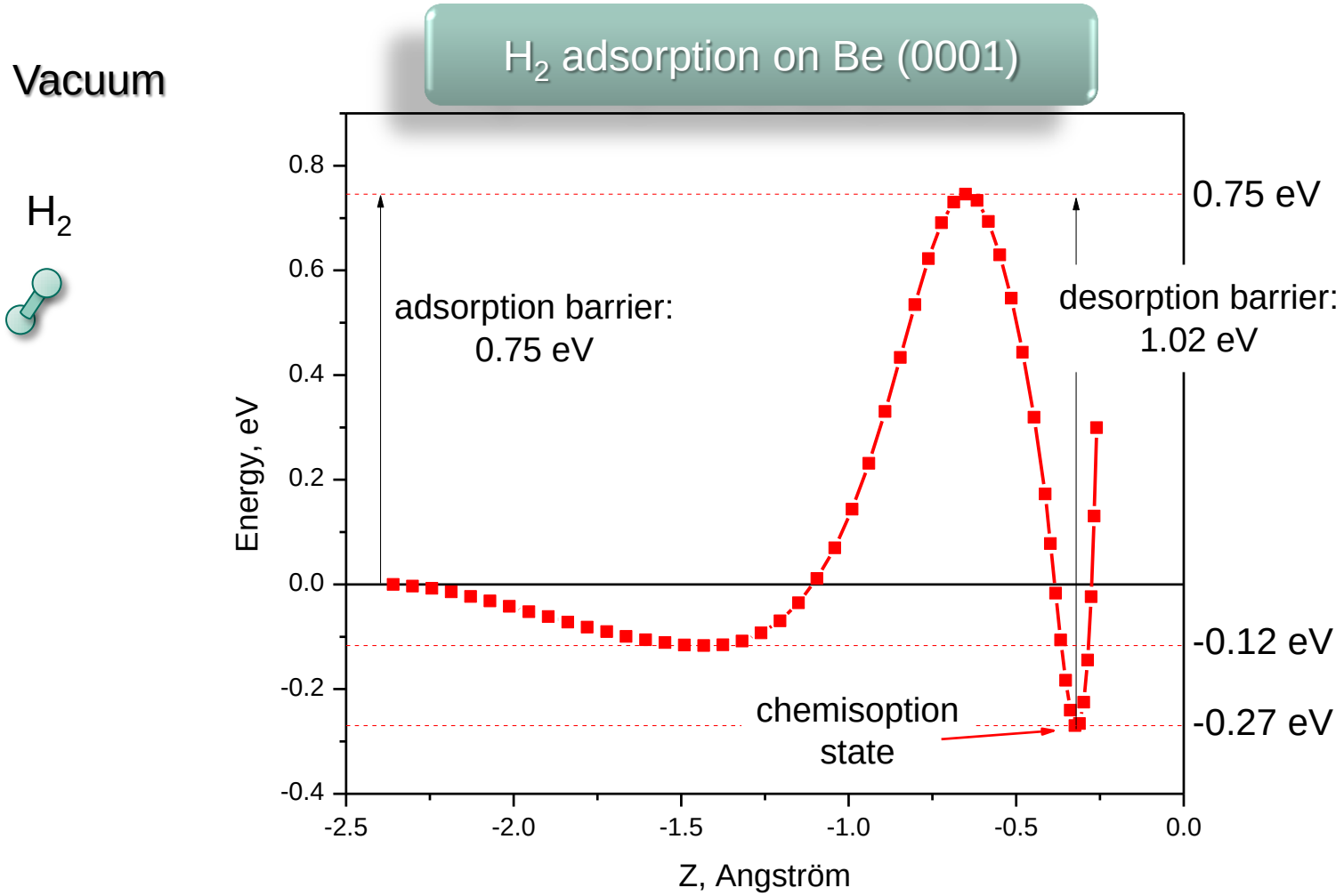
H_2



H_2 dissociative adsorption on (0001)Be

Vacuum

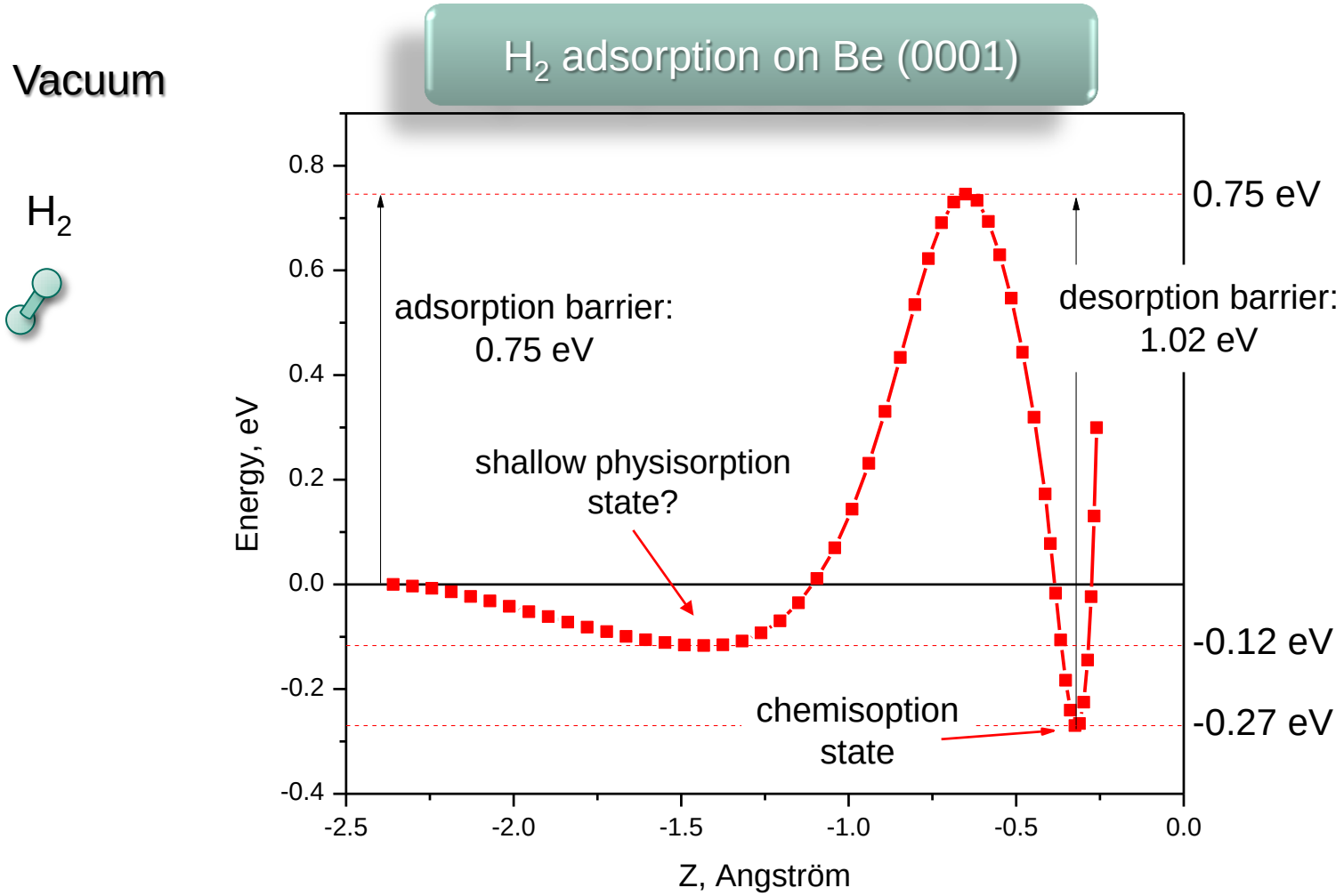
H_2



H_2 dissociative adsorption on (0001)Be

Vacuum

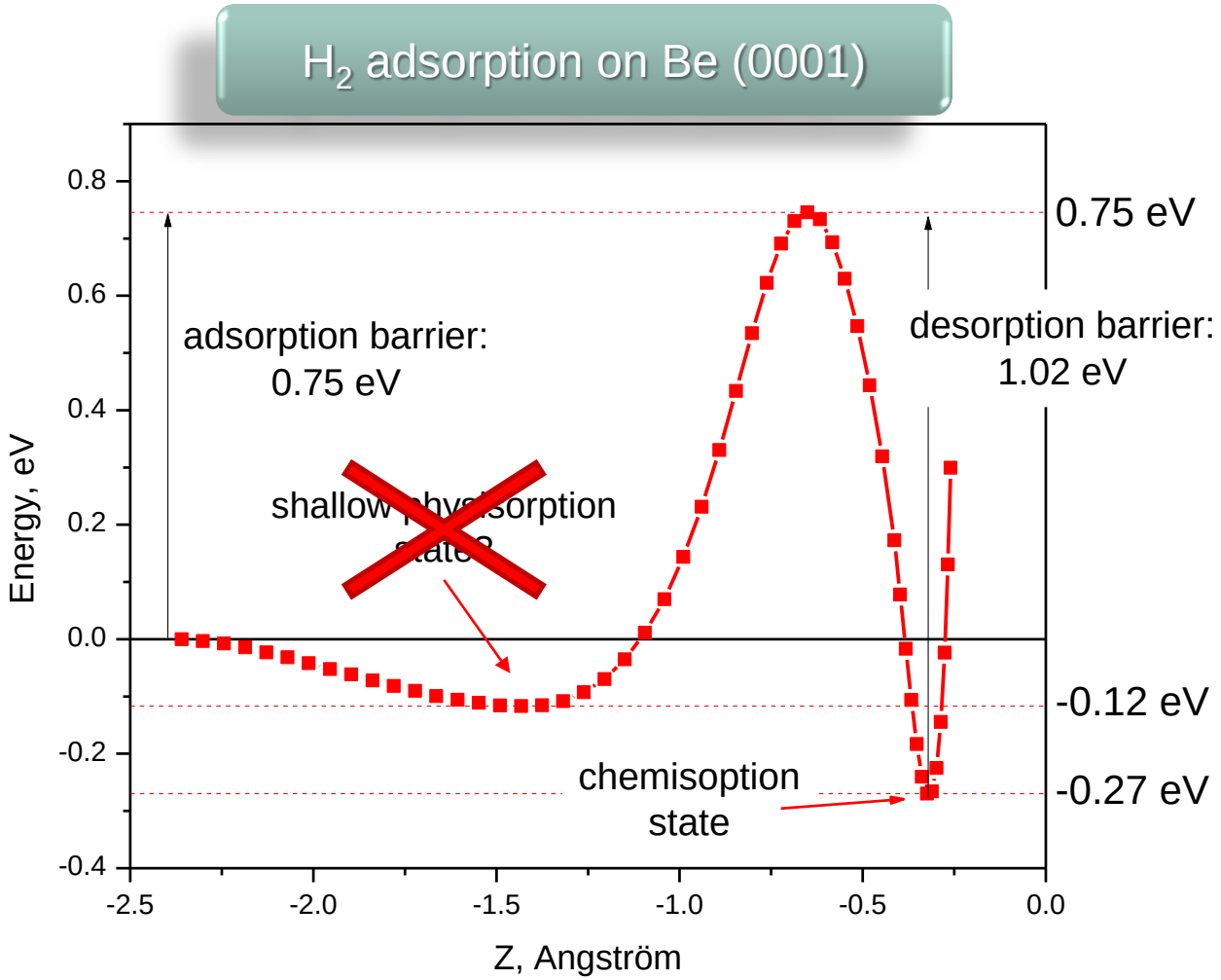
H_2



H_2 dissociative adsorption on (0001)Be

Vacuum

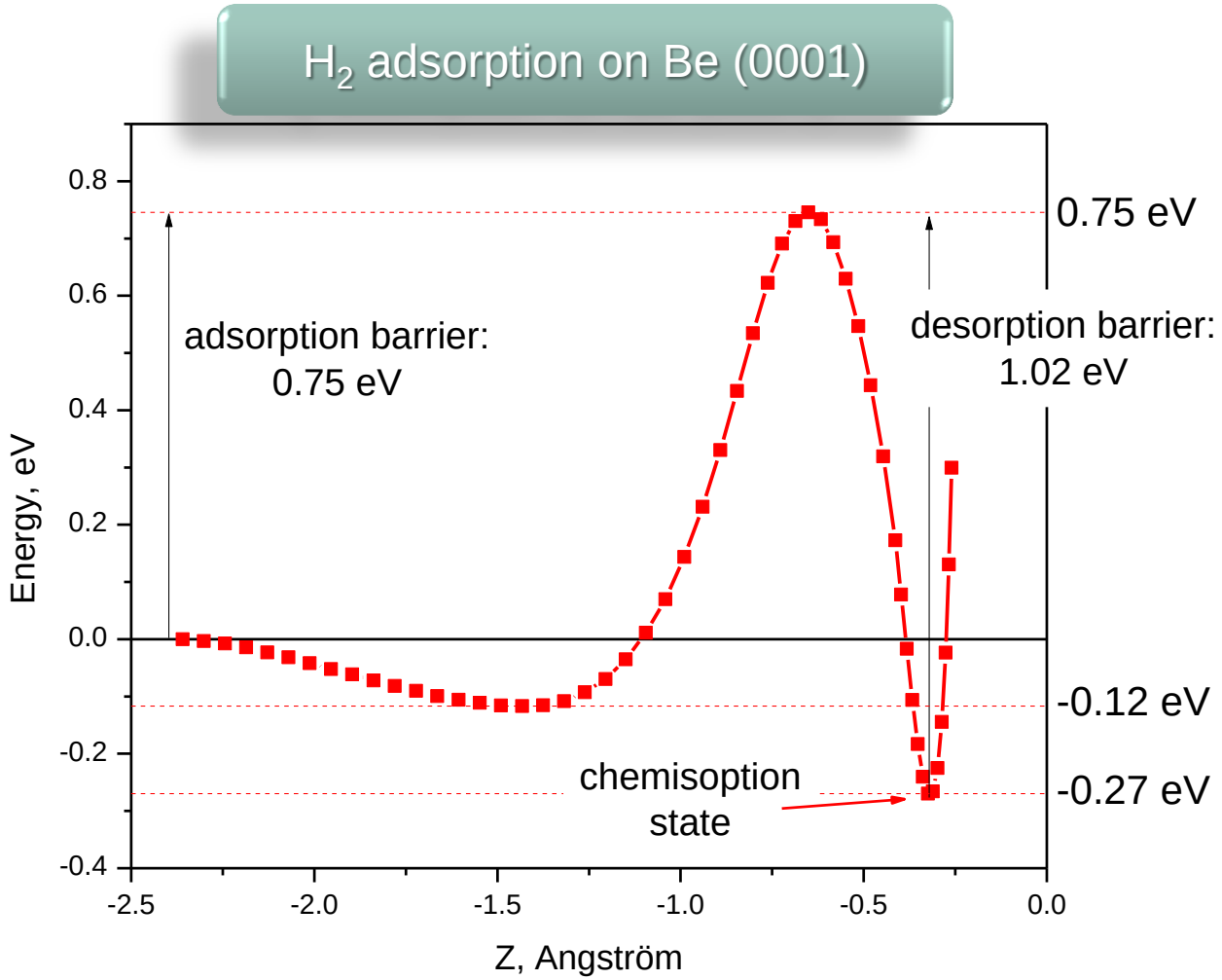
H_2



H_2 dissociative adsorption on (0001)Be

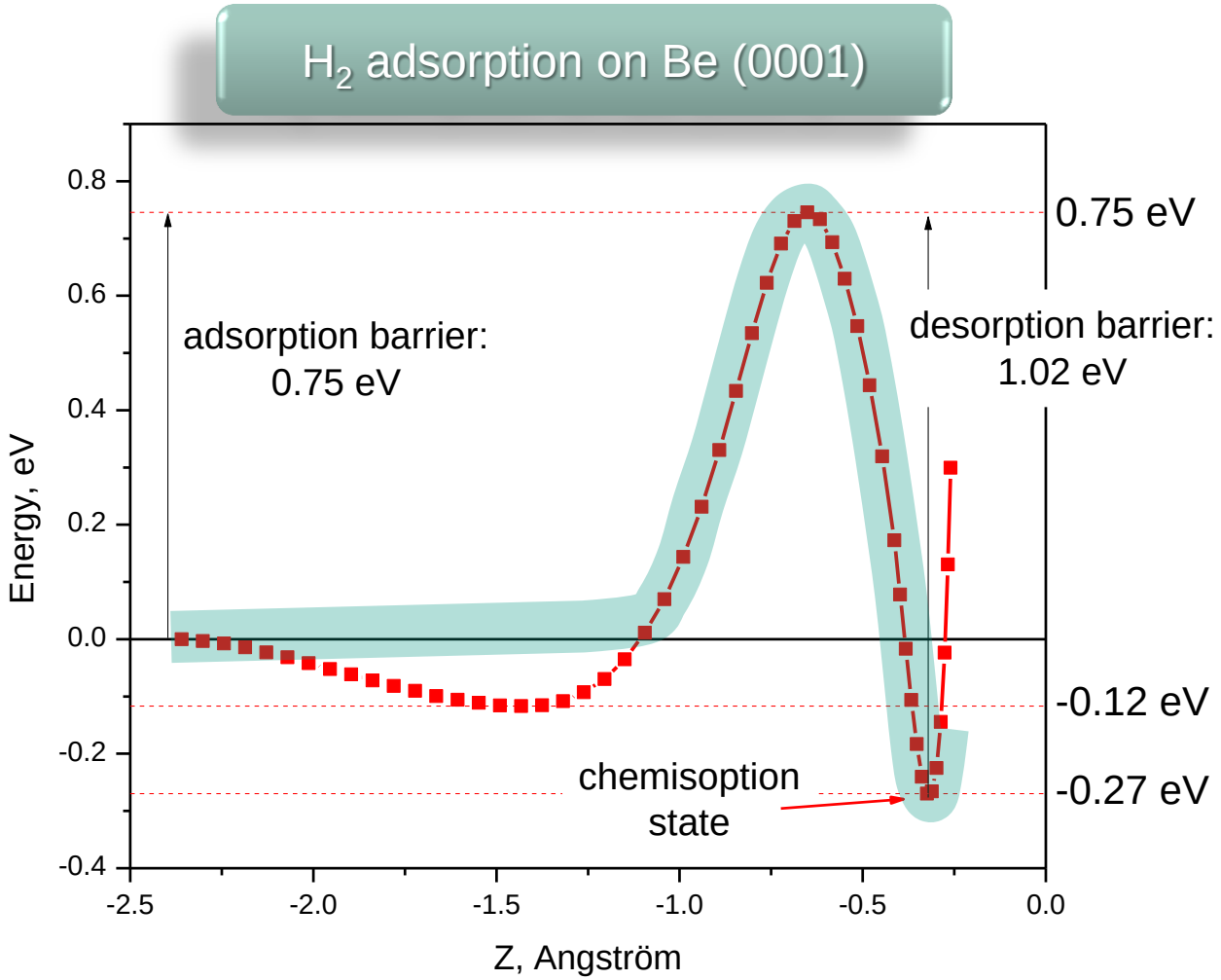
Vacuum

H_2

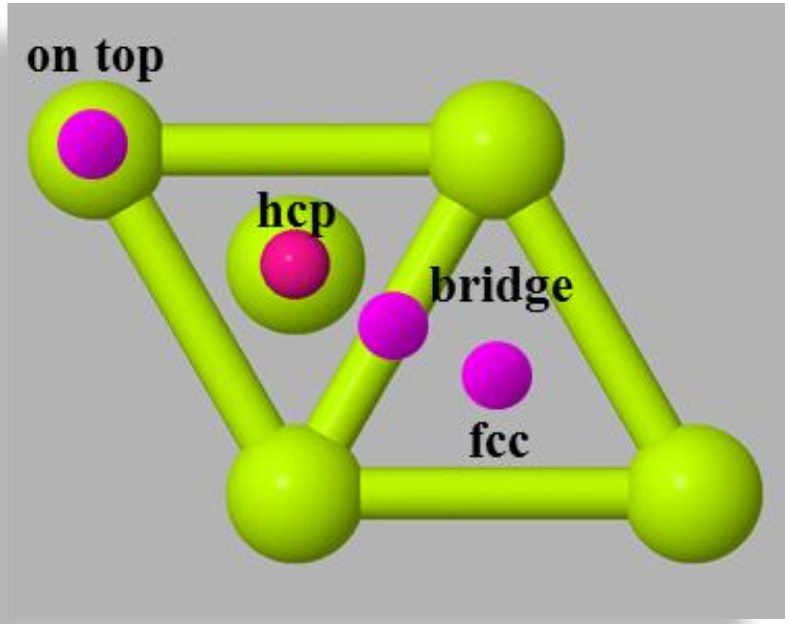


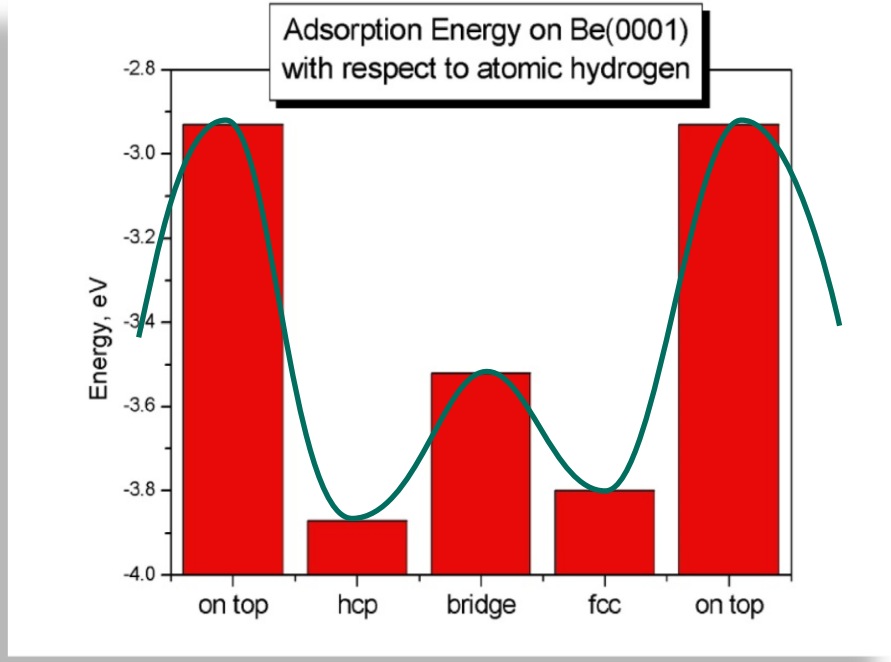
H_2 dissociative adsorption on (0001)Be

Vacuum

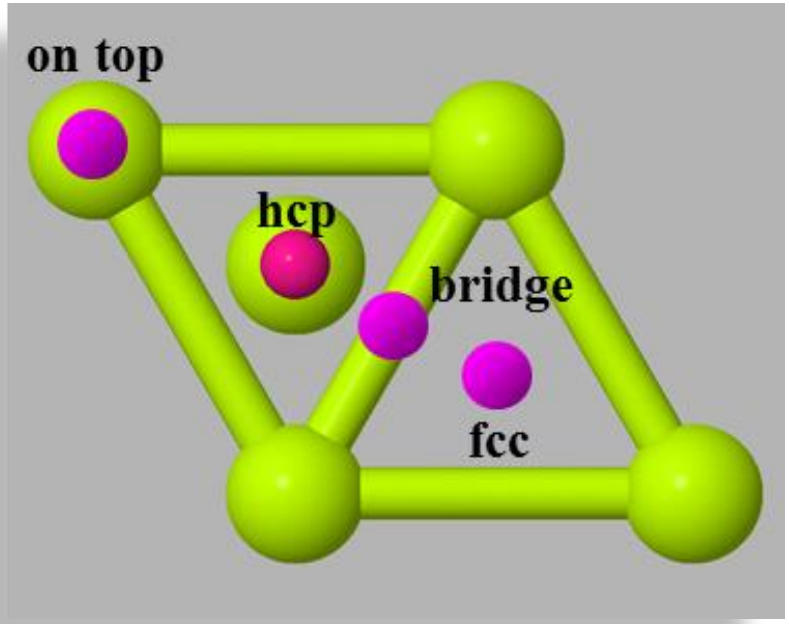


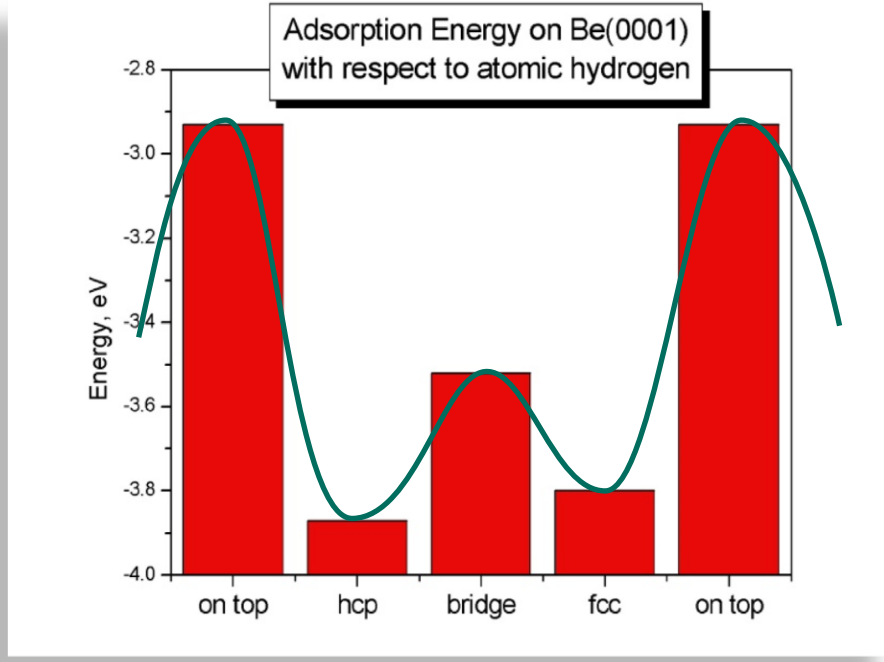
H on Be(0001) surface: Adsorption sites





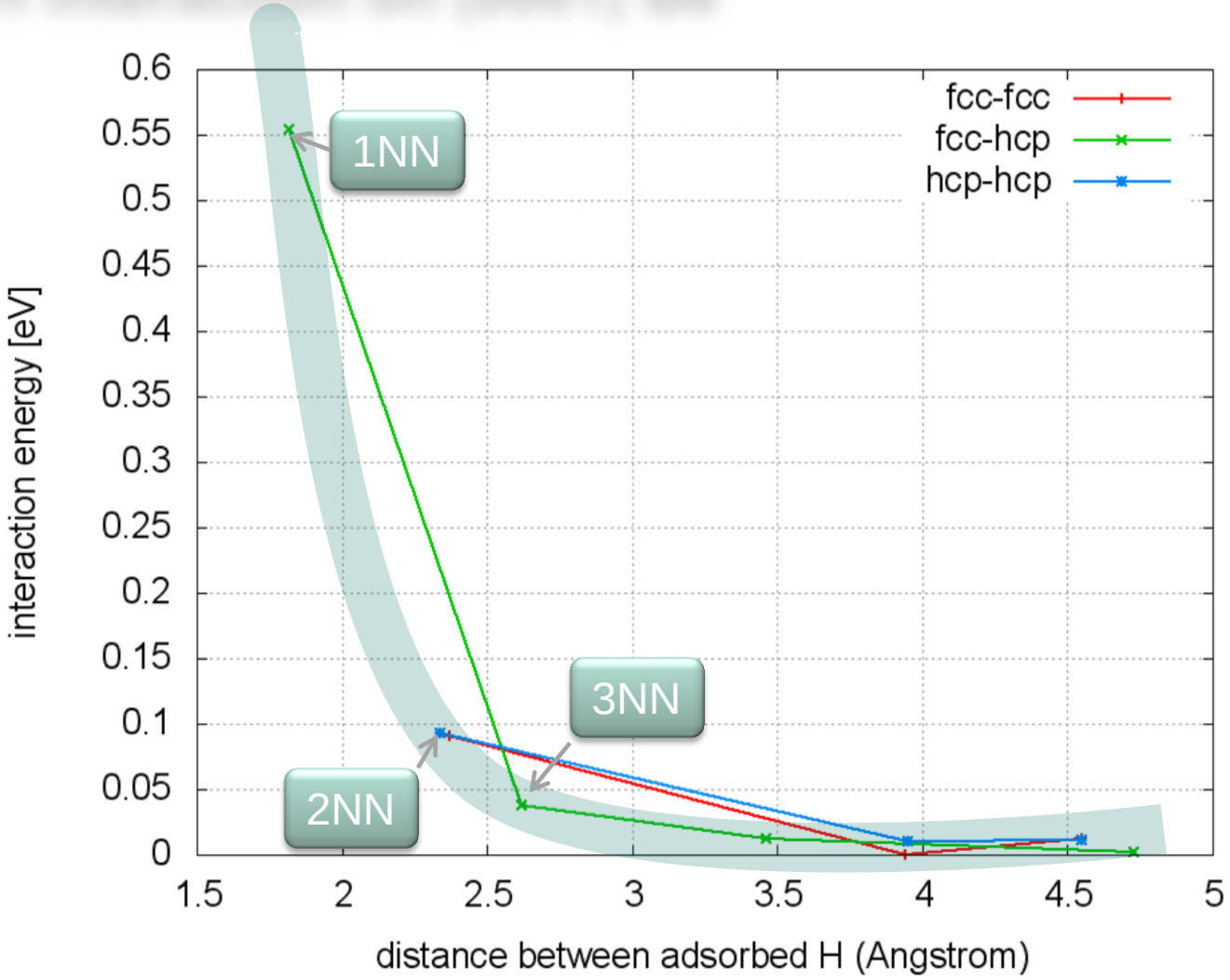
H on Be(0001) surface: Adsorption sites



