First-principles and semi-empirical potential calculations of He-vacancy complexes in silicon

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Motivations

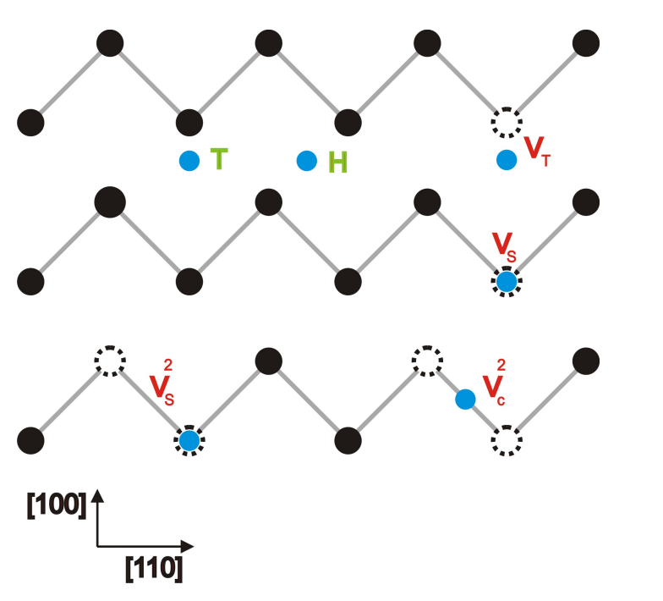
A light noble gas like He is characterized by several specific properties, such as the quasi absence of chemical reactivity. In fact the completeness of the valence electron shells makes the formation of chemical bonds very unlikely. However, despite this extremely low reactivity, it was shown to be able to induce significant structural modifications when it is introduced into many solid materials. The results appear to be similar in most of the cases. Depending on the conditions, He atoms tend to agglomerate, ultimately leading to the formation of cavities with disc or spherical shapes. The generally accepted driving force for this defect formation is the fact that He atoms are insoluble in most materials, their heat of solution being positive. Formed cavities can next be at the origin of several evolution mechanisms such as swelling, surface blistering, plane cleavage, which will irreversibly change the materials properties. This process can be clearly labelled ”multi-scale”, ranging from the formation of gas-filled cavities at the atomic scale to the possible exfoliation of the materials at the macroscale. Despite several dedicated works, the initial mechanisms leading to cavity formation are still not well characterized. Our investigations aim at providing new insights for a better understanding.

Methods

Density Functional Theory (DFT) + Perdew-Burke-Ernzerhof (PBE) GGA
- Pwscf code from the Quantum Espresso package
- Ultrasoft Vanderbilt pseudopotentials
- 3x3x3 k-points grid (64 atoms bulk), 2x2x2 (216 atoms bulk), and Γ (144 atoms, 9 layers surface system)
- Plane-wave cutoff energy of 30 Ry (bulk calculations) or 10 Ry (slab calculations)
- Optimized lattice constant of Si a_0= 5.468 Å (close to the experimental value of 5.43 Å)
- Nudged Elastic Band (NEB) technique for Minimum Energy Path (MEP) determination

Classical molecular dynamics with a home-designed interatomic potential

Behavior of one He in Si



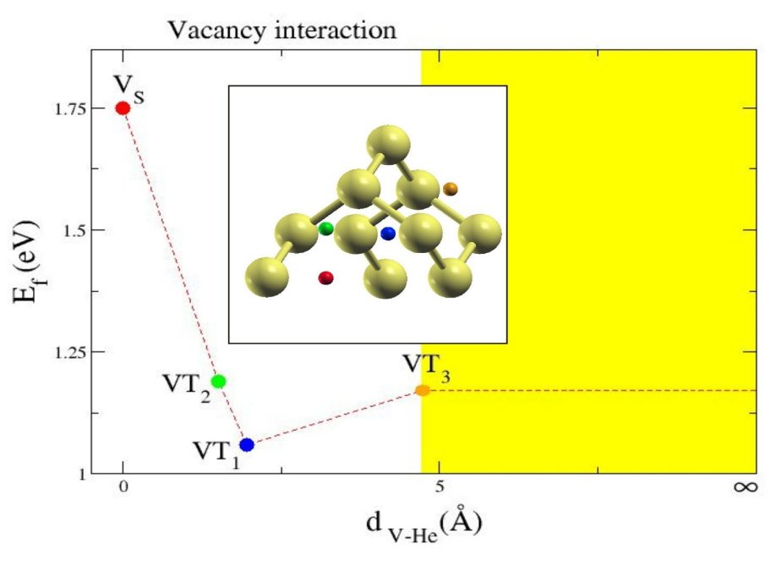
This figure represents several possible locations for He in Si, in presence or not of mono- (V) and di-vacancies (V_2), shown in the plane of the [110] zigzag chains of the Si lattice.

He – V interaction

The high formation energy for He in V could be due to an electronic repulsion between the He 1s electrons and the high electronic density in the vacancy center. Another explanation is that He prevents the Si vacancy reconstruction.

