The Kinetic Activation-Relaxation Technique

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Dresden, September 2016

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With the support of

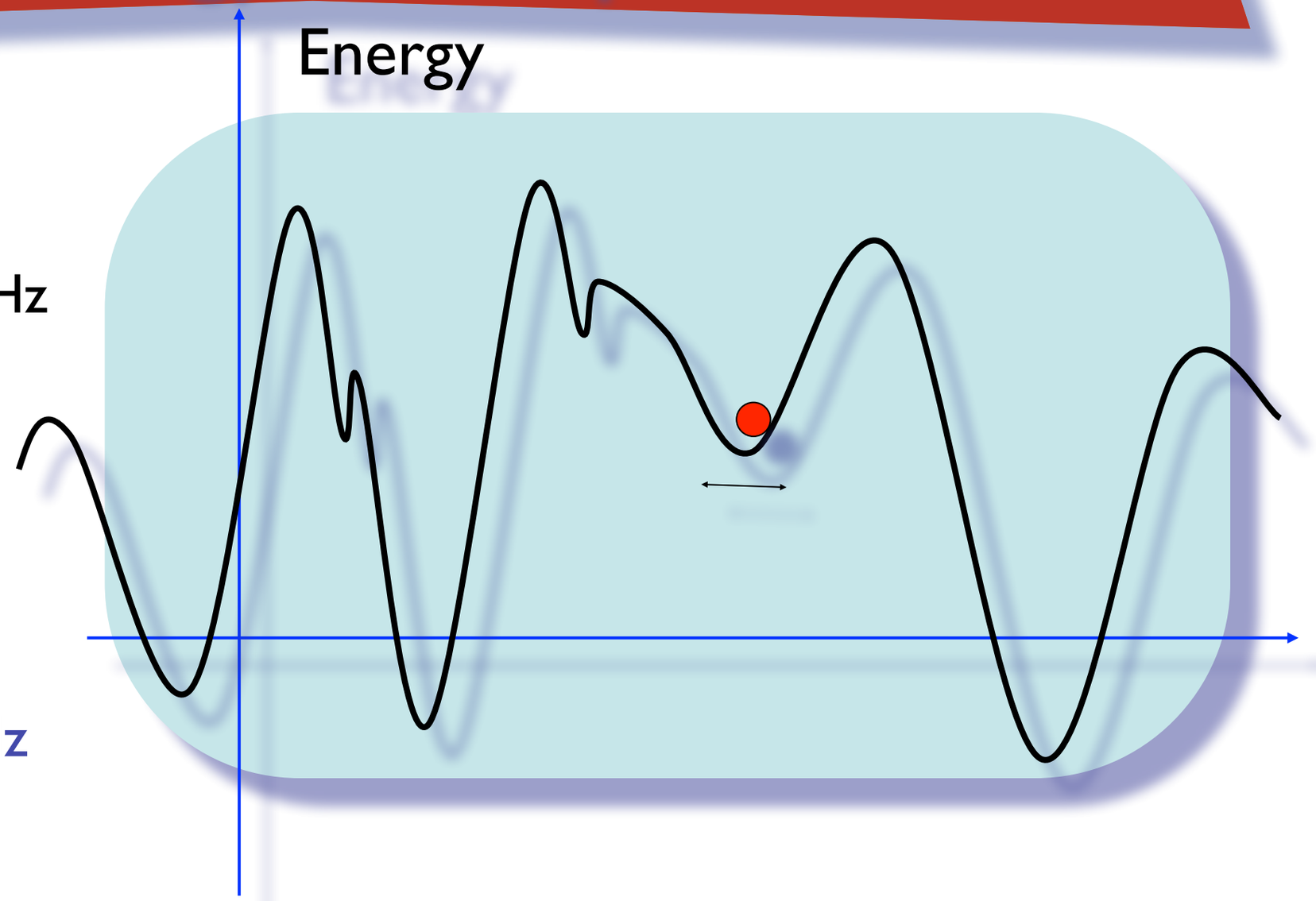
Natural Science and Engineering Research Council of Canada (NSERC)
Fonds de recherche du Québec - Nature et technologies
Canada Research Chair Foundation
Canadian Foundation for Innovation
Fondation NanoScience (Grenoble)
Qatar National Research Fund
Université de Montréal

Computer Time : Calcul Québec / Compute Canada

Energy landscapes

Atoms vibrate at 10^{12} Hz

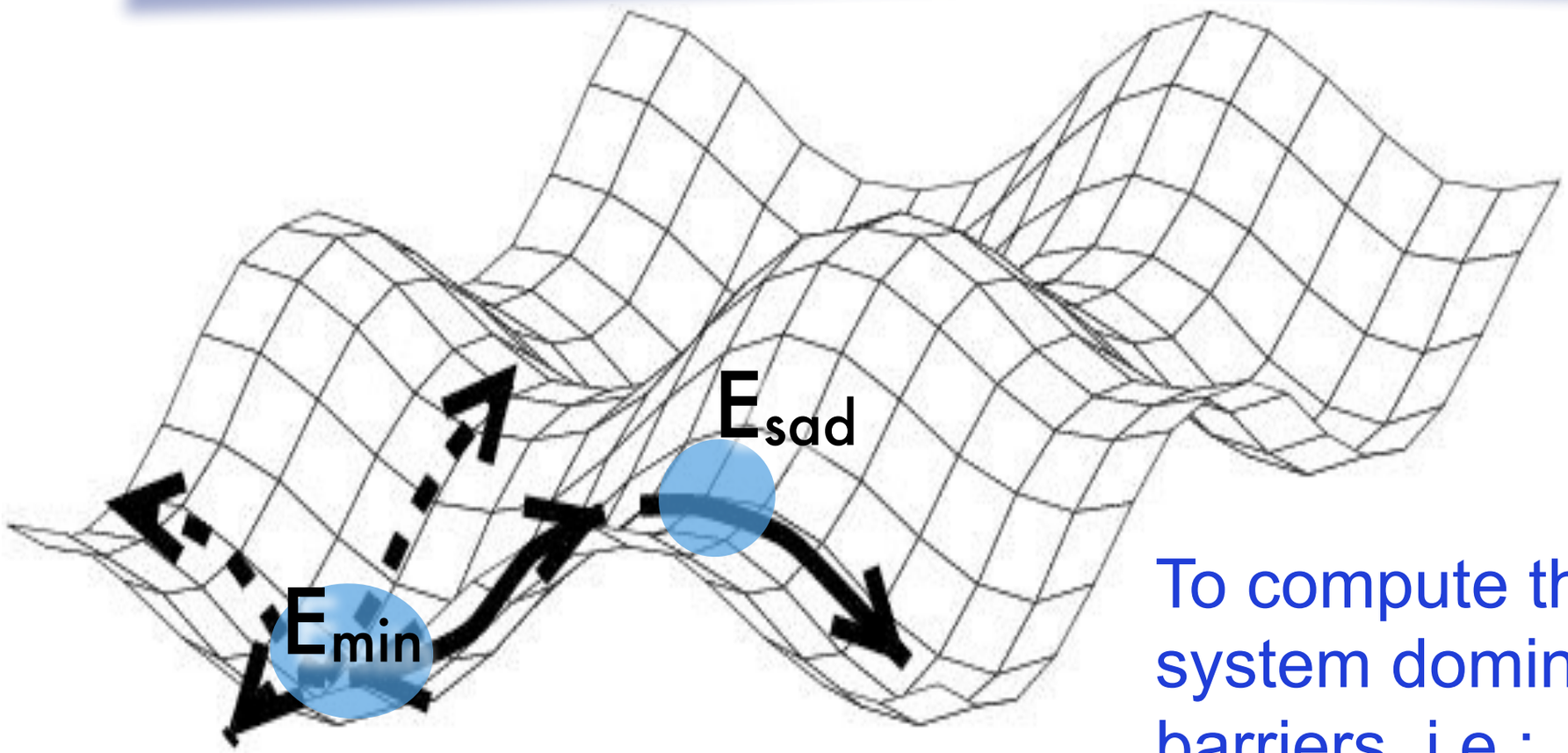
Rare events (activated events) occur at 10^{6} Hz or less



Generic problem:

How to explore the space of variables of a high dimensional cost function?

TST : activated dynamics



$$\Gamma = \Gamma_0 e^{-\Delta E / k_B T}$$

To compute the dynamics in a system dominated by activation barriers, i.e.:

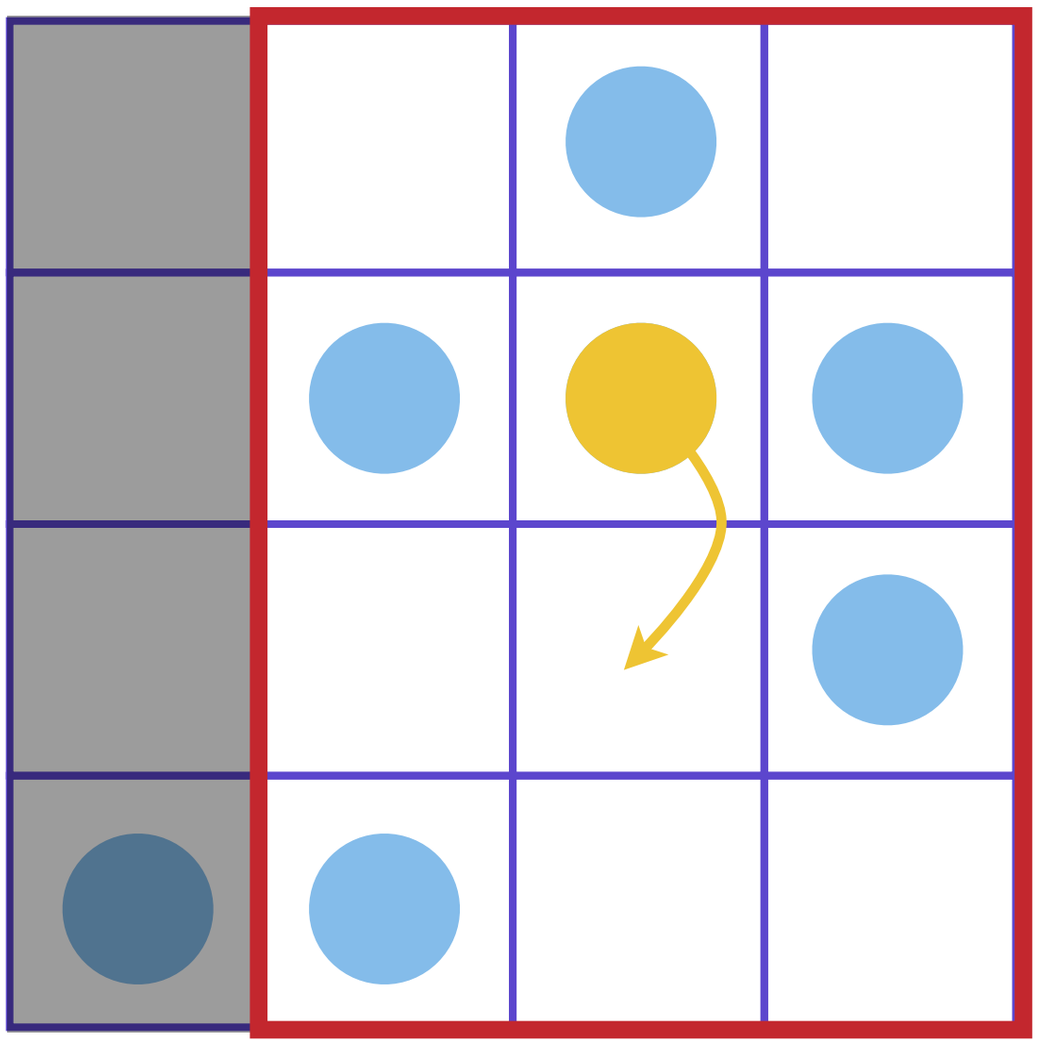
1. Uncorrelated jumps
2. High barriers wrt $k_B T$

we need to know:

1. Knowledge of saddle points
2. Prefactor

Standard Kinetic Monte Carlo

In standard KMC, the problem studied must be defined on a lattice



A. B. Bortz, M. H. Kalos, and
J. L. Lebowitz, J. Comput. Phys. (1975).

A list of events must then be constructed.

Including the final sites we get:

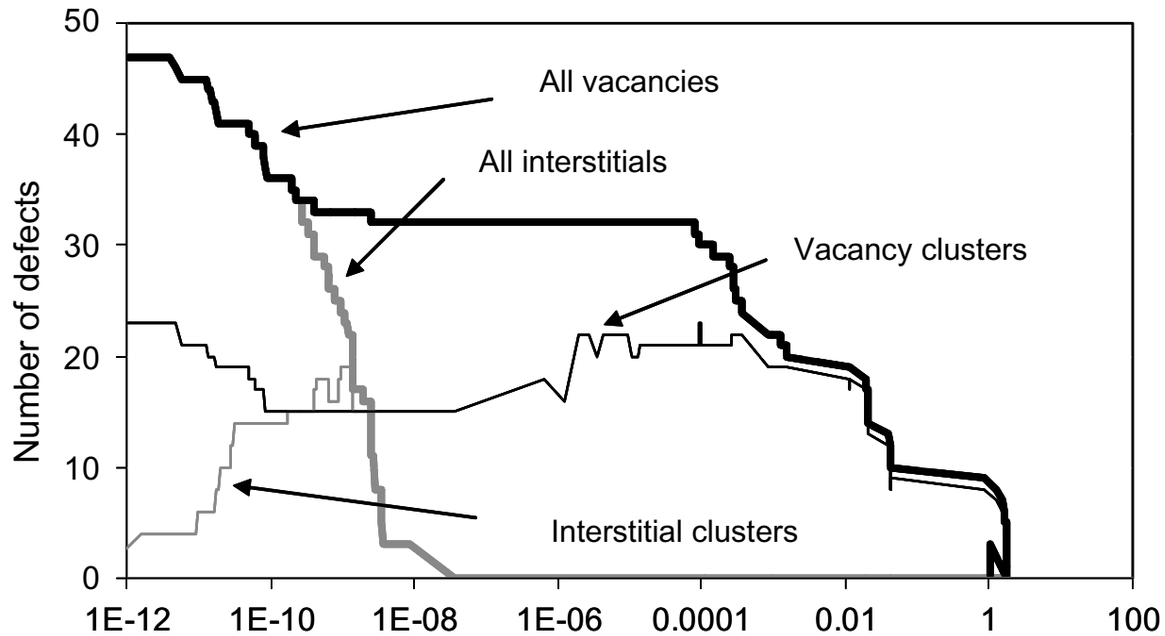
$2^{10} = 1024$ different events and barriers and prefactor

At a given moment, we select one of the possible events at random based on their rate *r of occurrence*

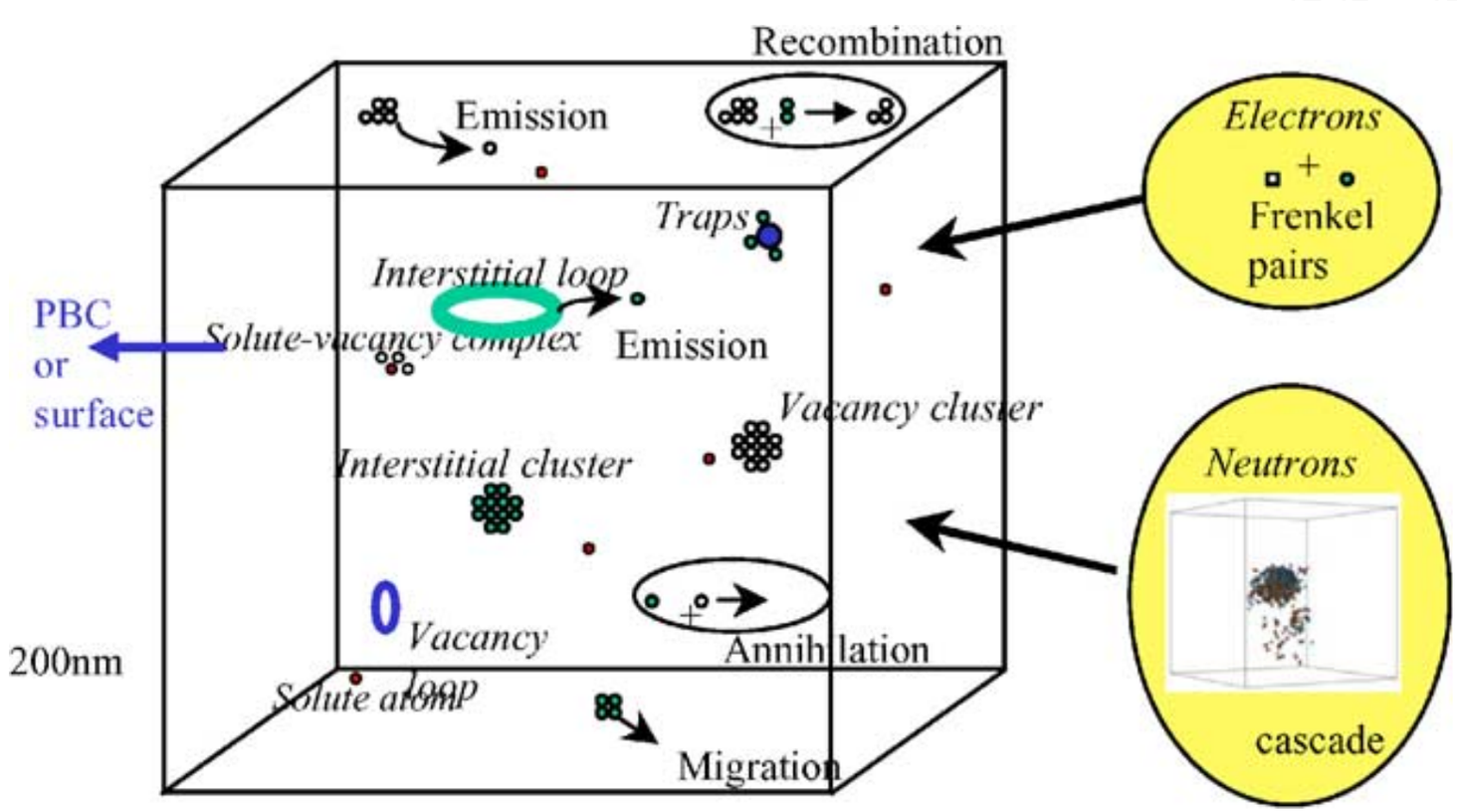
and make the move and update the clock according to

$$\Delta t = -\frac{\ln \mu}{\sum r_i}$$

Kinetic Monte Carlo simulation of the evolution of radiation damages in Fe



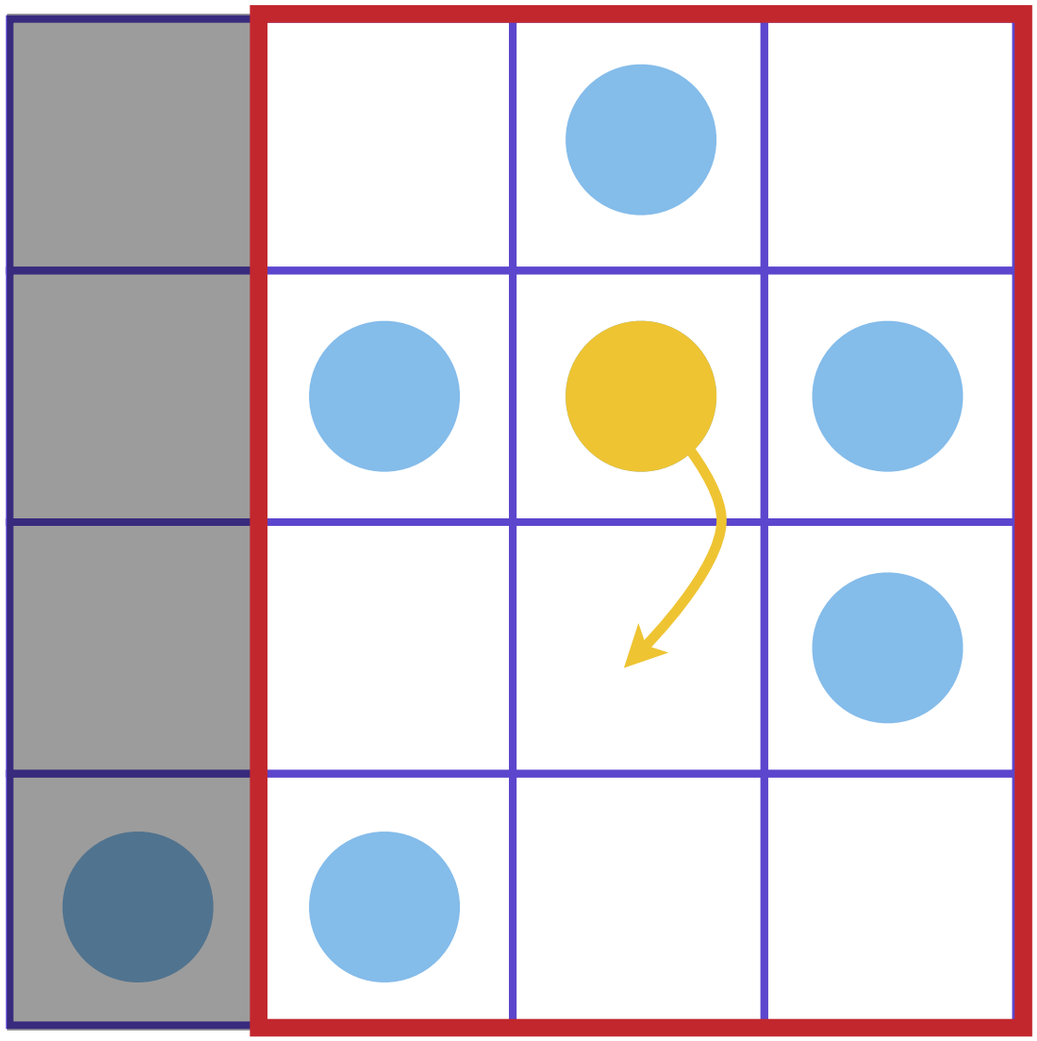
Different events included in the object-based catalog



