Accelerating time

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North Pole
Norwegian Sea
Norway
Polar Ice
Greenland Sea
UK
Russia
Arctic Ocean
Ellesmere Island
Alert
Iceland
Bering Strait
North Magnetic Pole
Kalaallit Nunaat (Grønland) (Denmark)
Arctic Circle
Beaufort Sea
Banks I
Resolute
Baffin Bay
Alaska (USA)
Inuvik
Victoria Island
Baffin Island
Davis Strait
Dawson
Great Bear Lake
Gjoa Haven
Yukon Territory
Mackenzie River
Iqaluit
Whitehorse
Northwest Territories
Nunavut
Labrador Sea
Atlantic Ocean
Baker Lake
Yellowknife
Ungava Bay
Fort Nelson
Great Slave Lake
CANADA
Nain
Newfoundland
British Columbia
Kuujjuaq
Fort McMurray
Churchill
Hudson Bay
Churchill Falls
St John's
Prince George
Alberta
Saskatchewan
Manitoba
Pacific
Fraser River
Edmonton
L. Winnipeg
Sandy Lake
James Bay
La Grande Rivière
Sept-Îles
Saint-Pierre et Miquelon (France)
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Quebec
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Victoria
Ocean
Regina
Winnipeg
Thunder Bay
Ontario
Québec
New Brunswick
Nova Scotia
Halifax
Fredericton
Montréal
United States of America
Lake Superior
Ottawa
Toronto
Lake Michigan
Lake Huron
Lake Ontario
Lake Erie
Atlantic Ocean
LEGEND
National capital
Provincial or Territorial capital
Other populated places
International boundary
Provincial or Territorial boundary
Exclusive 200 nautical mile Economic Zone (EEZ)
Scale
300 0 300 600 900
km km
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Quebec
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Salluit
Kangiqsujuaq
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ONTARIO
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La diffusion des connaissances liées à l'énergie pour ainsi contribuer à hausser le niveau des débats sociaux sur les questions énergétiques.

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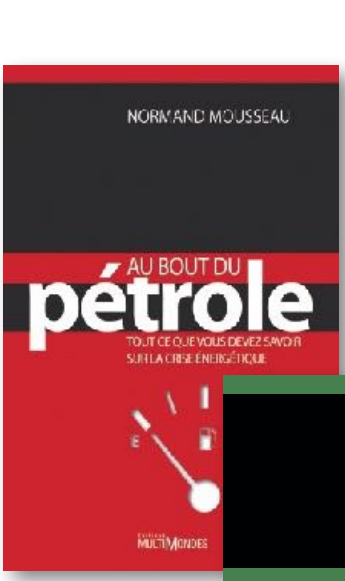
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MULTIMONDES


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L'AVENIR DU QUÉBEC PASSE PAR
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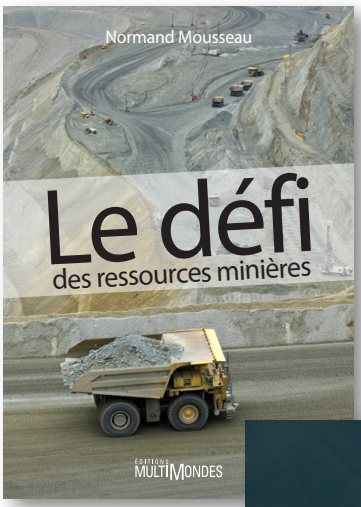
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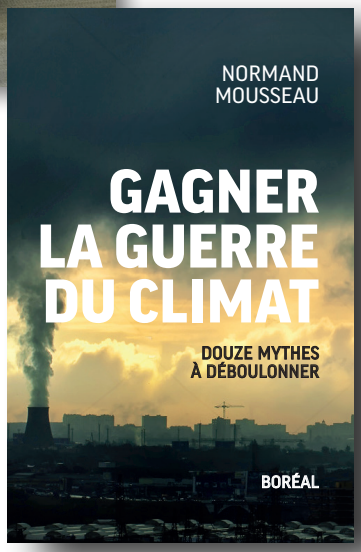
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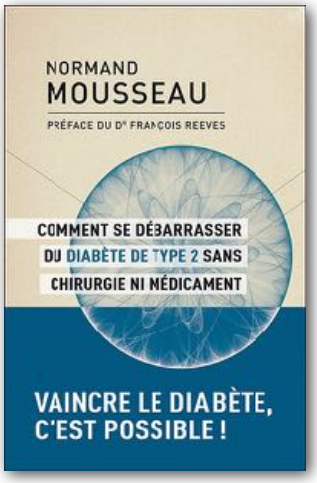
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COMMENT SE DÉBARRASSER
DU DIABÈTE DE TYPE 2 SANS
CHIRURGIE NI MÉDICAMENT
VAINCRE LE DIABÈTE,
C'EST POSSIBLE !

Commission sur les enjeux énergétiques du Québec

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Roger Lanoue
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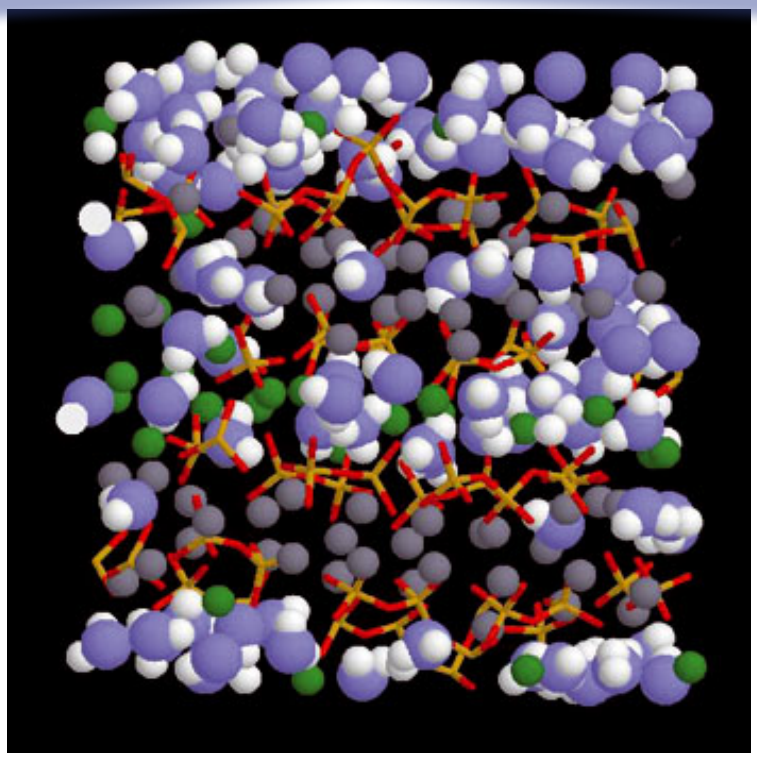
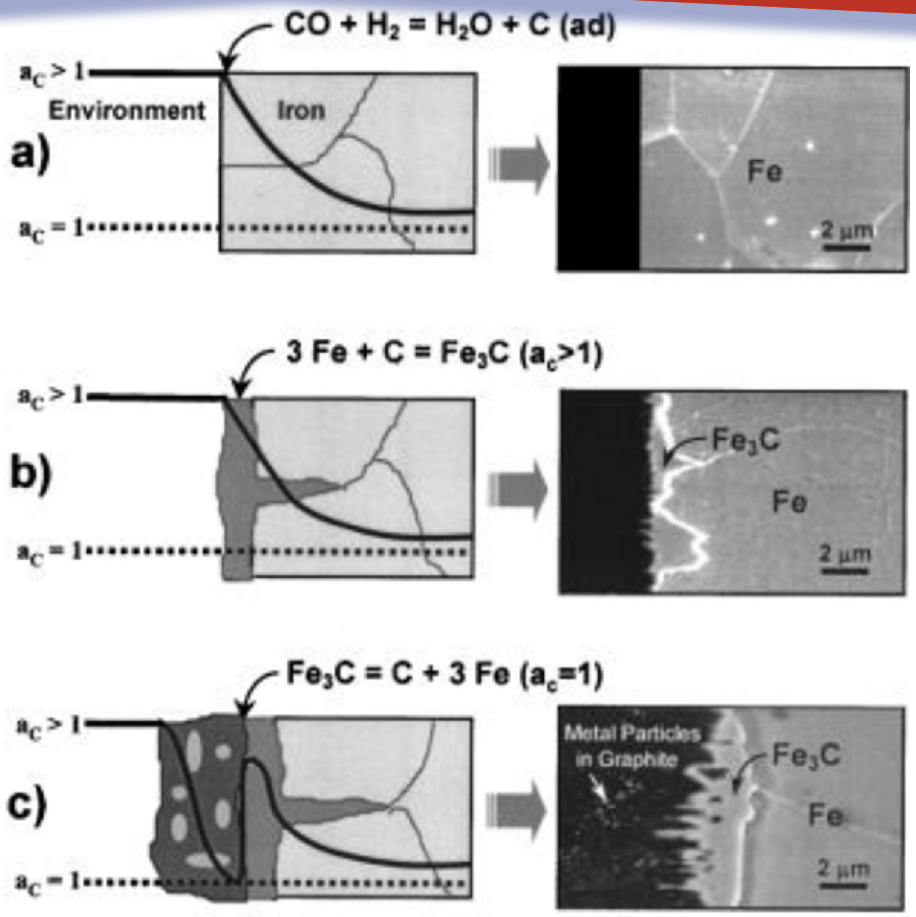
How does ciment microstructure evolve?