A slight shift in position induces the He migration in the vicinity of the V center. The interaction could be weakly attractive (left figure), or negligible depending on the accuracy of the simulations.

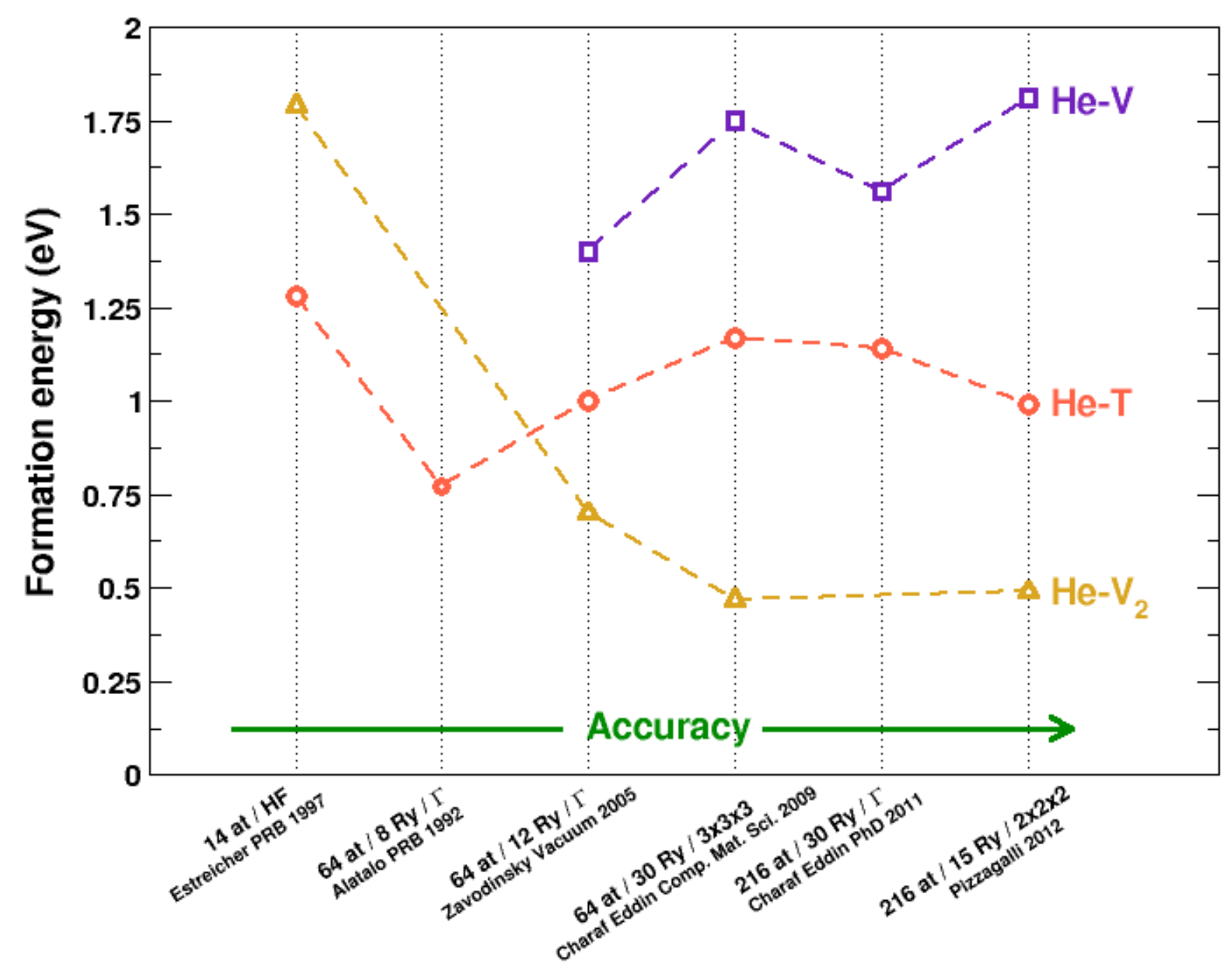
The formation of He-V complexe is then highly unlikely.



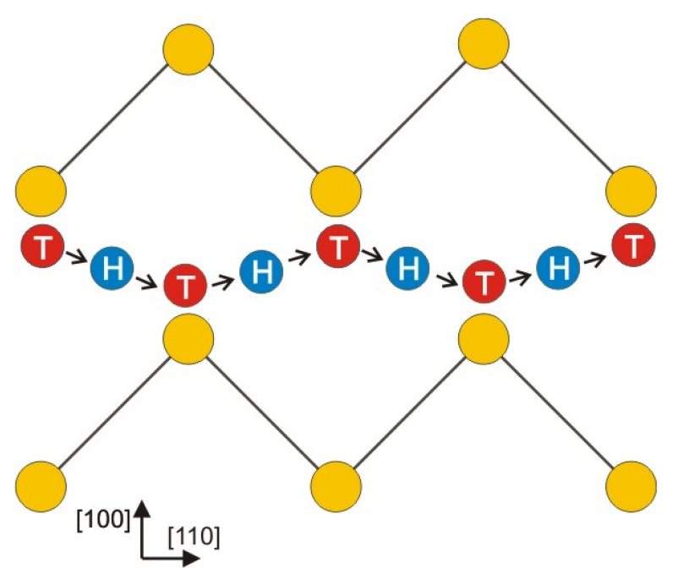
Stability

Our calculations yield the following results :