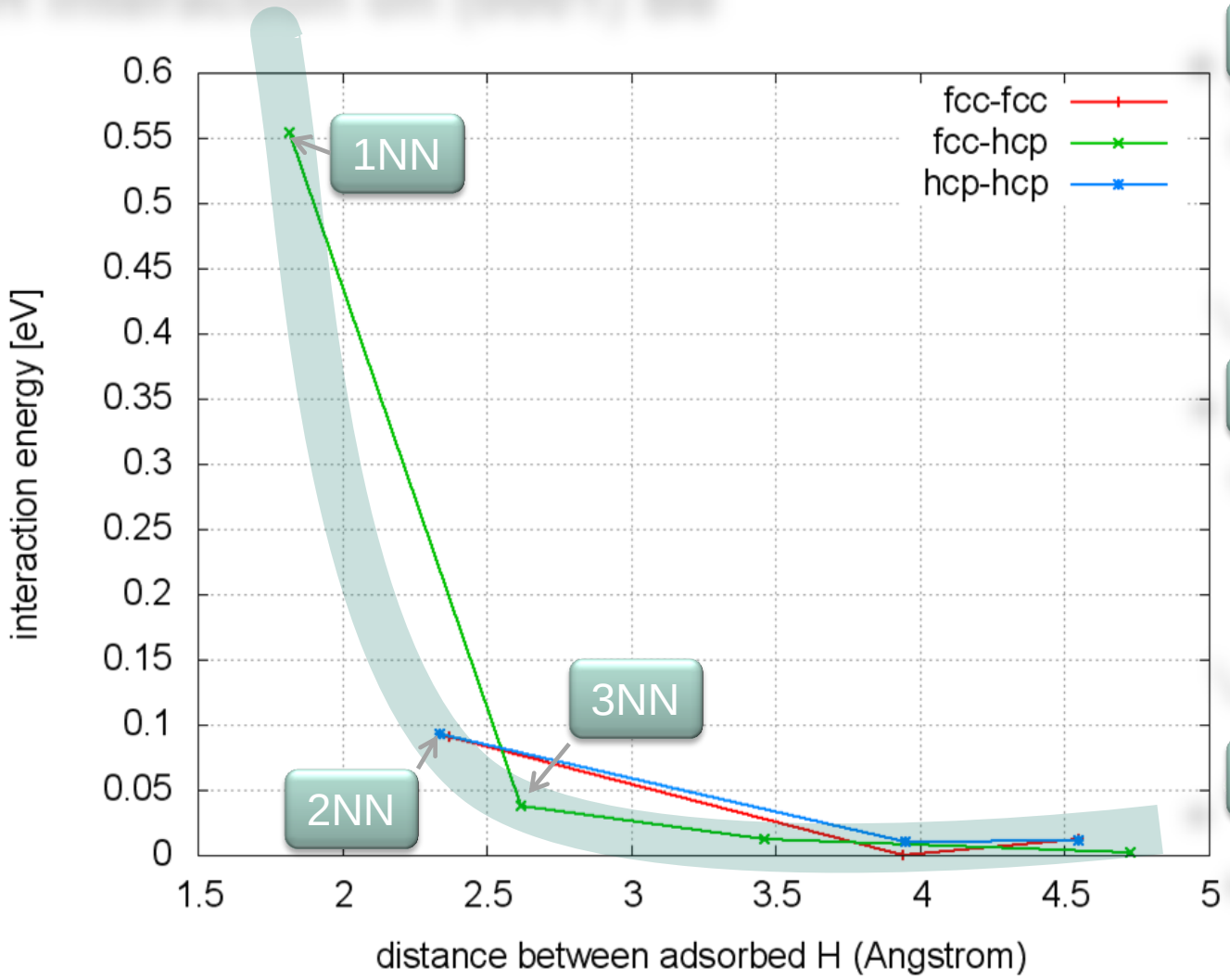


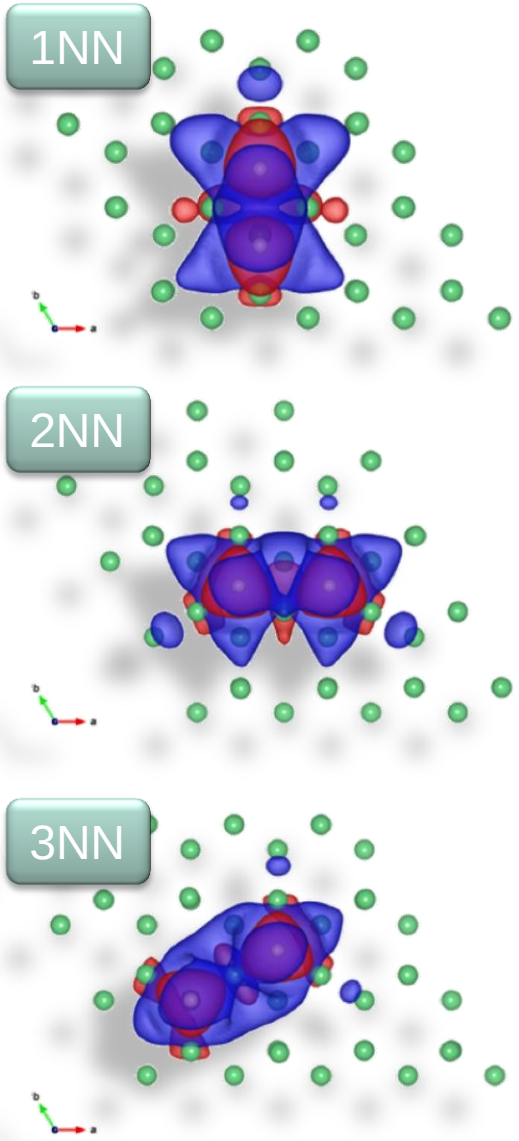
- Two stable adsorption sites for hydrogen (hcp and fcc) exist at (0001)Be surface
- Hydrogen coverage calculated as a fraction of occupied sites (1ML – all sites occupied)

H interaction on (0001) Be

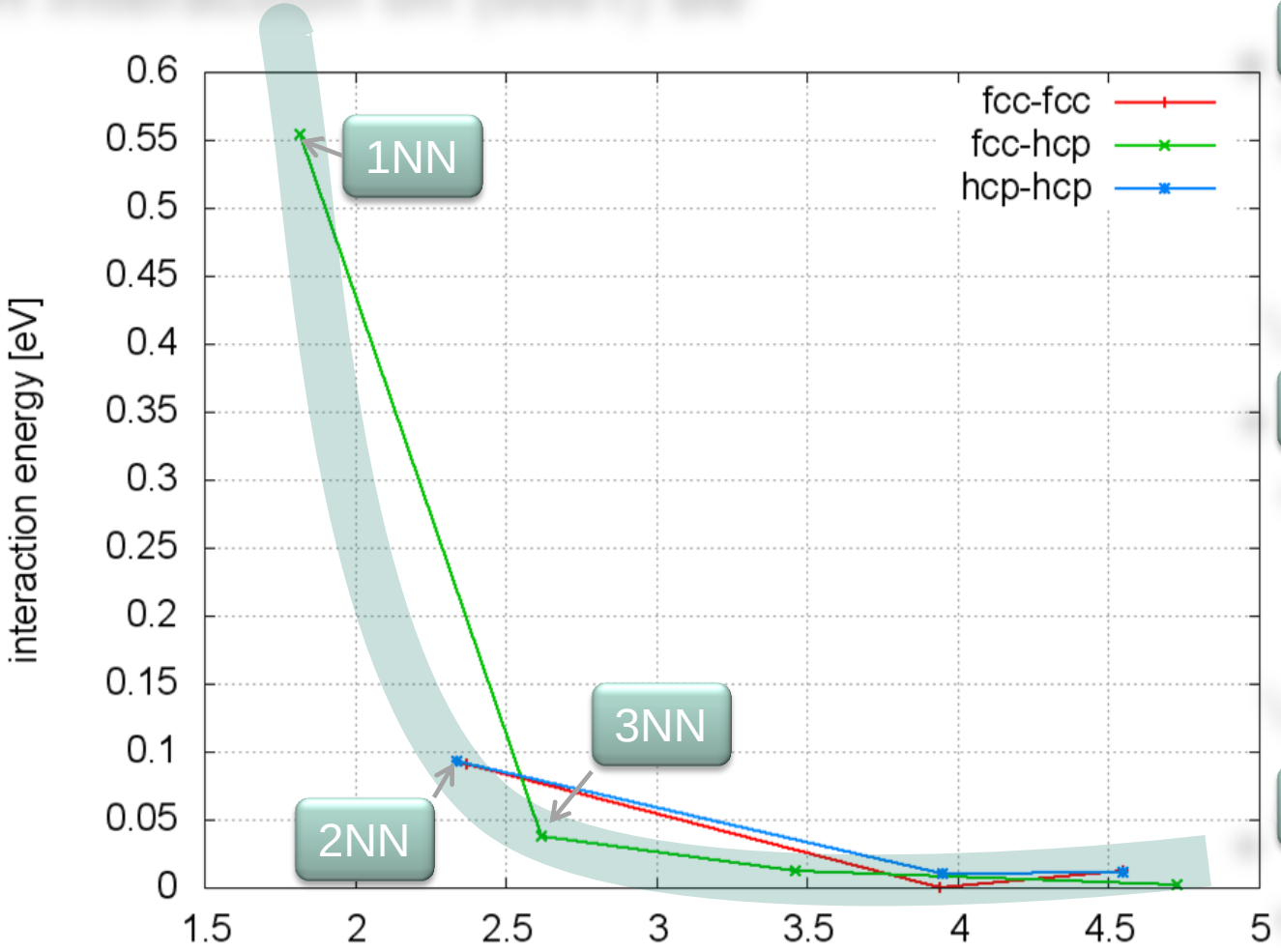


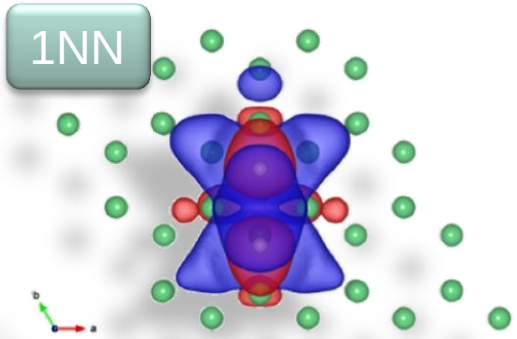
H interaction on (0001) Be

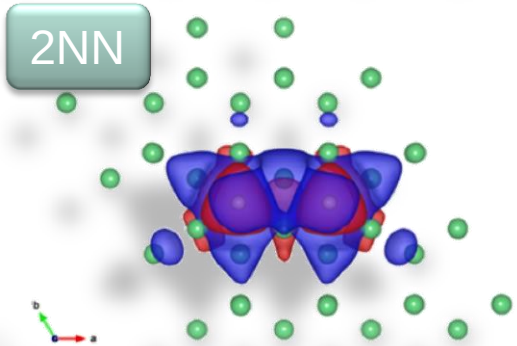


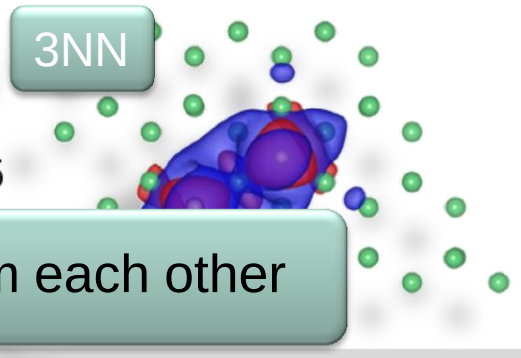


H interaction on (0001) Be



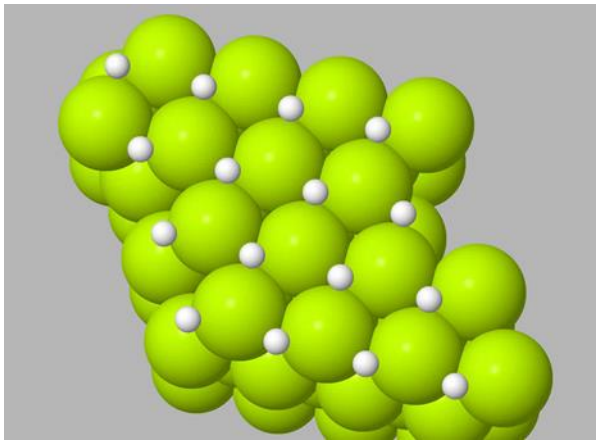




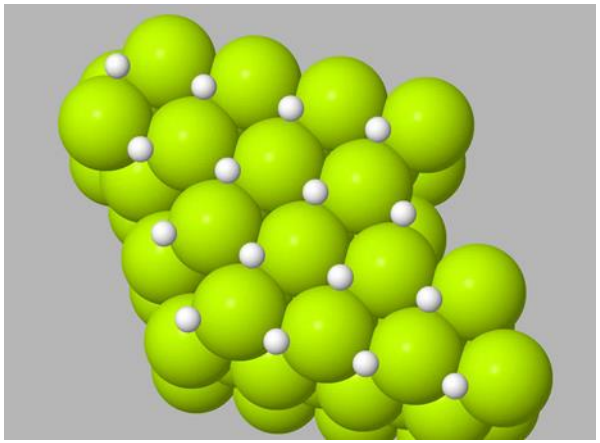


- Hydrogen atoms at the surface prefer to stay far from each other

H_2 adsorption on H pre-covered surface



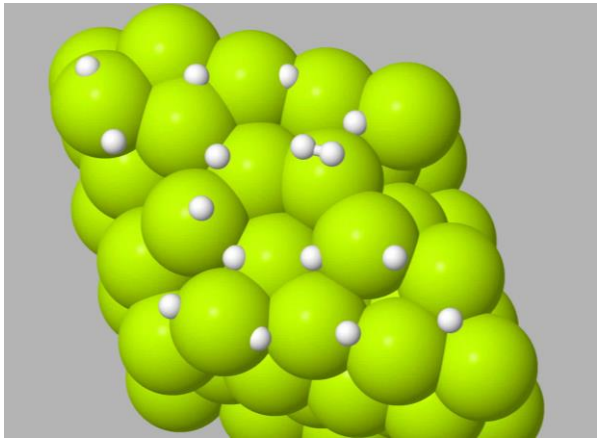