Example of a simulation at 600 K

C. Domain, C.S. Becquart & L. Malerba, J. Nucl. Mat. (2004)

Limitations of Standard Kinetic Monte Carlo



1. Uses a predefined and limited catalogue of known diffusions events and barriers at T=0

   can miss mechanisms

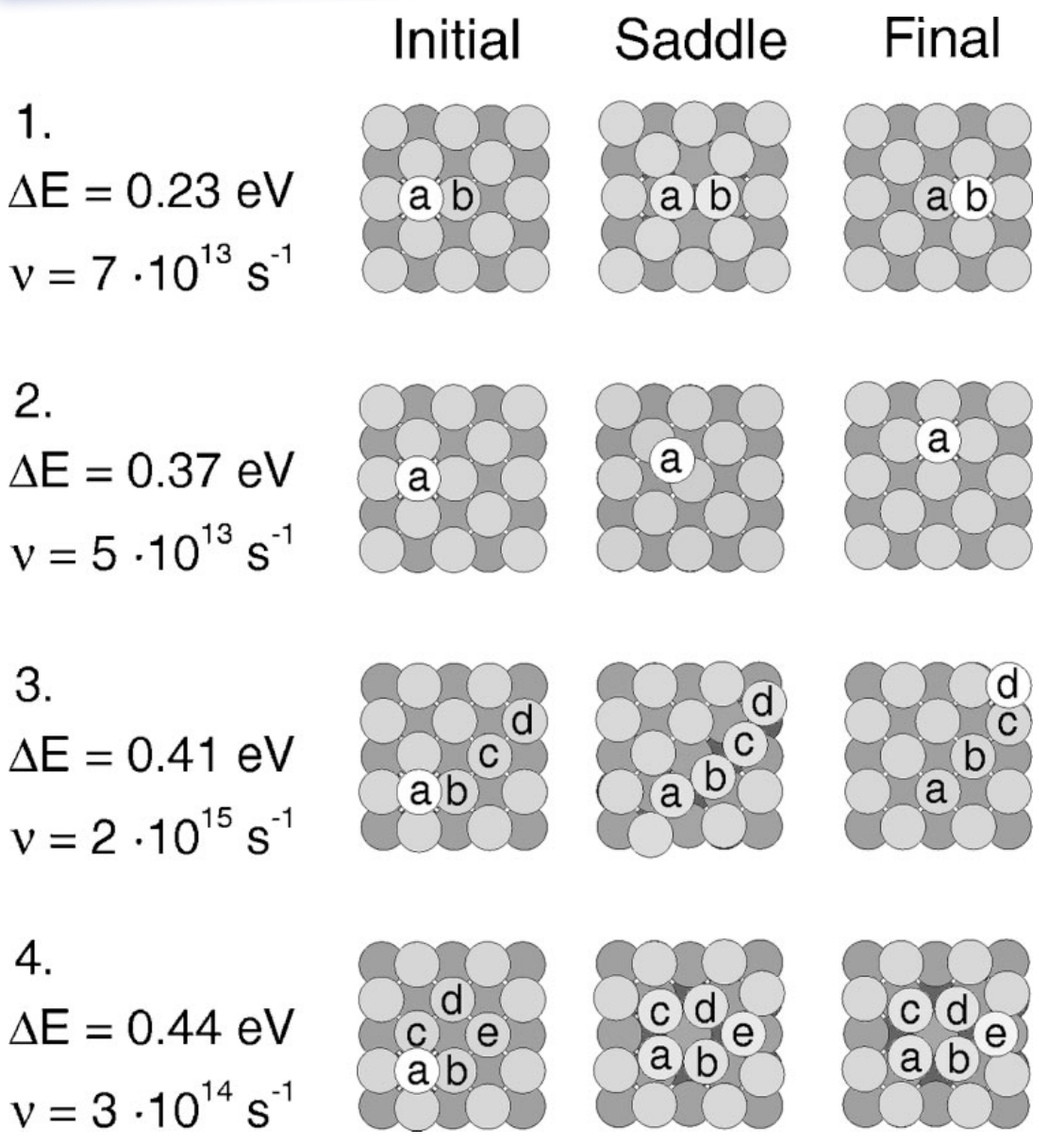
2. Constrains atoms to move only on a predefined lattice which can be real or effective

   atoms are not always on lattice

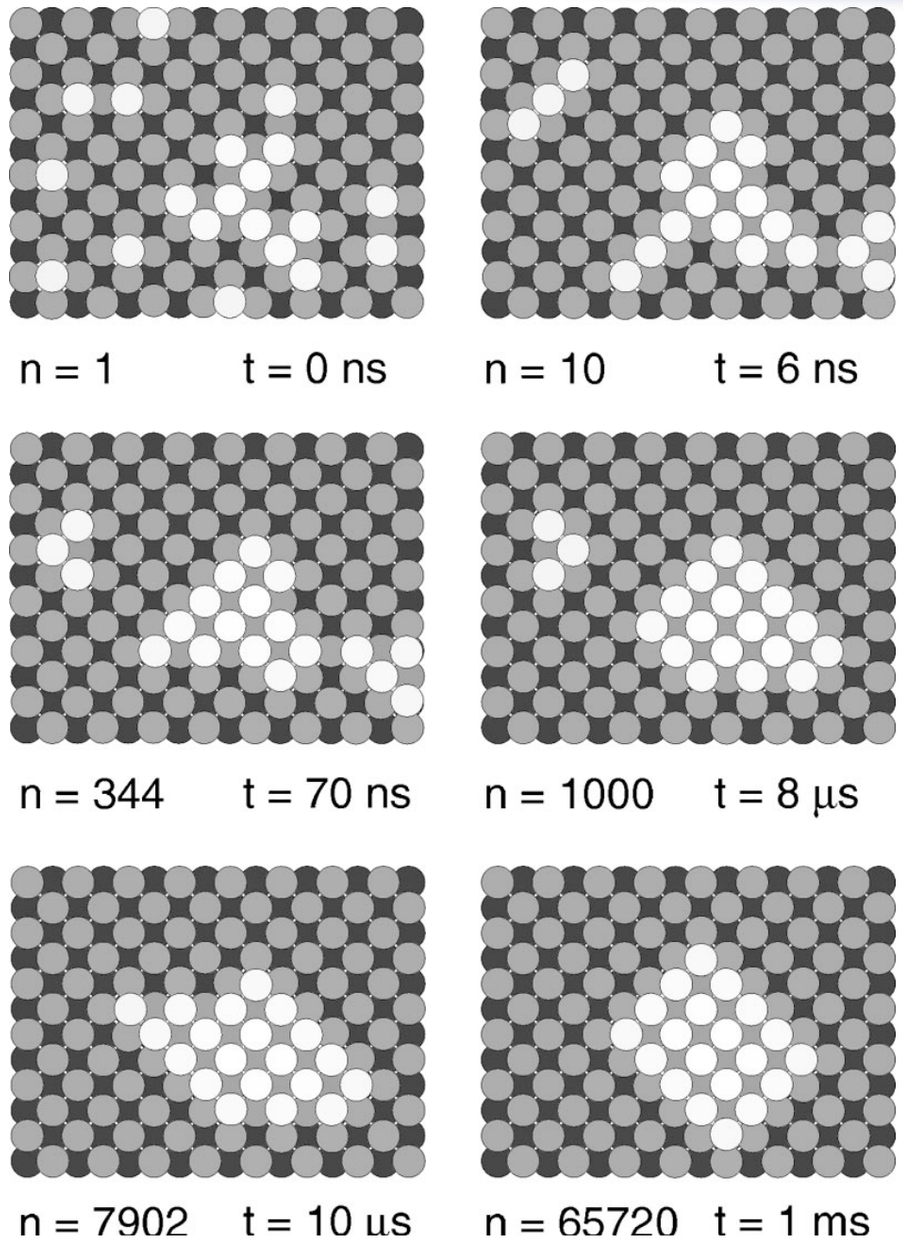
3. Supposes that there are no long-range interactions between defects

   elastic effects can be important

kMC with event list rebuilding at each step



Henkelman and Jonsson, JCP 2001



This method works well for small or simple systems. However, the number of barriers at each step much remain low.

Overcoming these limitations

Over the last few years, many methods have also tried to introduce a catalog with off-lattice configurations

Kinetic ART (El-Mellouhi, Lewis and Mousseau, PRB 2008)

- uses ART nouveau (currently, fastest saddle-point search method)
- Topological classification, handles any complexity and full elastic effects

Self-Learning KMC (Kara, Trushin, Yildirim and Rahman, JPCM 2009)

- limited saddle point searching capacities (drag + repulsive bias potential)
- pattern recognition based on the existence of a lattice (no elastic effects)

Self-evolving atomistic KMC (Xu, Osetsky and Stoller, PRB 2011)

- uses dimer method
- new searches in local environment (no elastic effects)

Local-environment KMC (Konwar, Bhute and Chatterjee, JCP 2011)

- NEB for predetermined mechanisms (biased catalog)
- Local geometrical classification (no elastic effects)

KINETIC ART

Can we recover the dynamics of relatively complex systems dominated by activated diffusion?

Kinetic ART

1) Generates the catalog and refines events with

ART nouveau

2) Classifies and reconstructs events with

Topological analysis - NAUTY

3) Evolves the system with

Kinetic Monte Carlo

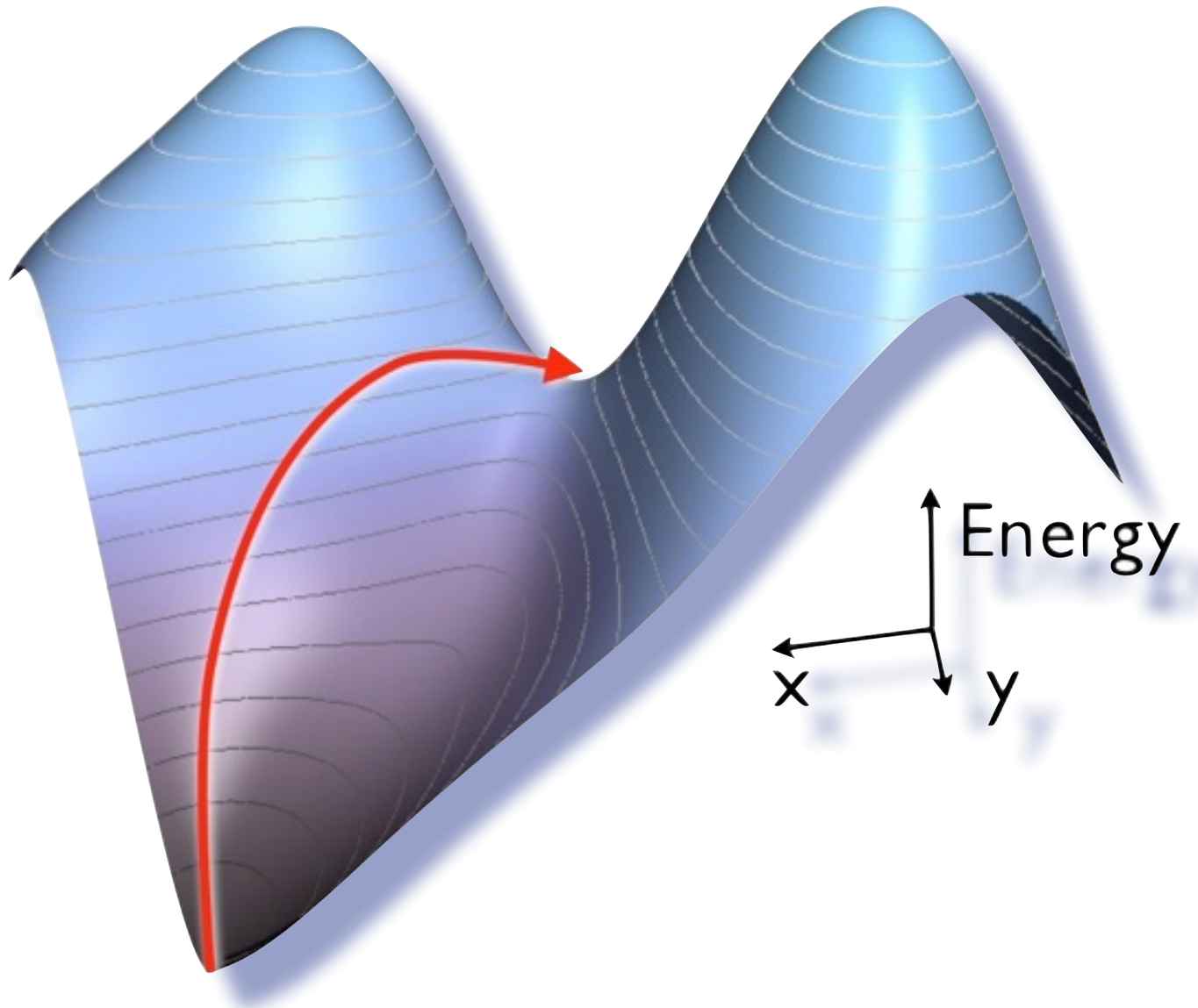
Example: Finding barriers with ART nouveau

The activation-relaxation technique is defined in three steps.

1) Leave the harmonic basin;
   threshold determined by value of lowest curvature

2) Push the configuration up along the corresponding direction;
   energy is minimized in the perpendicular hyperplane;
   can converge to the saddle point with any desired precision

3) Minimize the energy;
   bring the configuration into a new minimum



Barkema & Mousseau, Phys. Rev. Lett. 77 (1996);
Malek & Mousseau, Phys. Rev. E 62 (2000);

Systematic study of interstitials in Iron

M.-C. Marinica, F. Willaime and N. Mousseau, PRB (2011)

- Interstitial-type defects formed by the clustering of self-interstitials produced under irradiation have rather peculiar properties in α-iron by comparison with other body centered cubic (BCC) metals

- In α-iron isolated self-interstitial atoms (SIA) have a rather large migration energy, about 0.3 eV.

- Nanometer size clusters – or dislocation loops – have either ⟨111⟩ or ⟨100⟩ orientation in Fe.

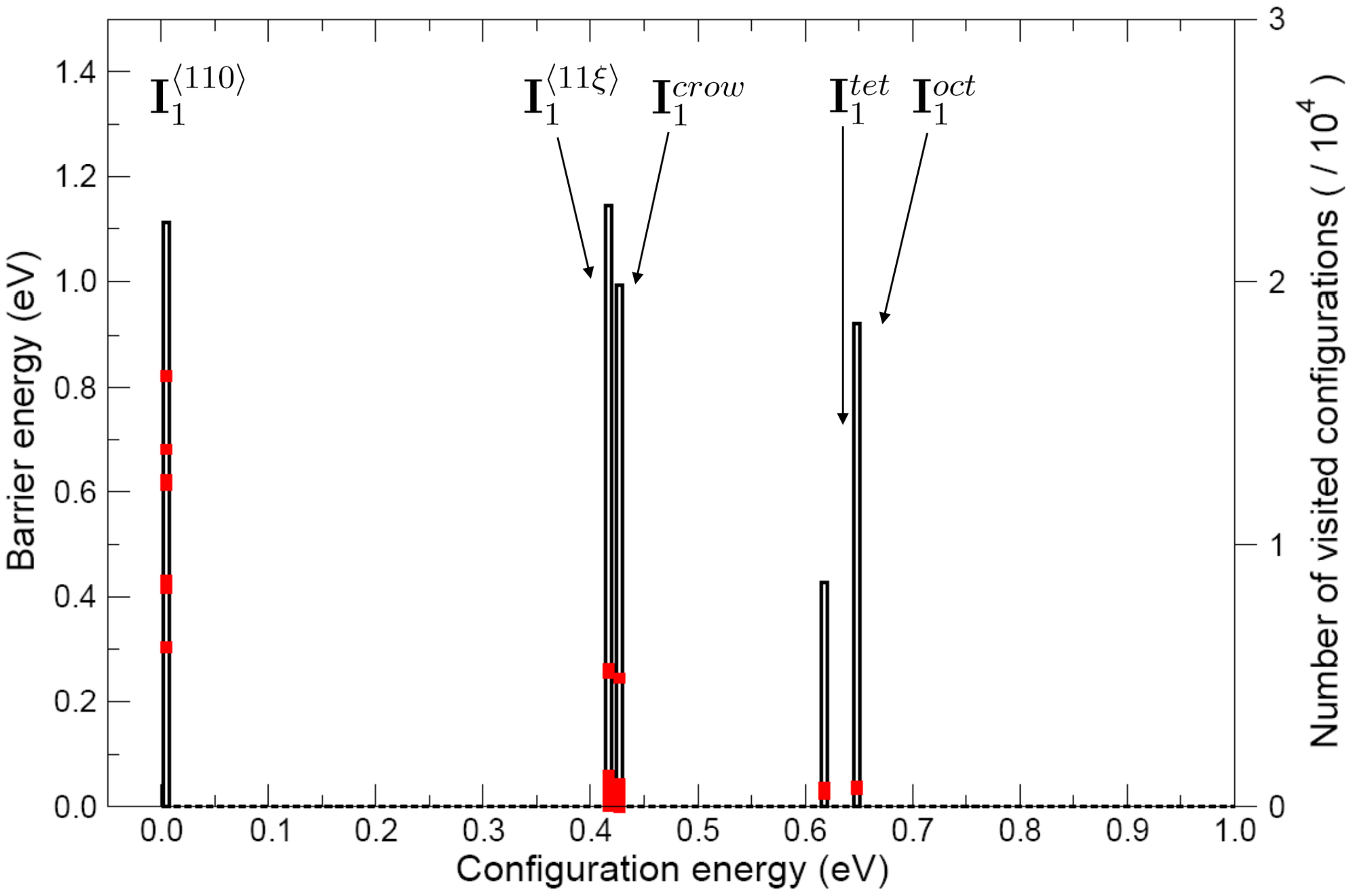
- The structure of interstitial clusters with intermediate size is largely unknown although they play a key role in the loop growth mechanism.

- The barrier height is such that MD can easily get trapped into specific minima, and not sample all mechanisms.