- He interstitials : the most stable configuration corresponds to He in a tetrahedral configuration. The hexagonal site is weakly stable, and a bond-centered configuration is not energetically favored. The accurate value of formation energy is 1.0 eV.
- He-V : He is only weakly stable at a vacancy location. The formation energy is much higher than in interstitial configuration
- He-V_2 : the most stable configuration corresponds to He in the middle of the divacancy, with a low formation energy



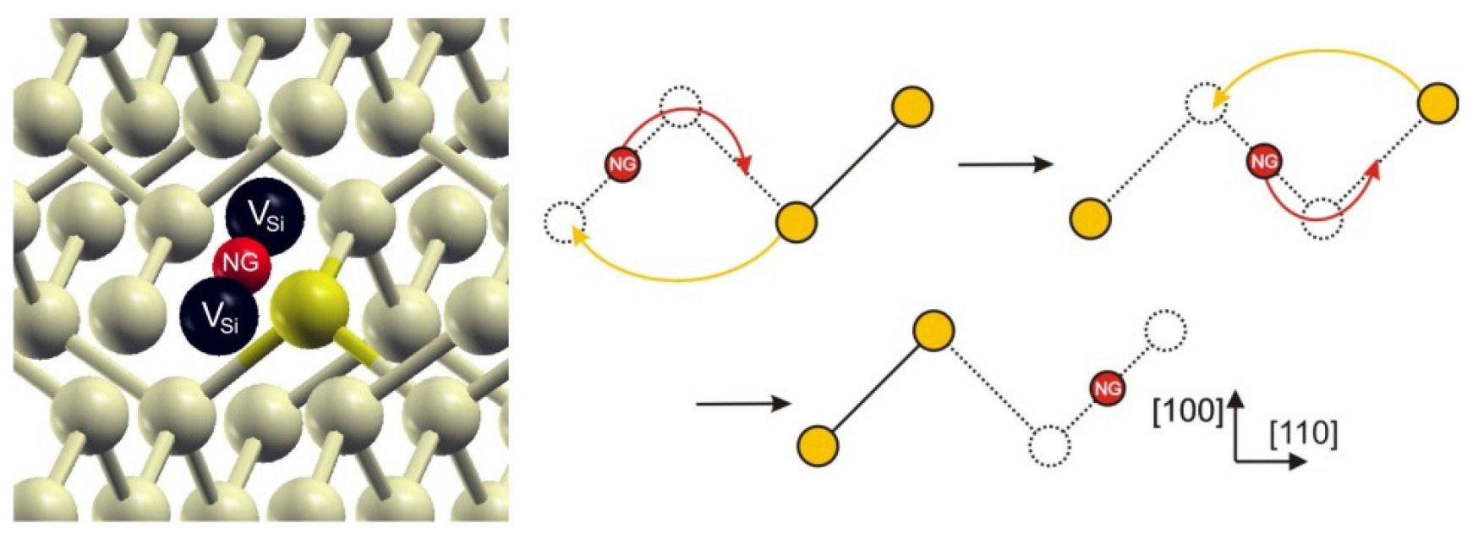
He and He – V_2 mobility



The migration of interstitial He occurs through successive visits of tetrahedral and hexagonal sites (H is almost a saddle point). Our computed migration energy is 0.65-0.70 eV depending on the accuracy. This value is in good agreement with permeation experiments by Jung *et al.* (0.80 eV, [NIMB 1994]), and confirms the earlier calculations from Alatalo *et al.* (0.84 eV, [PRB 1992]).

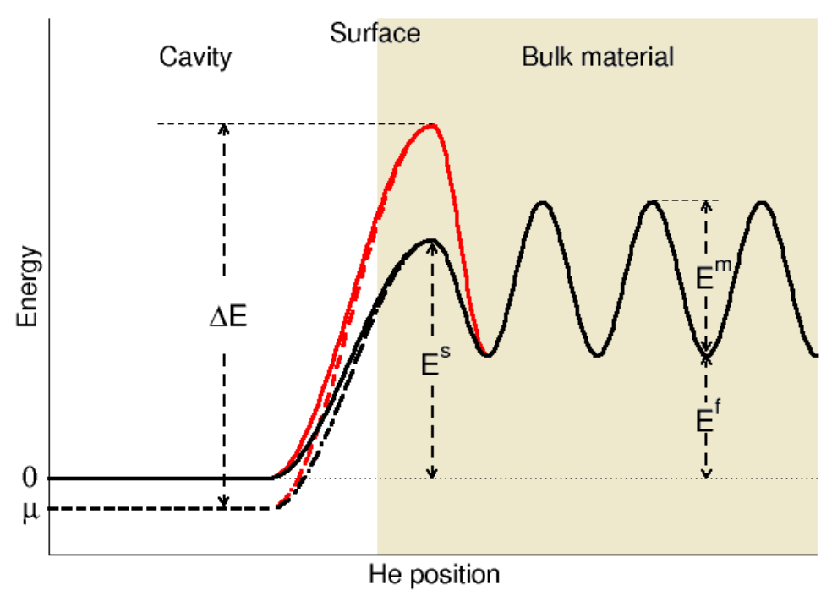
The migration of the He-V_2 complex has never been investigated. We computed the most simple mechanism, where there is a concerted motion of He and of one of the Si atom (see picture below). Our calculated activation energy is 2.50 eV.