H_2 adsorption on H pre-covered surface



- There is no hydrogen adsorption on fully precovered (0.5 ML) Be (0001) surface
- One H-vacancy is also insufficient for adsorption

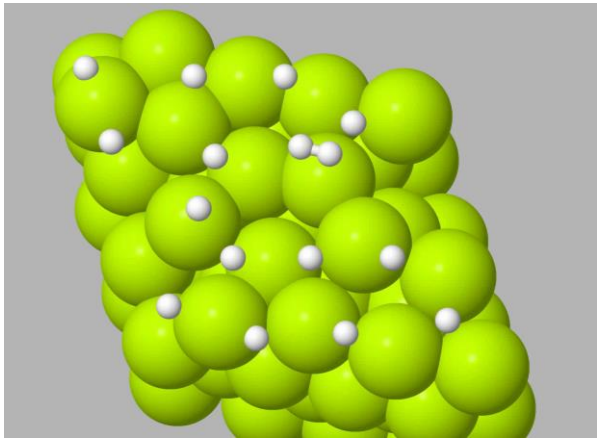
H_2 adsorption on H pre-covered surface

H coverage 0.5ML with two adjacent vacancies;
T=200K



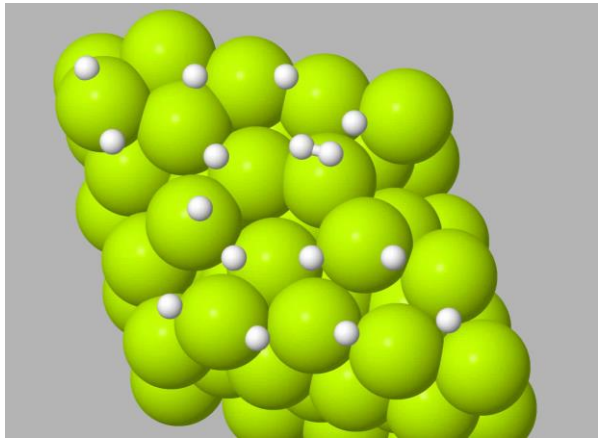
$E_k(H_2)$=2.0 eV

No adsorption



$E_k(H_2)$=4.6 eV

Adsorption!

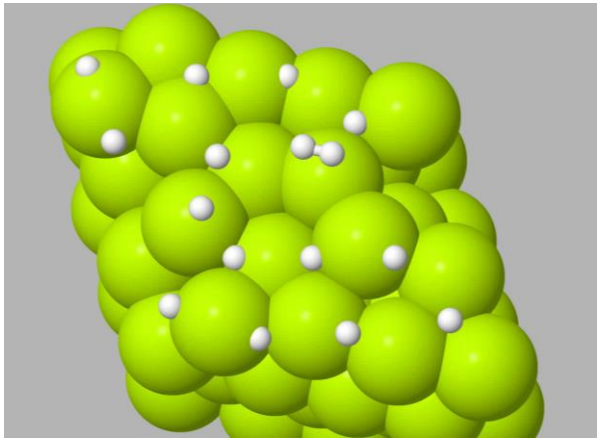


$E_k(H_2)$=8.2 eV

No adsorption

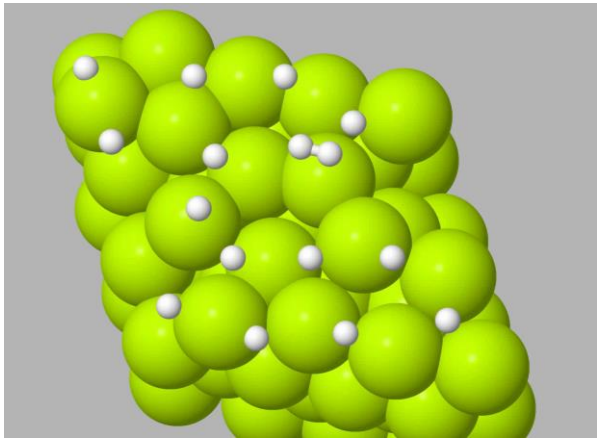
H_2 adsorption on H pre-covered surface

H coverage 0.5ML with two adjacent vacancies;
T=200K



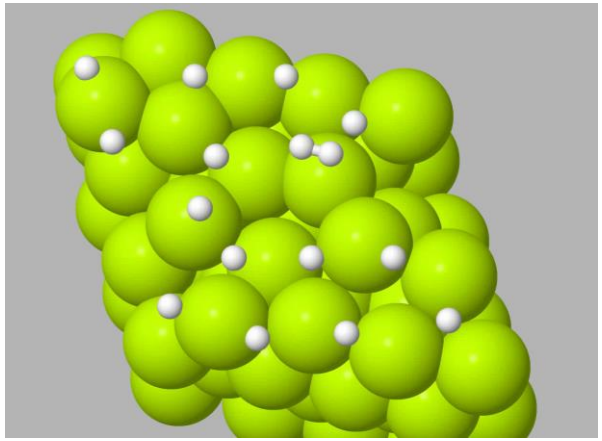
$E_k(H_2)$=2.0 eV

No adsorption



$E_k(H_2)$=4.6 eV

Adsorption!