R. Pellenq

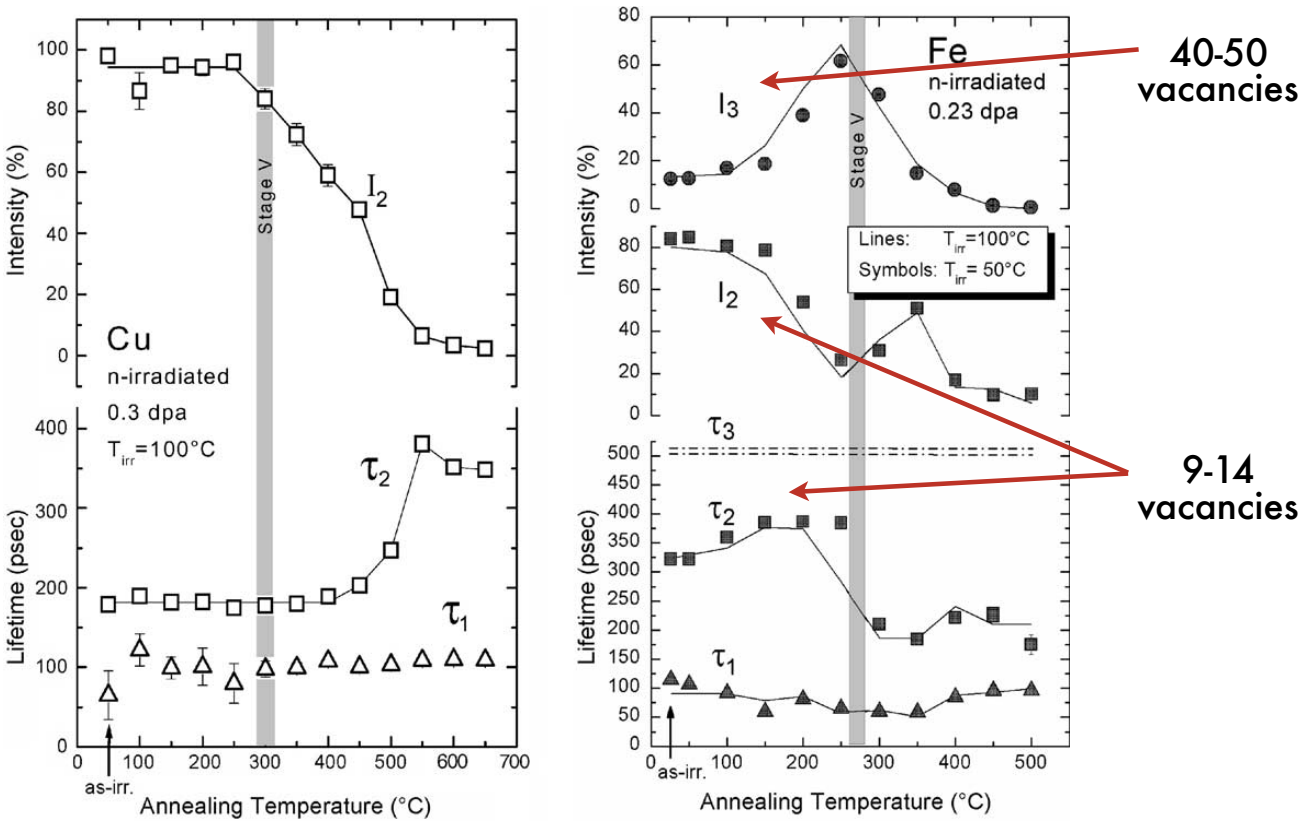
What is the microscopic origin of metal dusting?



Chun *et al.*, J. Electrochem. Soc. (2002)

kinetics of point defects

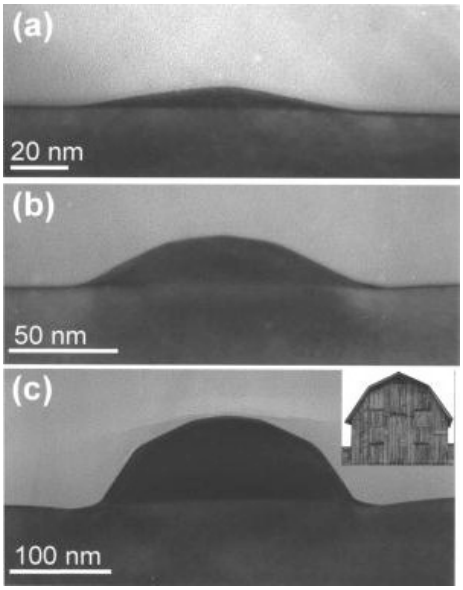
Accumulation of point defects and their complexes in irradiated metals as studied by the use of positron annihilation spectroscopy

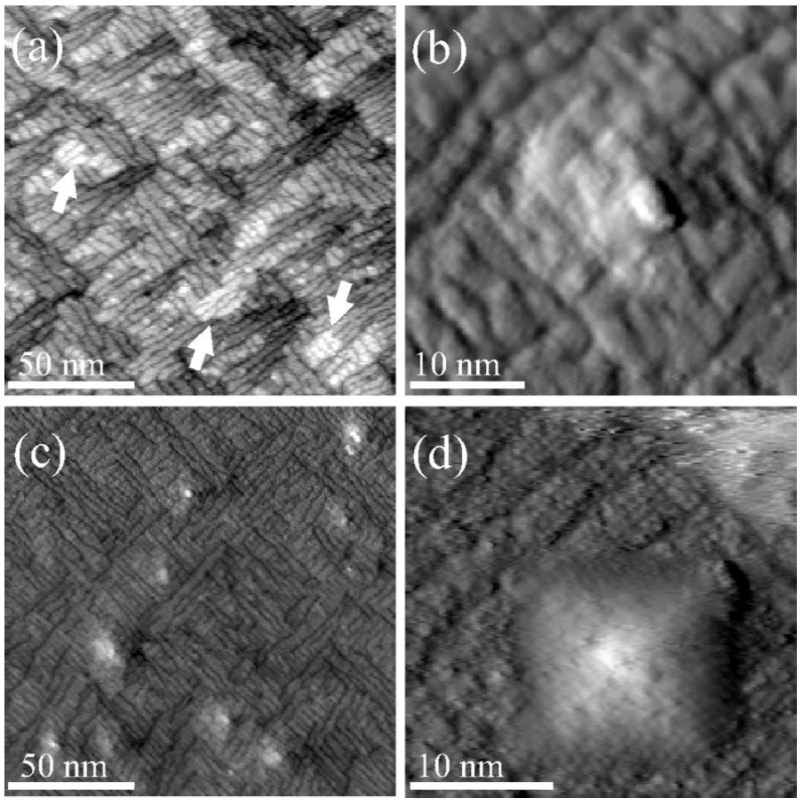


M. Eldrup and B.N. Singh, Journal of Nuclear Materials **323** (2003) 346–353.

Growth of nanostructures

Growth of Ge on Si leading to the formation of pyramids through Asaro-Tiller-Grinfeld instability.