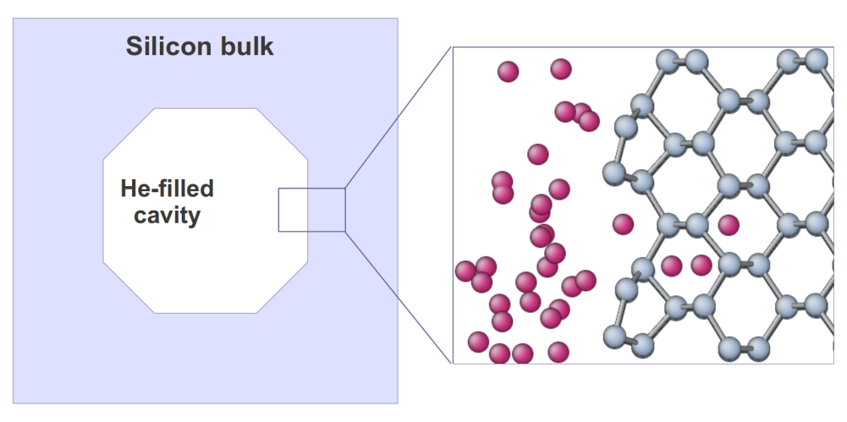
This high energy implies that it is energetically more favorable for He to dissociate from the vacancy and to migrate as an interstitial than to move as a He-V_2 complex. In fact, in that case the activation energy is about 1.25 eV. This suggests that this mechanism is occuring in earlier experiments from Van Wieringen *et al.* [Physica 1956], who found an activation energy for migration of 1.35 eV. It also tends to suggest that in the first step of bubble formation, Ostwald-Rippening would be preferred as a growth mechanism compared to migration of He-V complexes.



He desorption from a bubble in Si

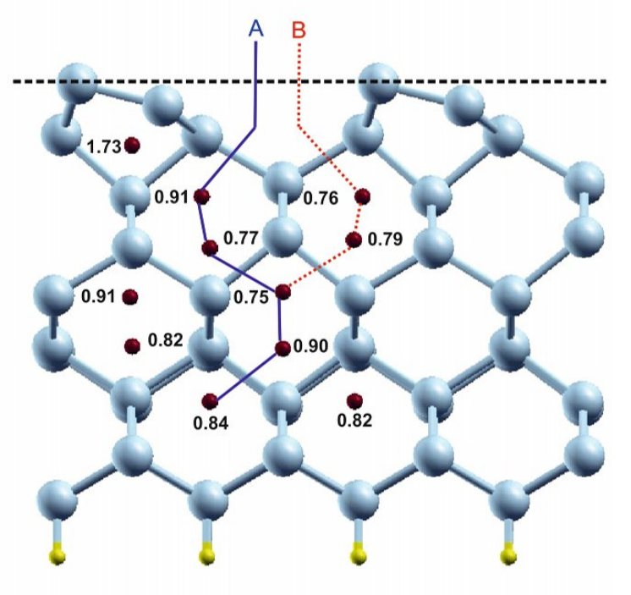
We investigated the desorption process at the atomic scale level of one He leaving a cavity, taking into account the effect of pressure and temperature on the desorption energy (μ in the model below), as well as the possible influence of the cavity surface.