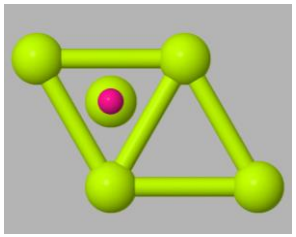
$E_k(H_2)$=8.2 eV

No adsorption

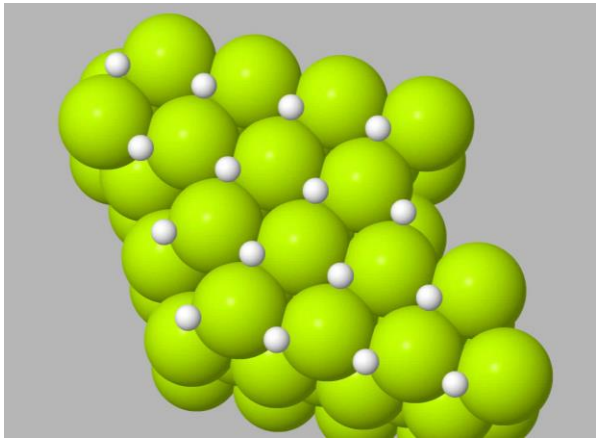
- Two hydrogen vacancies on H-covered surface are required for H_2 adsorption.
- The adsorption energy barrier on pre-covered surface is higher than for the clean surface.
- The energy of incident molecule should be in a rather narrow range!

Hydrogen at Be(0001) surface: Desorption

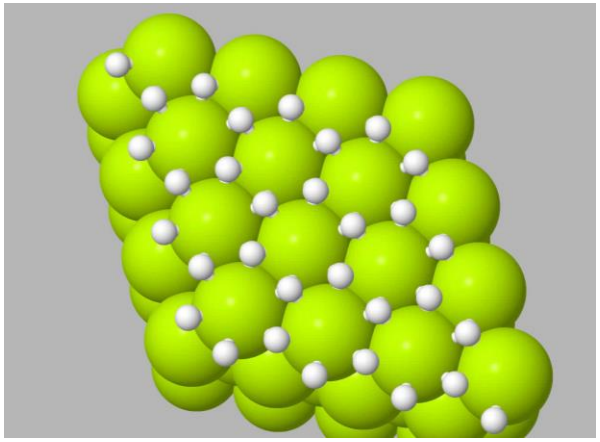
Surface coverage 0.5ML
(half of sites occupied by H)
hcp sites



T=900K



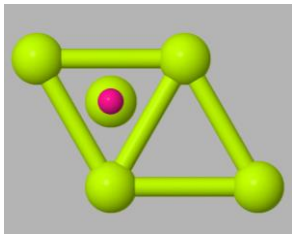
No desorption



Desorption!

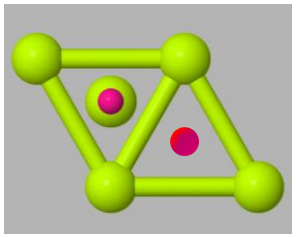
Hydrogen at Be(0001) surface: Desorption

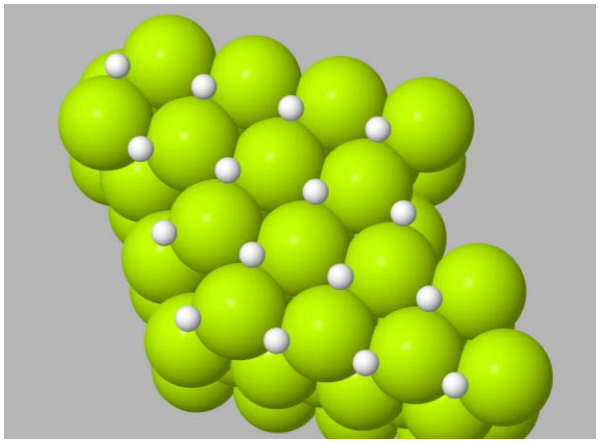
Surface coverage 0.5ML
(half of sites occupied by H)
hcp sites



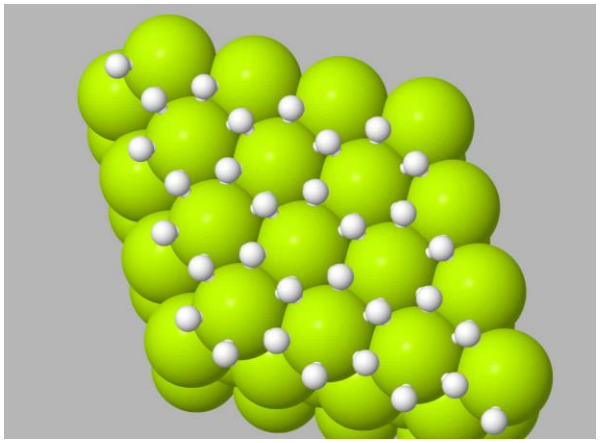
T=900K

Surface coverage 1.0ML
(all sites occupied by H)
hcp-fcc sites





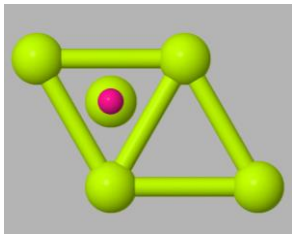
No desorption

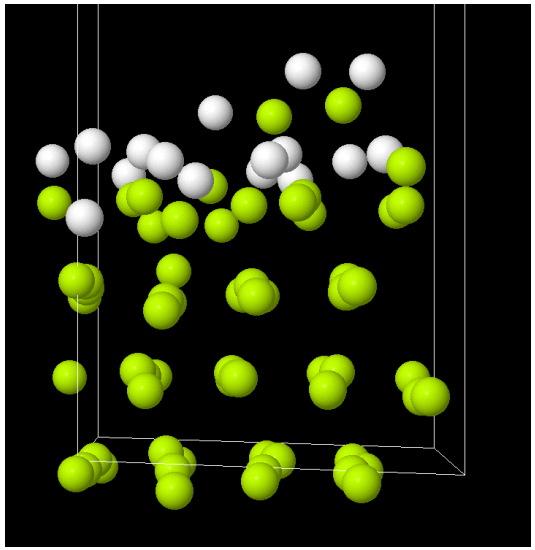


Desorption!

Hydrogen at Be(0001) surface: Desorption

Surface coverage 0.5ML
(half of sites occupied by H)
hcp sites

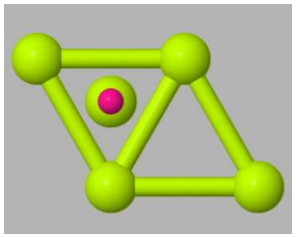


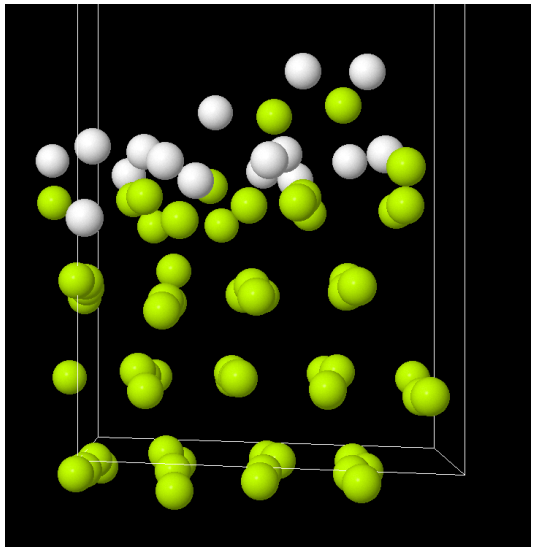


33 fs

Hydrogen at Be(0001) surface: Desorption

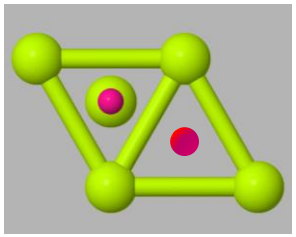
Surface coverage 0.5ML
(half of sites occupied by H)
hcp sites

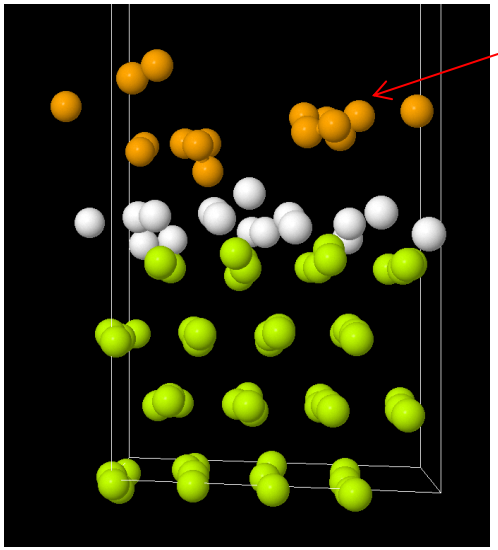




33 fs

Surface coverage 1.0ML
(all sites occupied by H)
hcp-fcc sites

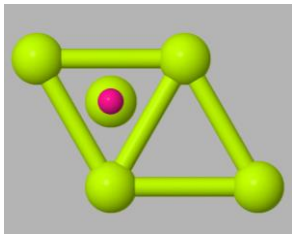


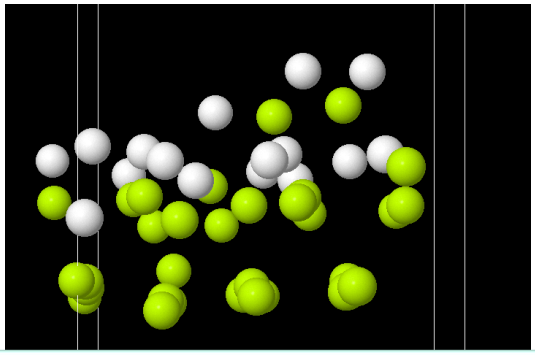


22 fs

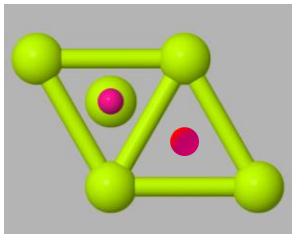
Hydrogen at Be(0001) surface: Desorption

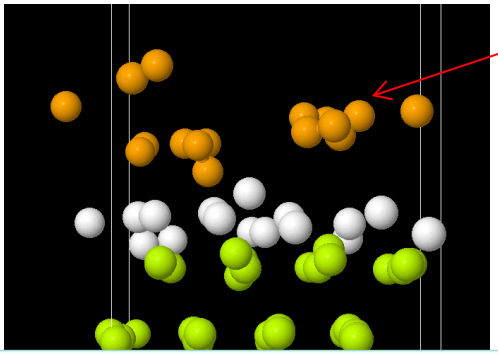
Surface coverage 0.5ML
(half of sites occupied by H)
hcp sites





Surface coverage 1.0ML
(all sites occupied by H)
hcp-fcc sites

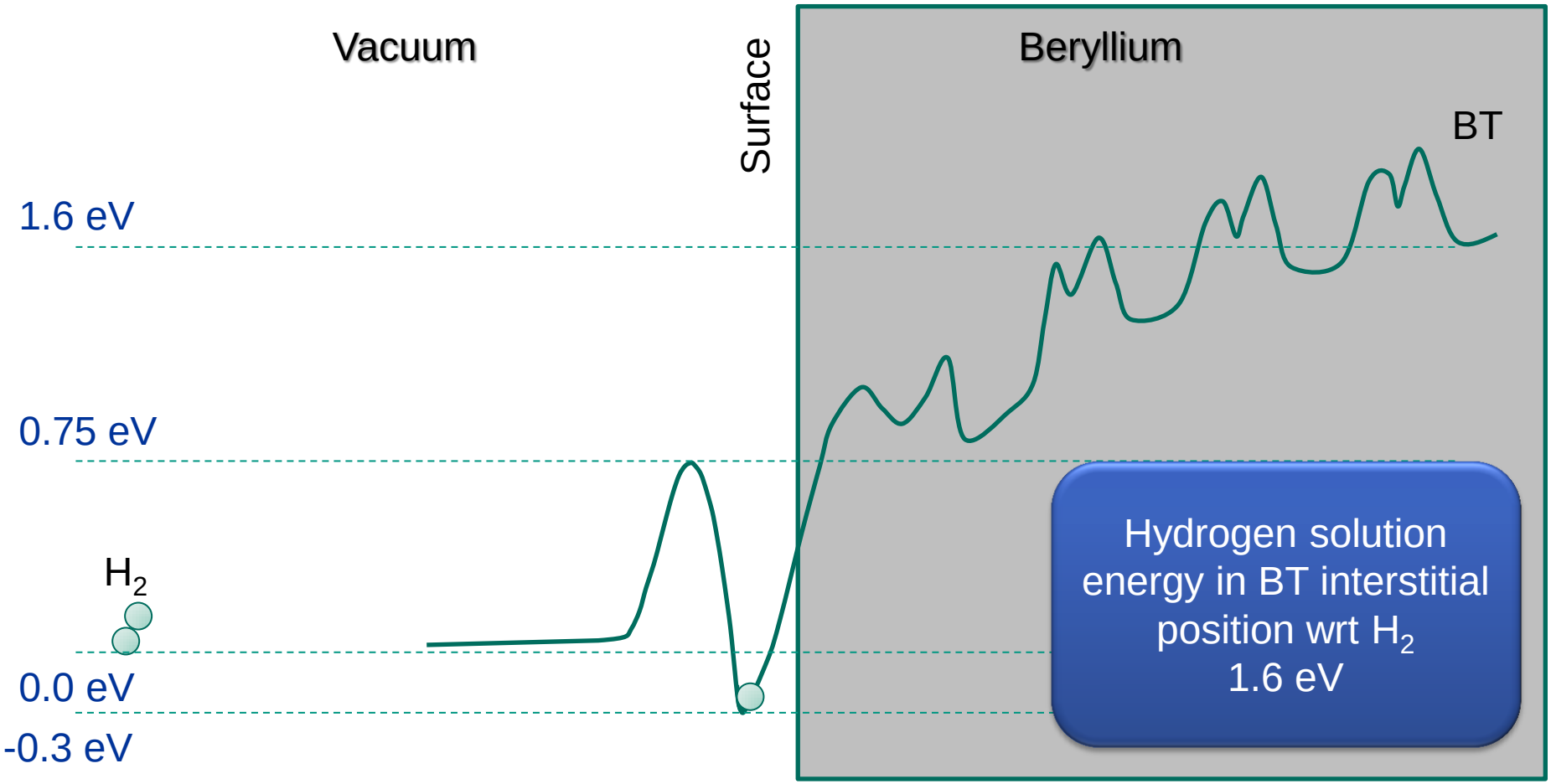




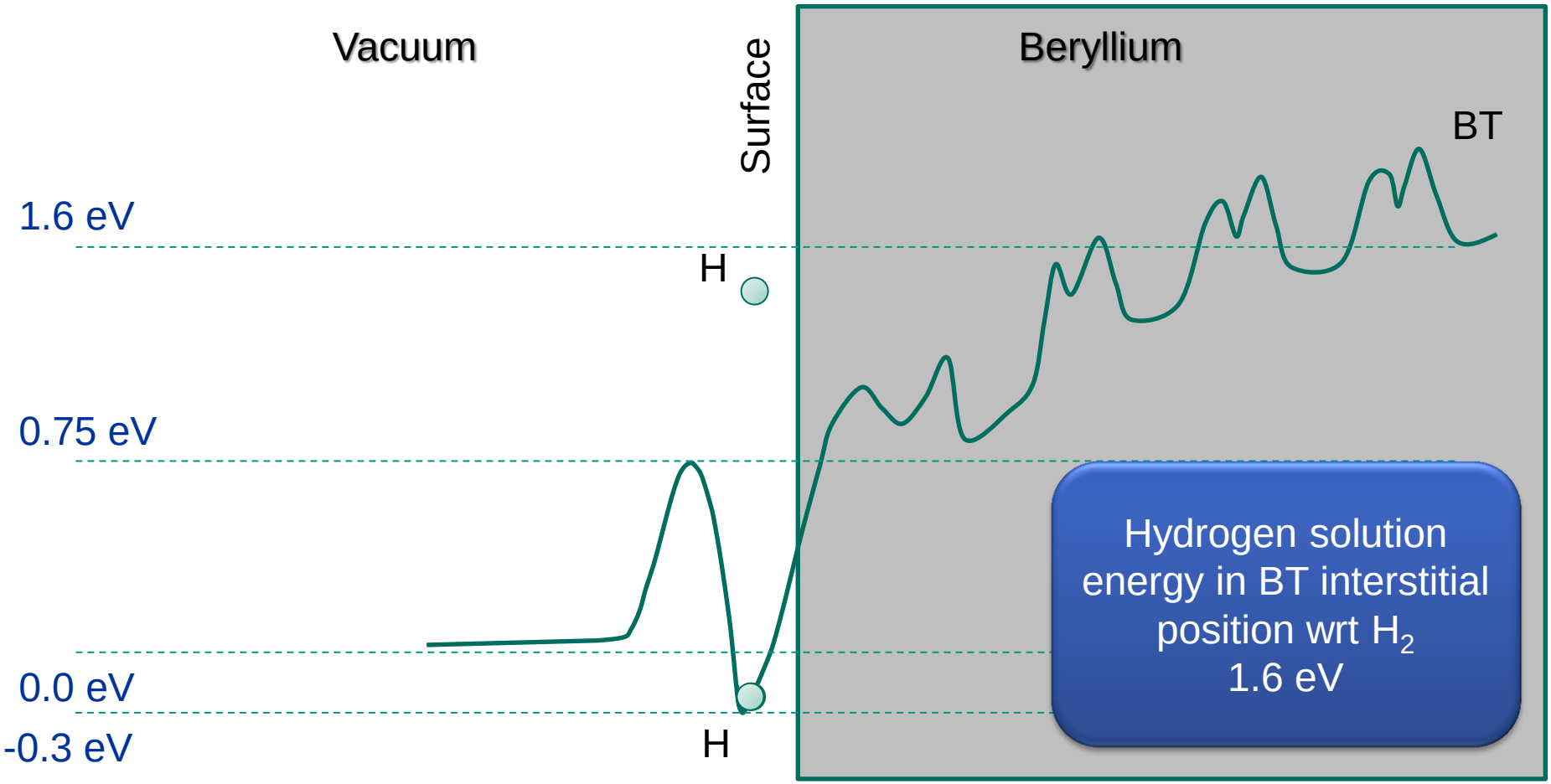
- At surface coverage of 0.5 ML severe surface reconstruction is observed, but no hydrogen desorption occurs.
- At surface coverage of 1.0 ML immediate associative desorption occurs.