A. Vailionis, B. Cho, G. Glass, P. Desjardins, D. G. Cahill, and J. E. Greene, Phys. Rev. Lett. 85, 3672 (2000).

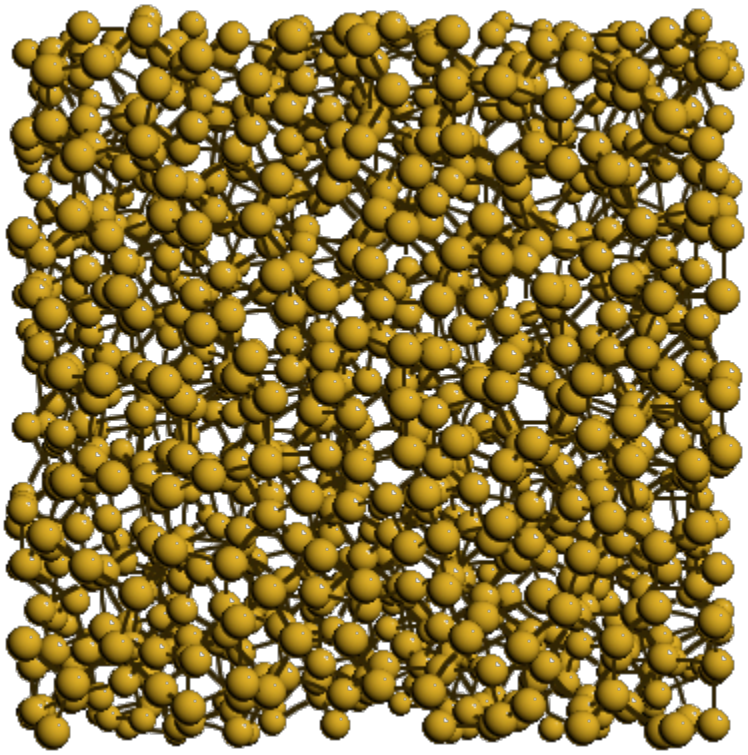
Kinetics of disordered systems

How do glasses relax at low T?

What are the defects?

What is the impact of impurities (e.g.: H in Si)

How do we understand the Si/SiO_2 interface?



Outline

1. The challenge of simulating over multiple time scales. Energy landscapes. The transition state theory. Overview of various methods for breaching these time scales.

2. Solving the problem for simple systems. The kinetic Monte Carlo approach. Various accelerated molecular dynamics methods.

3. Off-lattice kinetic Monte Carlo methods. The kinetic Activation-Relaxation Technique (part 1). Basic concepts. Searching for saddle points. Toplogical analysis. Constructing an event catalog.

4. The kinetic Activation-Relaxation Technique (part 2). Handling flickers. Limitations of current accelerated methods. Extending to large systems. Coming developments.

The challenges

- Thermodynamics
- Kinetics

Thermodynamics

We need to sample correctly the phase space

- access all relevant points in phase space
- establish their relative probability or, better, their absolute probability

Kinetics

We need to establish the dynamical evolution of the system

- focus on out-of-equilibrium property
- describe accurately the dynamical relation between points in phase space

The challenges

Equilibrium/Quasi-equilibrium systems

- Defects
- Polymers
- Multiphase materials

Difficult to identify the states, to establish their relative weight

Out-of-equilibrium processes

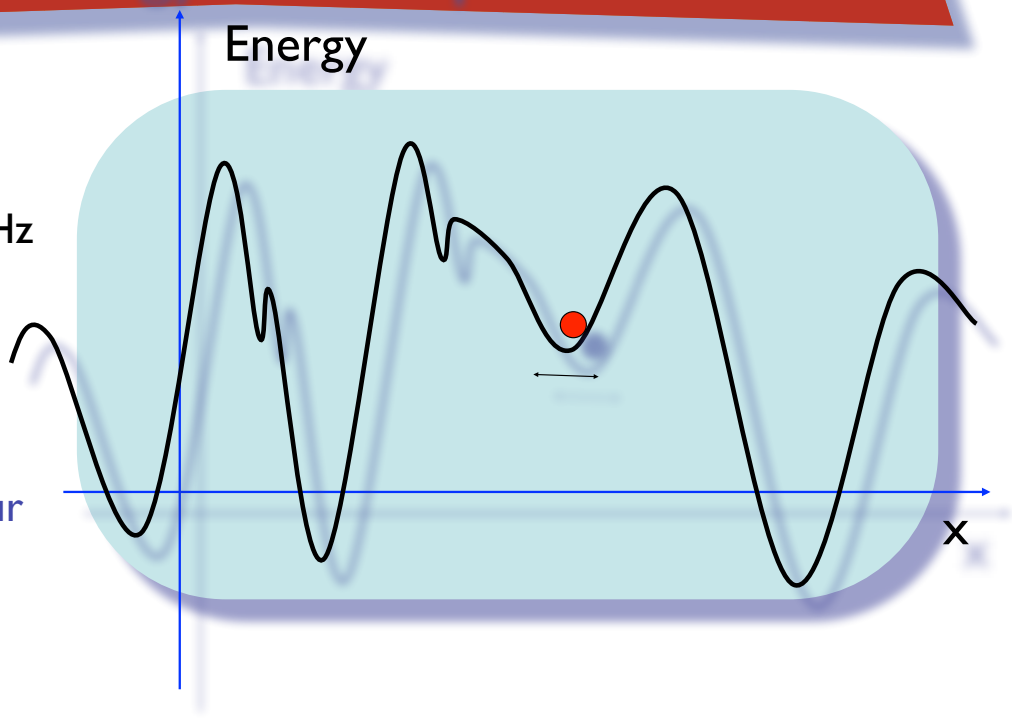
- Growth processes
- Self-Assembly
- Chemical reactions
- Glasses

How to find the pathways? How to access the right time scale?

Energy landscapes

Atoms vibrate at 10^{12} Hz

The evolution can occur on any scale

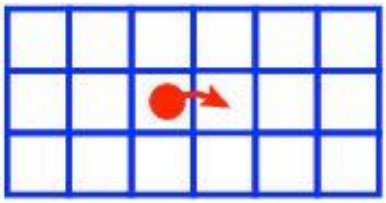


Generic problem: How to explore the space of variables of a high dimensional cost function?

Sampling states : discrete systems

In case of discrete systems, it is easy to identify basic mechanisms:

Spin networks	⇒	Spin flip
Adatom at surface	⇒	Atomic jump



Once barriers are known, it is possible to accelerate the dynamics

Swendsen and Wang	⇒	Flip of spin clusters
Voter, Barkema *et al.*	⇒	Rare event dynamics

Can we do the same thing for continuous systems ?