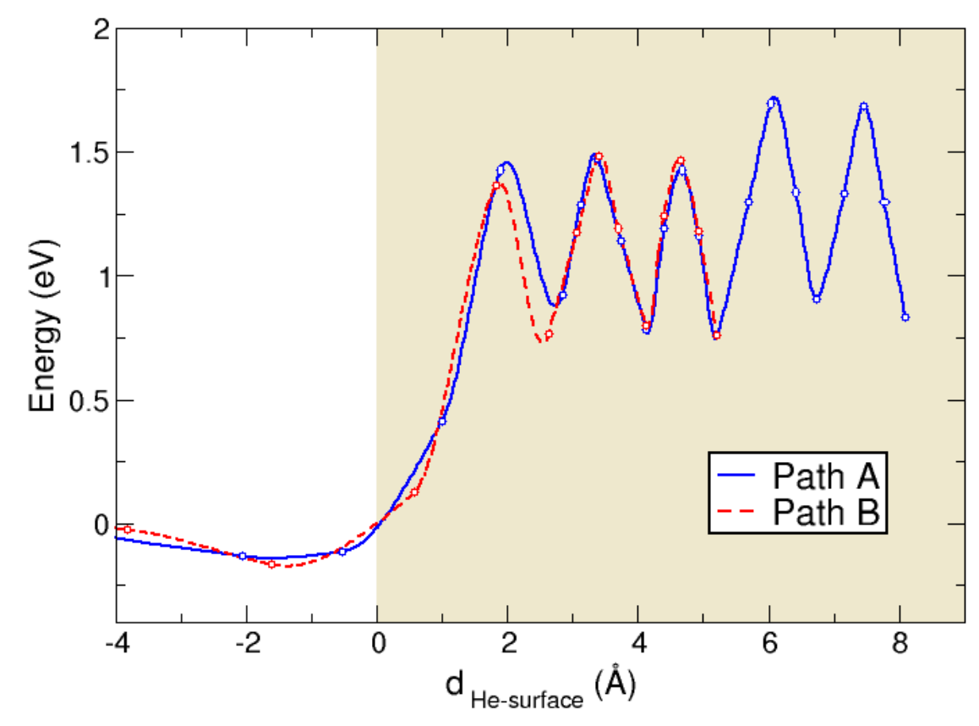


To perform our calculations within DFT framework, we model the cavity surface using a (001) surface slab model.

NEB DFT results



Two possible paths (above) have been found favorable for He migration from cavity to Si. The NEB computed energy variations show that the energy required for entering the surface is lower than the sum of the formation and migration energies for an interstitial He in bulk. Then, the cavity surface is not limiting desorption.



Taking into account pressure and He-density

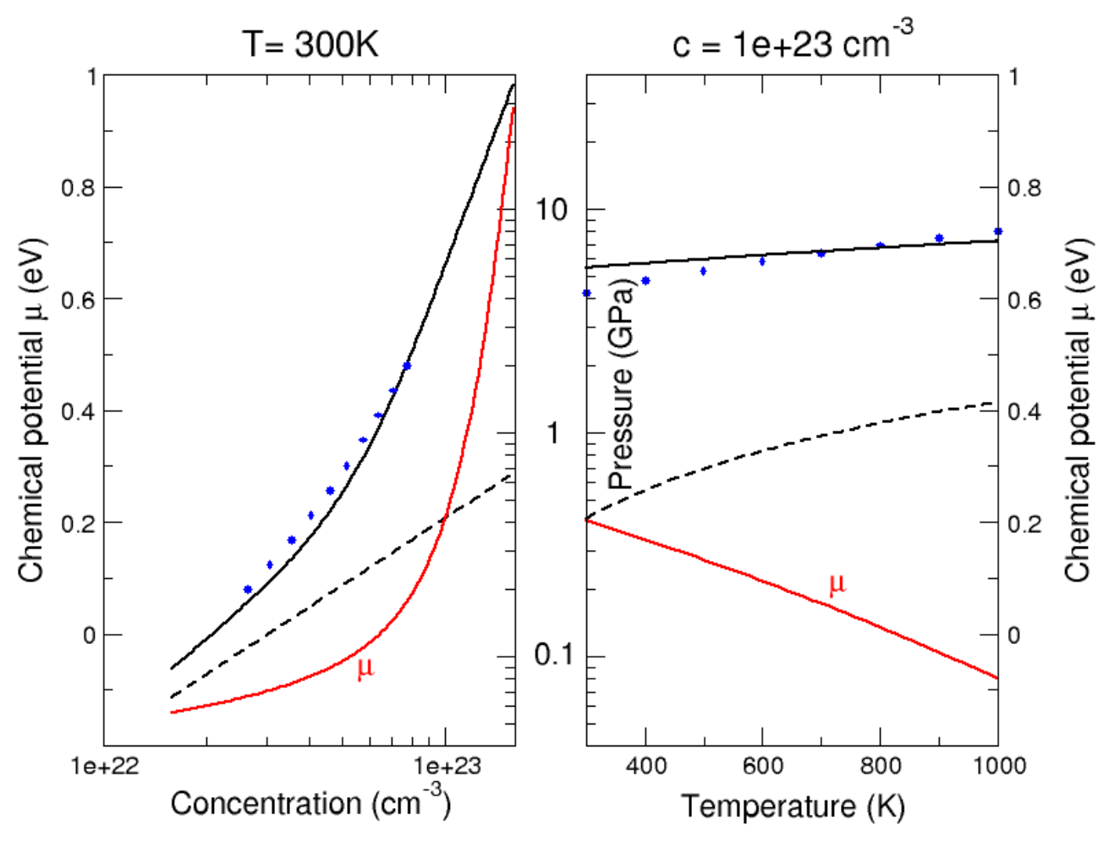
The activation energy for He to escape from the cavity is

$$\Delta E = E^f + E^m - \mu = E_H^f - \mu$$
$$\Delta E(T,P) = (E_H^f)_{T=0} + F(T) - \mu(T,P)$$
$$\Delta E(T,P) = 1.7\ eV + F(T) - \mu(T,P)$$

