Atomistic simulations of point defect diffusion in Si and SiGe

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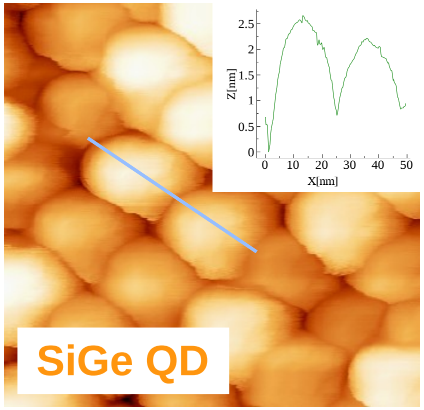
Partially founded by the OSiGe_Sim project ANR-05-NANO-004

Context and outline

Diffusion in the microelectronic material

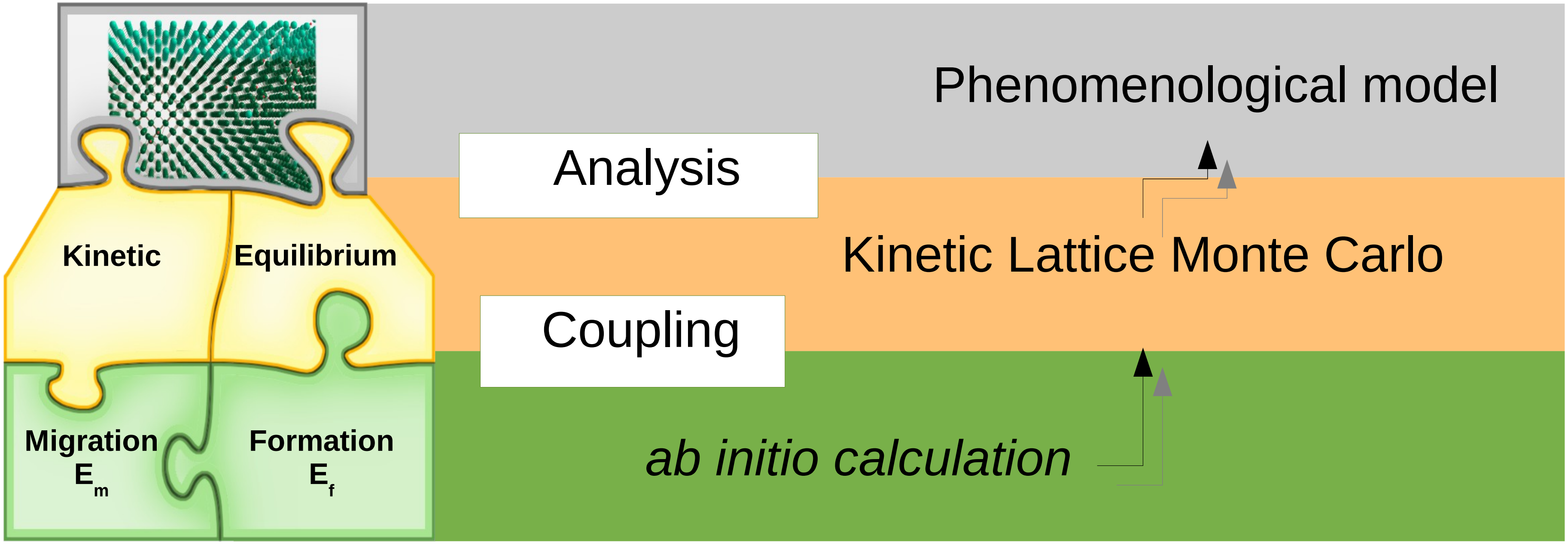
Ge & PD diffusion
Strain
Charge state
Dopant



The need of multi-scale for diffusion simulations !

- Some insight of Ge diffusion in SiGe
- The case of Si vacancy diffusion
- Summary and outlooks

The multi-scale method for diffusion studies



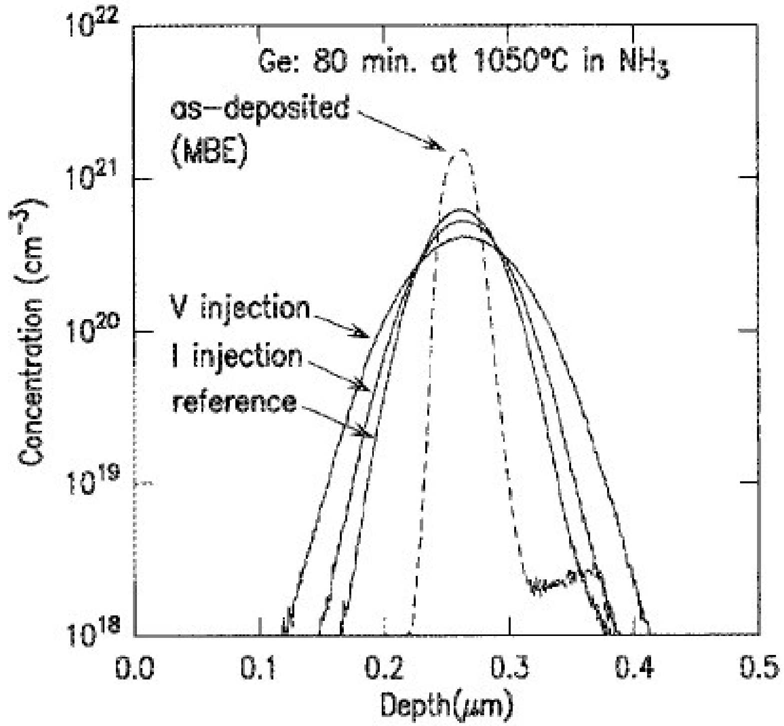
DFT (CPMD, SIESTA)**:** 216 atoms simulation box, Γ or 2x2x2, only some **typical configurations; NEB driver** for saddle point calculation

Coupling through **models** that reproduce the DFT energies for **all possible configurations**

BKL-type KLMC simulations (resident time)

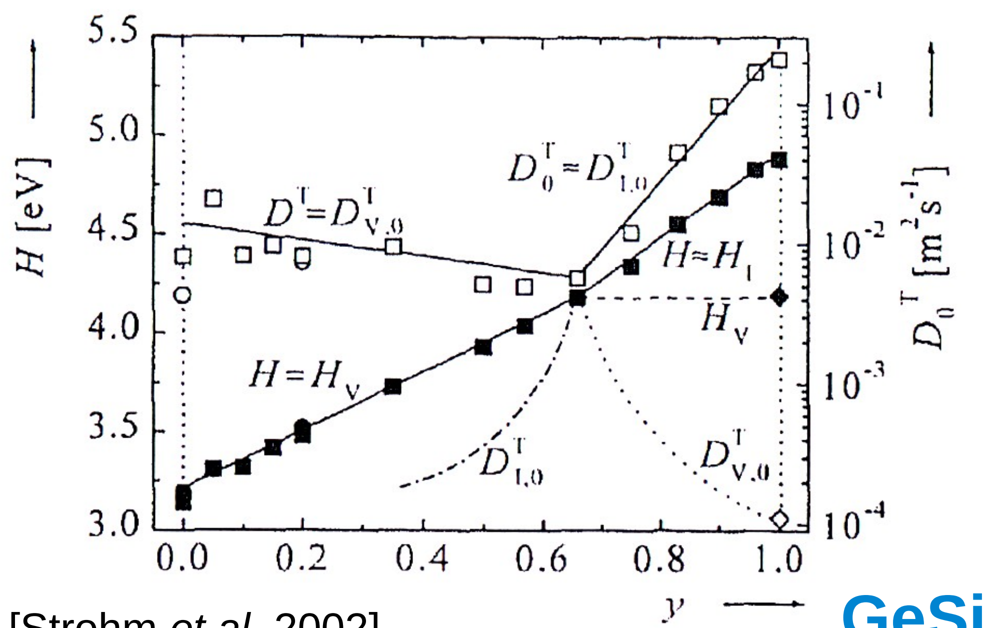
Diffusion in Si_y-Ge_{1-y} alloys (DFT step only)

Vacancy **and** interstitial diffusion



[Fahey *et al.* 1989]

Ge@Si



[Strohm *et al.* 2002]