But surfaces are not always symmetrical nor discrete

Standard approaches (at atomic scale)

Molecular dynamics

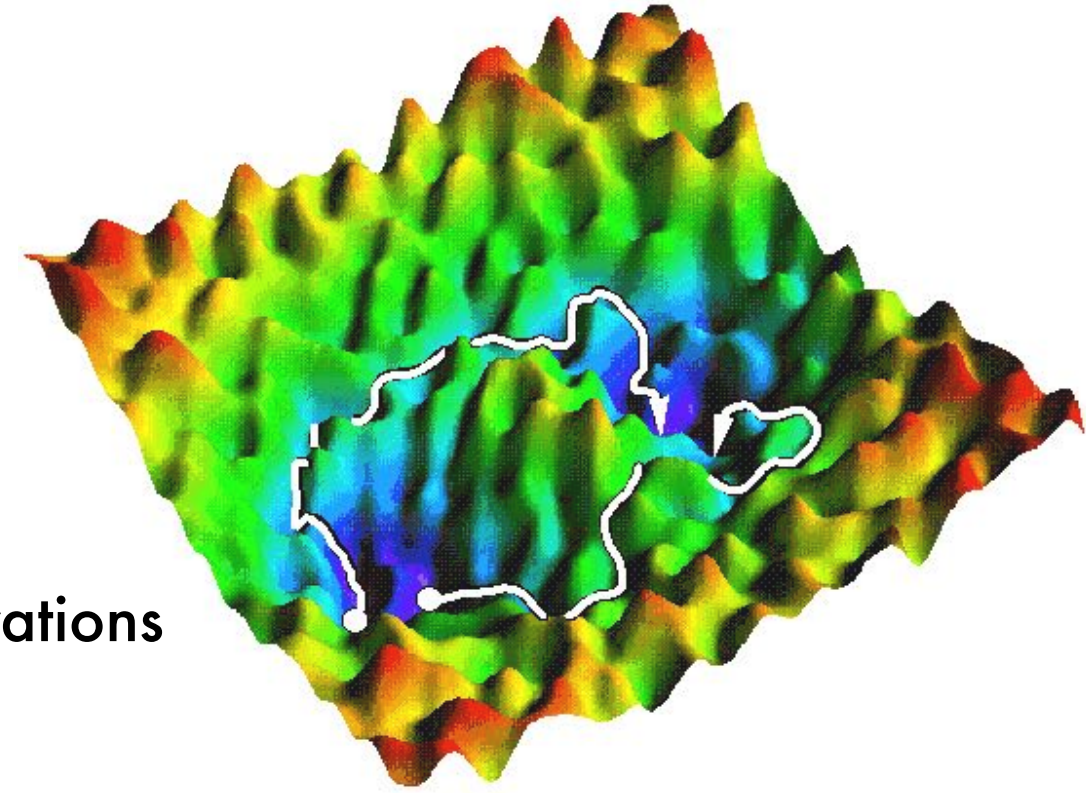
Monte Carlo

What are they?
What are their differences/ similarities?

Ensemble?

(Free) Energy landscapes

Let us go back to the landscape



- entropy
- state
- thermal vibrations

Transition State Theory

TST Escape rate is the equilibrium flux through the dividing surface

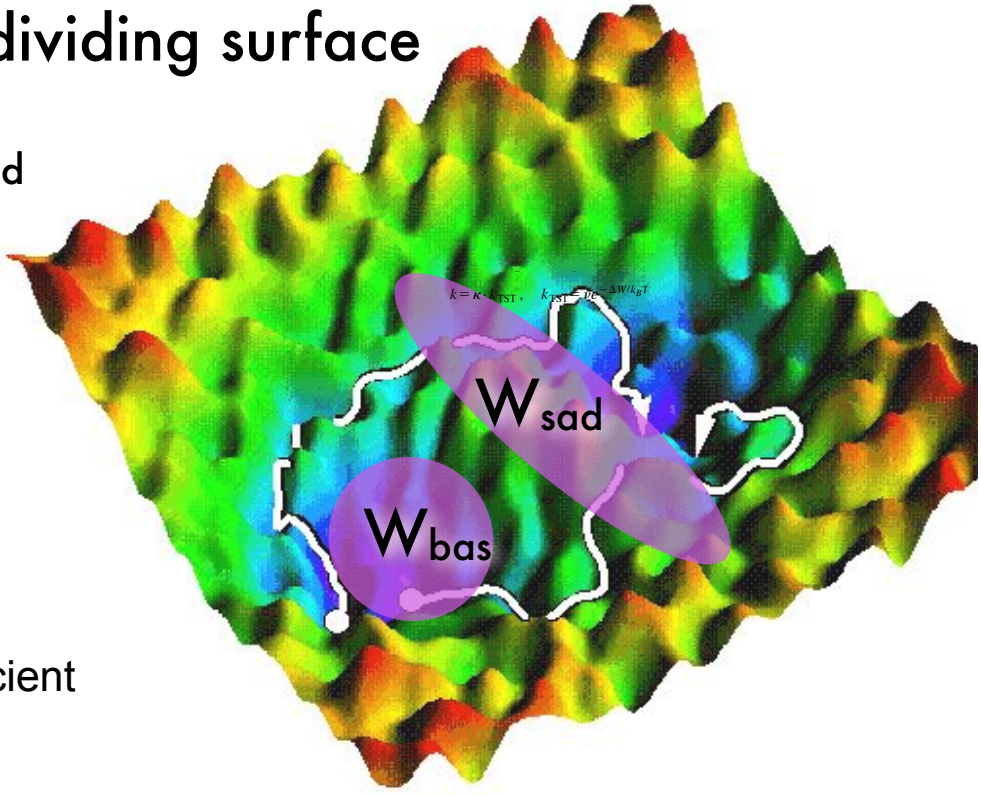
$\Delta W = W_{bas} - W_{sad}$

The rate is

$$k = \kappa \cdot k_{TST}$$

with

$$k_{TST} = \nu e^{-\Delta W / k_B T}$$



k : Crossing rate

κ : Transmission coefficient

ν : Attempt frequency

ΔW : Activation energy

Marcelin (1915), Eyring and Wigner (1930s)

Transition State Theory

The attempt frequency is defined as

$$\nu = \left[\frac{k_B T}{2\pi m}\right]^{1/2} \left[\int_{\text{well}} \exp\{-[W(x) - W(x_m)]/k_B T\} dx\right]^{-1}$$

Where $W(x)$ is the potential of mean-force

$$W(x) = \int_{x_m}^{x} \langle f(\lambda) \rangle_{\lambda = x'} dx'$$

where the averaged over the force is taken along the reaction pathway defined by the reaction coordinate λ

Transition State Theory

If we define

$$W(x) \simeq \alpha \frac{x^2}{2} - \beta \frac{x^3}{3}$$

with $W(x_m) = 0$ and $\Delta W = W(x_b) - W(x_m)$, we obtain

$$\nu(T) = \nu(0)\sqrt{\frac{\Delta E - T\Delta S}{\Delta E}}$$

If the barrier is simple and chosen correctly, $\kappa \approx 0.5$, we can ignore it and write the rate as :

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

with

$$\Gamma_0 = \nu e^{\Delta S/k}$$

Transition State Theory

While the transmission coefficient is given by

$$\kappa = \left\langle \Theta[x(+t) - x_b] - \Theta[x(-t) - x_b] \right\rangle_{t \gg \tau_{\text{vib}}}$$