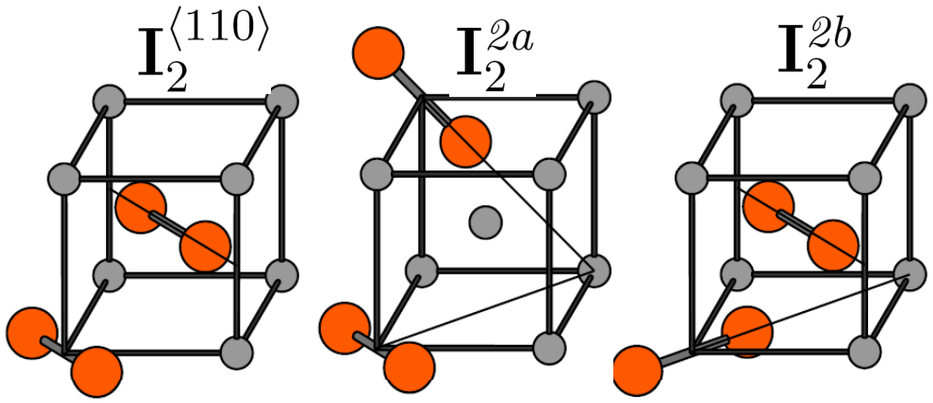
Systematic study of interstitials in Iron

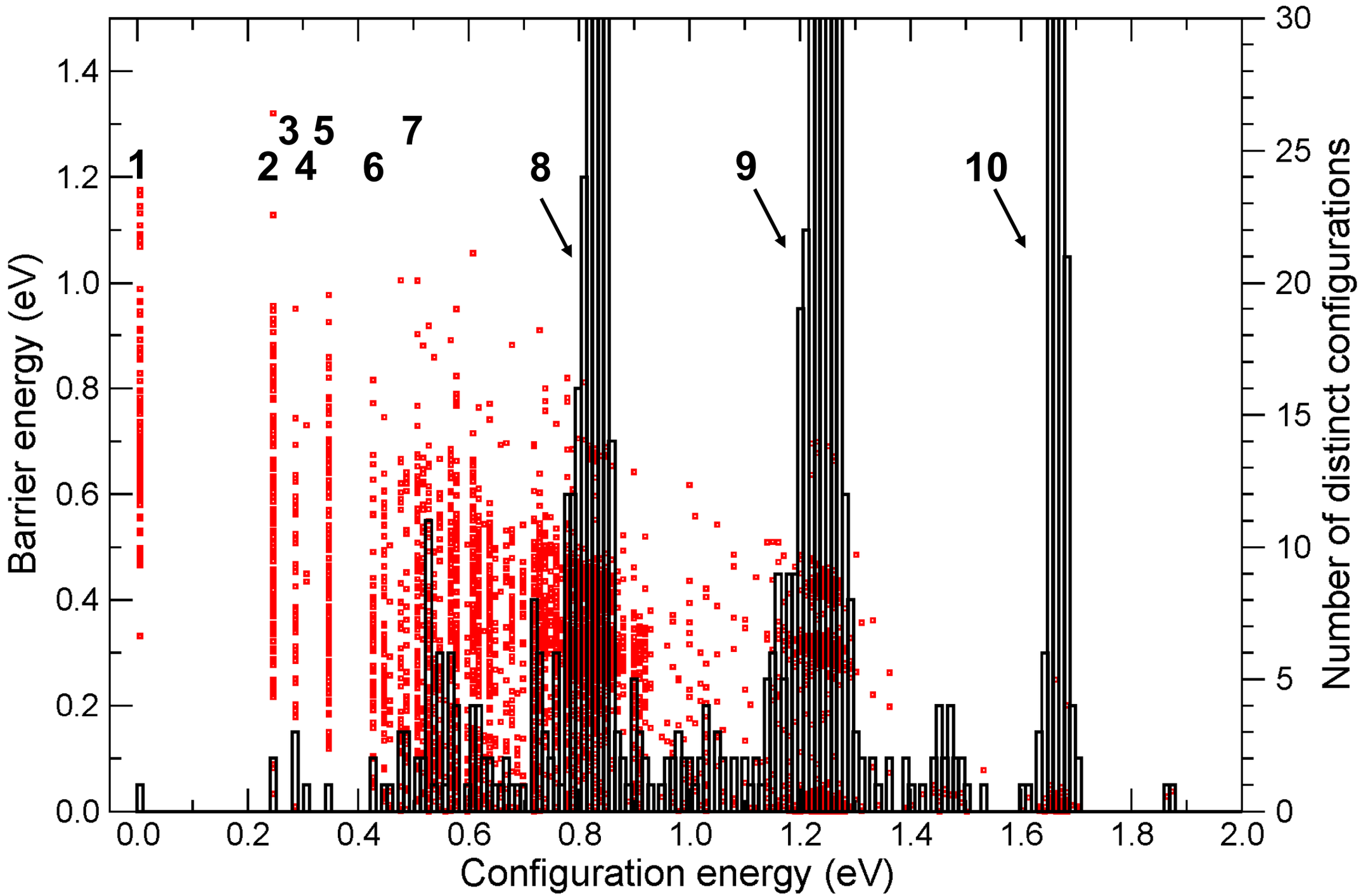
- Ackland-Mendelev potential
- ART nouveau
- 1024 atoms
- 50 trajectories which are stopped after 2000 successful activation events (each taking less than a week)

Mono-interstitials in Iron

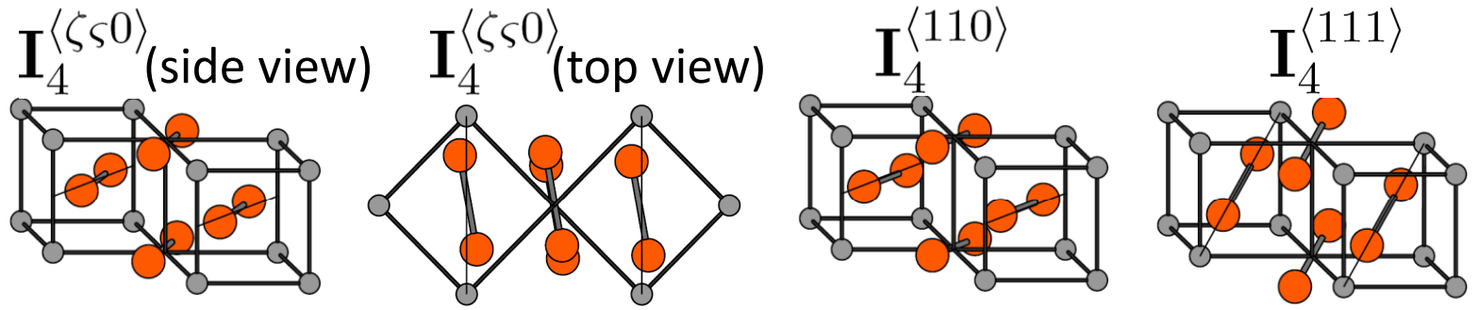


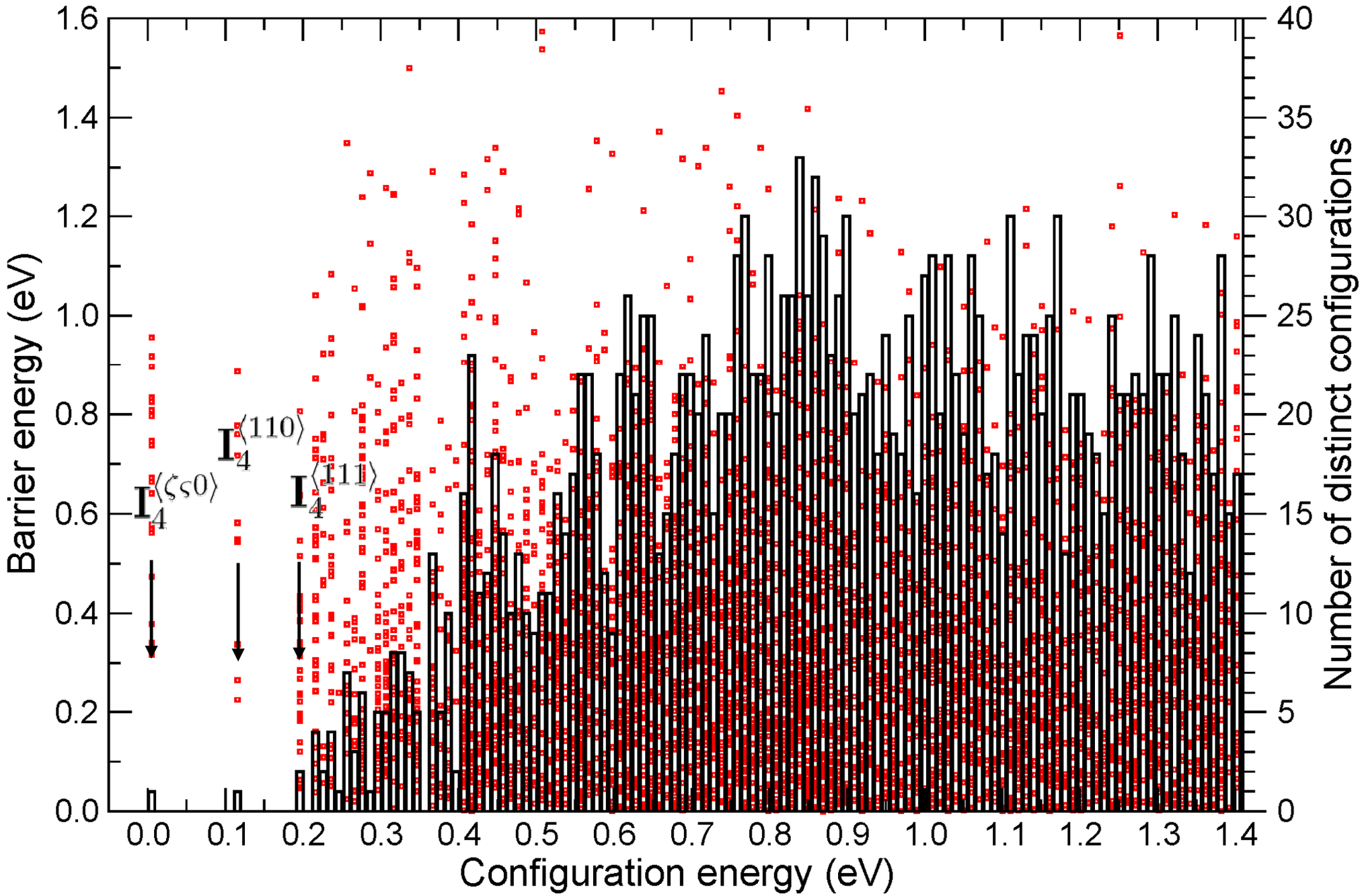
Di-interstitials in Iron





I_4 in Iron


$\mathbf{I}_4^{\langle\zeta\varsigma 0\rangle}$(side view)
$\mathbf{I}_4^{\langle\zeta\varsigma 0\rangle}$(top view)
$\mathbf{I}_4^{\langle 110\rangle}$
$\mathbf{I}_4^{\langle 111\rangle}$


Barrier energy (eV)
Number of distinct configurations
Configuration energy (eV)
$\mathbf{I}_4^{\langle\zeta\varsigma 0\rangle}$
$\mathbf{I}_4^{\langle 110\rangle}$
$\mathbf{I}_4^{\langle 111\rangle}$
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
5
10
15
20
25
30
35
40
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4

Some applications of ART nouveau

Ab initio calculation of defects diffusion mechanisms in Silicon, GaAs

El-Mellouhi and NM - PRB (2004, 2005), J. Appl. Phys.(2006); Malouin, PRB (2007)

Amorphous silicon - structure, relaxation and activated mechanisms

Barkema, Song, Malek, Kallel and NM - PRL (1996,1998, 2010), PRE (1998), PRB (2000, 2001,2003)

Amorphous gallium arsenide - structural properties

Lewis and NM - PRL (1997), PRB (1997), Barkema and NM, JPhys:CondMatt (2004)

Interstitials in Fe

M.-C. Marinica, F. Willaime and N. Mousseau, PRB (2011)

Silica glass - structural properties, activated mechanisms

Barkema, de Leeuw - NM - JCP (2000)

Lennard-Jones clusters and glasses

Brébec, Limoge, Malek and NM, PRB (2000), Def. Diff. Forum (2001)

Protein folding

Derreumaux, Wei and NM - J. Mol. Graph. (2001), JCP (2003), Proteins (2004);
St-Pierre, Derreumaux and NM (2008)

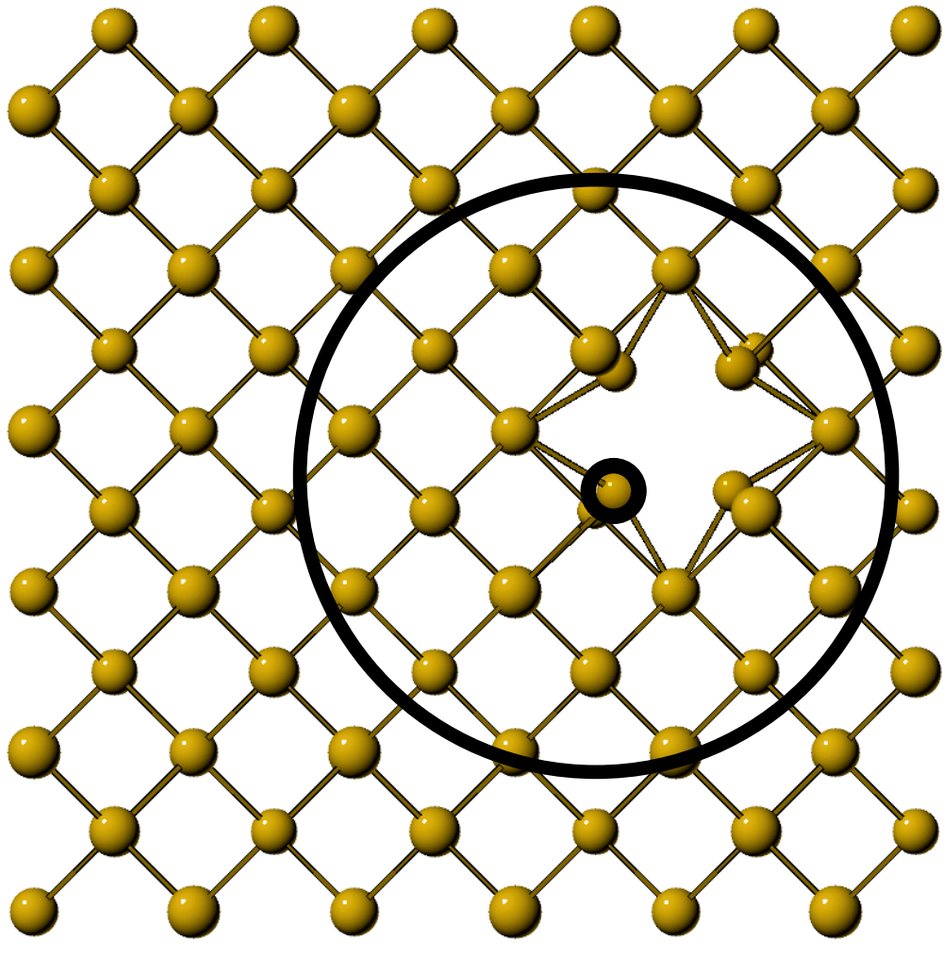
Protein aggregation

Boucher, Derreumaux, Melquiond, Santini and NM - JACS (2004), Biophys. J., Structure (2004), JCP (2005), Accounts Chem. Res.(2005), Proteins(2006), JCP (2006,2007)

A topological classification

We suppose that all configurations can be classified in terms of their topology and that the events generated will have the same topological evolution.

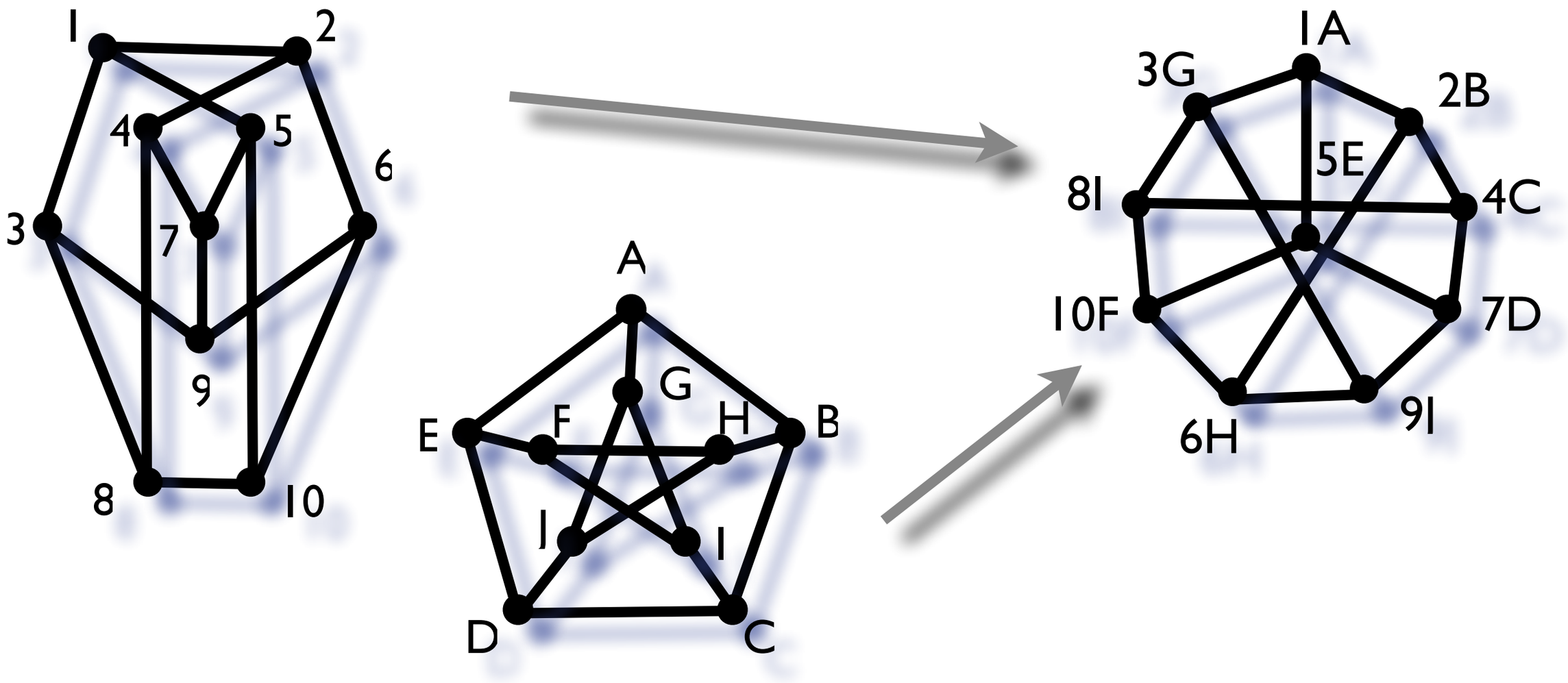
1. Using the neighbour list, a graph is generated
2. The graph is analysed at its topology identified
3. All graphs with the same topology belong to the same class



F. El-Mellouhi, NM and L.J. Lewis, PRB **78**, 153202 (2008).

NAUTY

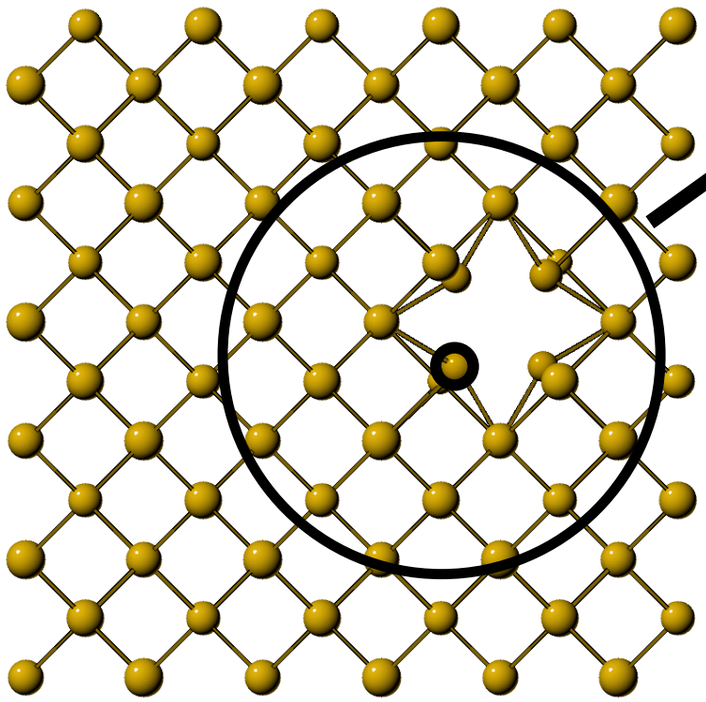
NAUTY is a program for computing automorphic groups of graphs; it can also produce a canonical labelling taking into account symmetry operations of the graph.