GeSi

* **Vacancy** diffusion for **y < 0.70** and T < ~ 1000 °C

* **Dual diffusion** for lower concentration

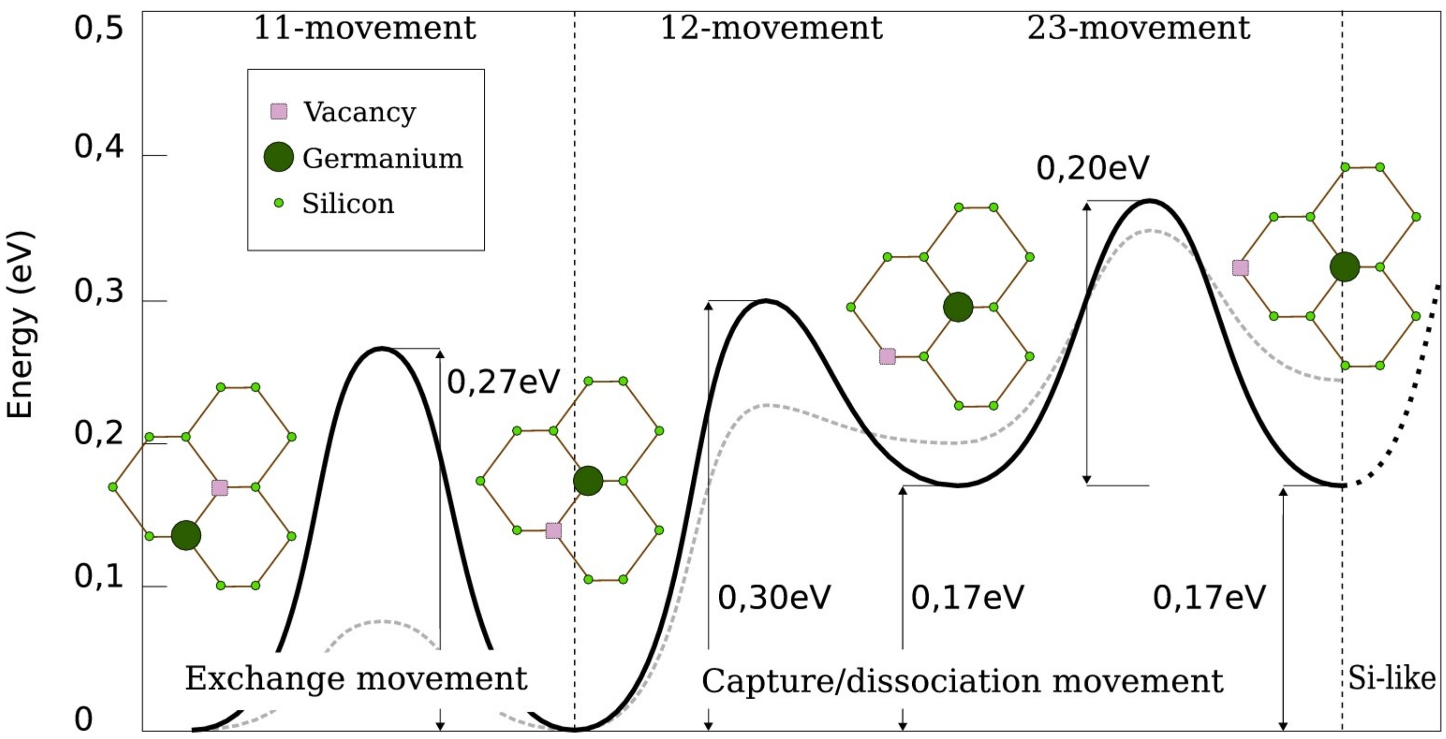
DFT study of Ge diffusion in Si

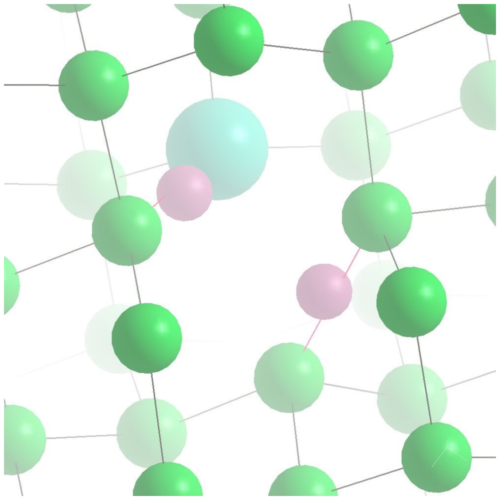
The vacancy mechanisms

Only one Ge in the Si box

Formation energy E_f = 3.6 eV *(216-2k)*

Migration path with a ring mechanism





Jahn-Teller effect

- Ge
- Si
- pairing

$<E_m> = 0.37$ eV

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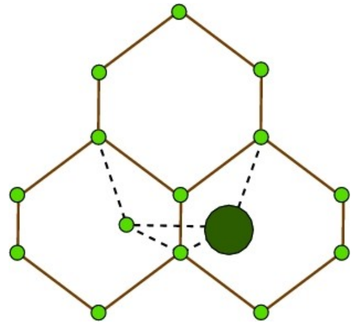
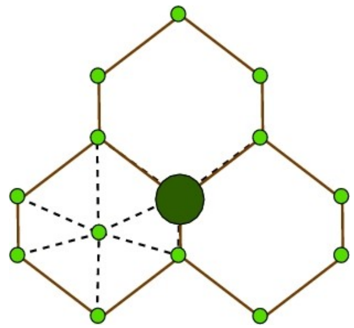
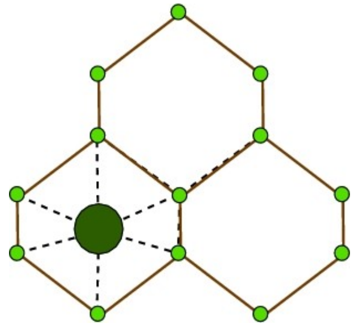
The interstitial formation

Mixed dumbbell $d_{\langle 110 \rangle}$	**3.16 eV**	
Hexagonal Si^H	**3.33 eV**	
Hexagonal Ge^H	**3.45 eV**	

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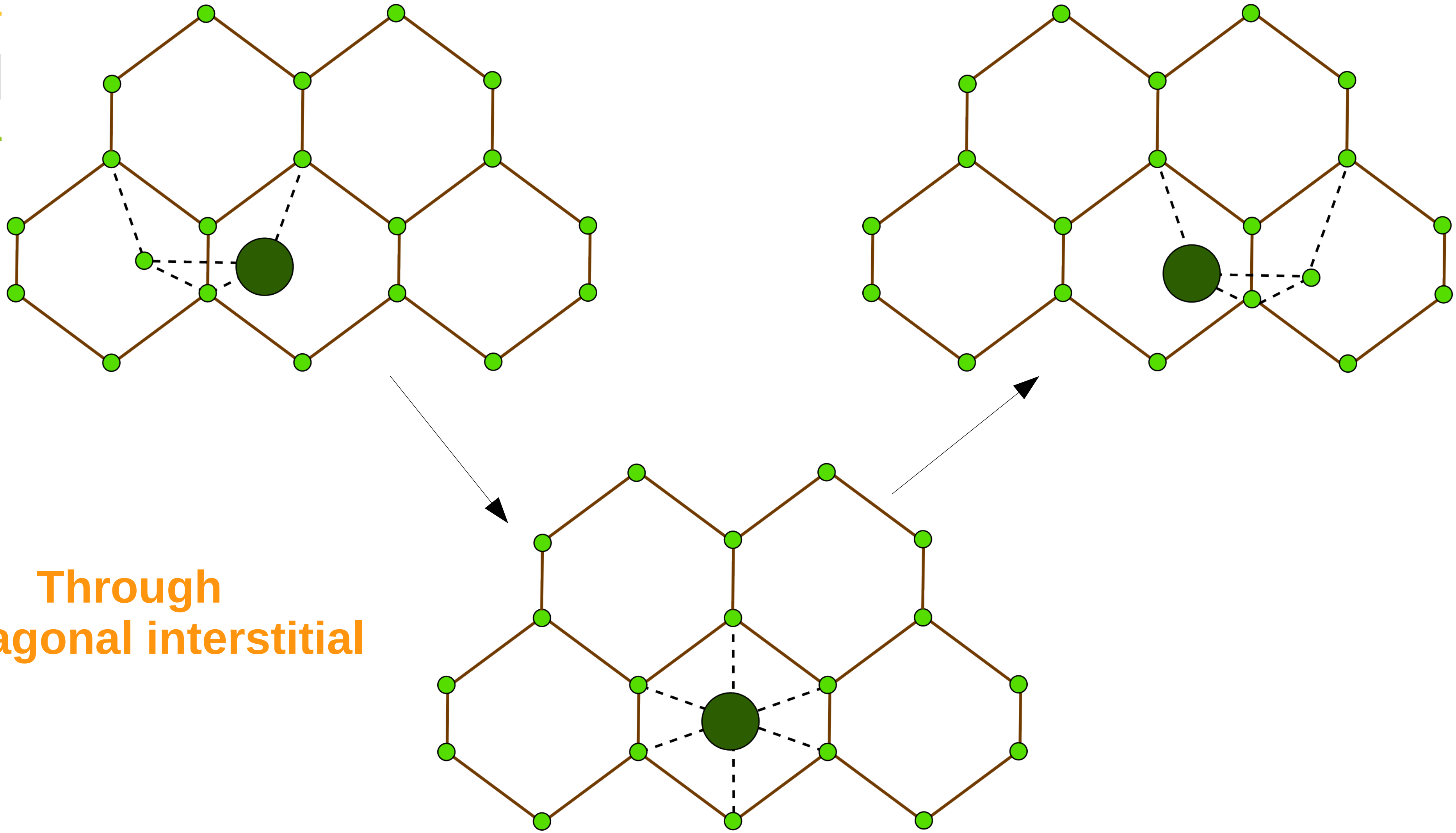
The migration mechanism of the <110> dumbbell