Computing the pre-factor : The harmonic approximation

We have seen that the transition rate is given by

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

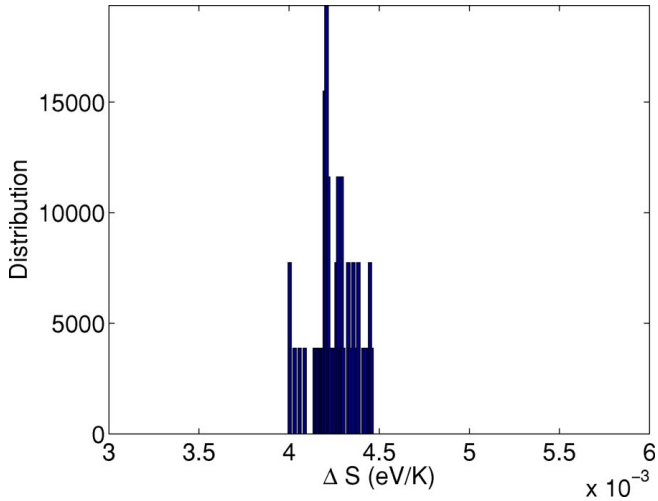
where

$$\Gamma_0 = \nu e^{\Delta S / k}$$

In the harmonic approximation, the entropy is related to the phonon frequencies and the prefactor becomes:

$$\Gamma_0 = \frac{\prod_i^{3N} \nu_i^{\min}}{\prod_i^{3N-1} \nu_i^{\mathrm{sad}}}$$

Computing the pre-factor : A constant value

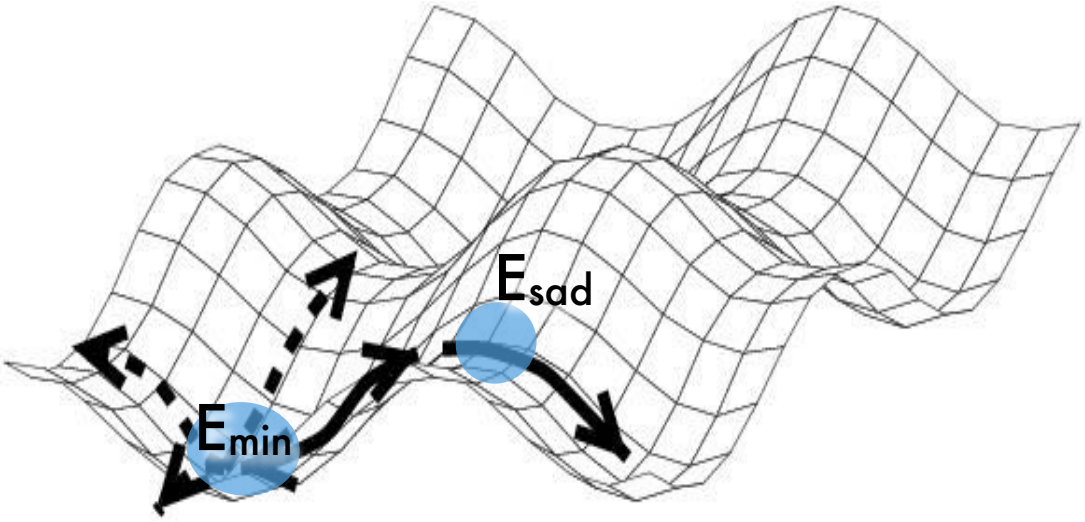


Amorphous silicon

FIG. 9. Distribution of the entropy barrier at the saddle point evaluated in the harmonic limit, for 50 different events selected at random.

Francis Valiquette and Normand Mousseau, Phys. Rev. B 68, 125209 (2003)

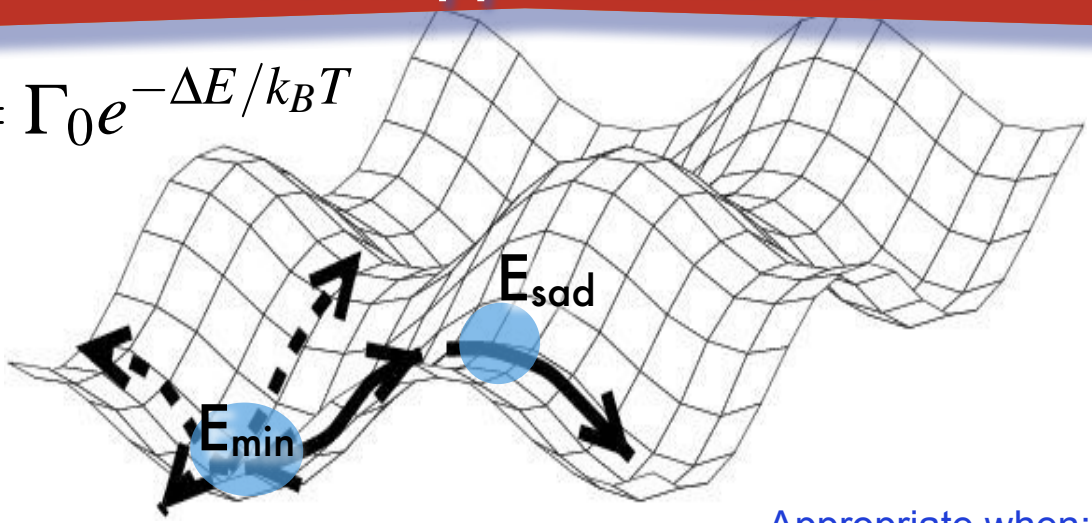
TST : The simplified version



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

TST: Approximations

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



we need to know:

1. Knowledge of saddle points
2. Prefactor

Appropriate when:

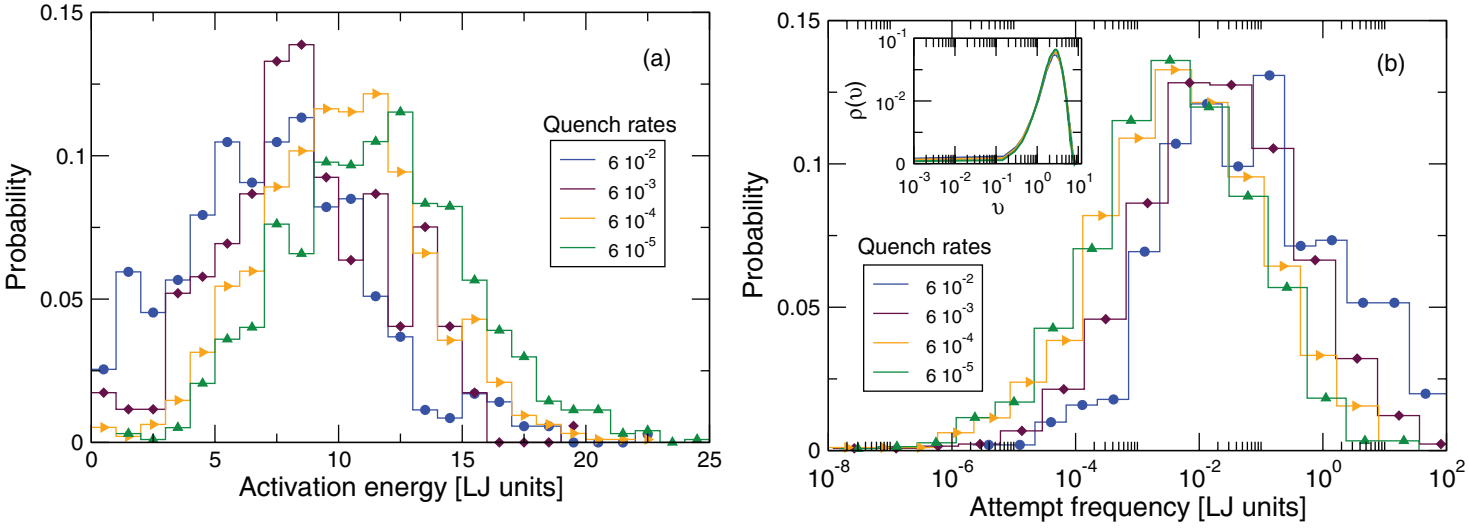
1. Uncorrelated jumps
2. High barriers wrt $k_B T$
3. No diffusive mechanisms