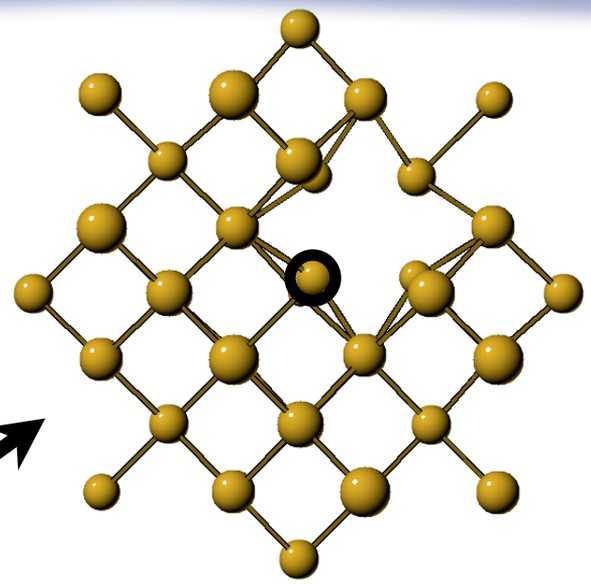
Brendan D. McKay, *Practical Graph Isomorphism*, Congressus Numerantium, **30** (1981) 45-87.
http://cs.anu.edu.au/~bdm/nauty/

Topological analysis with NAUTY

Take a sphere around each atom



(a)



(b)

Prepare the graph of connectivity between atoms and label them

(c)

NAUTY

(d)

[912419]

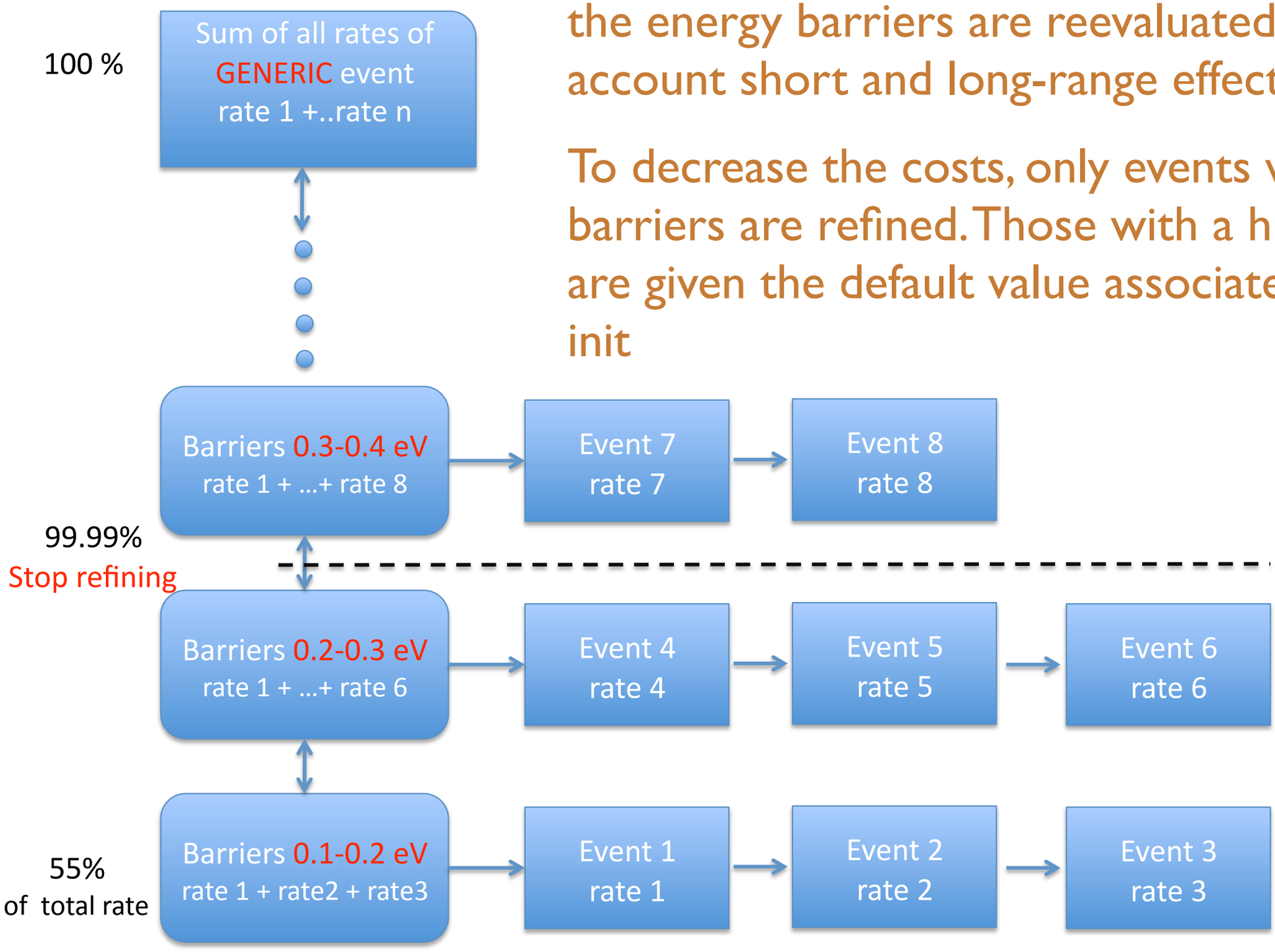
1. Store the topology label in a hash table, rehash the label if clustering occurs;
2. Update the occurrence of the topology;
3. If topology is completely new, store it and find the events and rate lists associated with it.

The algorithm

After an event :

1. The topology of all the atoms within the active part of the event is evaluated again;
2. If the topology is known, import the list of events; if not, generate ART events;
3. If some of the old topologies do not have enough events, try a few more ART steps;
4. Store these new topologies.
5. Relax all relevant barriers to take into account elastic effects
6. Compute rate and apply KMC

Taking into account long-range elastic effects



After each event, saddle points are refined and the energy barriers are reevaluated to take in to account short and long-range effects.

To decrease the costs, only events with low-barriers are refined. Those with a high barrier are given the default value associated with the

Taking care of low-energy barriers

Separate states in

transient states

- low-energy barriers
- fast transitions between t.s.

absorbing states

- final states: after some time the system will end up in a a.s.

- high-energy barriers

The Mean Rate Method

Puchala et al., JChP **132**, 134104 (2010)

LK Béland, P Brommer, F El-Mellouhi, J-F Joly and NM, PRE **84**, 046704 (2011).

Other features

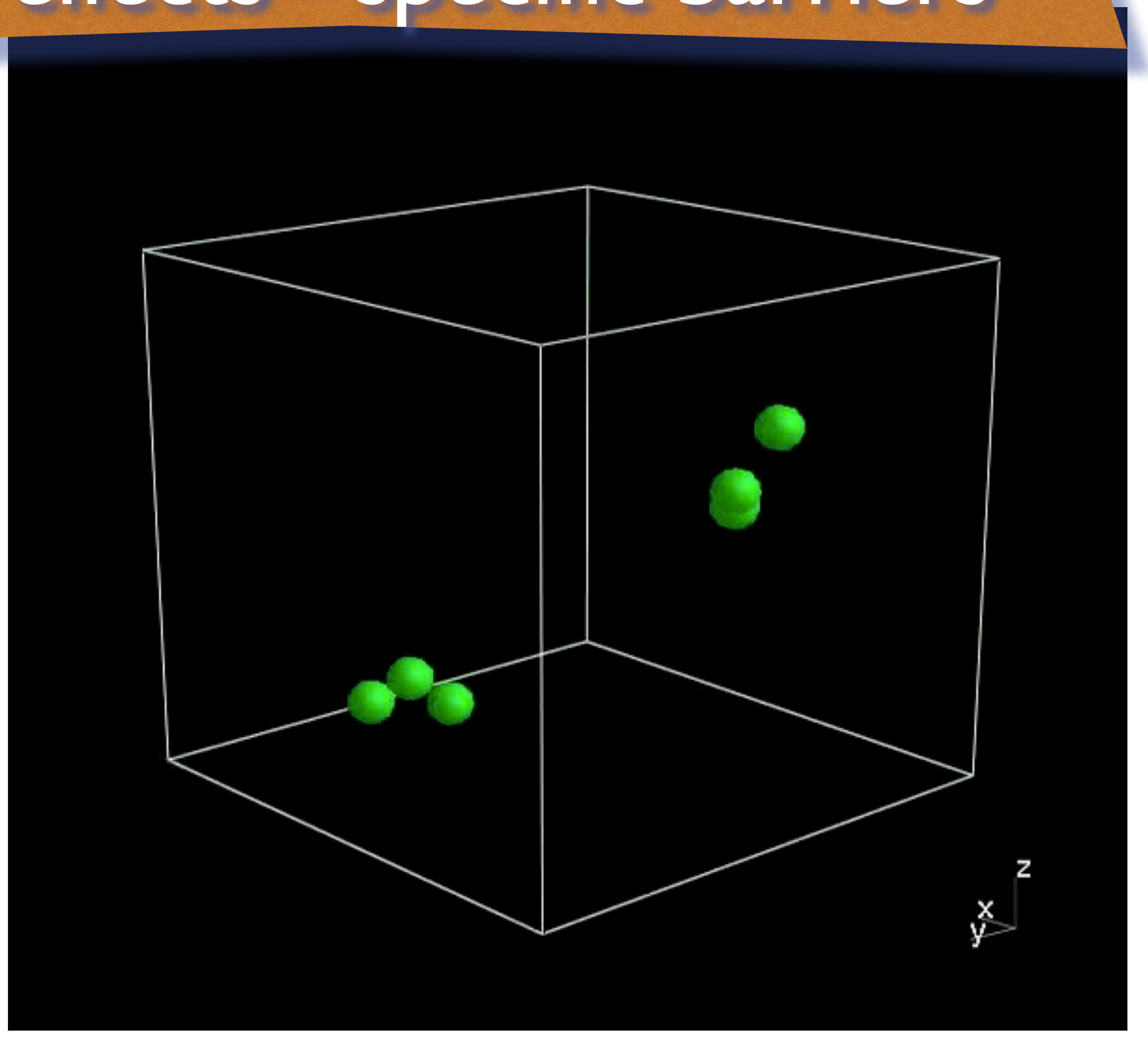
- Use the LAMMPS forcefield library
- Fixed prefactor (typically 10^{13} s^{-1})
- Handles alloys directly
- Parallelized for events and forcefield
- Order (1) force calculations
- Various capabilities at selecting events, species, etc.
- Flexible handling of boundary conditions, including surfaces

Elastic effects - specific barriers

~1000 atoms
Stillinger-Weber potential
6 vacancies
500 K

~1200 events

120 μs



Only generic events

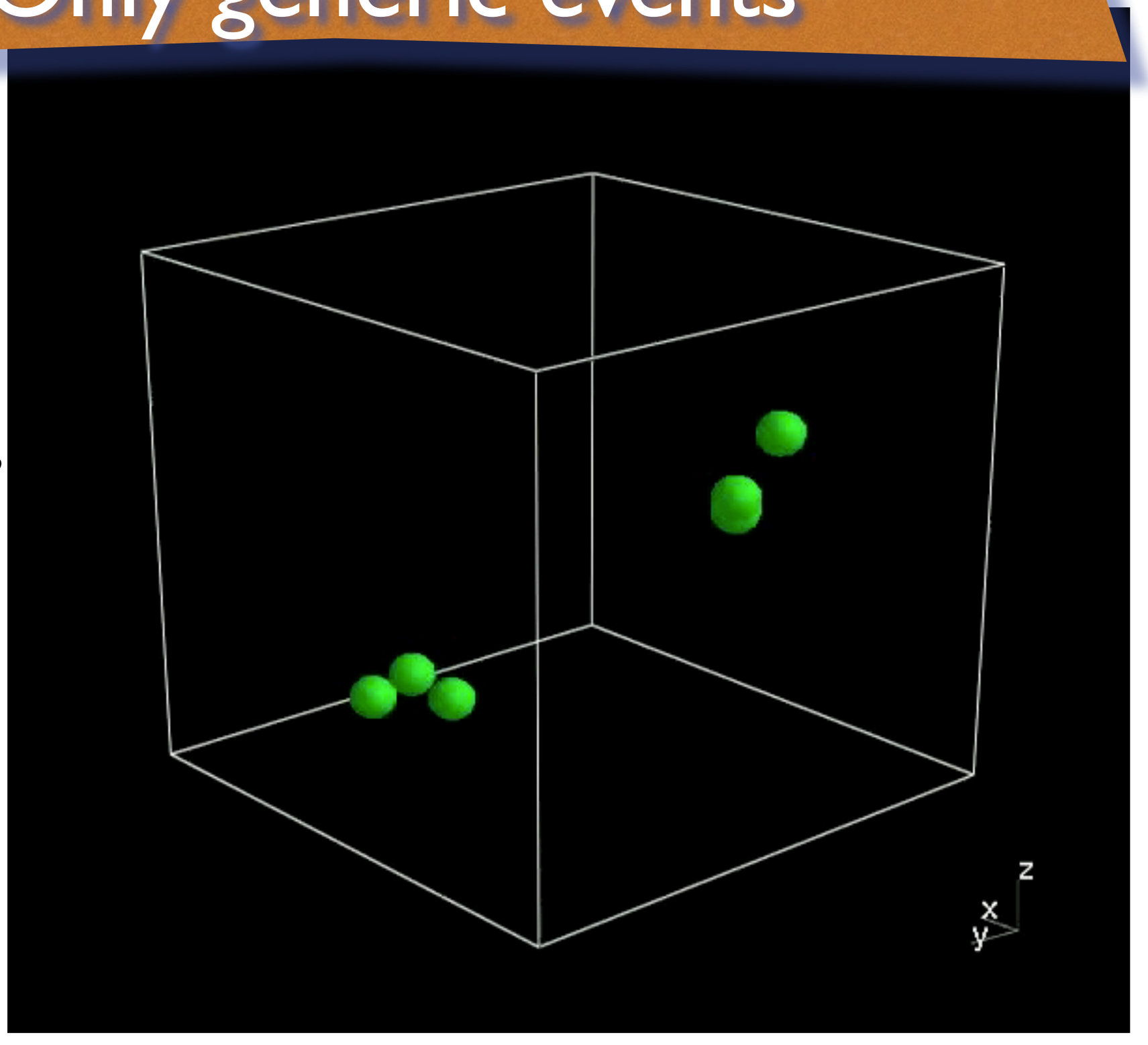
~1000 atoms
Stillinger-Weber potential
6 vacancies

Only generic events, no relaxation for barriers

500 K

~5000 events

0.001 s



C-

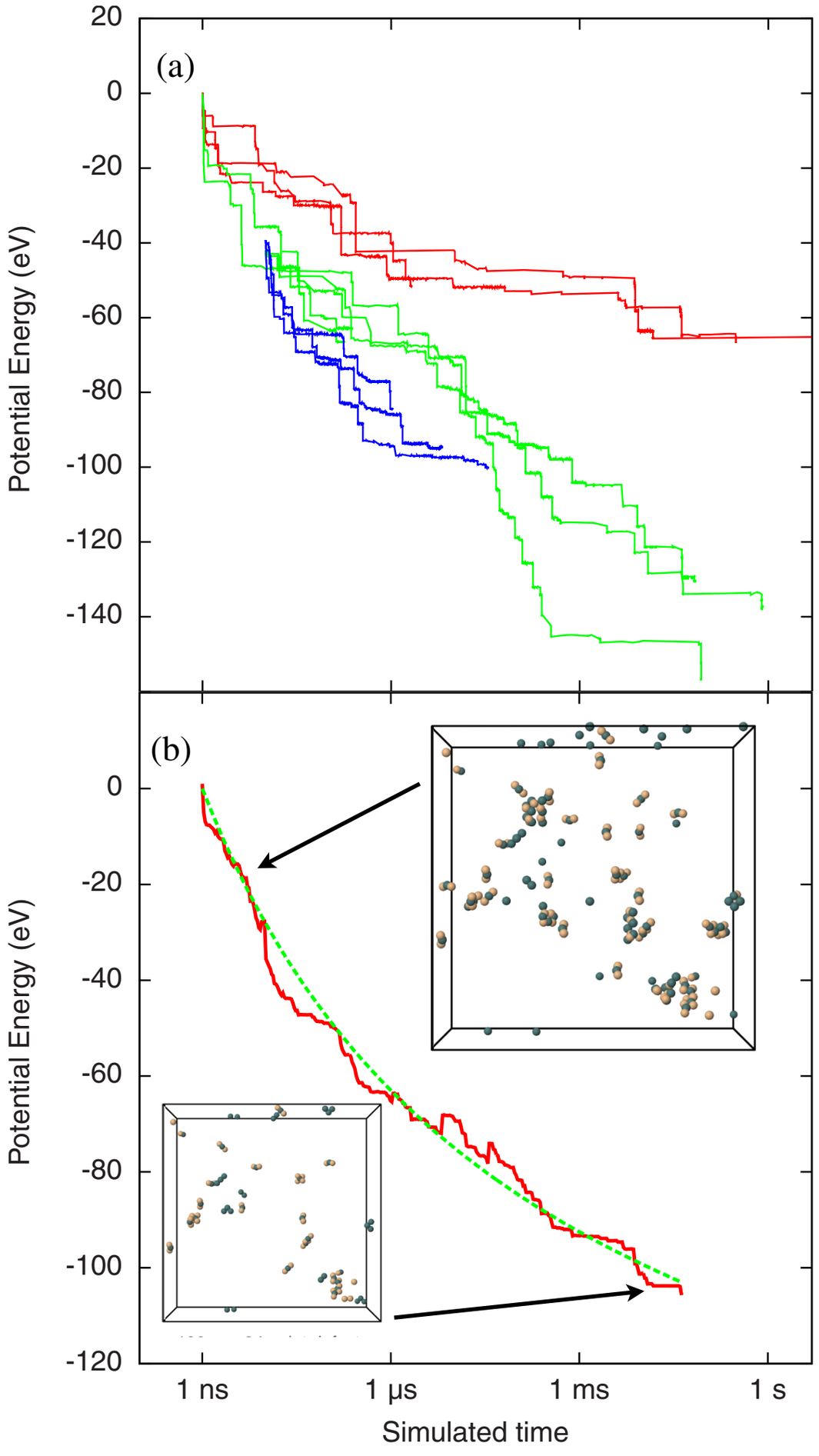
Si anneal after ion

27000 atoms box, 300 K, 1 atom implanted at 3 keV

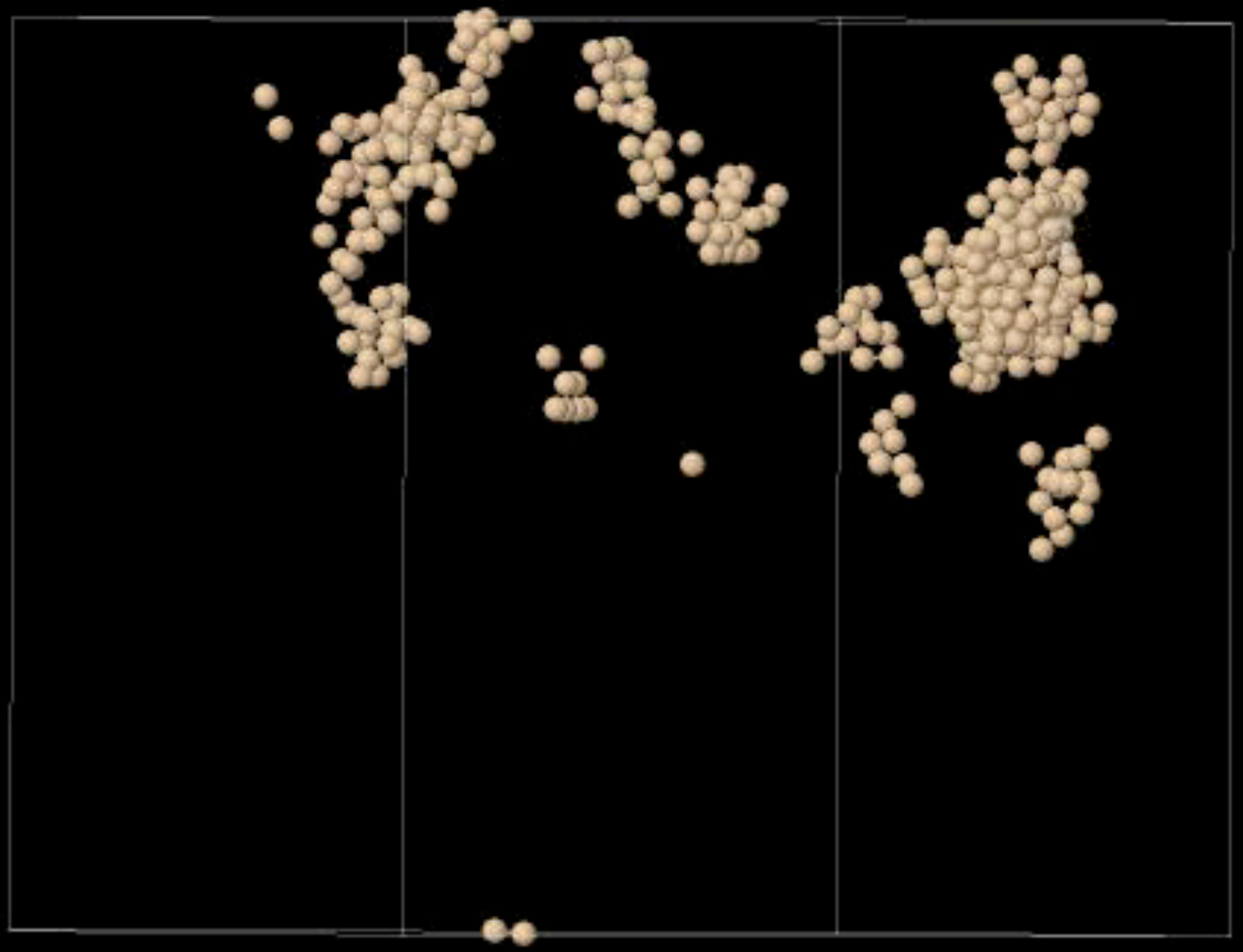
1 ns simulated with MD, serves as initial configuration for kART run