Second neighbor diffusion



Through hexagonal interstitial

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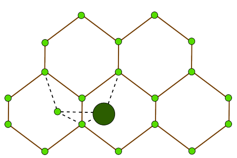
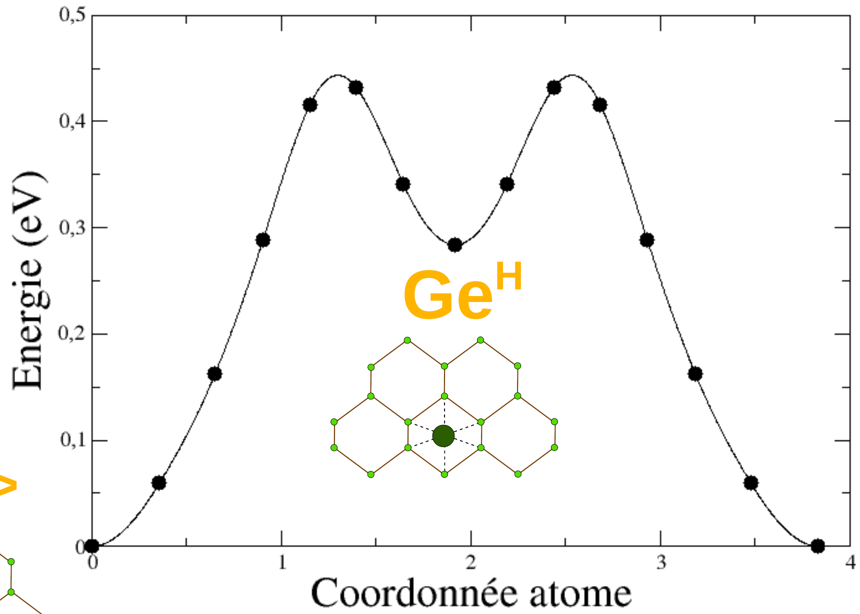
The interstitial migration mechanism

$d_{\langle 110\rangle}$ --> Ge^H $E_m = 0.44$ eV

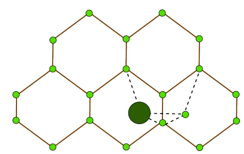
$d_{\langle 110\rangle}$ --> Si^H $E_m = 0.37$ eV

$d_{\langle 110\rangle}$





$d_{\langle 110\rangle}$



Direct migration of Ge^H : $\langle E_m \rangle \sim 0.10$ eV

Back movement Ge^H --> $d_{\langle 110\rangle}$: $E_m = 0.15$ eV

Kick-off scheme diffusion

but with a dumbbell to hexagonal ratio is not << 1 !

$\langle E_m \rangle = 0.44$ eV

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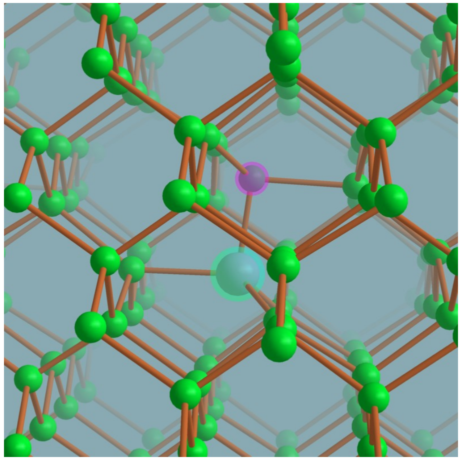
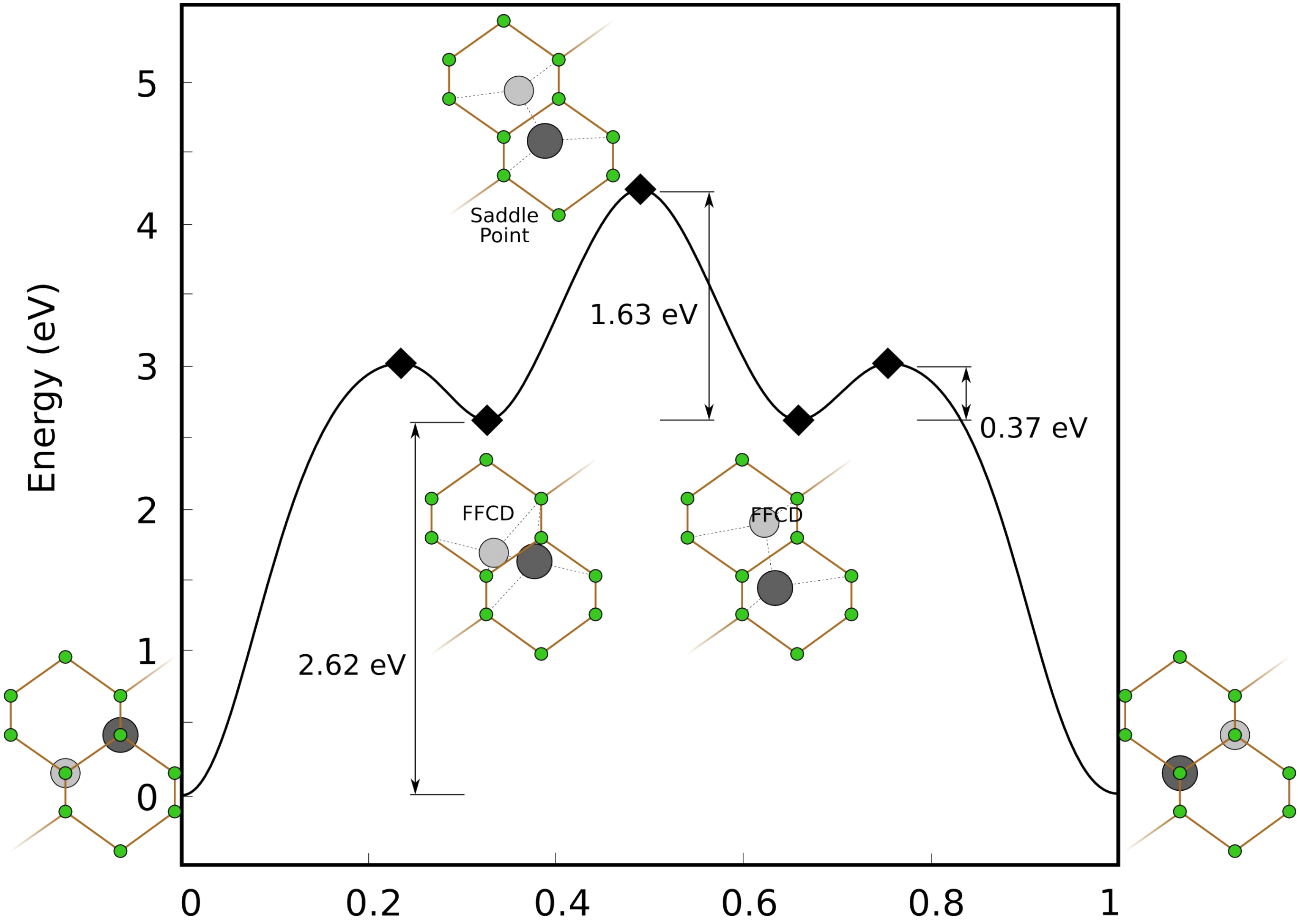
The FFCD mechanism: an intrinsic mechanism

~ SW in C_{60}



[Pandey, PRL **57**, 2287 (1986) and Goedecker, PRL **88**, 235501 (2002)]



Low formation energy:

$E_f = 2.62$ eV

High migration energy:

$E_m = 1.63$ eV

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Ge diffusion in Si (comparison with experiments)

Direct use of ab initio value: ***1 mediator only***

For FFCD	$E_a = 4.2$ eV	Saddle point	unknown
For interstitials	$E_a = 3.7$ eV	$E_a = E_f + \langle E_m \rangle$	unknown
For vacancies	$E_a = 4.0$ eV	$E_a = E_f + \langle E_m \rangle$	4.18 eV [Strohm et al. 2002]

All mediators might contribute to diffusion as observed in experiments but the Ge diffusion activation energy is ~ **5 eV ?!**

For complex diffusion mechanism, **effective activation energies** could be higher than the **direct sum** of individual one ?

Need of Monte Carlo step for correct physical average !

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The case of Si vacancy

An old but controversial story for migration energy ...

Watkins **E_m = 0.45 eV** direct measurement of E_m

[MSS. Proc. 3, 227-235 (2000)]

Bracht *et al.* **E_m = 1.8 eV** measurement of E_a

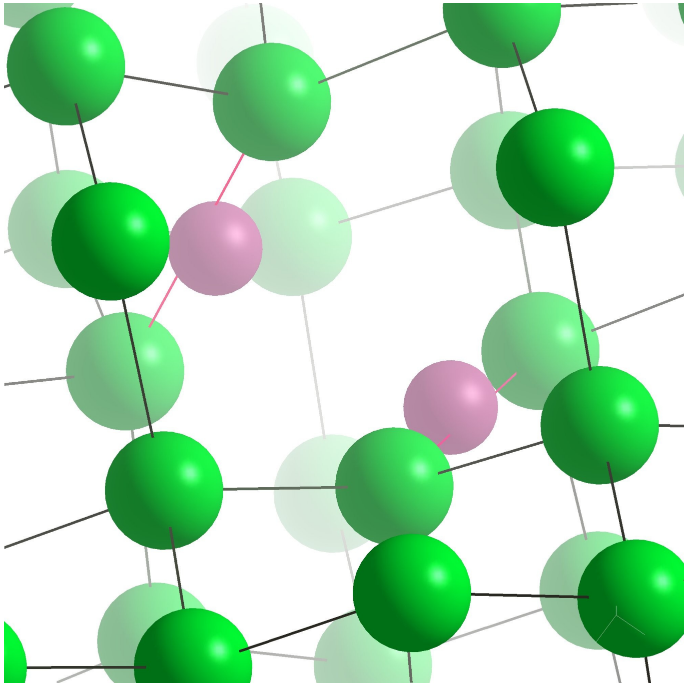
[PRL 91, 245502 (2003)]

Ranki *et al.* **E_m = 1.2 eV** measurement of E_a

[PRL 93, 255502 (2004)]

Can we explain these scattered data from effective phenomena ?