Prefactor approximation

1. Homogeneous
2. Well-separated pathways

Failures

Inverse Meyer-Neldel behavior for activated processes in model glasses



Pawel Koziatek, Jean-Louis Barrat, Peter Derlet, and David Rodney
Phys. Rev. B 87, 224105 (2013

TST

Beyond trivial results as a function of temperature

For thermodynamics : need entropy of each state + state

For kinetics : even with constant prefactors, competing phenomena, may lead to complex changes

Many methods have been proposed

There are many approaches to increase the efficiency of sampling the phase space of slow systems :

- parallel tempering
- entropic sampling
- transition path sampling
- hyper molecular dynamics
- temperature-assisted dynamics
- biased methods such as Laio and Parrinello

The methods have provided important results. There are still problems with complex materials with continuous distribution of barriers

Replica-exchange MD

1. launch n molecular dynamical simulations in parallel, at n different temperatures
2. at regular intervals, try an exchange of configurations between two adjacent temperatures using a Metropolis accept-reject criterion

$$p(i,j) = \min\left\{1.0,\ \exp\left[\frac{1}{kBT_i} - \frac{1}{kBT_j}\right](E_i - E_j)\right\}$$

REMD accelerates sampling (in some cases) for the cost of losing dynamical information.

REMD still provides thermodynamical information

Accelerating time
Part 2

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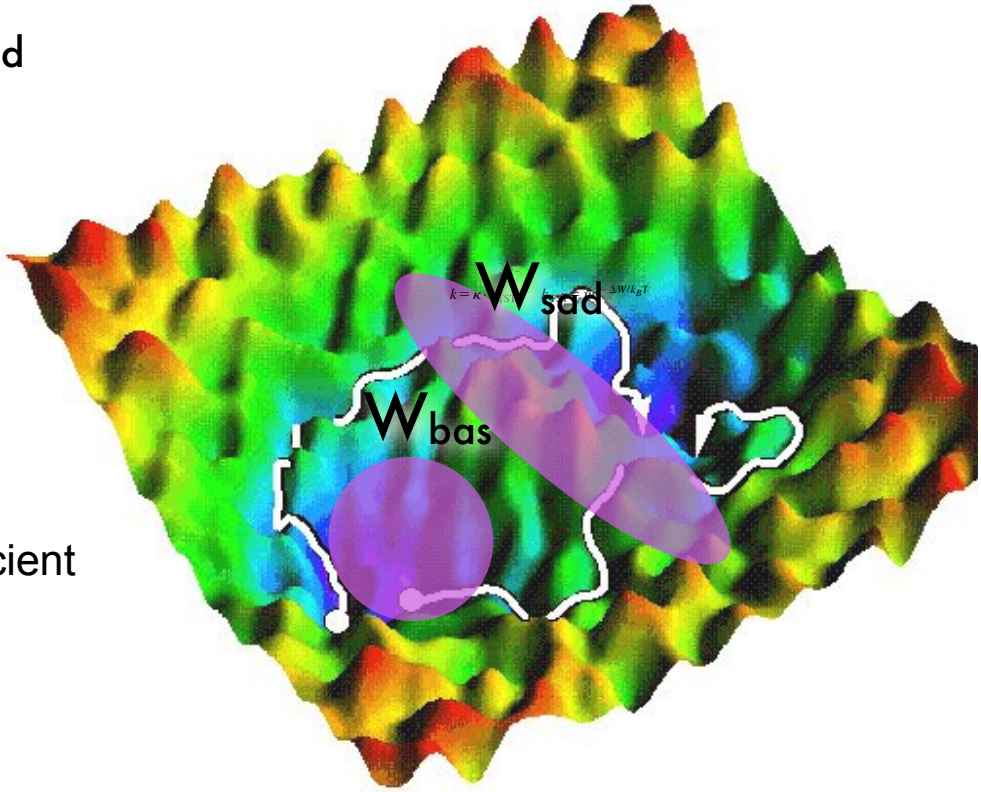


Marcelin (1915), Eyring and Wigner (1930s)

Transition State Theory

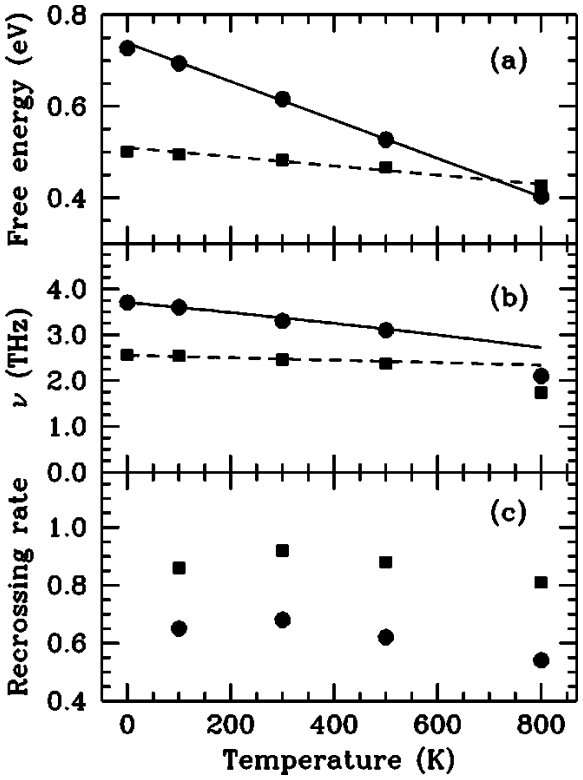
The law of compensation or the Meyer-Neldel Rule:

W. Meyer and H. Neldel, Z. Tech. Phys (Leipzig)12, 588 (1937).

Cu on Cu (EAM) with two mechanisms:

- Jump
- Exchange

(Feibelman, end of 1980's)



Boisvert, Mousseau and Lewis, PRB **58,** 12667 (1998)

Transition State Theory

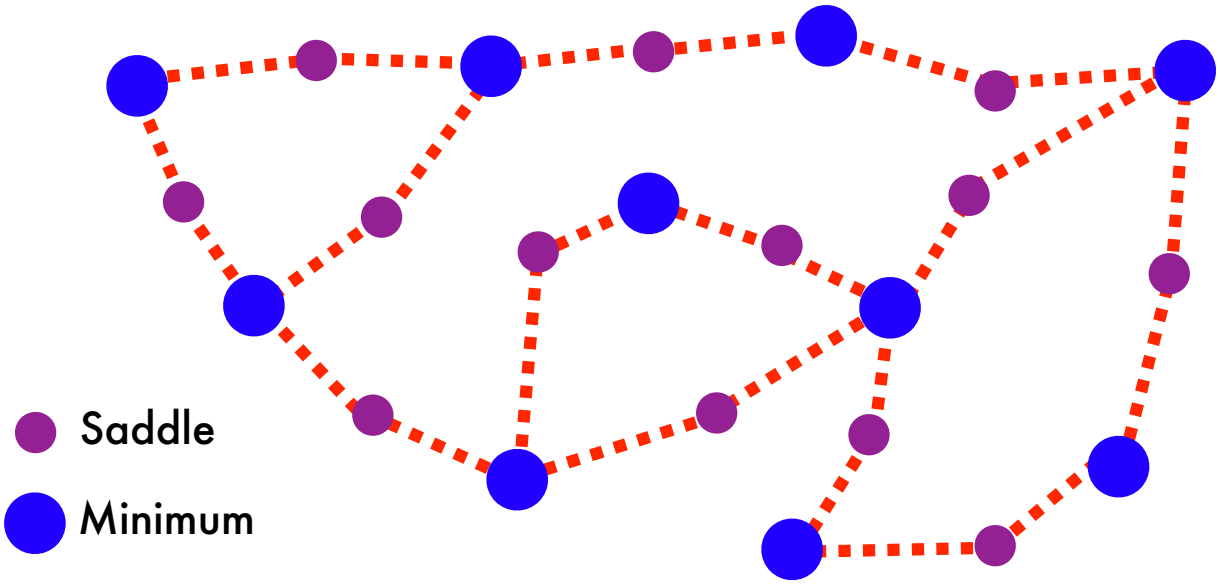
TABLE I. Comparison between TI and MD results for the jump (J) and exchange (X) diffusion activation barriers ΔE (in eV) and rate prefactors Γ_0 (in THz); also given are the entropy ΔS (in k_B) and the static energy barrier, $\Delta E(0)$. Estimated errors are given in parenthesis.