Comparison with nanocalorimetry experiments is possible

Handling of low-barrier by basin mean-rate method makes these runs even faster



Béland et al, PRL 2013; PRB 2013

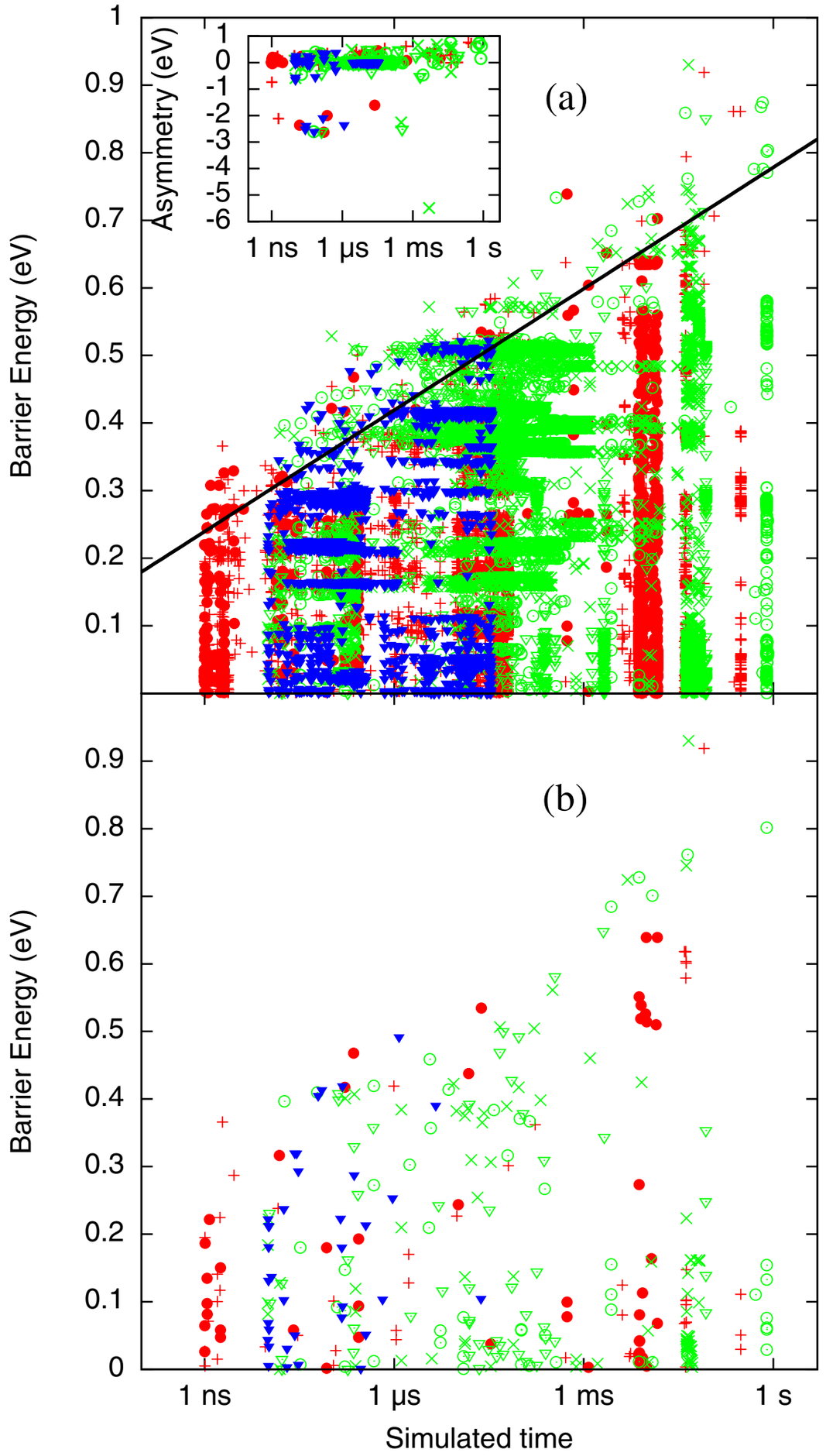


C- Si anneal after ion

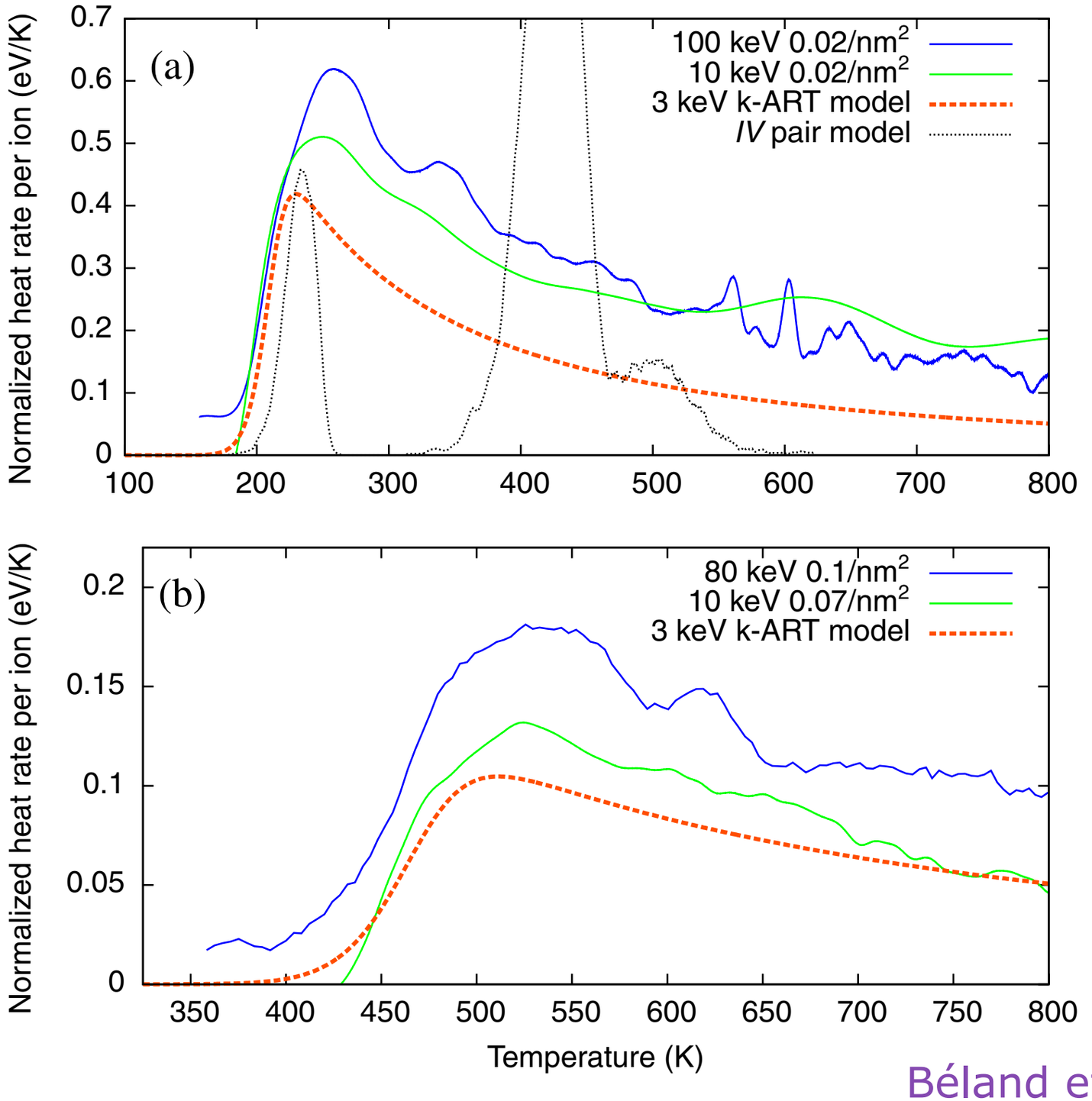
The jumps in time are caused by the basin method acceleration.

A large number of topologies must be explored to describe the correct PES (potential energy surface) and kinetics.

We show that the damaged system can execute transitions with a quasi-continuum of energy barriers



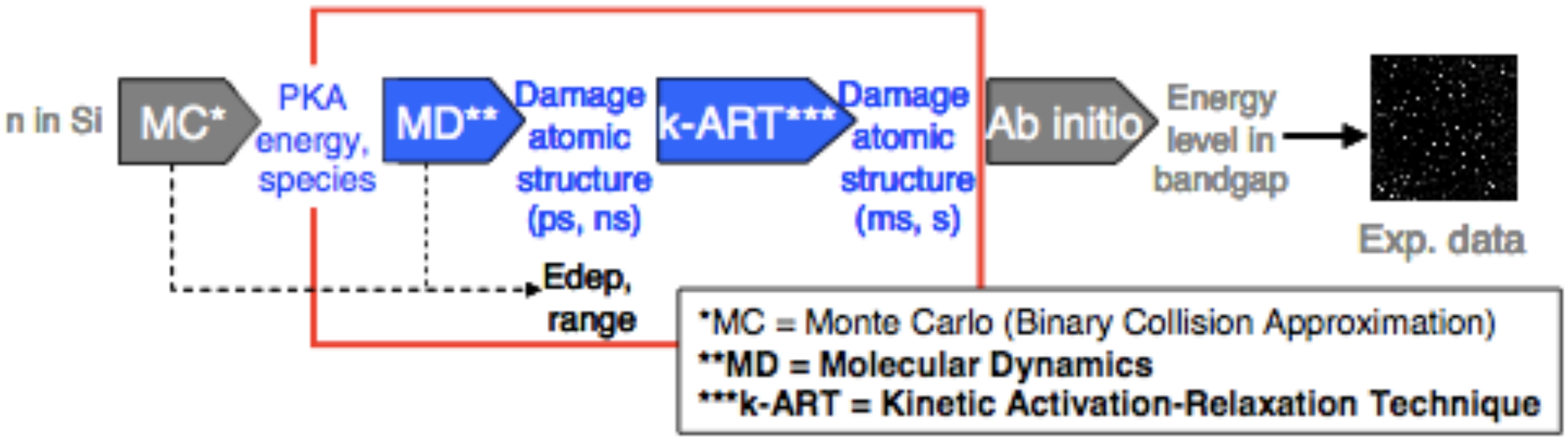
Nanocalorimetry measurements : *c*-Si



Béland et al, PRL 2013

Revisiting: understanding telegraph noise

With Antoine Jay, Mélanie Rayne, Anne Hémeryck, Vincent Goiffon, Nicolas Richard and Pierre Magnan



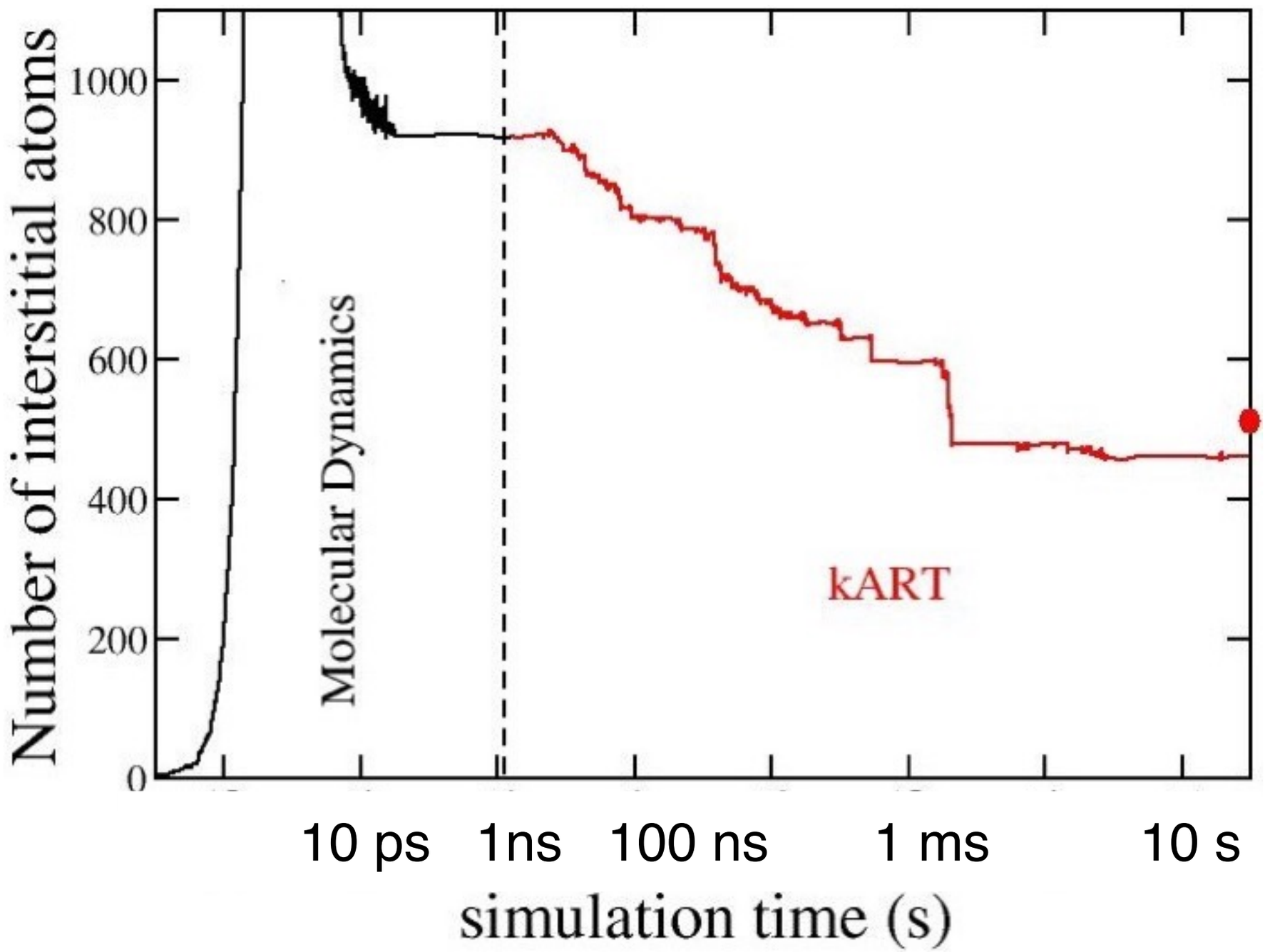
1. 1 million atoms initially

2. 10 to 100 keV

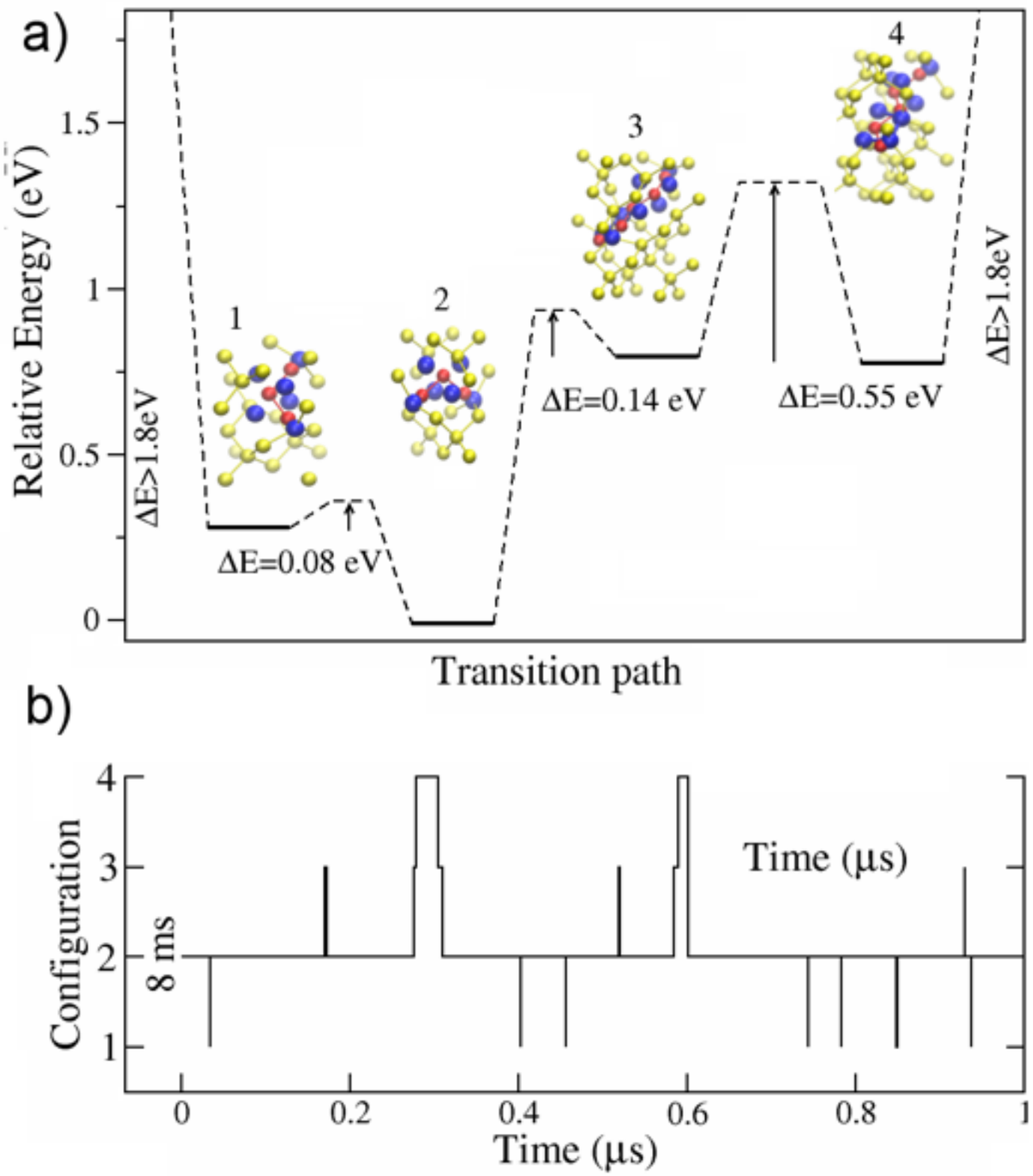
3. Relaxation first with MD (1 ns) then k-ART