DFT step: vacancy formation energy



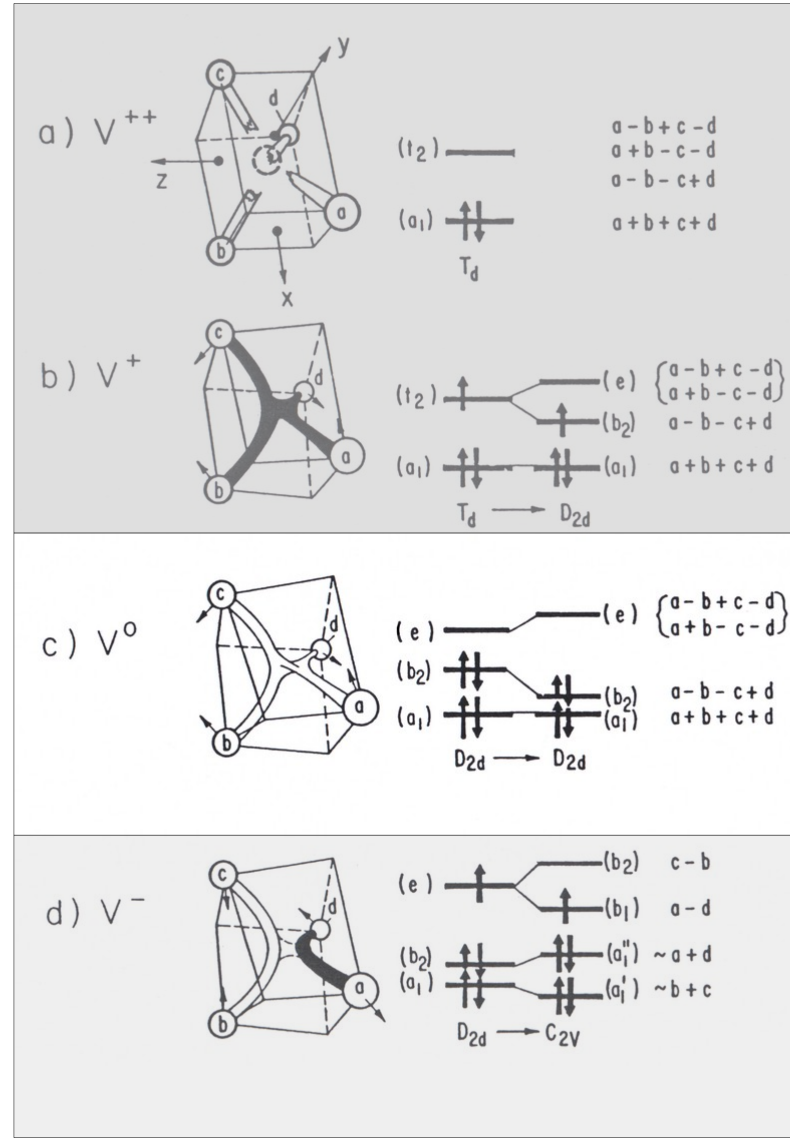
Si pairing

3.52 eV (*216-1k*) ***3.6 eV*** (Dannefaer 1986)

In Si, DFT fit well with exp

[D. Caliste PhD (2005); see also Wright (2006)]

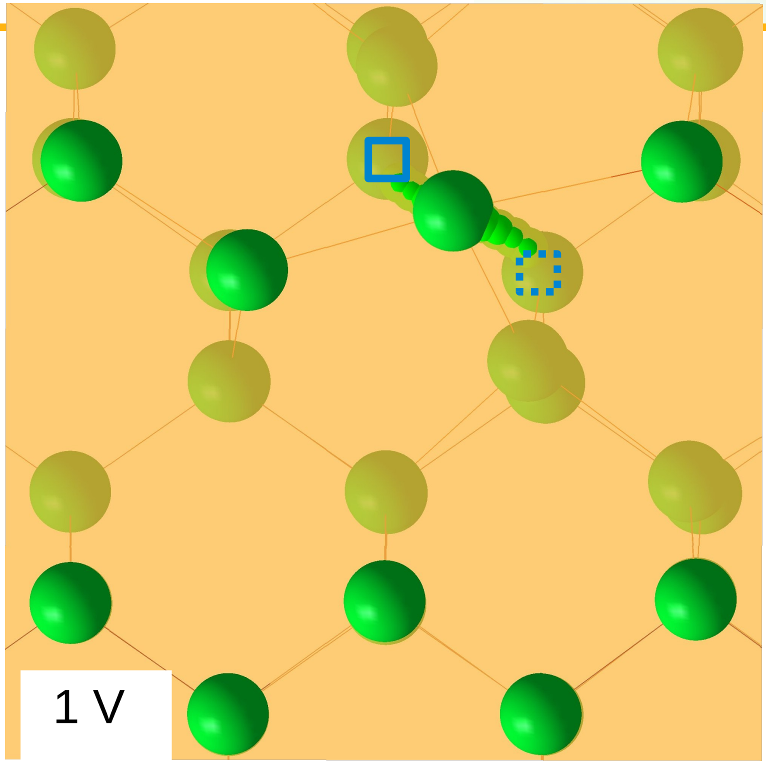
Only neutral vacancy !

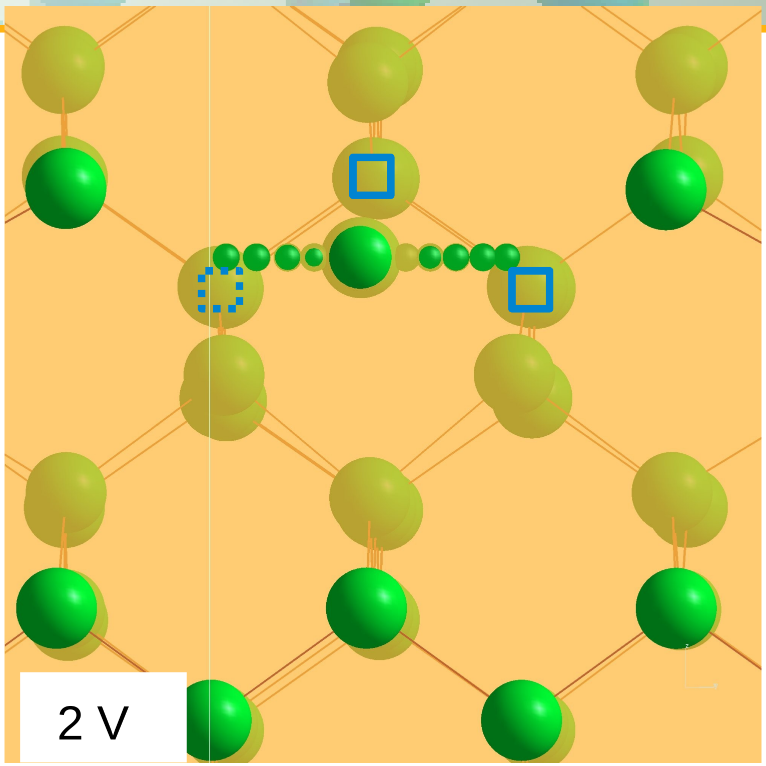


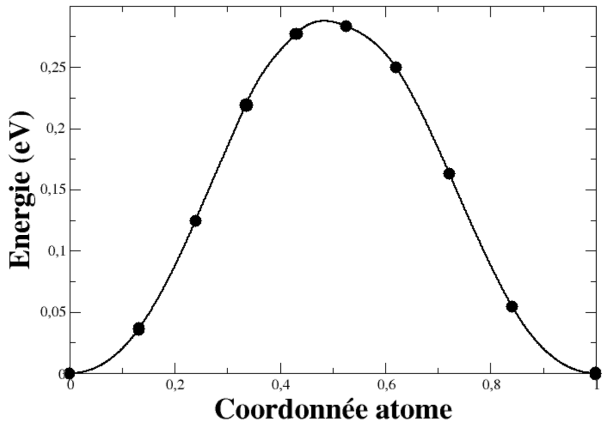
Jahn-Teller effect [G. Watkins 1992]

DFT step: vacancy migration energy

NEB+DIIS 216-1k



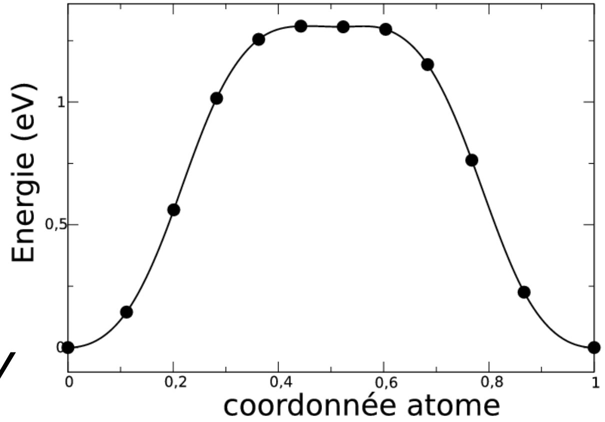




0.30 eV

Exp: 0.45 eV

[Watkins '79]