Vibrational contributions *F(T)* for He interstitials in Si are obtained with a simple harmonic oscillator

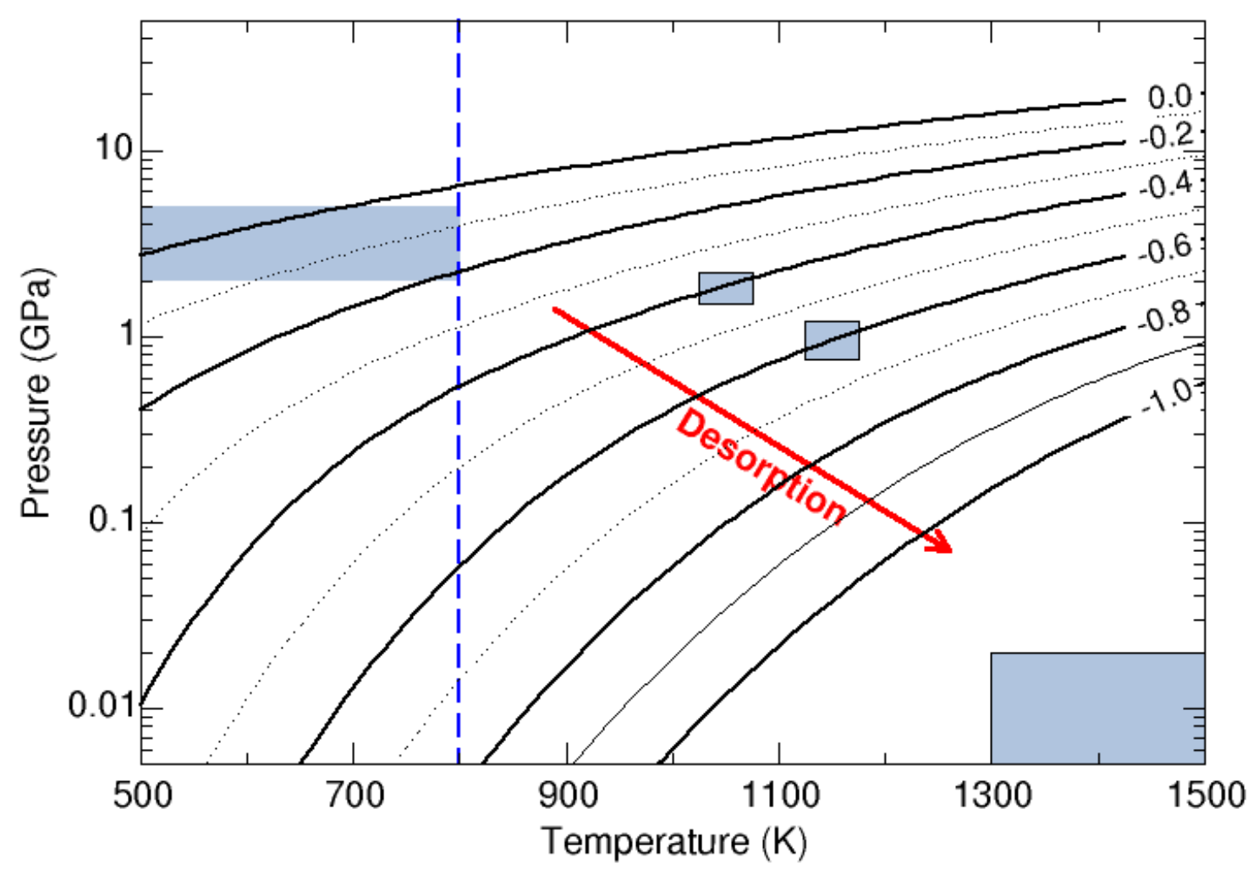
$$F(T) = 3kT \ln\left[\sinh\left(\frac{h\nu}{2kT}\right)\right]$$

The temperature and density dependent chemical potential μ of He in the cavity is computed thanks to the ultradense fluid model of Cerofolini *et al.* [Mat. Sci. Eng. Rep. 2000]. It is built from a vdW model, in which finite-size effects are included by associating a defined temperature and density dependent volume to each particle (the covolume), and by including the interaction energy between all particles.



Pressure calculation

Different (P,T) states of He in bubbles during desorption (blue shaded areas) are shown below. At temperatures below 800 K, no desorption occured and the pressure in bubble is in the 2-5 GPa range depending on the preparation conditions. At temperatures greater than about 1300 K, very few He is left in Si and there is a very low pressure in bubbles. At intermediate temperatures, the two small rectangles show the states corresponding to desorption measurements at 1050 K [Griffioen NIMB 1987], and 1150 K [Oliviero APL 2002]. The lines represent the isoenergy curves for μ (in eV per He atom) as a function of temperature and pressure.



Our model indicates that the maximum of desorption corresponds to a bubble pressure of 1-2 GPa.