⇒ Maximum critical H coverage of 0.5 ML

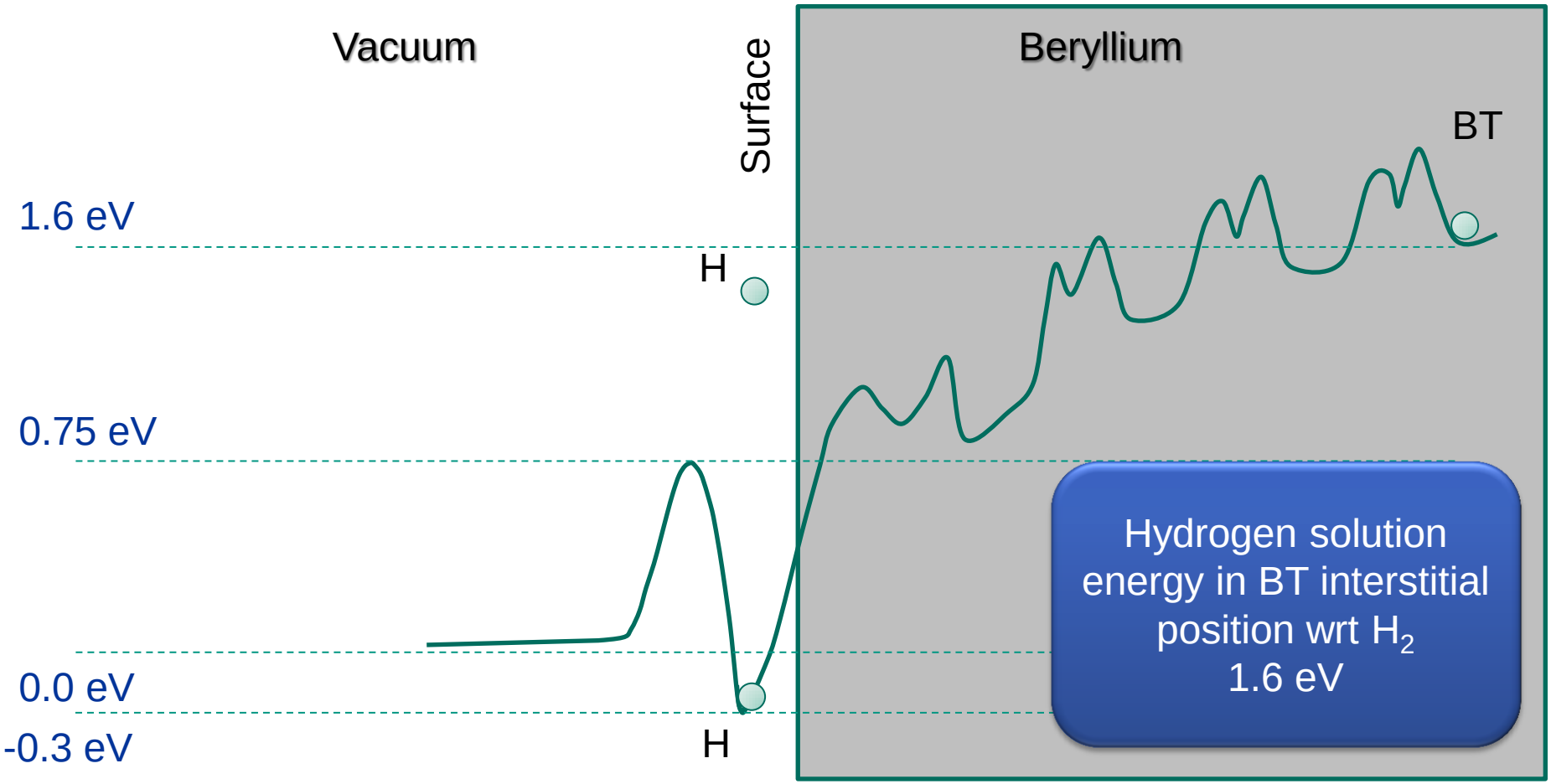
Energy landscape for H_2 absorption



Energy landscape for H_2 absorption



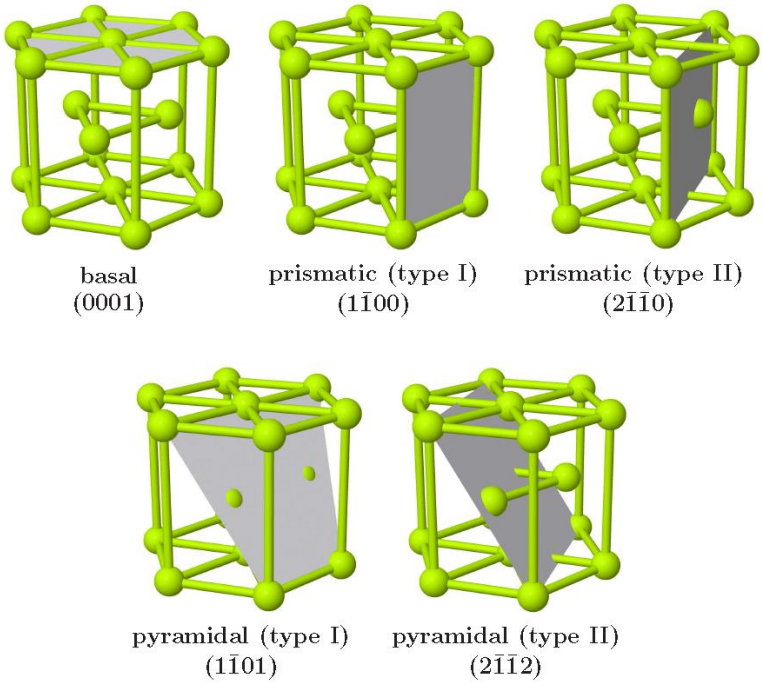
Energy landscape for H_2 absorption

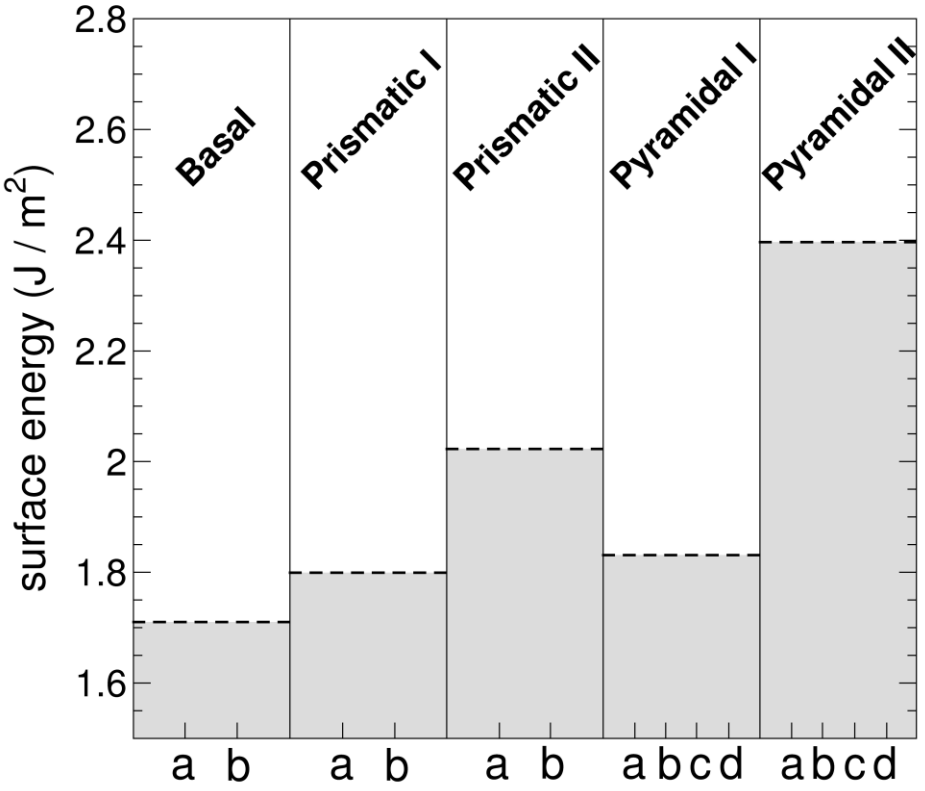


Outline

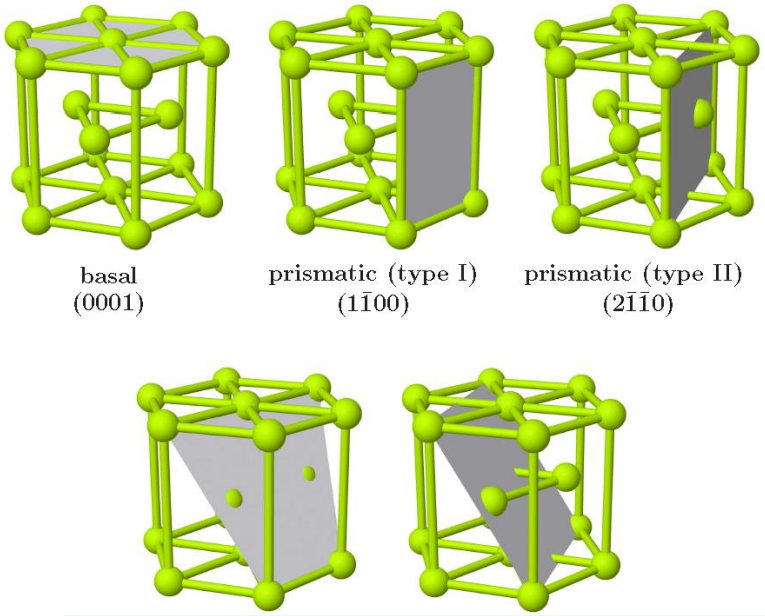
- Beryllium in Fusion Reactor
  - Be as plasma facing material
  - Be in T-breeding pebble bed
- Simulation method
- Adsorption and desorption
  - H_2 dissociative adsorption on (0001)Be
  - Hydrogen surface adsorption sites
  - H_2 adsorption on precovered surface
  - Hydrogen interaction on Be surface
  - Hydrogen associative desorption
  - Hydrogen absorption in bulk
- Surface energy modification
  - Clean surface energies
  - Surface energy with hydrogen
  - Faceting of H-covered bubble
- Conclusions

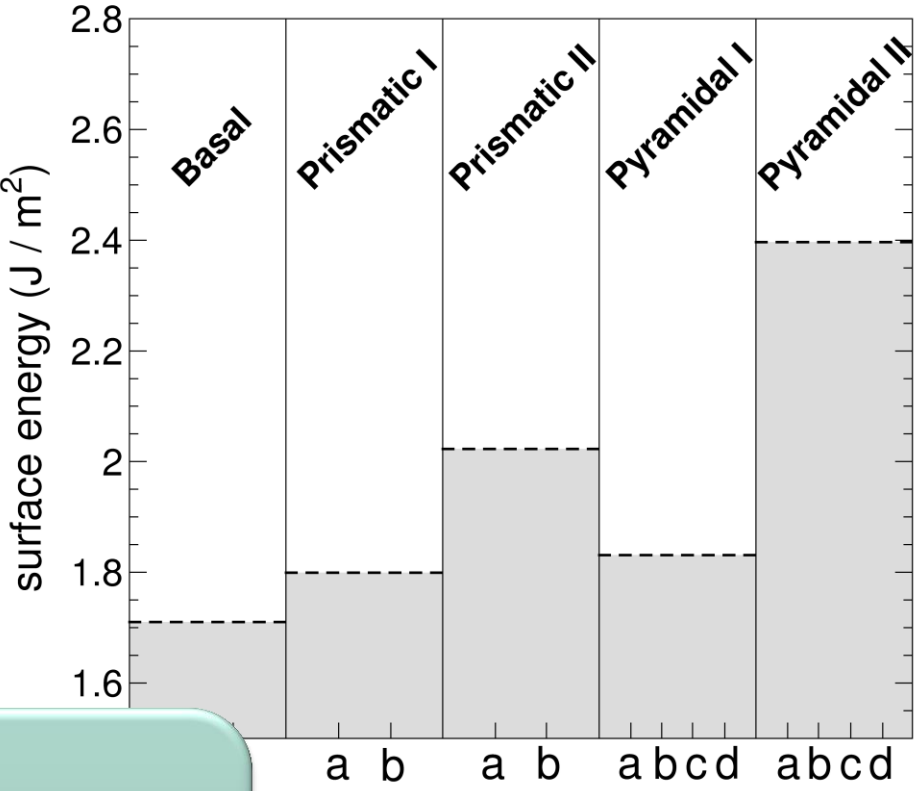
Be principal surfaces





Be principal surfaces



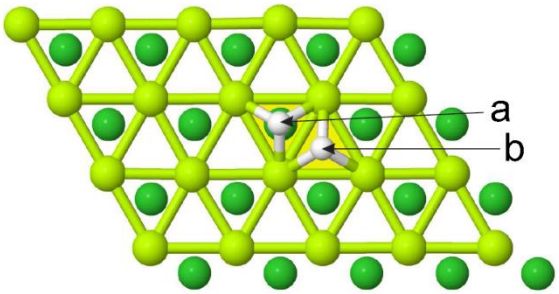


The lowest surface energy has

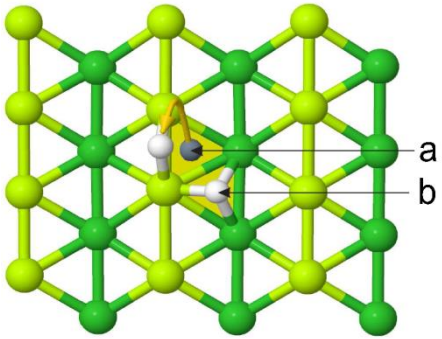
- basal (0001) plane,
- followed by prismatic I (1$\bar{1}$00) and
- pyramidal II ($\bar{2}$112) surfaces

The last two being very close in energy.