4. Stillinger-Weber

Revisiting: understanding telegraph noise



A possible candidate: a tri-interstitiel flicker

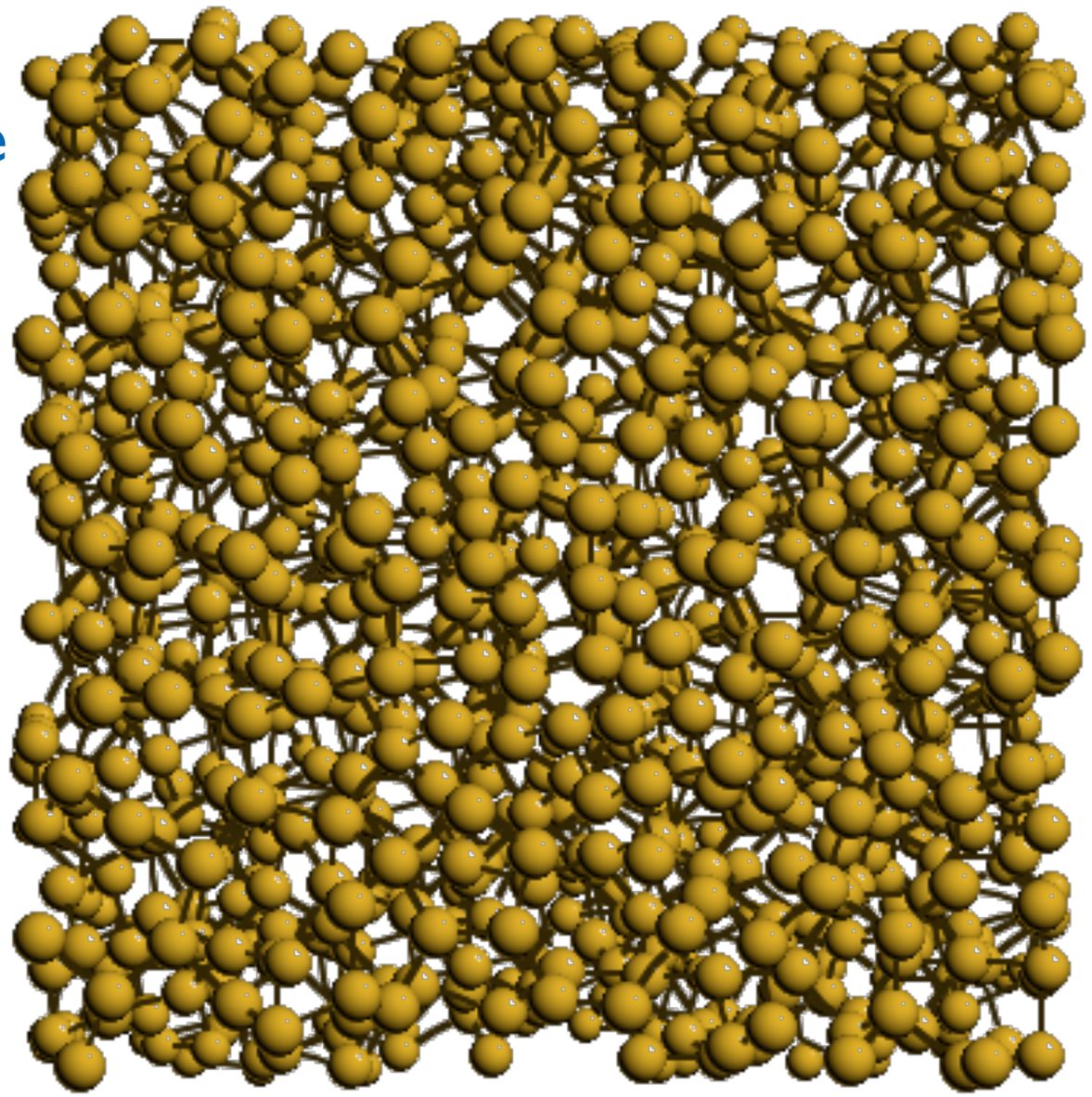


Application to amorphous silicon

1. What is the relation between average coordination (i.e. defects) and relaxation?

2. How do defects move?

3. No accelerated technique has been applied to these disordered materials

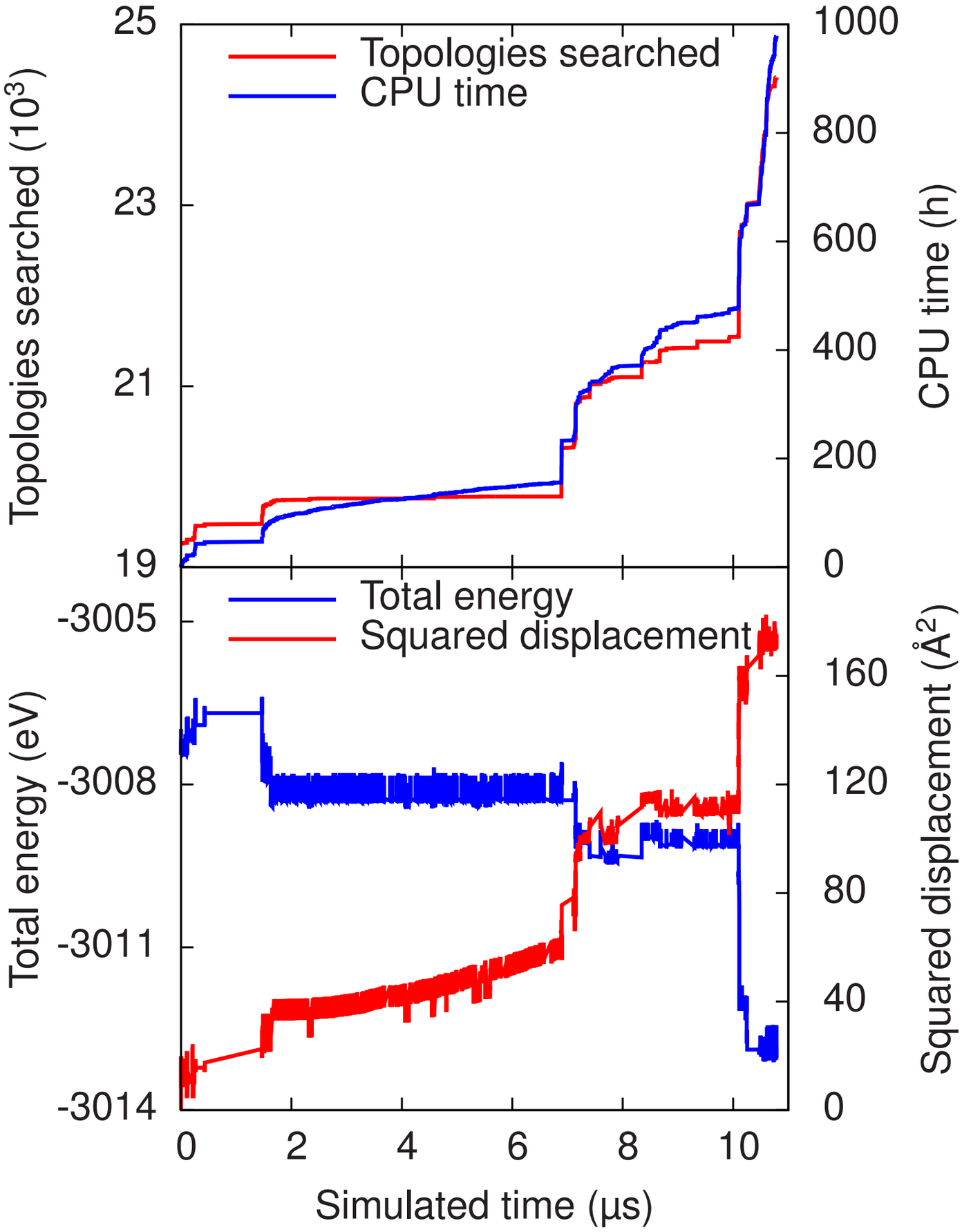


Joly *et al*, PRB 2013; PRB (submitted 2015)

Application to amorphous silicon

1000-atom box

modified Stillinger-Weber potential



Stability of vacancies

999-atom box (1 vacancy)

modified Stillinger-Weber potential

T=300 K

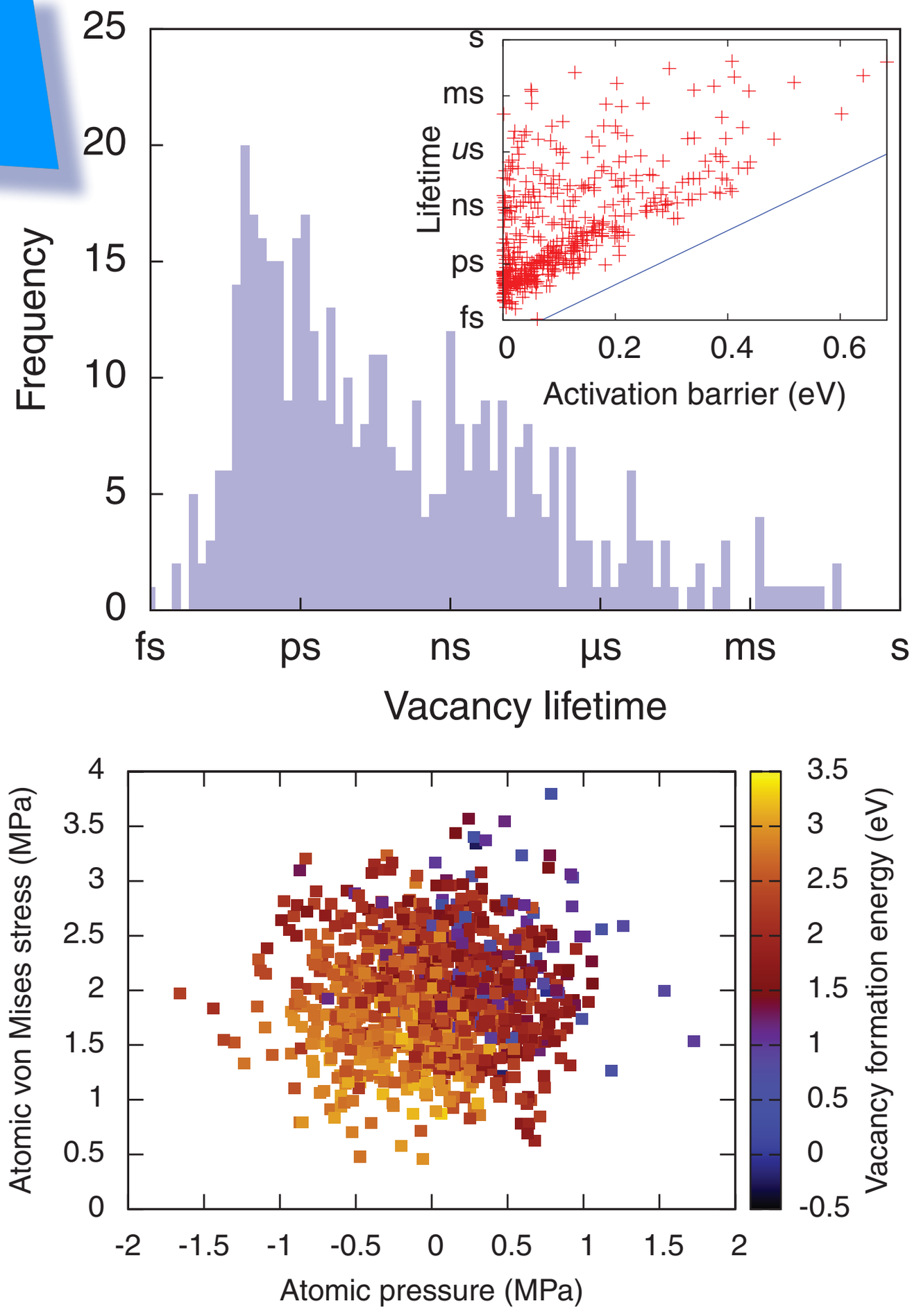
Initial catalog: 32 120 events

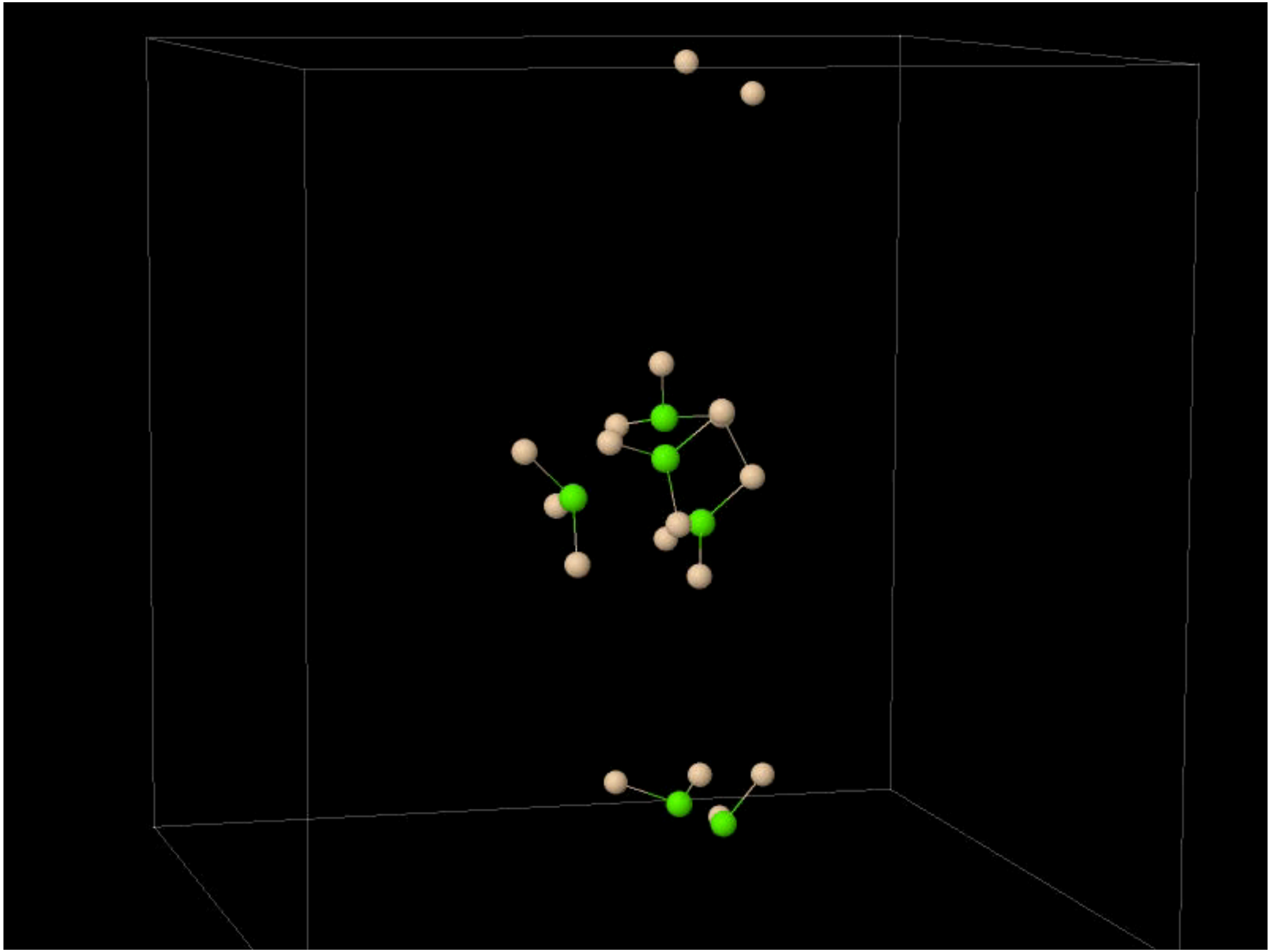
E_{basin} = 0,45 eV

24 processors (Intel Westmere-EP).

Most vacancies disapear within 1 ns

Here, vacancy survives after 120 µs





Vacancies in Iron

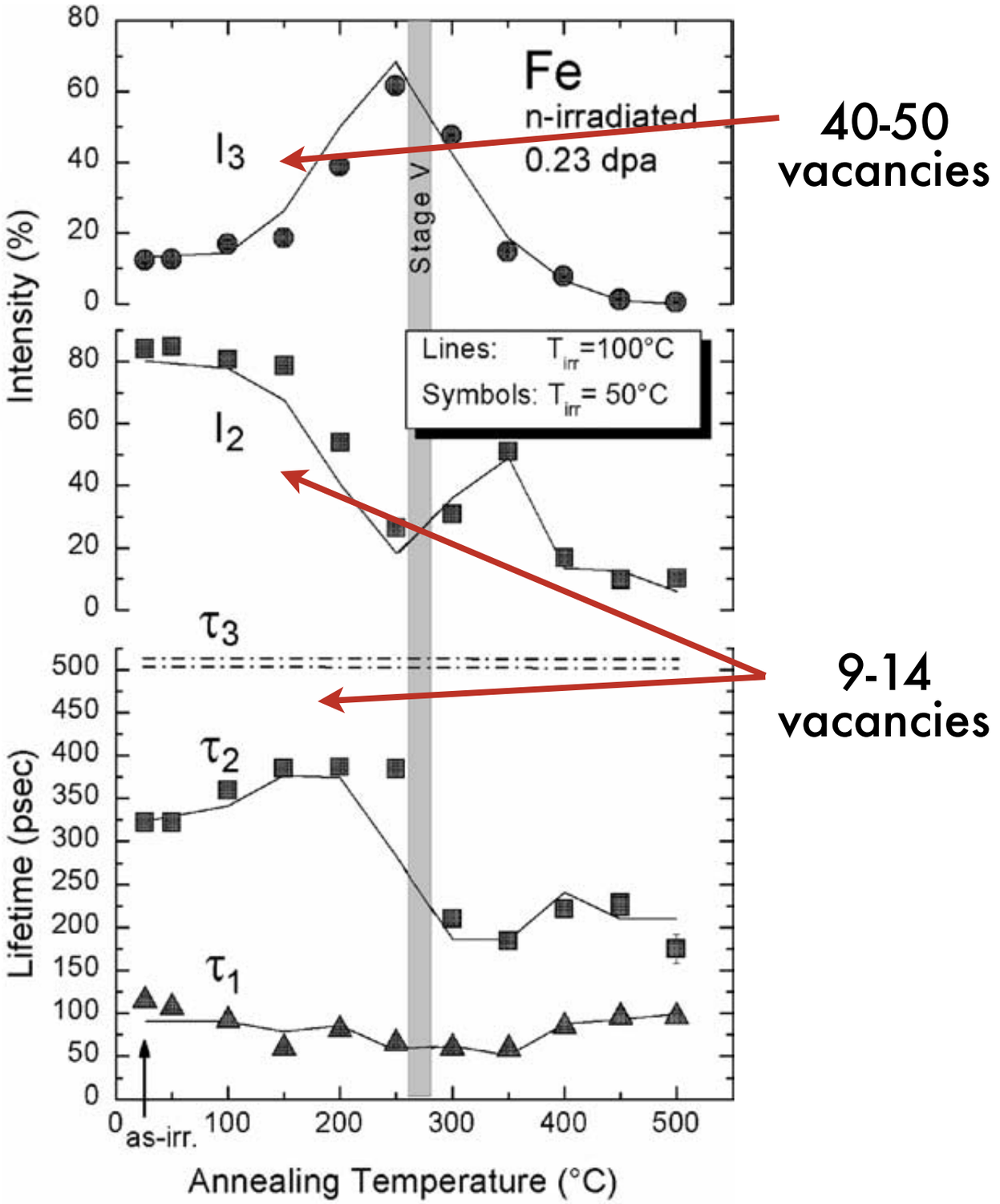
Accumulation of point defects and their complexes in irradiated metals as studied by the use of positron annihilation spectroscopy