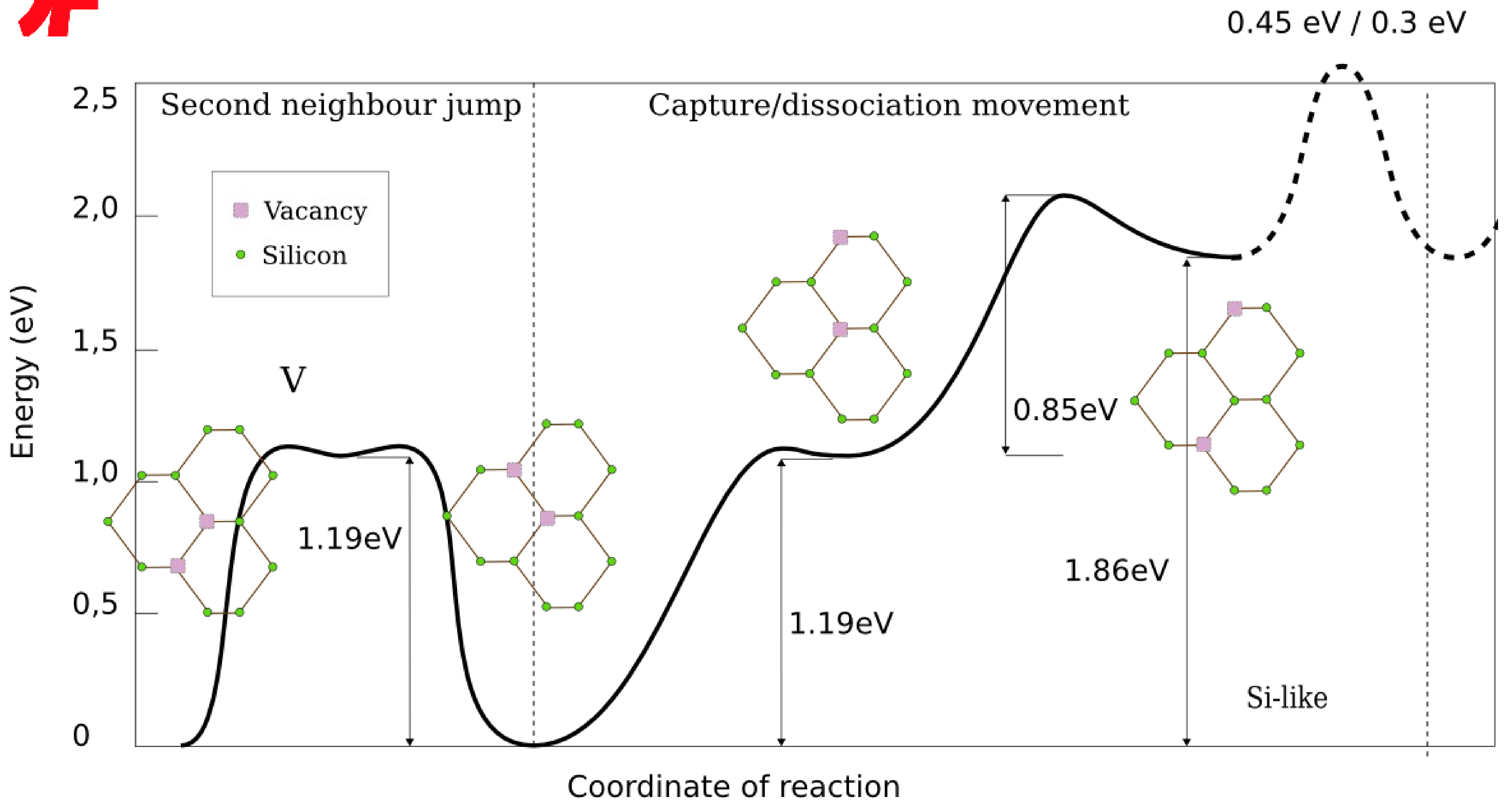


1.19 eV

Exp: 1.3 eV

[Watkins '65]

Coupling step: migration landscape



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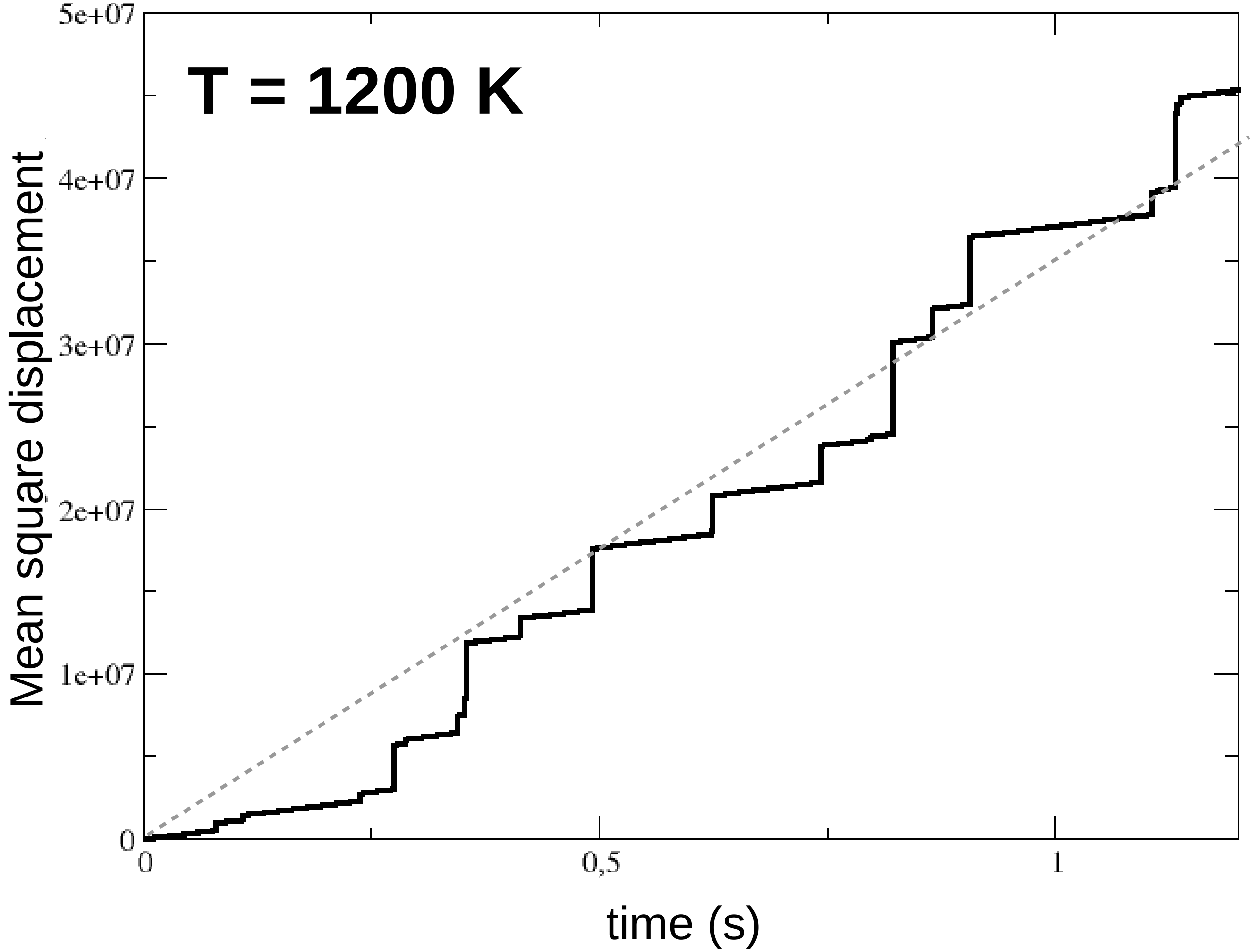
Monte Carlo step