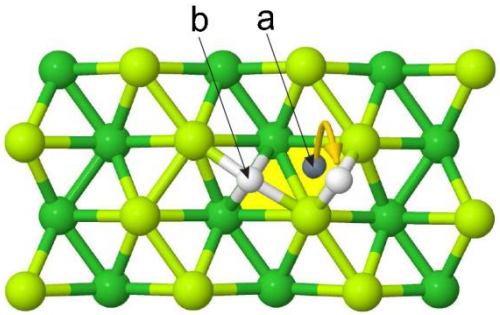
H adsorption sites on Be principal surfaces



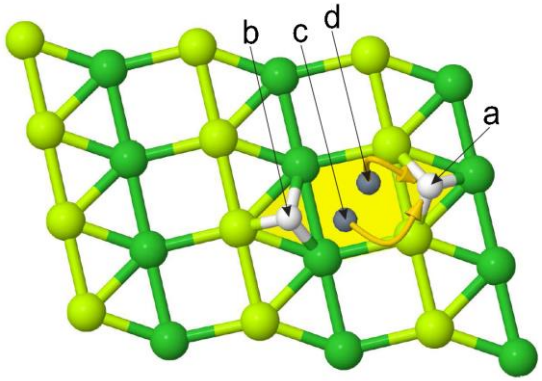
basal
(0001)



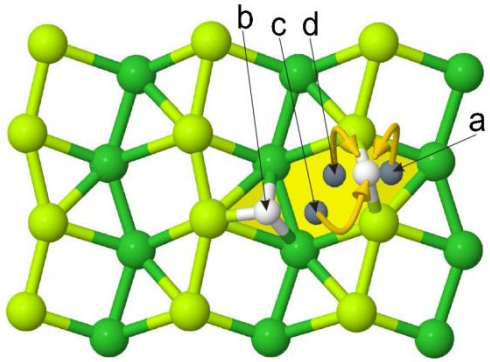
prismatic (type I)
$(1\bar{1}00)$



prismatic (type II)
$(2\bar{1}\bar{1}0)$

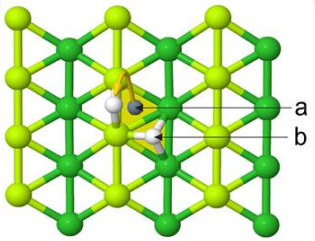


pyramidal (type I)
$(1\bar{1}01)$

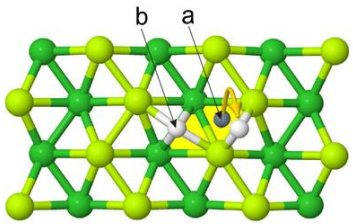


pyramidal (type II)
$(2\bar{1}\bar{1}2)$

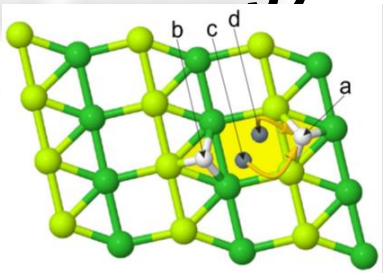
Adsorbed hydrogen modifies surface energy



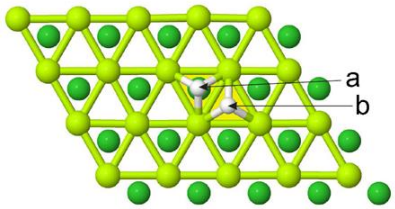
prismatic (type I)
$(1\bar{1}00)$



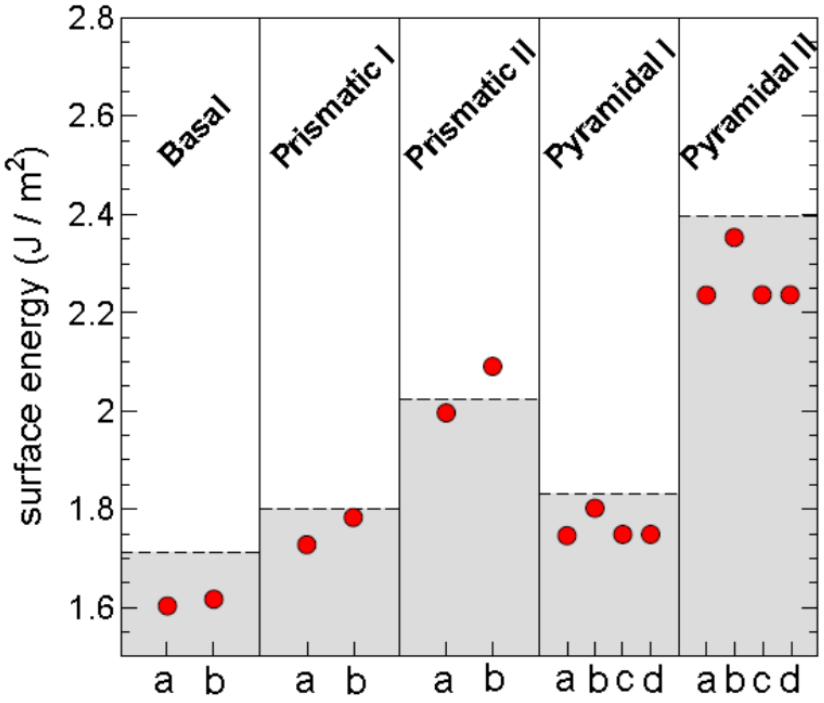
prismatic (type II)
$(2\bar{1}\bar{1}0)$

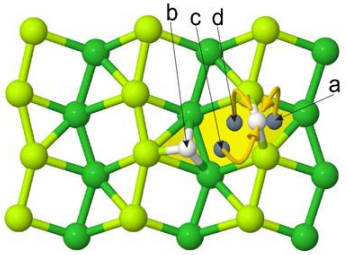


pyramidal (type I)
$(1\bar{1}01)$



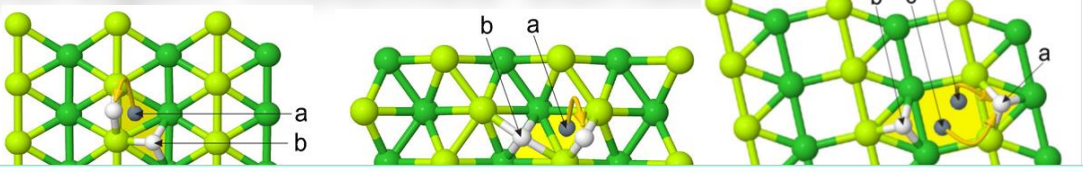
basal
(0001)



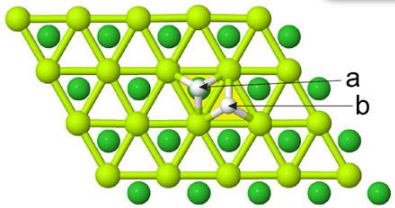


pyramidal (type II)
$(2\bar{1}\bar{1}2)$

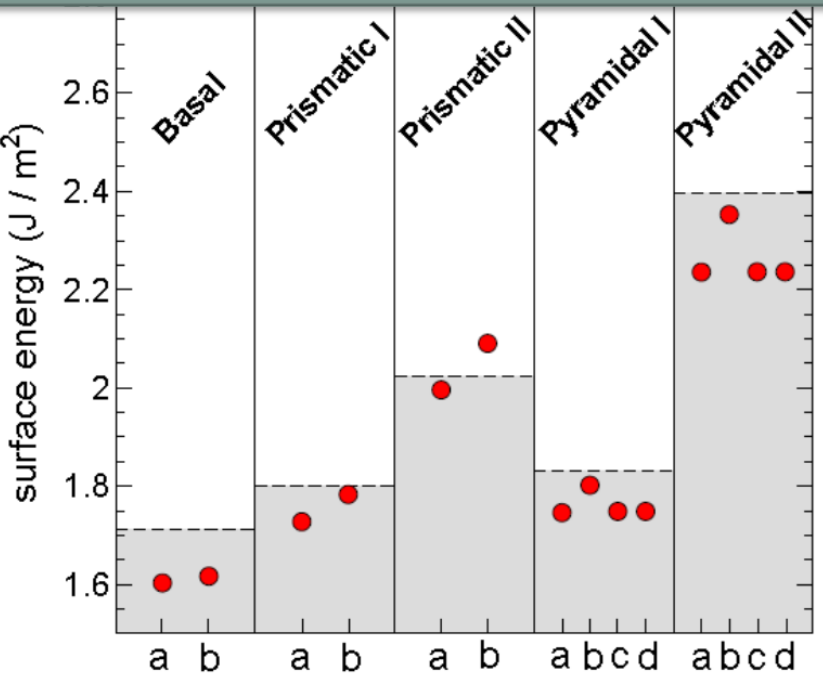
Adsorbed hydrogen modifies surface energy

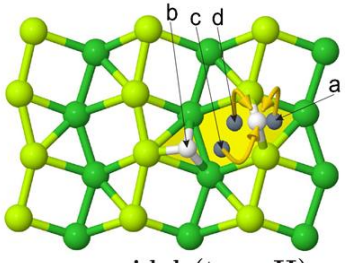


Single hydrogen atom adsorption results in notable decrease of surface energy in most of the cases.



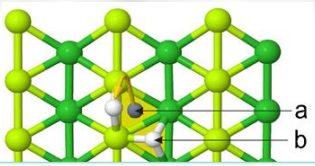
basal
(0001)

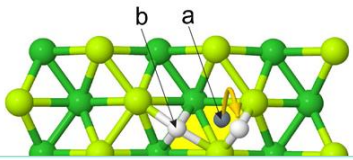


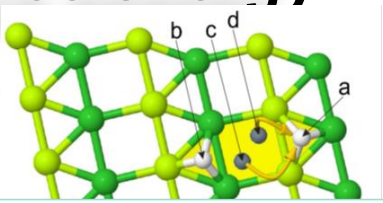


pyramidal (type II)
$(2\bar{1}\bar{1}2)$

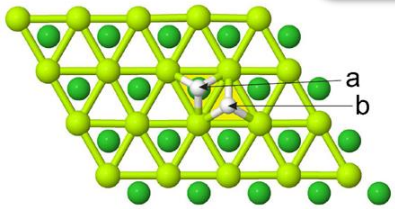
Adsorbed hydrogen modifies surface energy



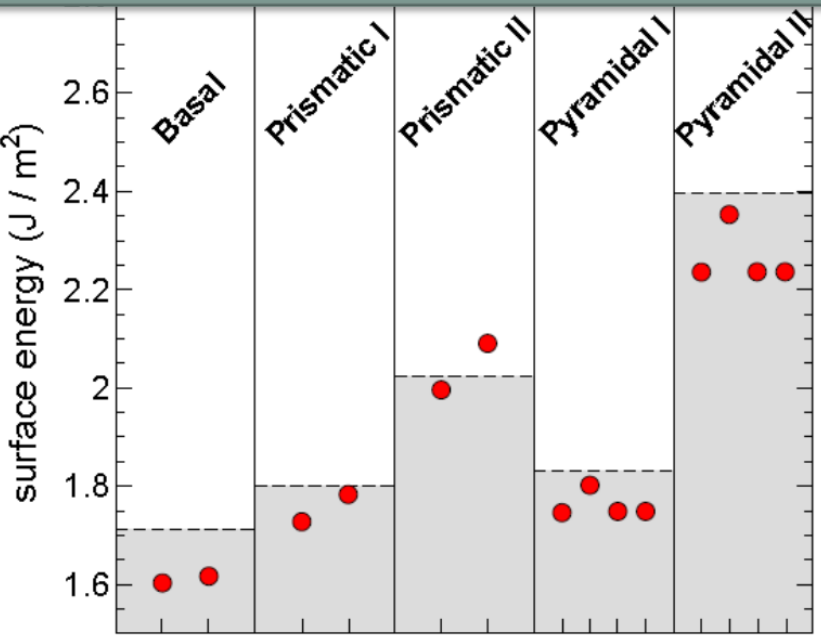


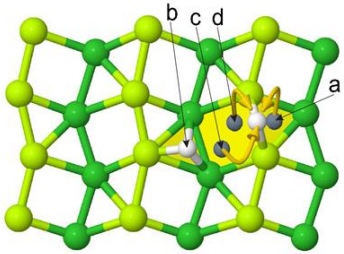


Single hydrogen atom adsorption results in notable decrease of surface energy in most of the cases.



basal
(0001)

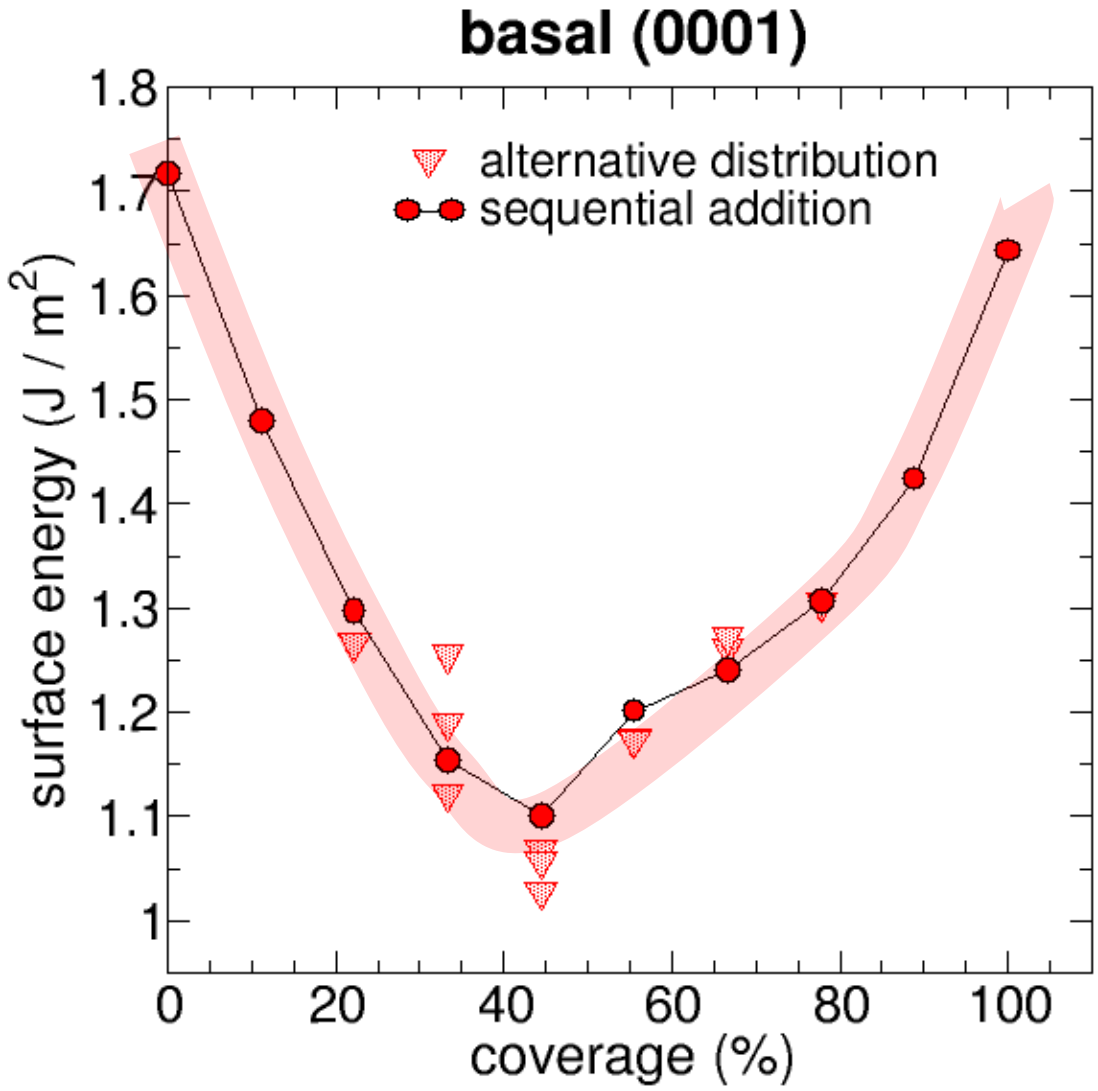




pyramidal (type II)
$(2\bar{1}\bar{1}2)$

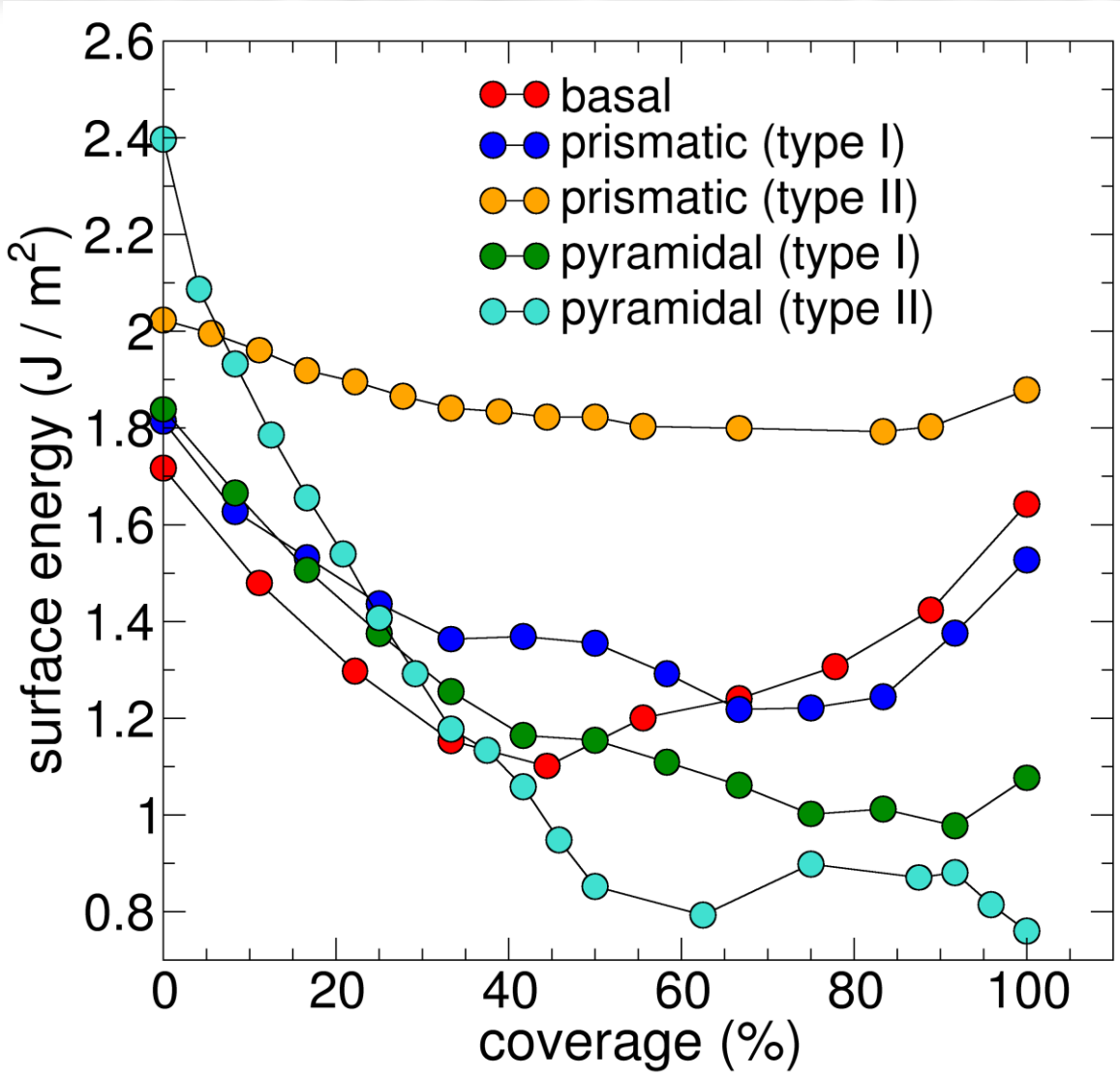
How multiple hydrogen adsorption would affect the surface energy?