M. Eldrup and B.N. Singh, Journal of Nuclear Materials **323** (2003) 346–353.

OUR APPROACH:

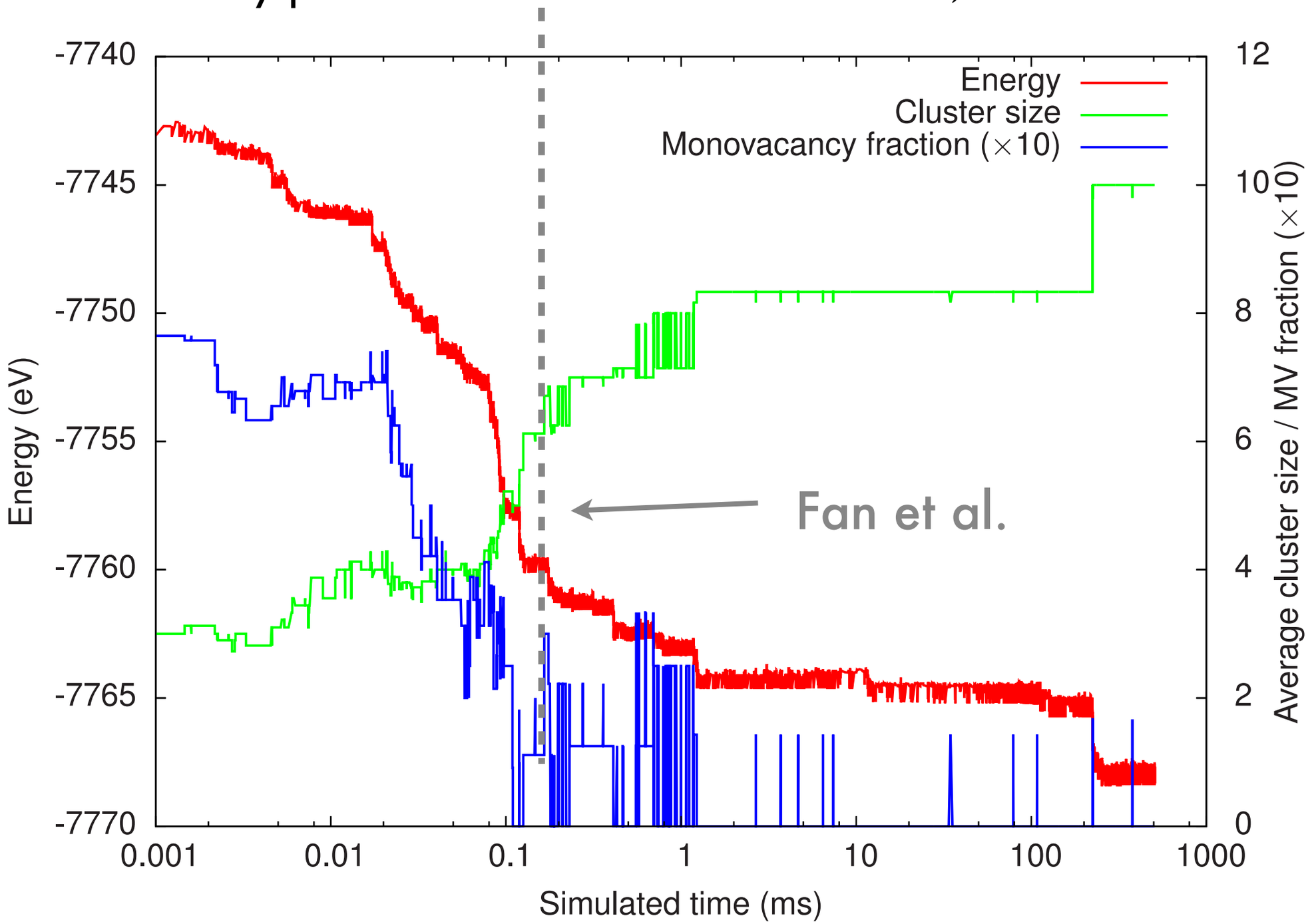
50 randomly placed vacancies in 2000-atom box;

Mendeleev Potential.

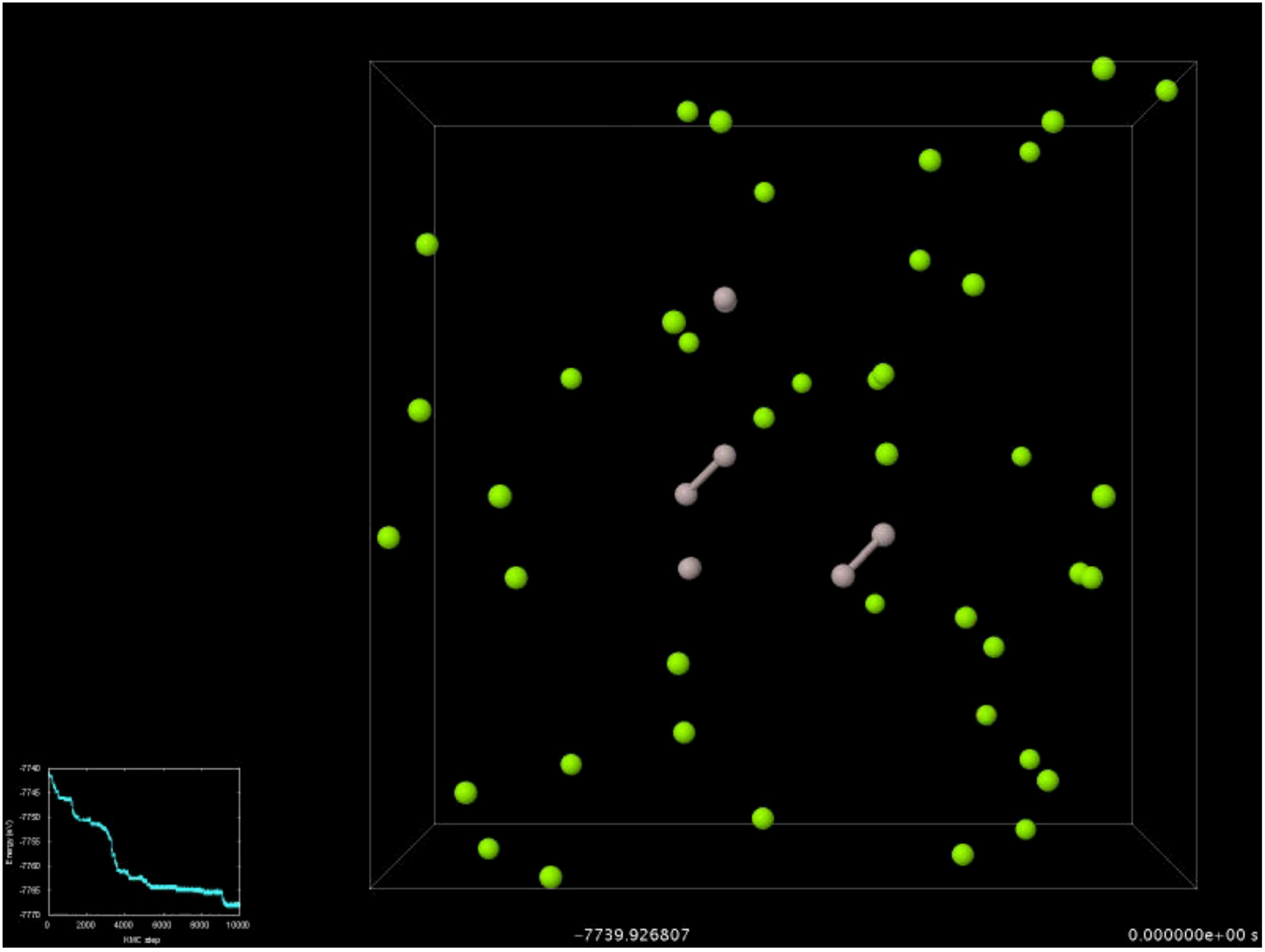


Vacancies in Iron

50 randomly placed vacancies in 2000-atom box; Mendeleev Potential.



Brommer *et al.* PRL (2011); PRB (2014)


-7740
-7745
-7750
-7755
-7760
-7765
-7770
Energy (eV)
0
2000
4000
6000
8000
10000
KMC step
-7739.926807
0.000000e+00 s

C diffusion in Fe (in progress)

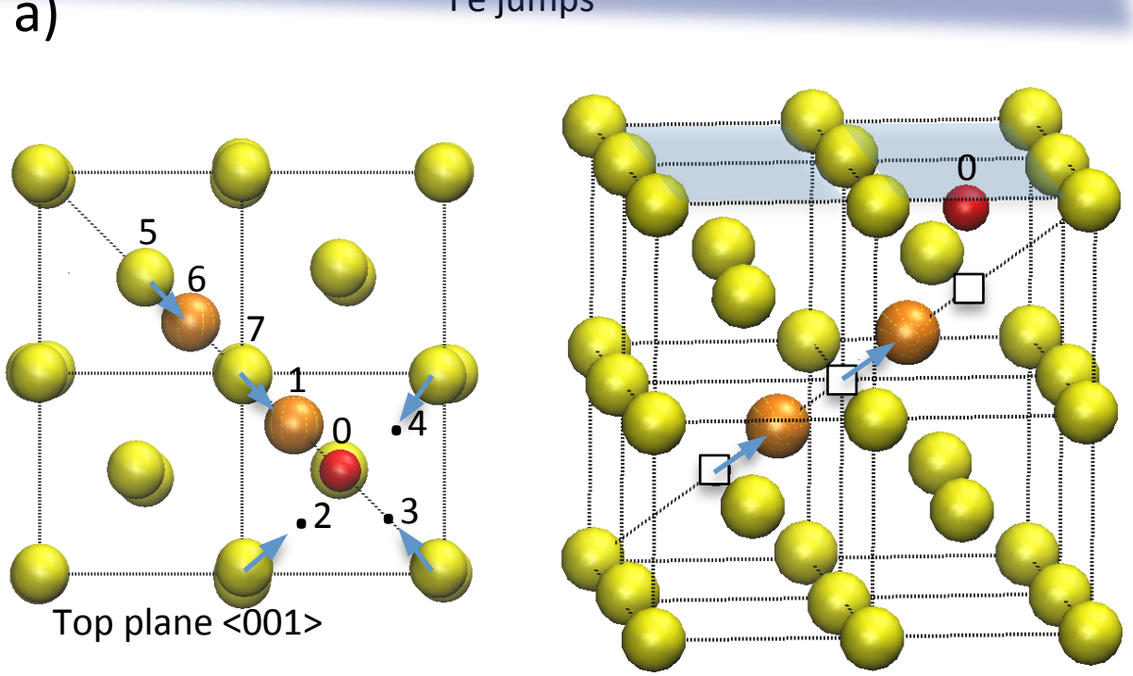
What are the fundamental mechanisms responsible for metal dusting ?

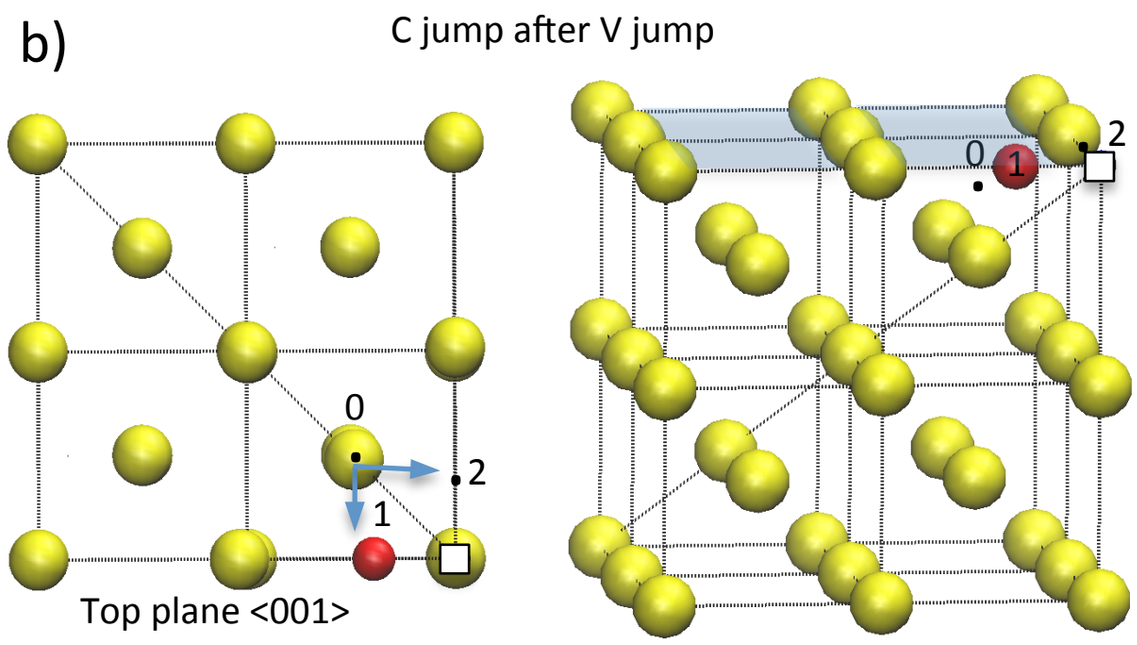
1. Use Becquart's C-Fe EAM potential

2. Start with simple defects :

   1. C interstitials

   2. C subsitutionals





O.A. Restrepo, N. Mousseau, F. El-Mellouhi, O. Bouhali, M. Trochet, C. S. Becquart, Computational Materials Science **112**, Part A, 96-106 (2016).

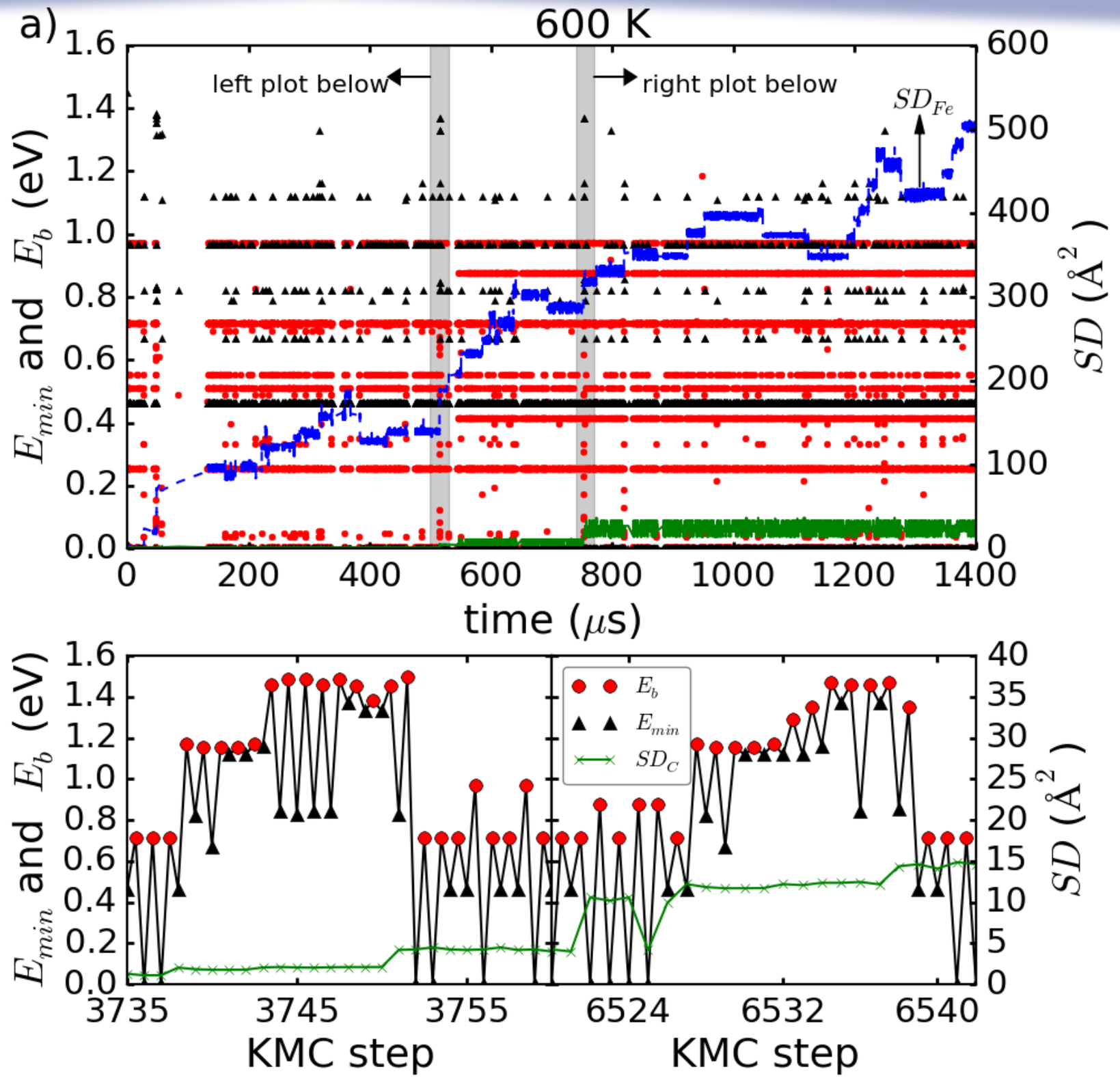
C-substitutional in Fe

A complex diffusion:

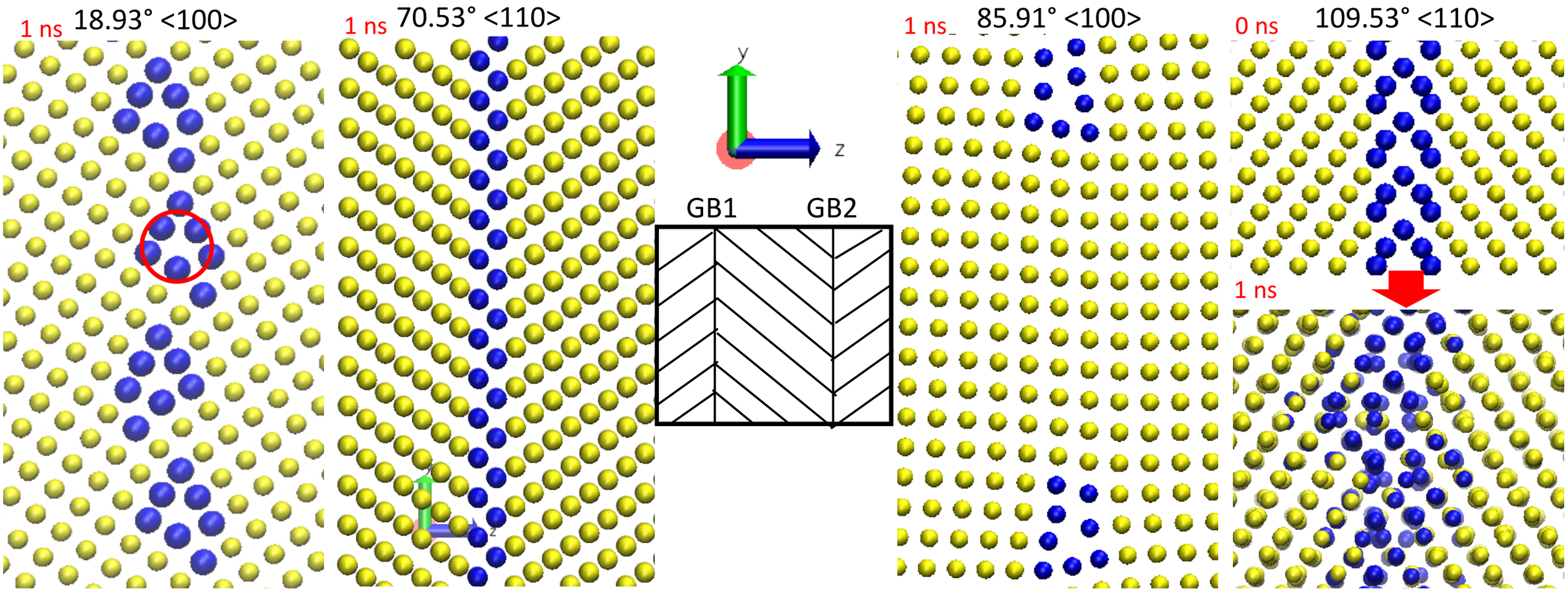
C-interstitial diffusion barrier: 0.81 eV