Accumulation of He in Si

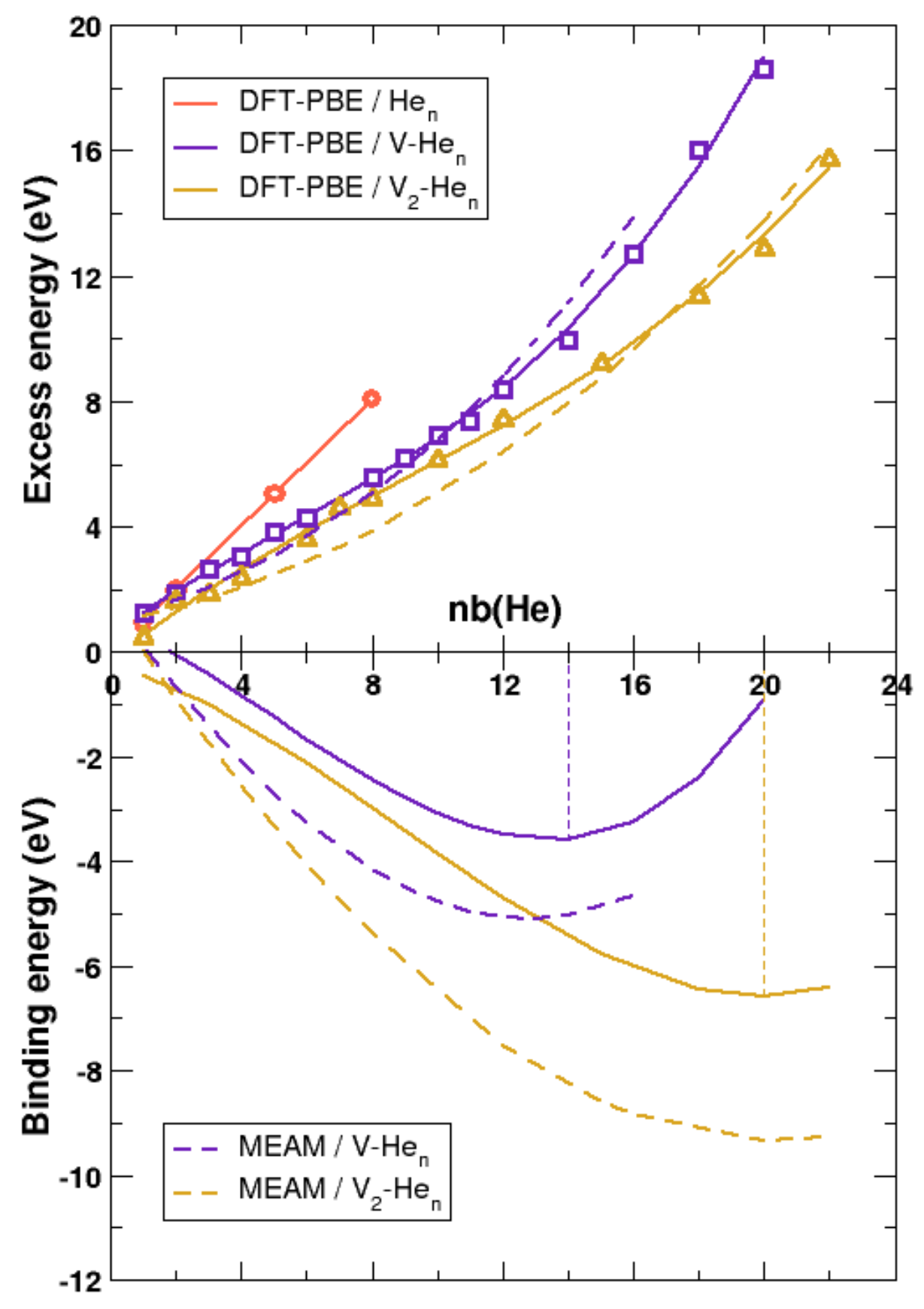
Investigating the properties of He_n-V_m complexes is difficult with DFT due to the fastly increasing number of possible configurations.

To overcome this issue, we designed an interatomic potential able to describe He-Si interactions. This potential is built according to the following rules :

- Use of the MEAM formalism. This is required for describing the repulsive nature of the vacancy center, which cannot be captured with a pair potential.
- Fit on the high pressure properties of He in solid state, from measurements, to describe the repulsive part of He-He interaction
- Fit on small molecules data obtained by the accurate Tang-Toennies potential [JCP 2003], to describe the attractive part of He-He interaction.
- Accurate description of the first-principles results obtained for one He (shown in the first part above)

The potential is then used to explore efficiently the potential energy surface of He_n-V_m complexes. The best configurations are then used as input for ab initio calculations.