Adsorbed hydrogen modifies surface energy



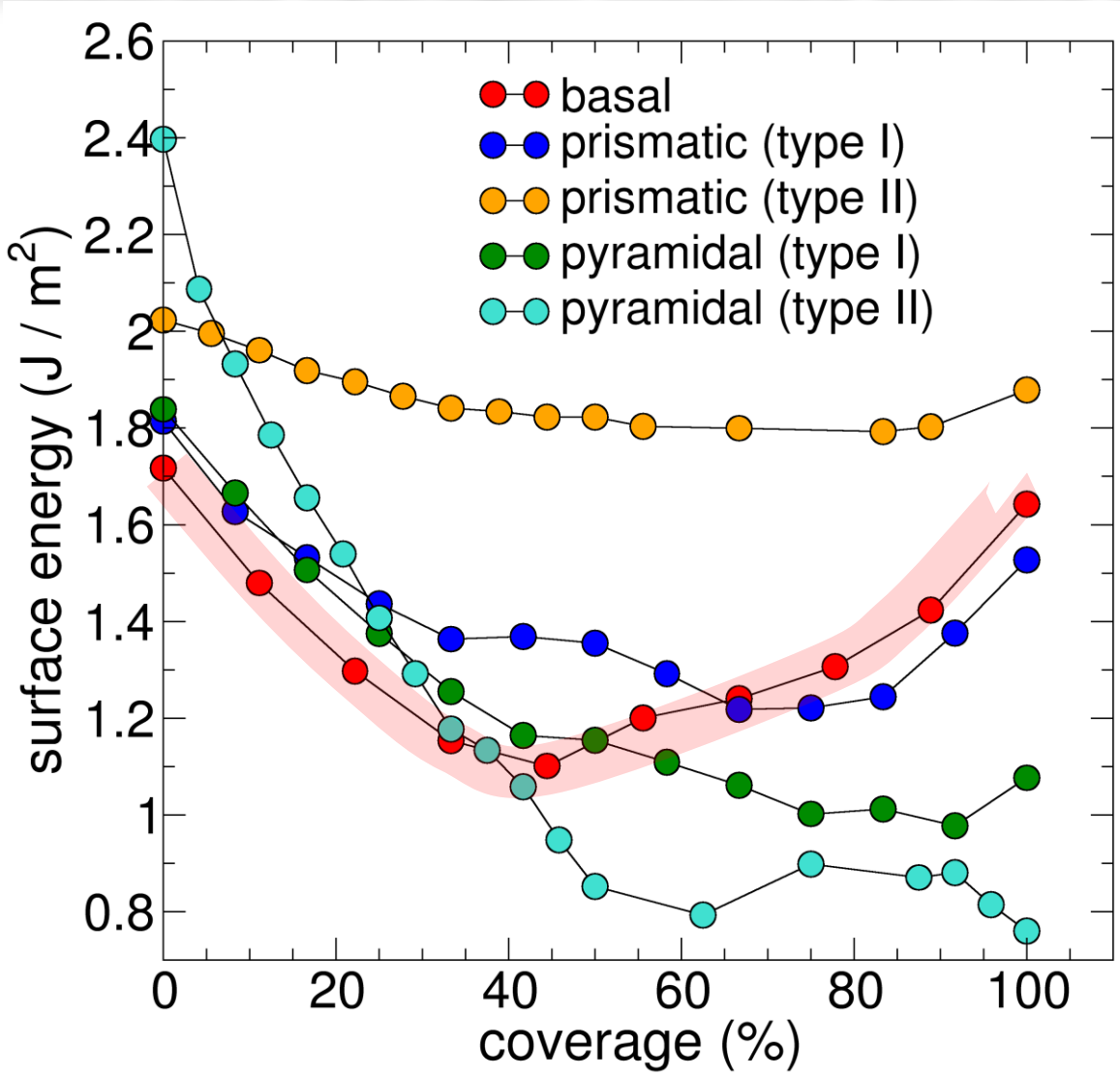
- At low coverage:
  Decrease of E_{surf} due to single H adsorption
- At high coverage:
  Increase of E_{surf} due to H-H repulsion

Adsorbed hydrogen modifies surface energy



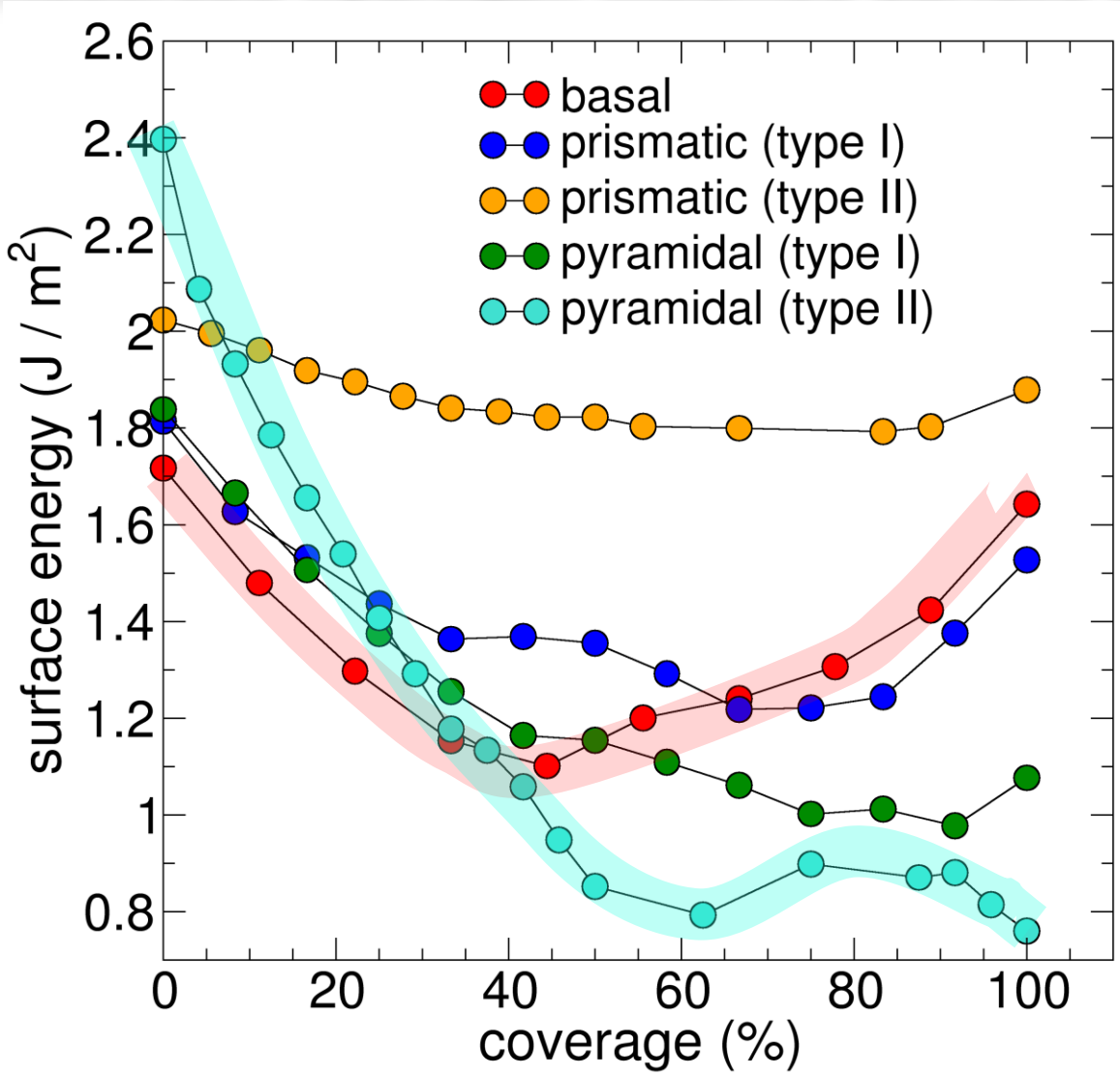
- At low coverage: Decrease of E_{surf} due to single H adsorption
- At high coverage: Increase of E_{surf} due to H-H repulsion

Adsorbed hydrogen modifies surface energy



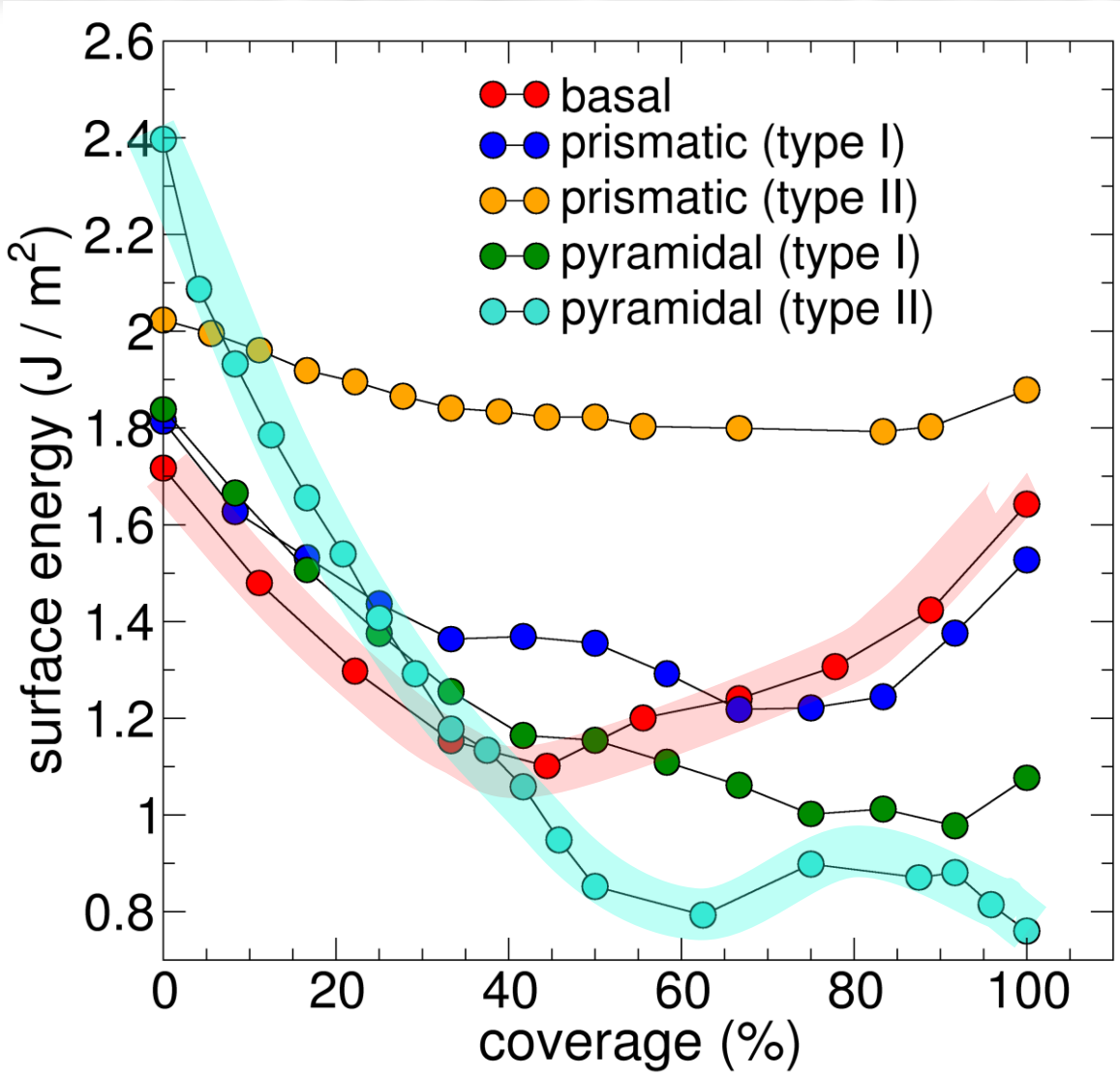
- At low coverage: Decrease of E_{surf} due to single H adsorption
- At high coverage: Increase of E_{surf} due to H-H repulsion

Adsorbed hydrogen modifies surface energy



- At low coverage: Decrease of E_{surf} due to single H adsorption
- At high coverage: Increase of E_{surf} due to H-H repulsion

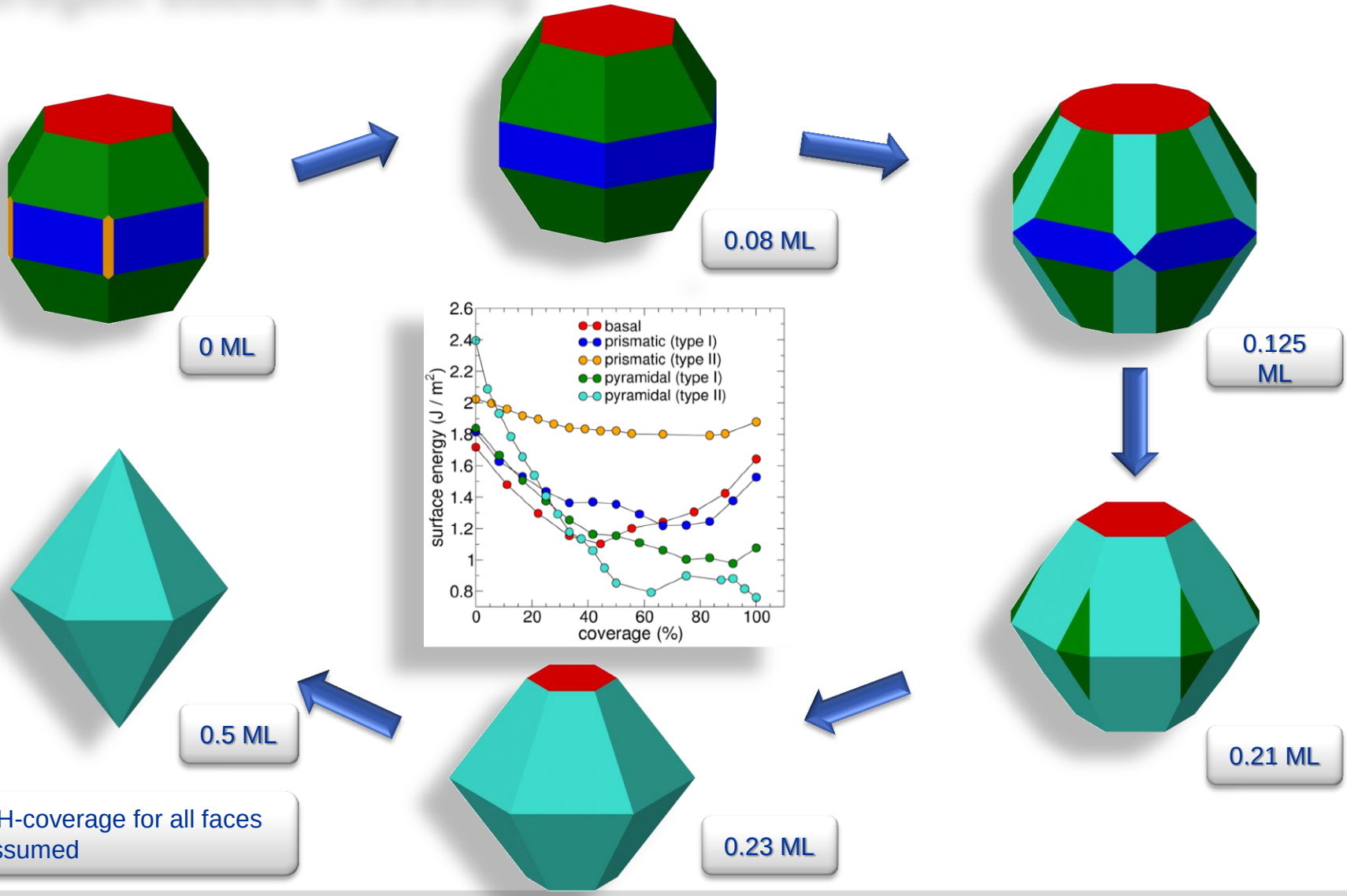
Adsorbed hydrogen modifies surface energy