The vacancy diffusion barrier: 0.64 eV

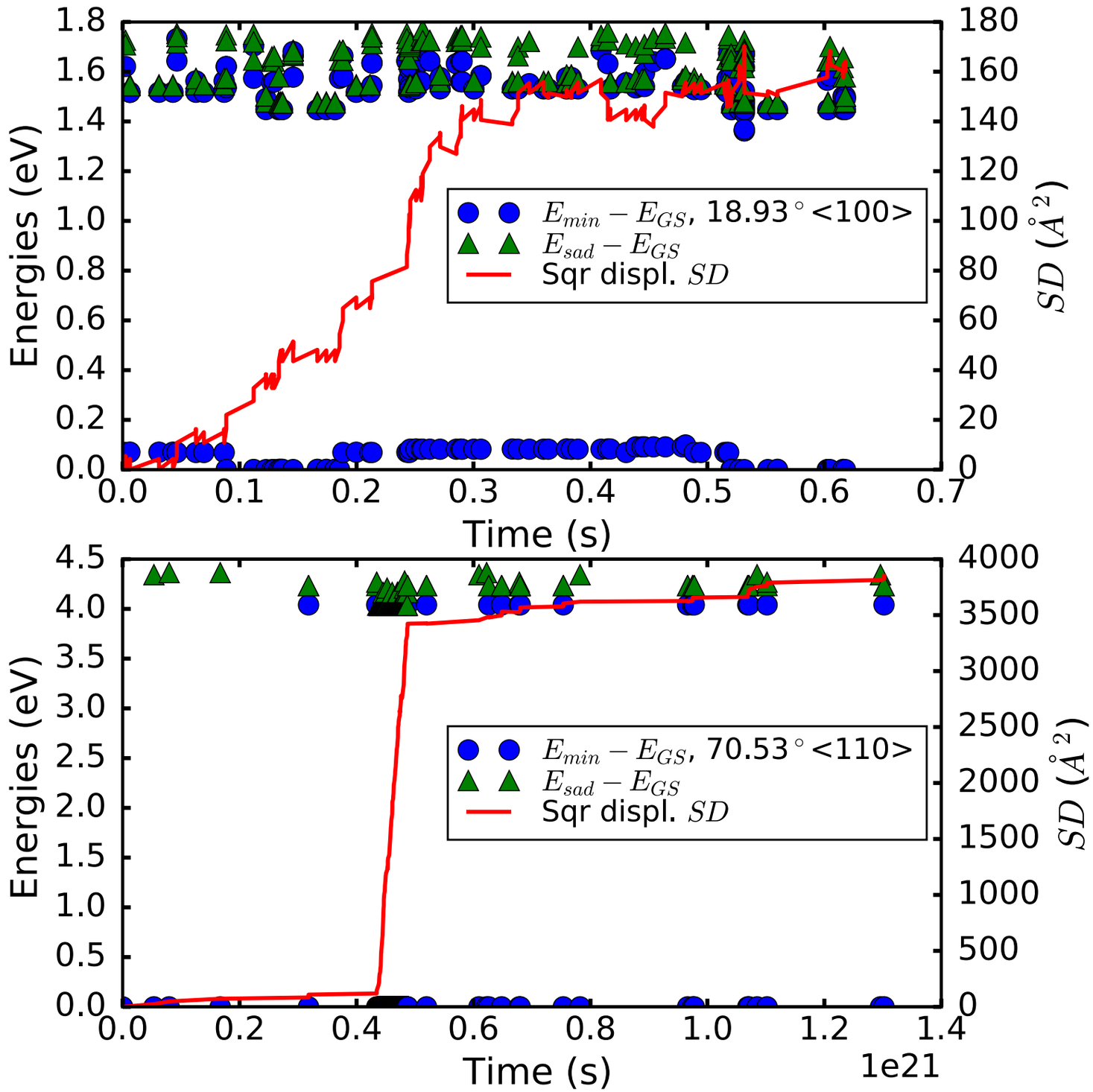
Vacancy-C bound state barrier: 1.5 eV



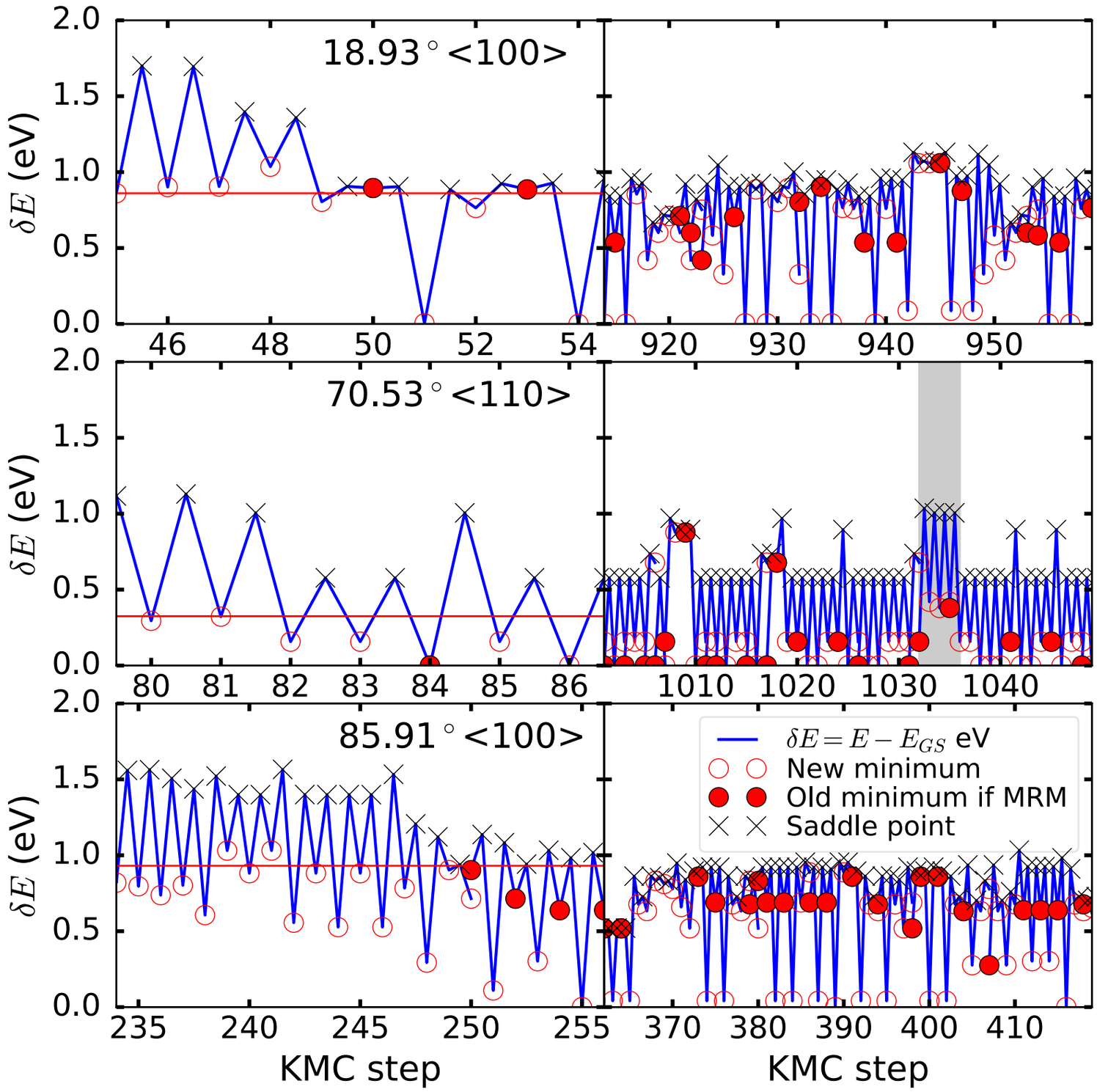
Effects of Grain Boundaries



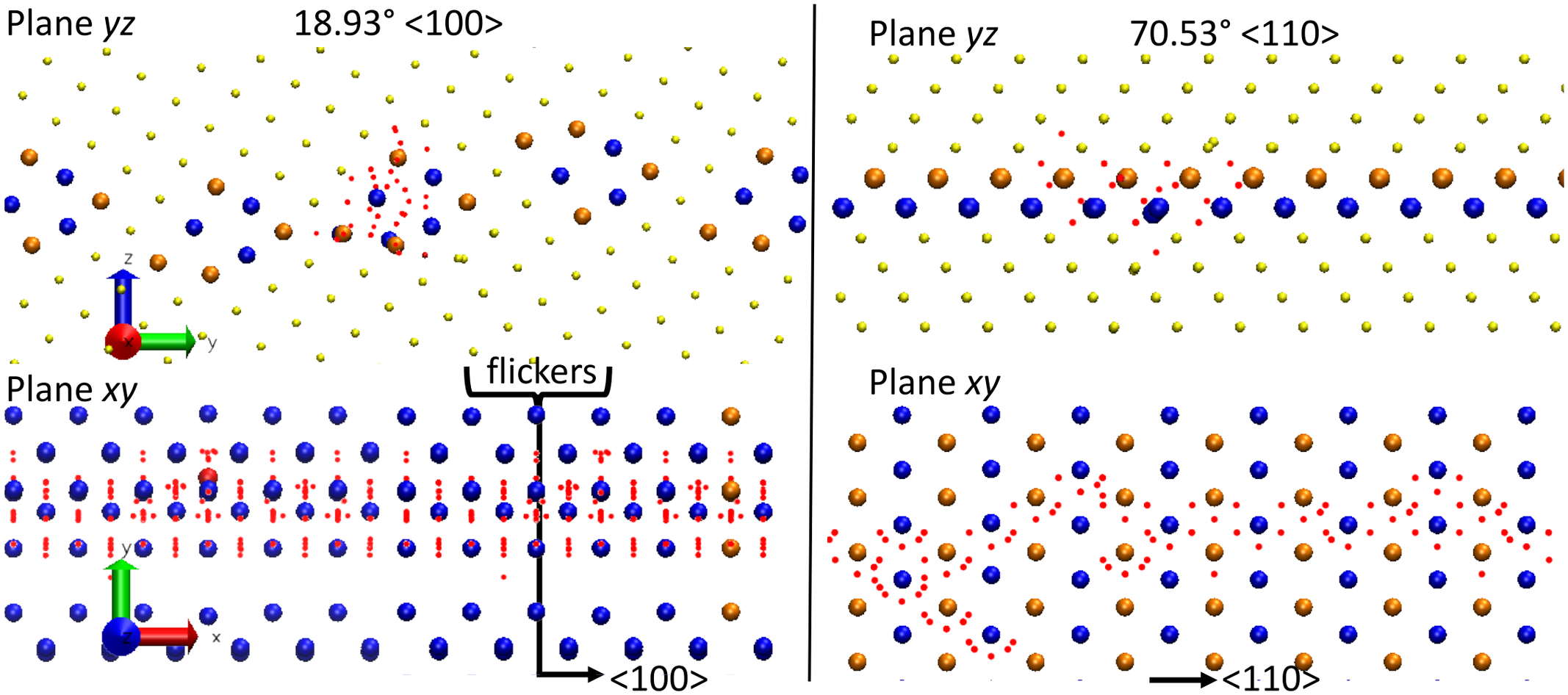
Diffusion of Grain Boundaries



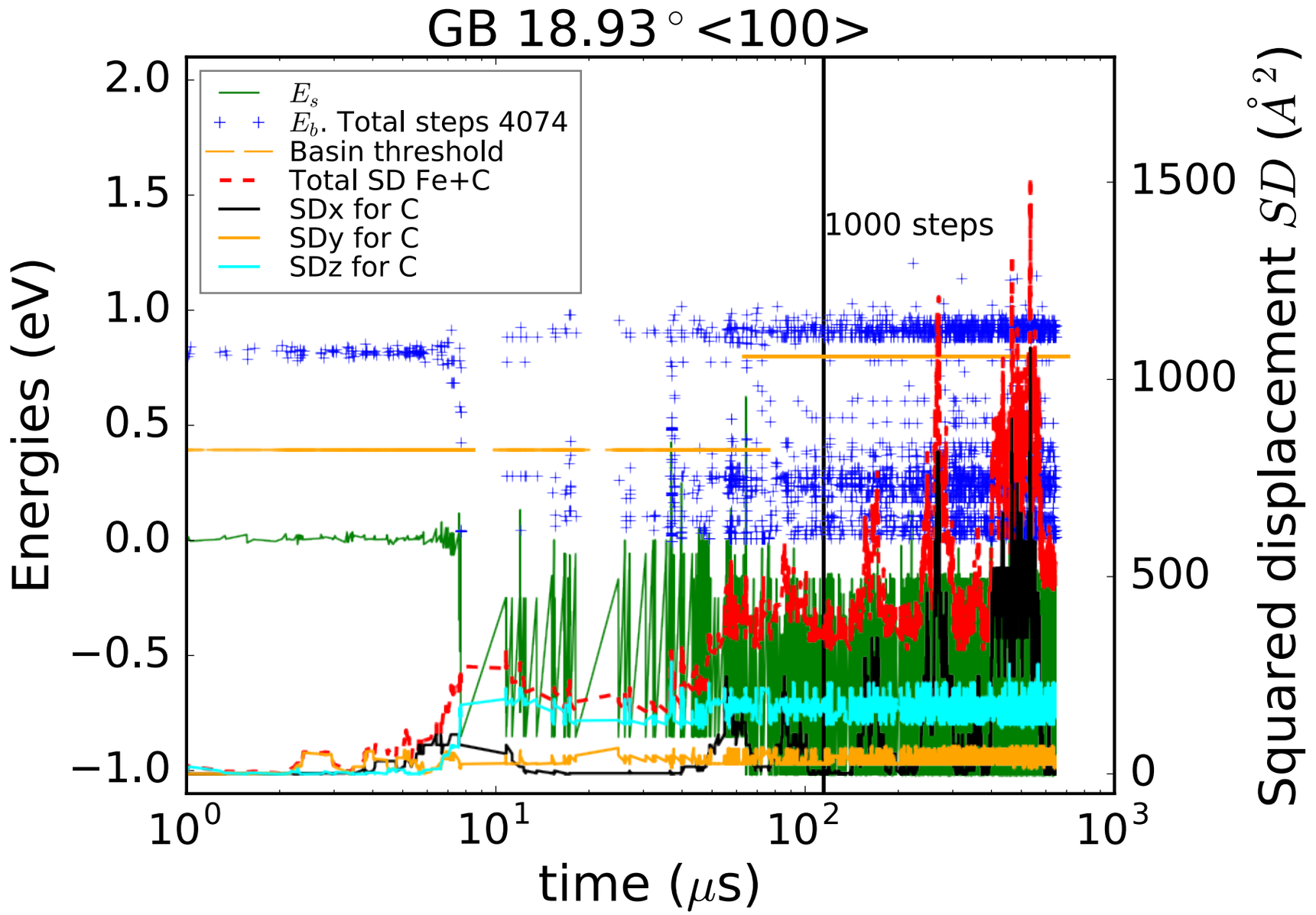
C diffusion at grain boundaries



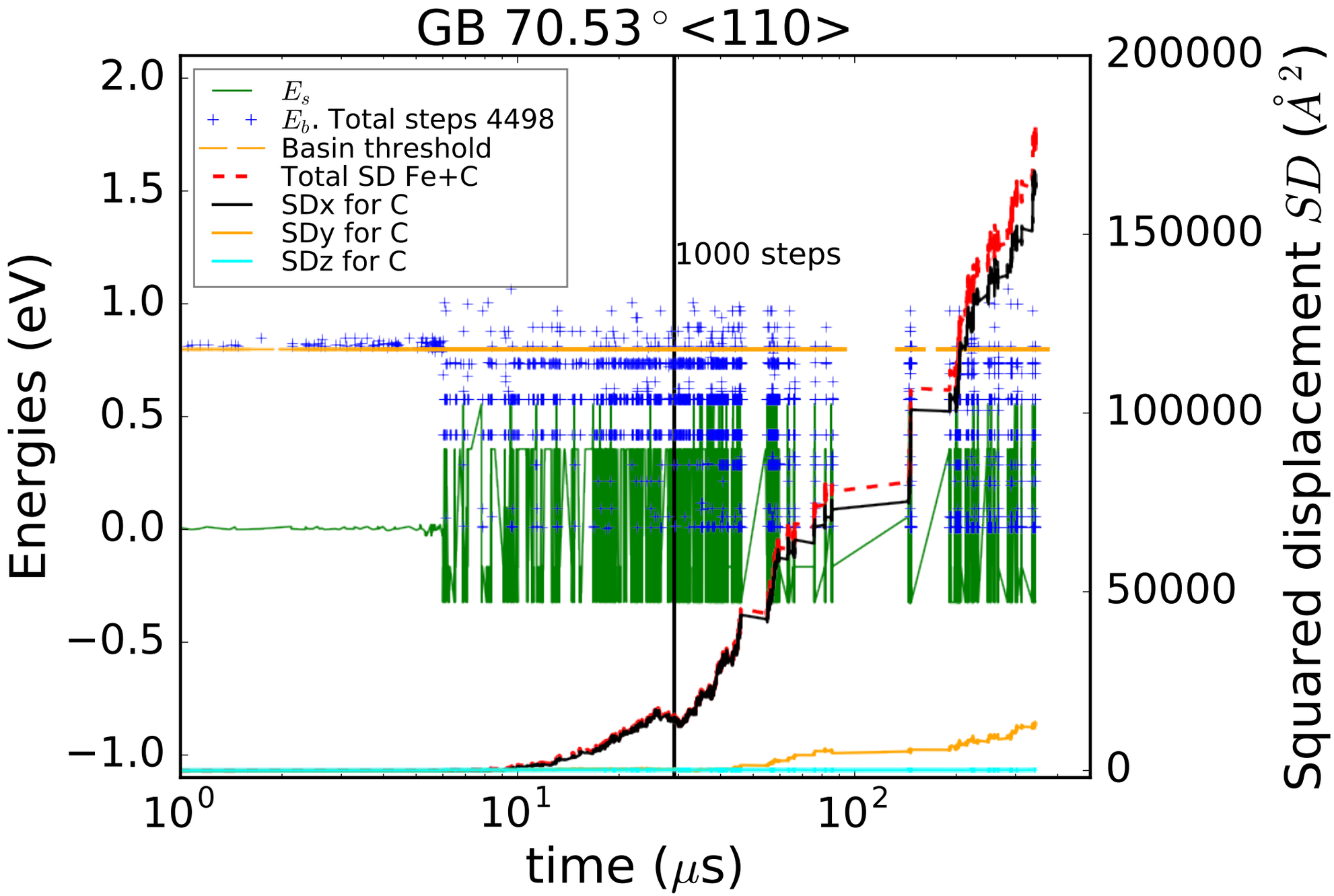
C diffusion at grain boundaries



C diffusion at grain boundaries



C diffusion at grain boundaries



CONCLUSIONS

- Kinetic ART is an efficient on-the-fly kinetic Monte-Carlo algorithm
- It uses a topological description for the classification of events; the flexibility of nauty allows us to take into account multiple components and more
- It defines two classes of events:
  - low-energy barriers that must be refined after each event
  - high-energy barriers which are treated as ensemble

- Kinetic ART is particularly useful for the study of diffusion in when strain effects are important or asymmetries prevent the use of standard KMC (e.g. presence of defects, interface, etc.).
- It is ideal for problems where
  - where the type of barriers evolves with time — self-organisation and aggregation phenomena
  - with complex environments - alloys, grain boundaries, disordered systems
- A number of details make the method efficient:
  - parallelization
  - recycling of low-energy barriers
  - handling of highly symmetric events
  - handling of blinkers
  - use of local forces for O(1) calculations

K-ART CODE

- available at normand.mousseau@umontreal.ca
- distributed freely/collaboration preferred for first project

THANK YOU