2 vacancies and 0,1 à 18 M silicon atoms



Einstein formula

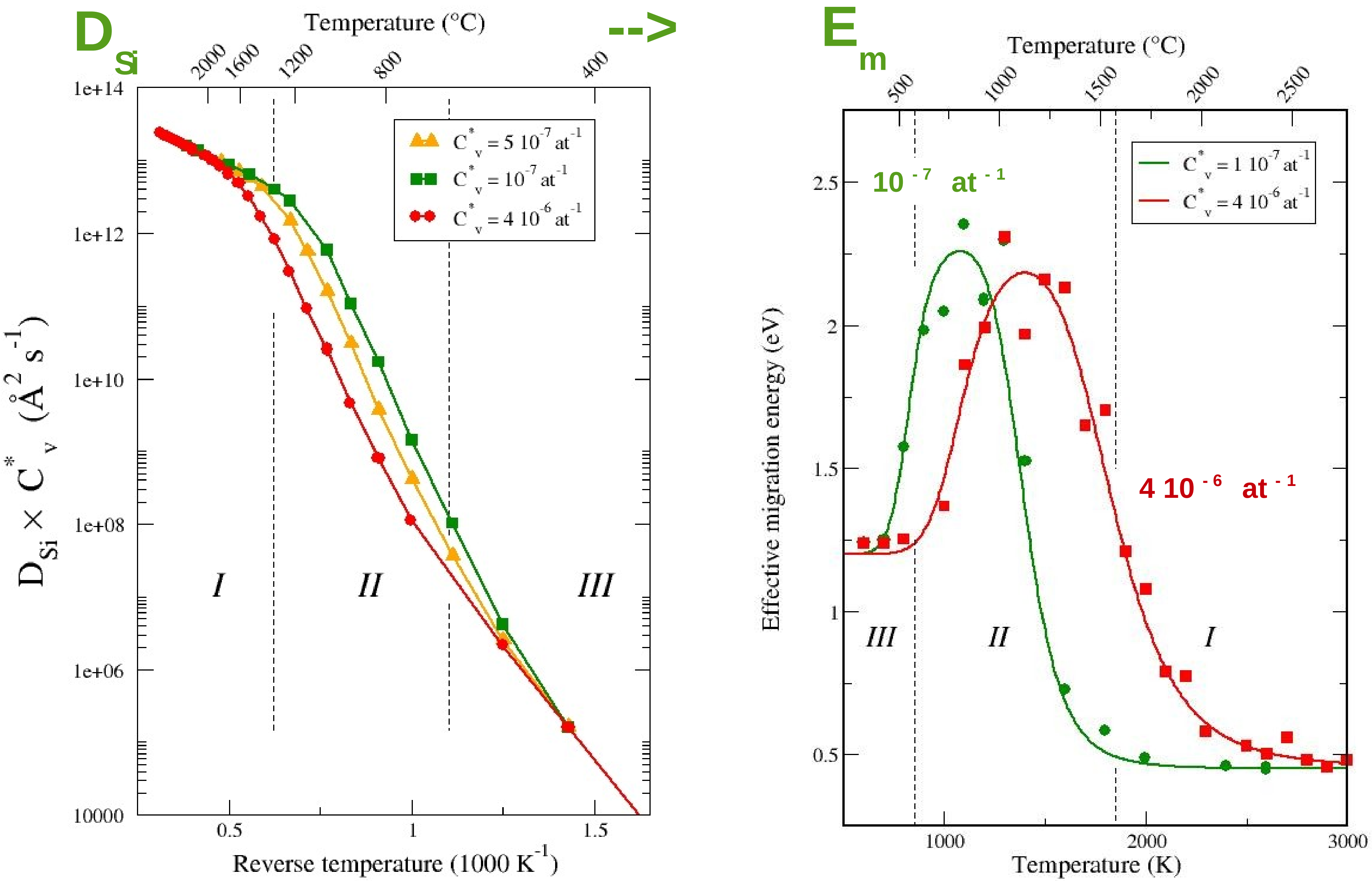
$$\langle r^2(t)\rangle = 2\,dDt$$

Average on 20 trajectories

--> D as function of T and C_v

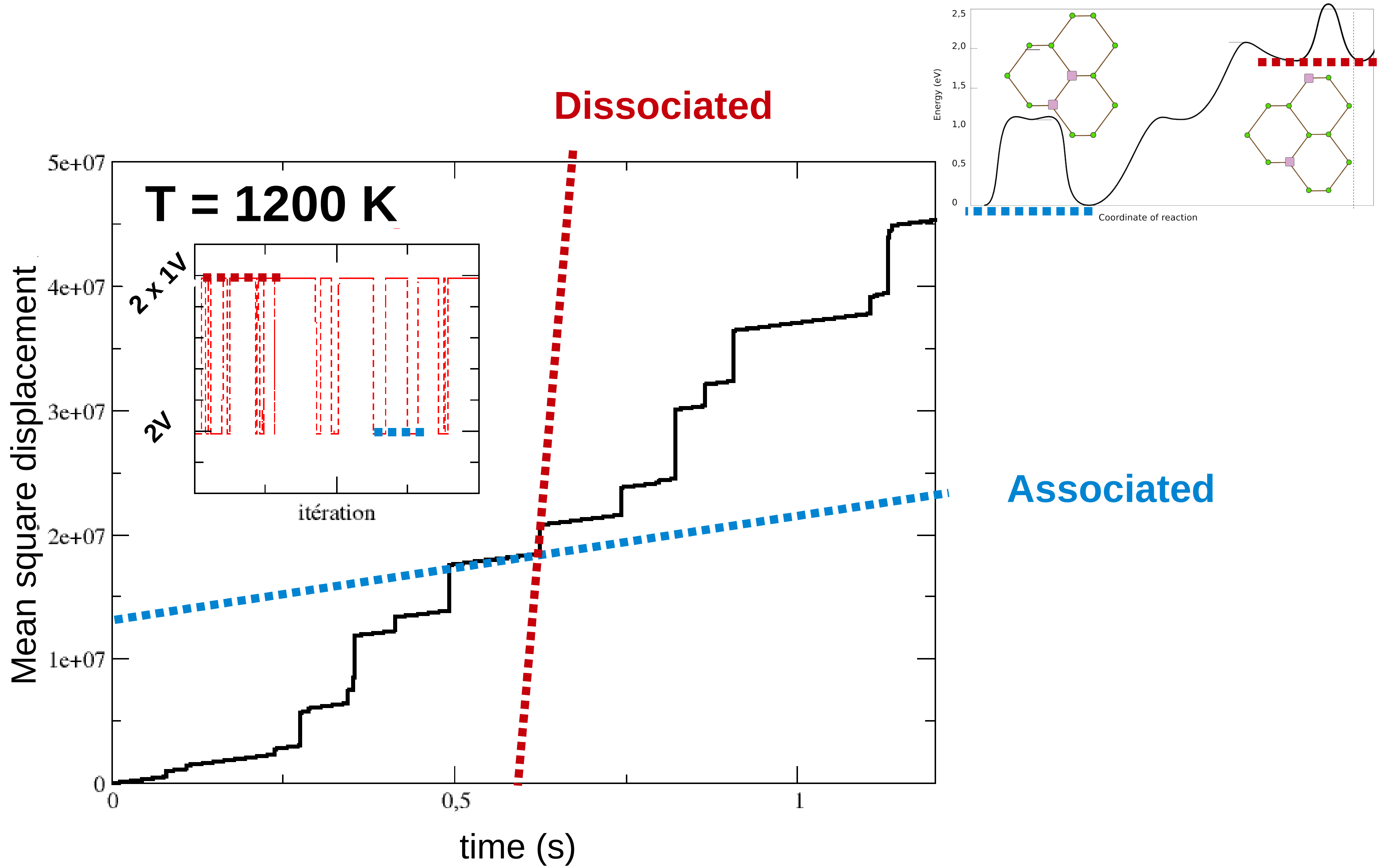
Non-Arrhenius diffusion is predicted !

D_{Si} --> E_m



3 diffusion regimes !

Step-like trajectory in intermediate temperature ?



Three temperature regime rationalization

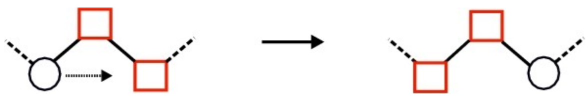
Concurrent diffusion in 1V or 2V

$$\tilde{D}(T, C_v^*) = f_\tau(T, C_v^*) \times D_{1v}(T) + [1 - f_\tau(T, C_v^*)] \times D_{2v}(T)$$

2V dissociation

1V migration (fast)

2V migration (slow)



Analytical derivative gives a model for effective migration energy

$$\tilde{E}^m(T, C_v^*) = f_\alpha E^m_{1v} + f_\beta(2E^f_{1v} - E^f_{2v}) + (1 - f_\alpha)E^m_{2v}$$