- At low coverage:
  Decrease of E_{surf} due to single H adsorption
- At high coverage:
  Increase of E_{surf} due to H-H repulsion

$\Rightarrow$ Complex modification of hydrogen-filled gas bubble faceting

Hydrogen bubble faceting

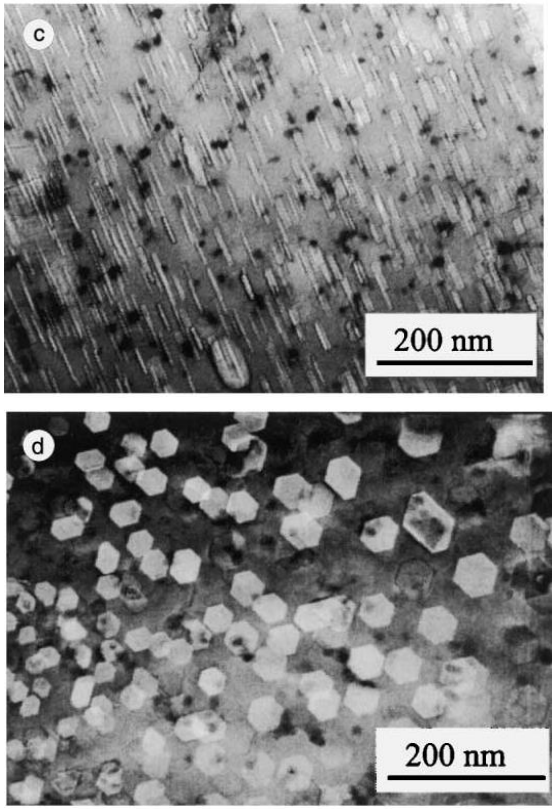


Equal H-coverage for all faces was assumed

Shape of gas bubbles in Be

n-irradiated (He-bubbles)

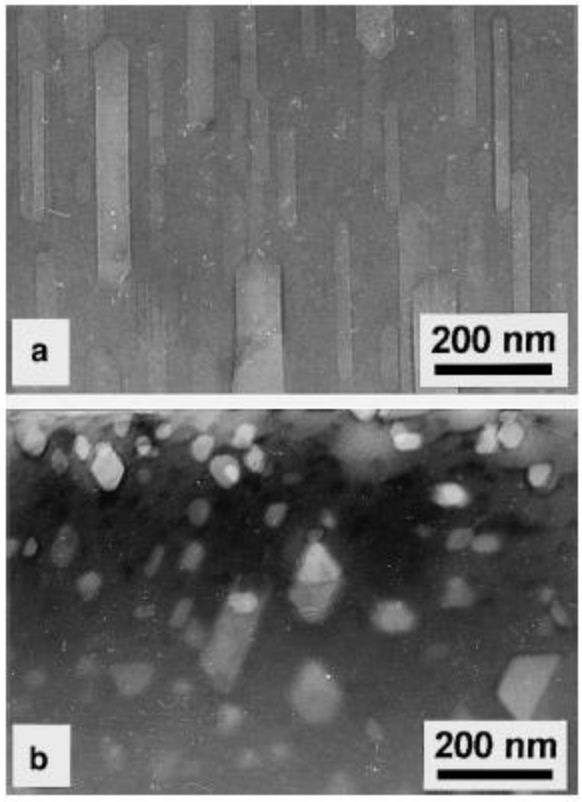
<0001>



V. Chakin, Z. Ostrovsky, J. Nucl. Mater. **307–311** (2002) 657–663

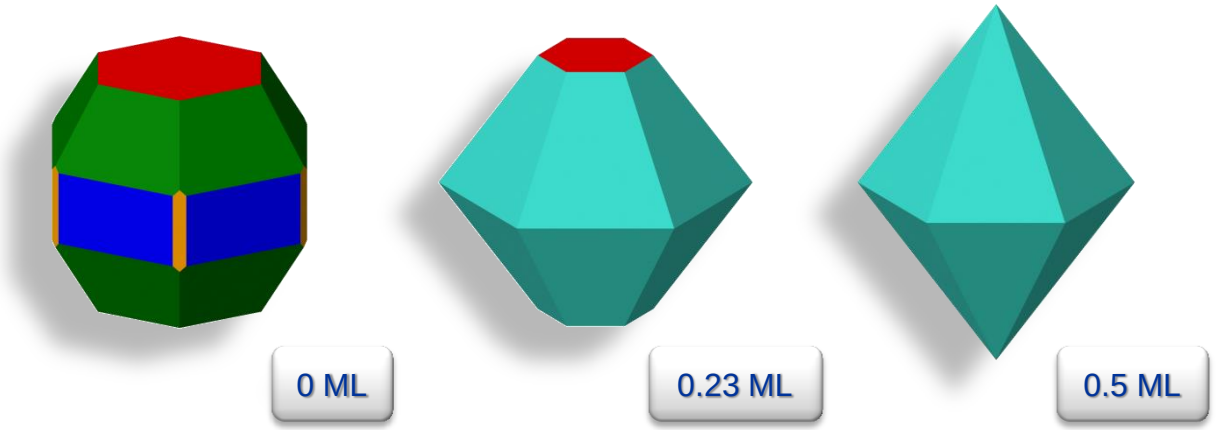
H-implanted (H-bubbles)

<0001>

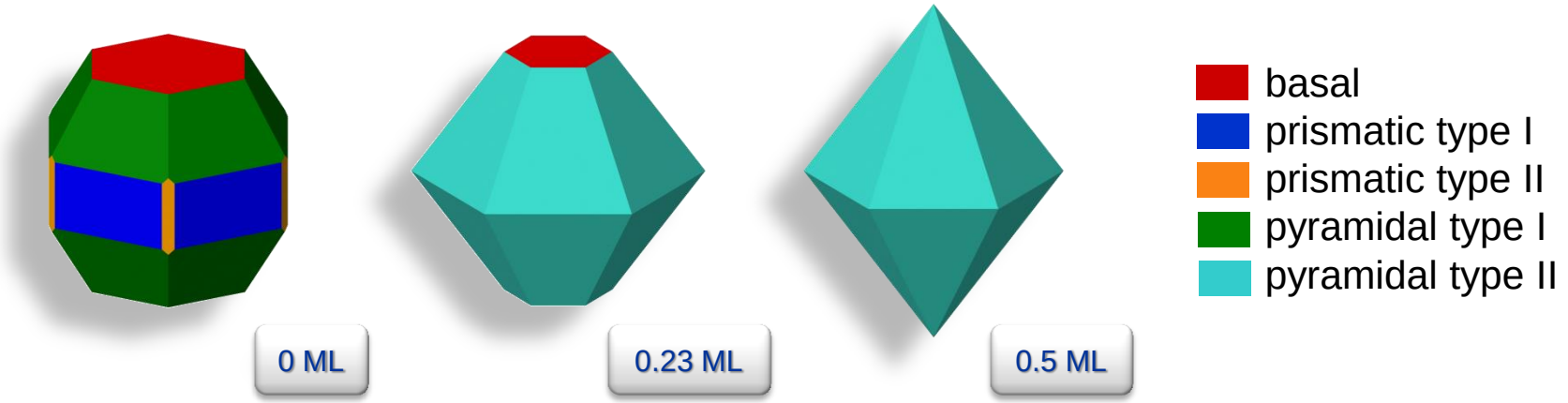


S.P. Vagin et al. J. Nucl. Mater. **258-263** (1998) 719-723

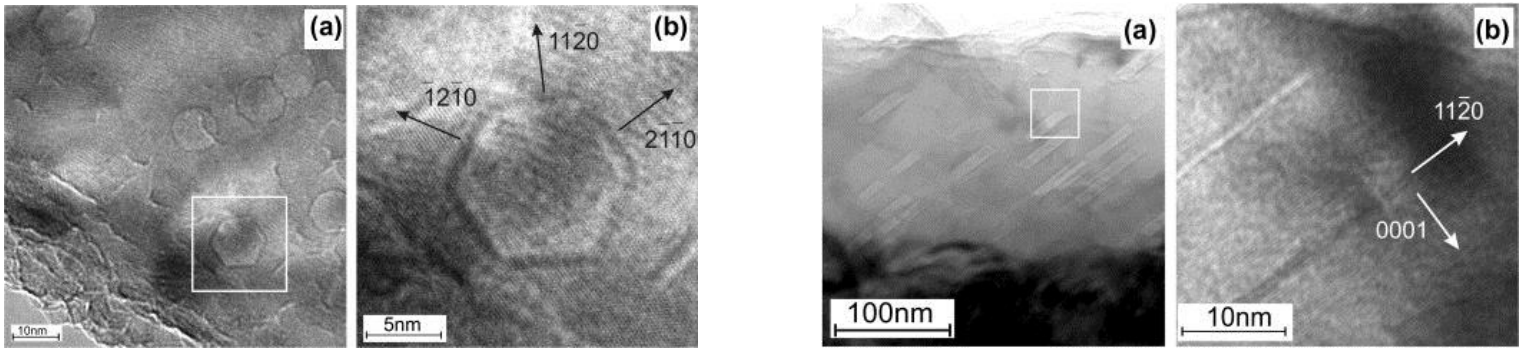
Equilibrium shape of bubbles (Wulff construction)



Equilibrium shape of bubbles (Wulff construction)



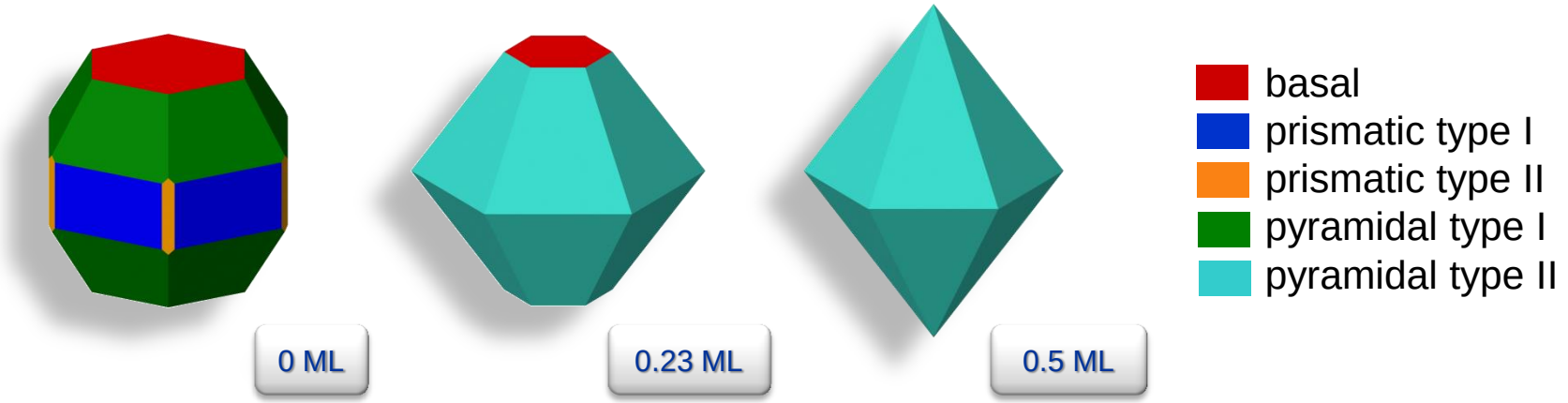
"Comparison" with experiment



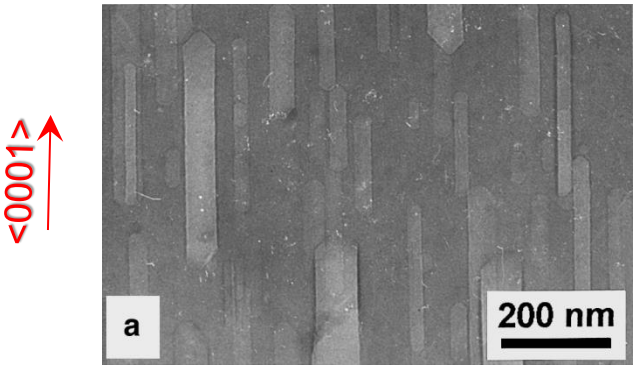
HRTEM investigations of a 8 nm bubble in a pebble irradiated at 686 K: the bubble with a regular hexagonal form and with an elongated shape

Taken from: M. Klimenkov et al. J. Nucl. Mat. 443 (2013) 409-413.

Equilibrium shape of bubbles (Wulff construction)



“Comparison” with experiment

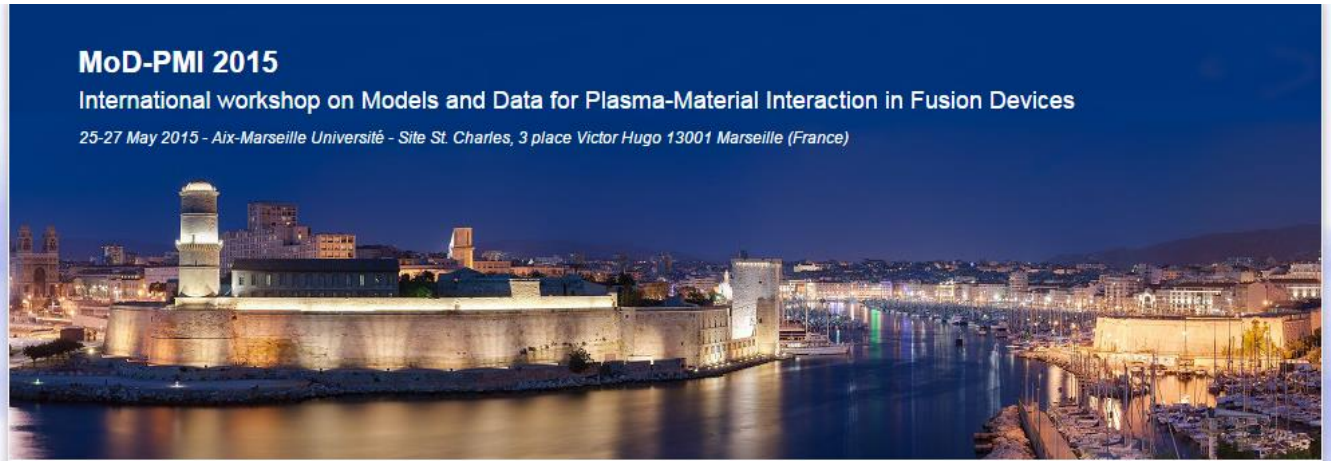


Cavities in hydrogen-implanted beryllium after annealing for 15 min at 600°C.

Taken from: S.P. Vagin et al. J. Nucl. Mat. 258-263 (1998) 719.

Conclusions

- H_2 adsorption and desorption on clean and H precovered Be(0001) surface has been studied
- Hydrogen atom is adsorbed without barrier, while ~0.8 eV should be overcome during H_2 molecule adsorption
- Hydrogen adsorption is completely blocked by H-coverage of 0.5 ML
- At least two vacant sites are necessary for H_2 adsorption on H precovered surface
- There is a critical H surface coverage of 0.5ML, above which non-activated H_2 desorption occurs
- H repulsion on the surface results in severe surface reconstruction
- Adsorbed H significantly modifies surface energy of various Be surfaces, so that equilibrium shape of H-covered bubble is changed drastically



Thank you for your attention!