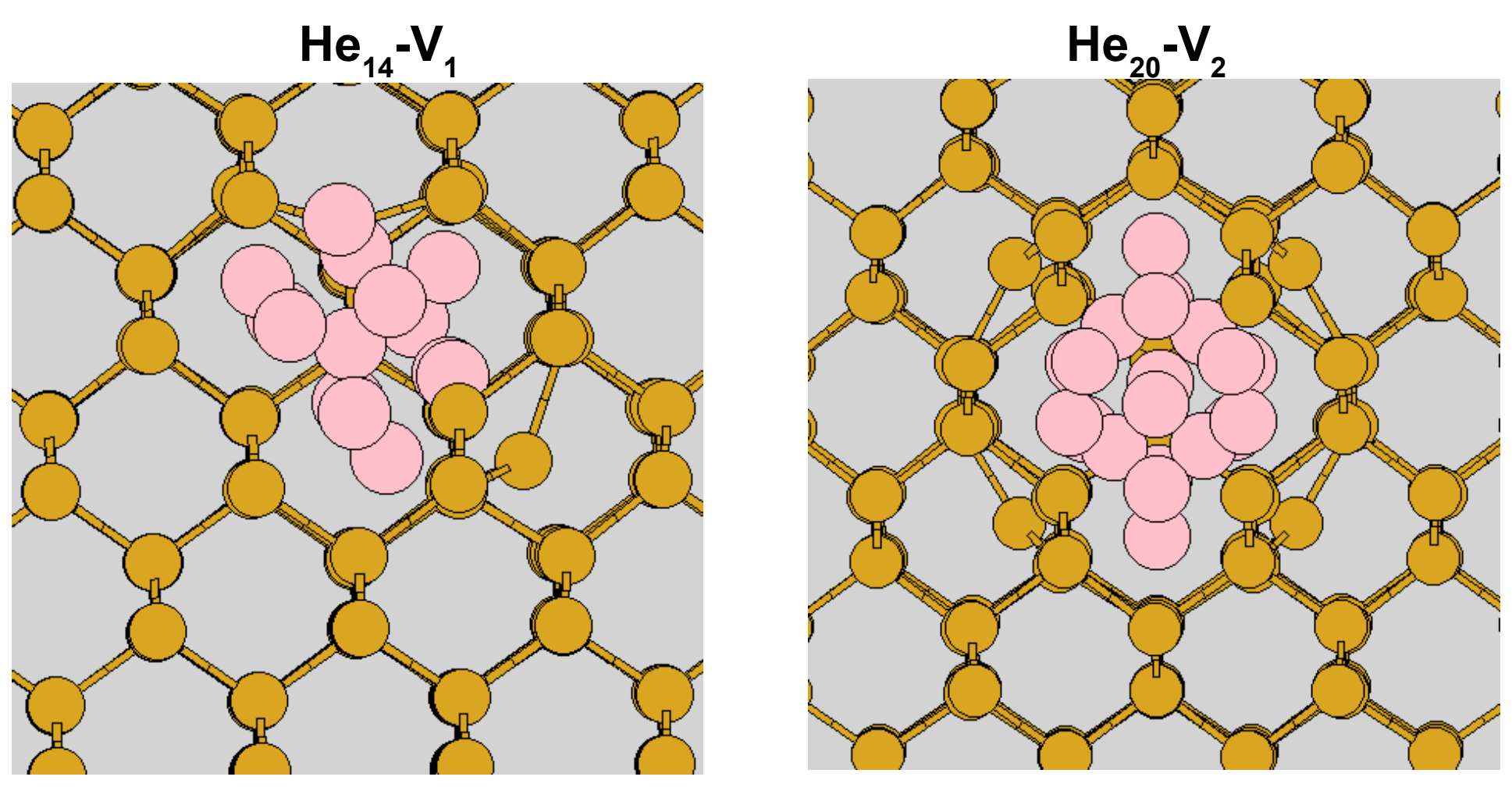
DFT and potential results



The formation energies of He_n-V_1 and He_n-V_2 complexes first increase linearly as a function of n, then as a power of n^3. The inflexion point (or equivalently, the plateau in the binding energies variation) corresponds to the more favorable filling of V_1 and V_2 by He.

DFT results indicate a filling of 14 He for V_1, and 20 He for V_2.

Similar results are obtained using the empirical potentials, albeit with larger binding energies.



He_{14}-V_1

He_{20}-V_2

The best configuration corresponds to He atoms organized on a HCP lattice, with distortions due to the cubic diamond matrix.

Conclusions

Using DFT calculations, we have investigated the properties of He in Si. Our works lead to the following conclusions :

- He is stable as an interstitial and in a divacancy, but not in a monovacancy.
- He migrates as an interstitial, even if it is initially located in a divacancy.
- The desorption from a cavity solely depends on the conditions into bulk Si (temperature) and into the cavity itself (He density and temperature).
- Analysis of earlier experiments suggests a bubble pressure of 1-2 Gpa during desorption
- The investigation of the formation of small He_n-V_m complexes reveal that a large number of He atoms can be accommodated in a mono- or a di-vacancy.

Future directions

- Classical molecular dynamics investigations of the first steps of He_n-V_m complexes as a function of temperature and (He,V) concentrations
- Modelling of He_n-V_m energy variations
- Determination of He_n-V_m complexes mobility
- Calculation of pressure in small bubbles