With f_α and f_β being [0-1] bounded

$$f_\alpha = \frac{D_{1v} f_\tau}{D_{1v} f_\tau + D_{2v} \times (1 - f_\tau)}$$

$$f_\beta = f_\alpha - f_\tau$$

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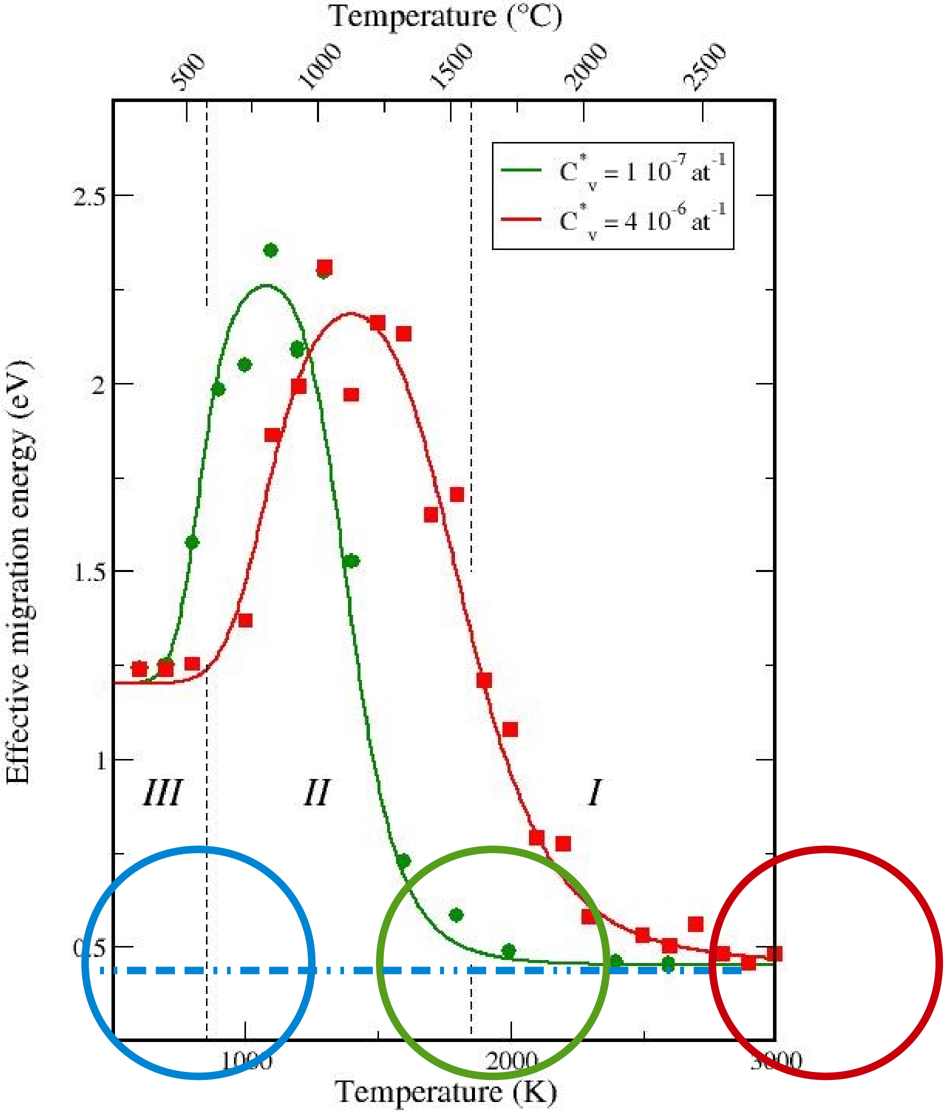
Model vs MC simulations (high T)

$$\tilde{E}^m(T, C_v^*) = f_\alpha E^m_{1v}$$



low C_v <-- medium C_v <-- high C_v

region I

0.45 eV

> **high T** or **low C_v**

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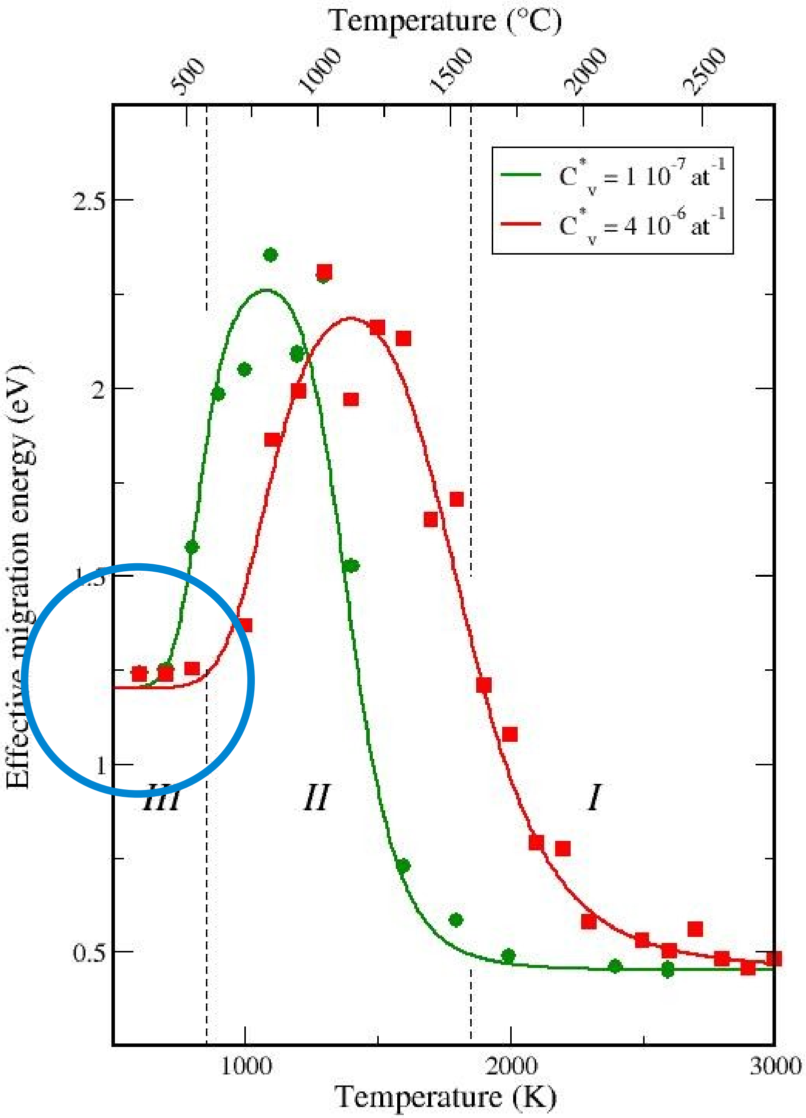
Model vs MC simulations (low T)

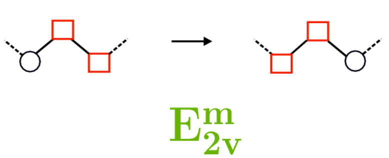
$$\tilde{E}^m(T, C_v^*) = \quad \cdot (1 - f_\alpha) E^m_{2v}$$



region III

< 850 K for C_v =10^{-7} at^{-1}

1.25 eV



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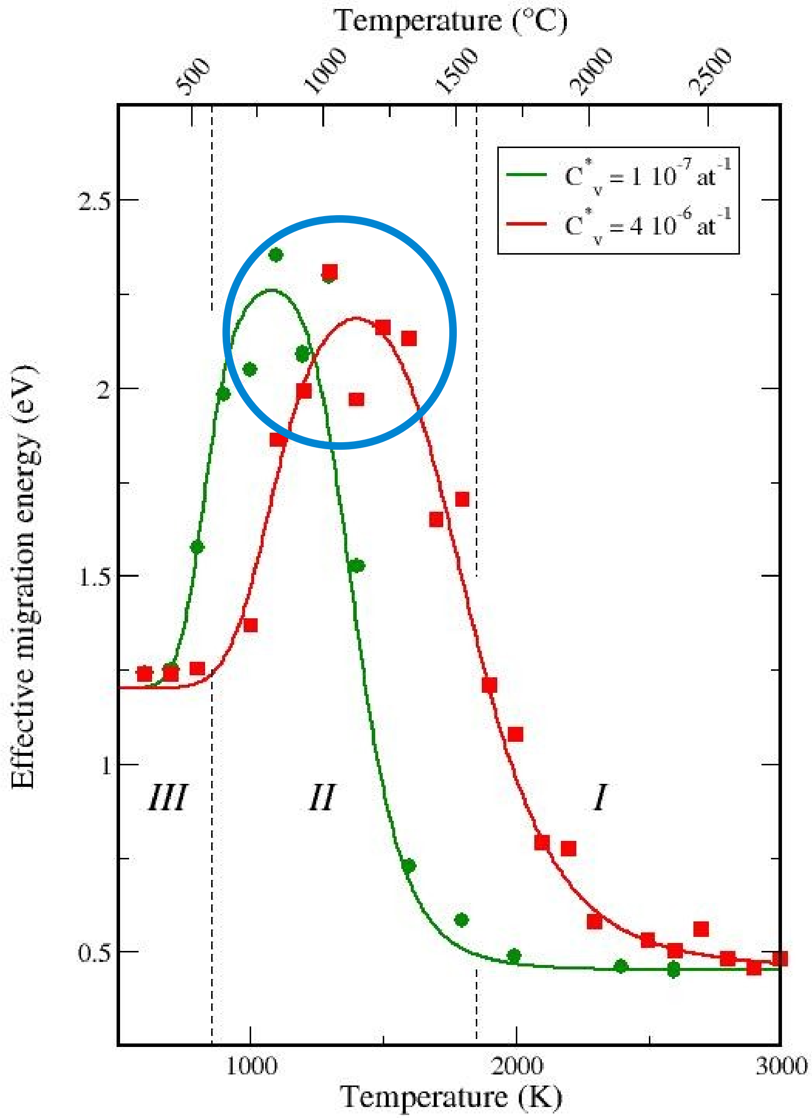
Model vs MC simulations (intermediate T)

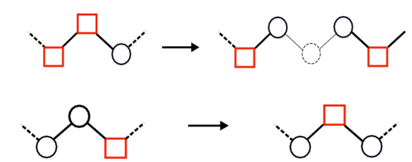
$$\tilde{E}^m(T, C_v^*) = f_\alpha E^m_{1v} + f_\beta (2E^f_{1v} - E^f_{2v})$$



region II

850-1300 K for $\mathbf{C_v=10^{-7}\ at^{-1}}$

2.1 eV



$$E^m_{1v} + (2E^f_{1v} - E^f_{2v})$$

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Experiment reconciliation

T < 200 K
~ équilibium
E_m = 0.45 eV
[Watkins '79]

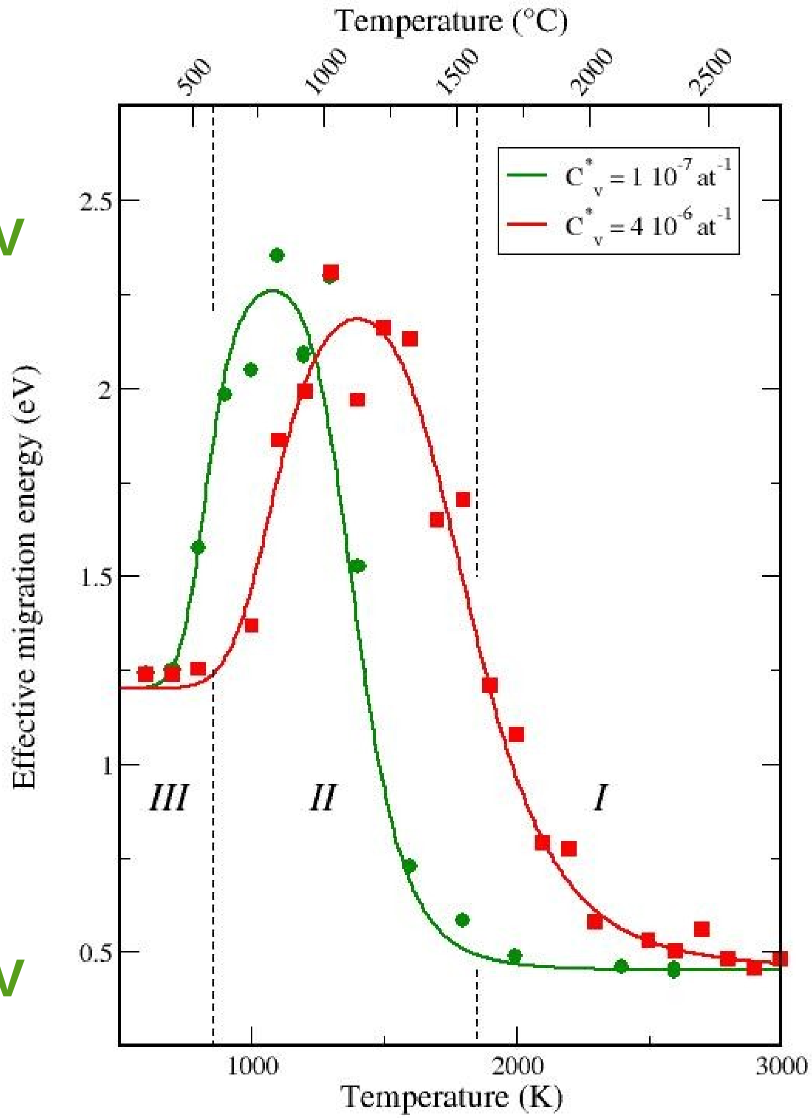
E_m = 0.45 eV

1050-1150 K
e^- irradiation
E_m = 1.8 ± 0.5 eV
[Bracht '03]

E_m = 2.1 eV

650-900 K
Highly doped
E_m = 1.3 eV
[Ranki '04]

E_m = 1.25 eV



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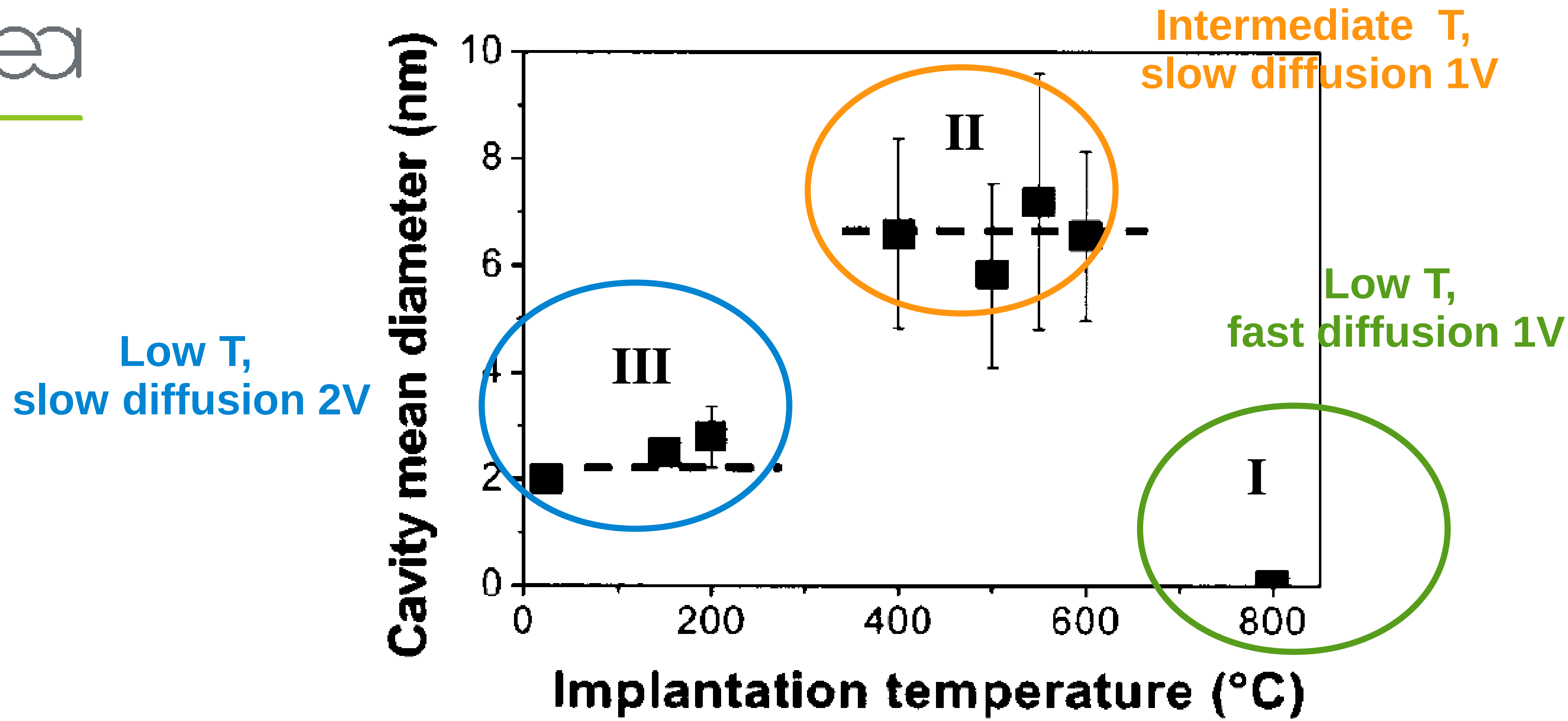
3 temperature regimes already observed in Si !

Evolution of the He cavity radius as function of implantation T

[M. L. David *et al* JAP **93** 1438 (2003)]



Fast diffusion allows effusion; slow diffusion allows cavity formation.
The slower the diffusion the bigger the mean cavity radius.

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Summary

In complex diffusion mechanism **effective activation energies** might be higher than the **direct sum** of individual one !

Multi-scale simulation is a powerful tool for diffusion studies

DFT step is not enough when concurrent mechanisms are involved.

Coupling between DFT and KLMC is a good solution

Effective mechanisms might explain simulation/experiment discrepancy

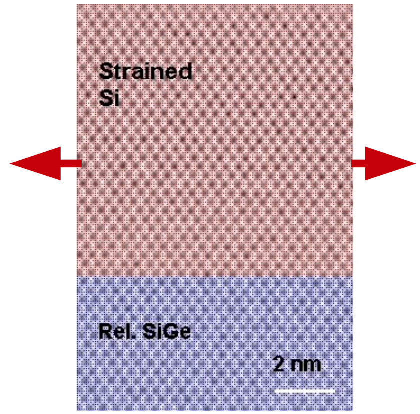
Drawbacks:

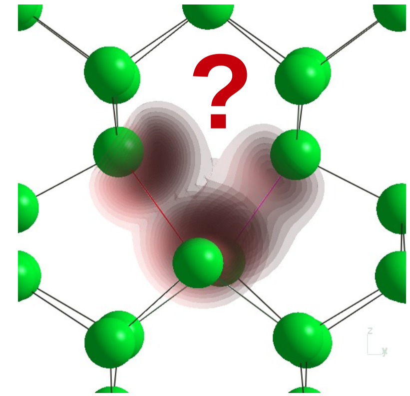
On lattice simulations

Pre-calculated events database

Outlooks

Strain effect:





Work in progress to go above our first analysis

[K. Z. Rushchanskii, *et al.* APL **92**, 152110 (2008)]

Charge effect:

Work in progress to develop an accurate *ab initio* scheme

Growth on Ge QD on Si using *ab initio* and off-lattice *on-the-fly* KMC

[N. Mousseau *et al.* (2008)]

MUSCADE project founded 2010-2012

Study of possible mechanisms of LID in SOG silicon (cf 4.3)

Acknowledgments

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References:

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K. Z. Rushchanskii, P. Pochet and F. Lançon APL **92**, 152110 (2008)