	ΔS	ΔE	ΔE	$\Delta E(0)$	$\ln \Gamma_0$	$\ln \Gamma_0$
	(TI)	(TI)	(MD)		(TI)	(MD)
J	1.1(0.2)	0.51(0.02)	0.49(0.01)	0.50	2.9(0.2)	3.0(0.2)
X	4.9(0.6)	0.74(0.02)	0.70(0.04)	0.73	6.5(0.6)	6.1(0.7)

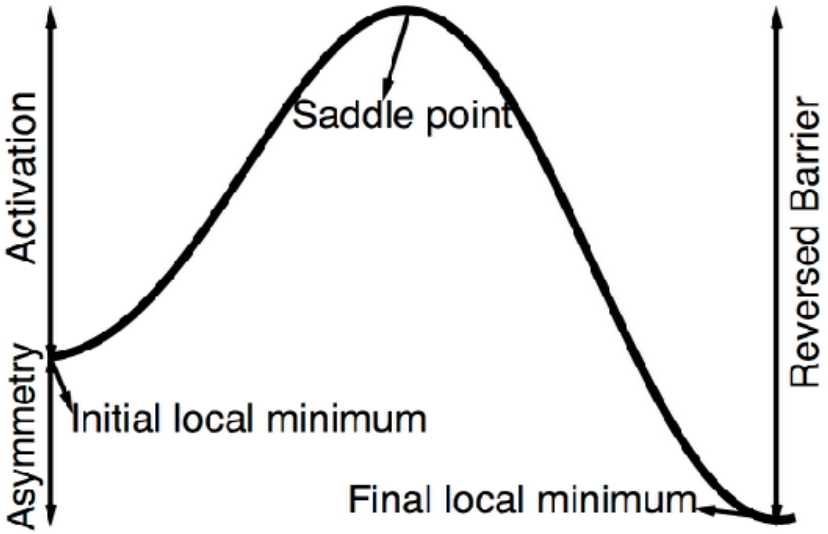
Boisvert, Mousseau and Lewis, PRB **58,** 12667 (1998)

Simplifying the search

Reduce phase space to trajectories between minima going through saddle points



A few definitions...



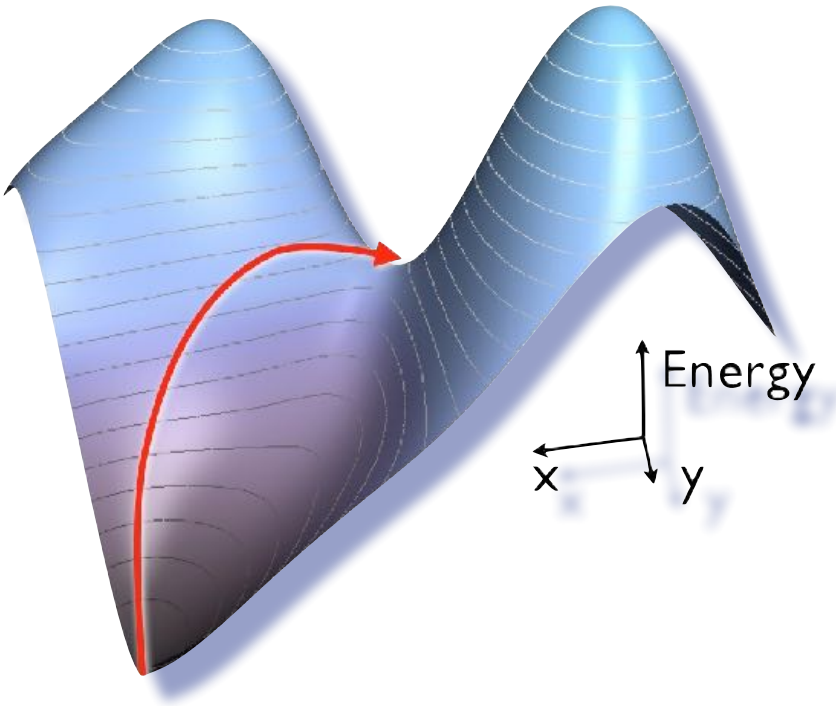
Example: Finding barriers with ART nouveau

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);

Generating an event

ART nouveau can be used to identify barriers

1. Start from a local minimum

2. Select the atom in the center of the local topological region; displace this atom and its neighbours slowly.

3. Follow this direction until an eigenvalue become negative.

4. Push along the corresponding eigenvector until total force is zero. (Saddle point)

5. Converge to a new minimum (event).

6. Assign the event to the atom that has moved most.

7. Repeat, from (2) a desired number of times.

8. Move to the next atom and start at (2)

Lanczos

The Hessian matrix is defined as

$$H_{i\alpha,j\beta}[\mathbf{q_0}] = \frac{\partial^2 E[\mathbf{q}_0]}{\partial q_{i\alpha}\partial q_{j\beta}},$$

It is possible to extract its lowest eigenvalue and corresponding eigenvector through an iterative process first proposed by Lanczos. We first generate a random vector $\mathbf{u_0}$ and compute $\mathbf{u_1}$ from:

$$\mathbf{H}\mathbf{u}_0 = a_0\mathbf{u}_0 + b_1\mathbf{u}_1$$

and, iterating:

$$\mathbf{H}\mathbf{u}_1 = a_1\mathbf{u}_1 + b_1'\mathbf{u}_0 + b_2\mathbf{u}_2,$$

Because the Hessian is symmetric:

$$\mathbf{u}_1 \cdot (\mathbf{H}\mathbf{u}_0) = \mathbf{u}_0 \cdot (\mathbf{H}\mathbf{u}_1)$$

So that b_l'=b_l giving the relation:

$$\mathbf{H}\mathbf{u}_k = a_k\mathbf{u}_k + b_k\mathbf{u}_{k-1} + b_{k+1}\mathbf{u}_{k+1}$$

Closing can be done simply as :

$$\mathbf{H}\mathbf{u}_{l-1} = a_{l-1}\mathbf{u}_{l-1} + b_{l-1}\mathbf{u}_{l-2}$$

Lanczos

And, in the end, we only have to diagonalize:

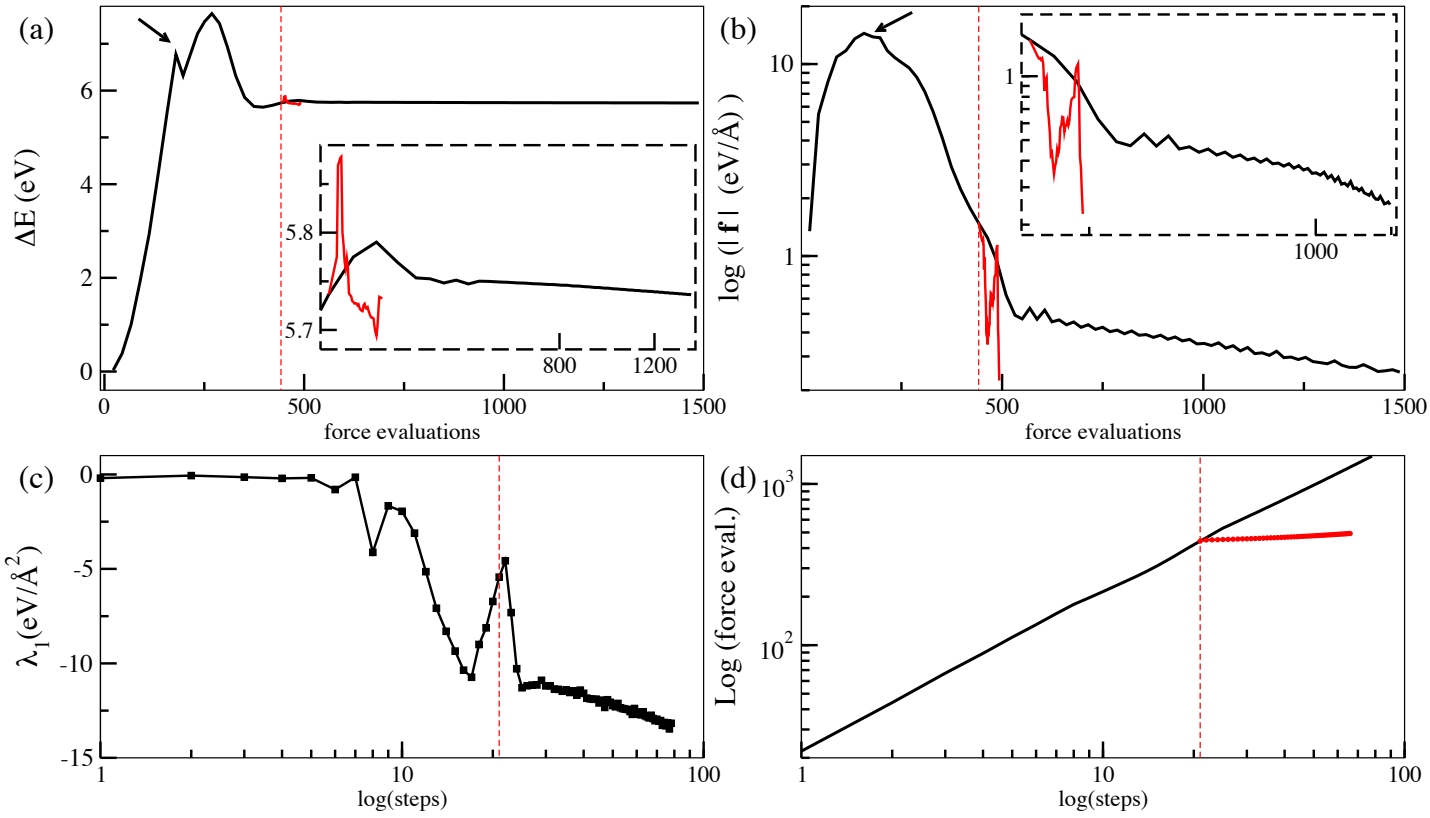
$$\mathbf{T}_l = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & \cdots & 0 \\ 0 & b_2 & a_2 & \cdots & 0 \\ 0 & \ddots & \ddots & \cdots & 0 \\ 0 & & b_{l-2} & a_{l-2} & b_{l-1} \\ 0 & & 0 & b_{l-1} & a_{l-1} \end{pmatrix}$$

Because of the properties of linear algebra, the lowest eigenvalue (and its corresponding eigenvector) comes out exponentially fast from the Lanczos aglorithm. By reusing the final eigenvector as $\mathbf{u_0}$, only a matrix of 12x12 is sufficient to obtain the desired vector and eigenvalue, irrespective of the system's size.

Moreover, the Hessian does not have to be computed directly, only the forces are needed:

$$\mathbf{H}[\mathbf{q}_0]\mathbf{u} = -\frac{\mathbf{f}(\mathbf{q}_0 + \delta_L \mathbf{u}) - \mathbf{f}(\mathbf{q}_0 - \delta_L \mathbf{u})}{2\delta_L} + O\left(\delta_L^3\right)$$

Details of the algorithm

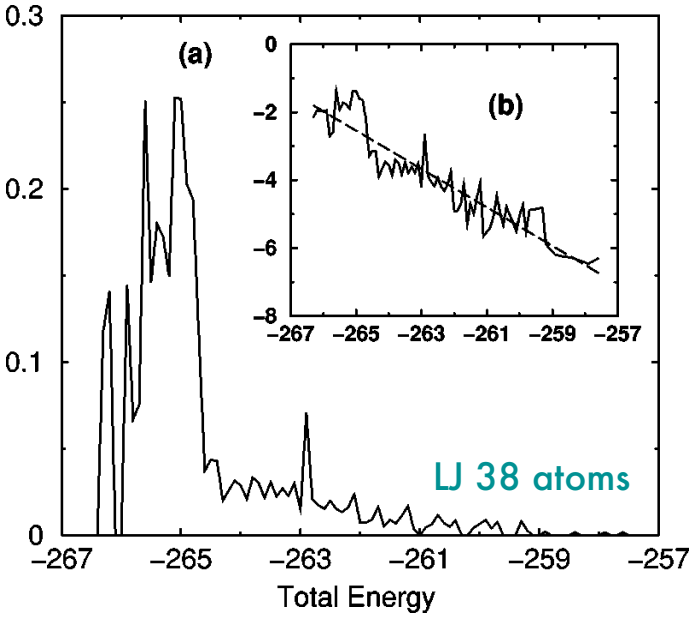


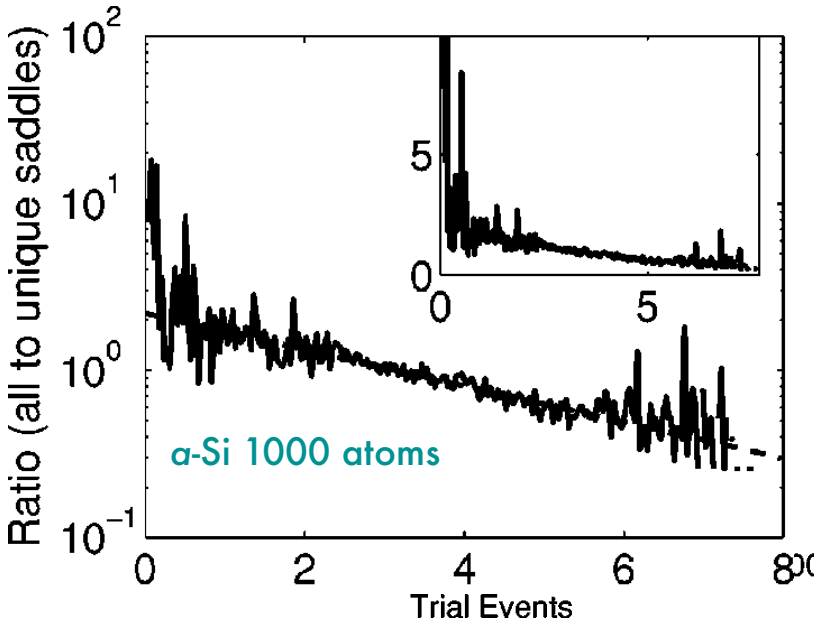
E Machado-Charry, LK Béland, D Caliste, L Genovese, NM and P Pochet, J. Chem Phys. (2011).

Features of ART

not sensitive to the real space complexity of activated jump nor the height of the activation energy barrier, which can be very high

not biased toward pre-determined





very efficient numerically

seems to sample all classes of events (ergodic)

events are reversible

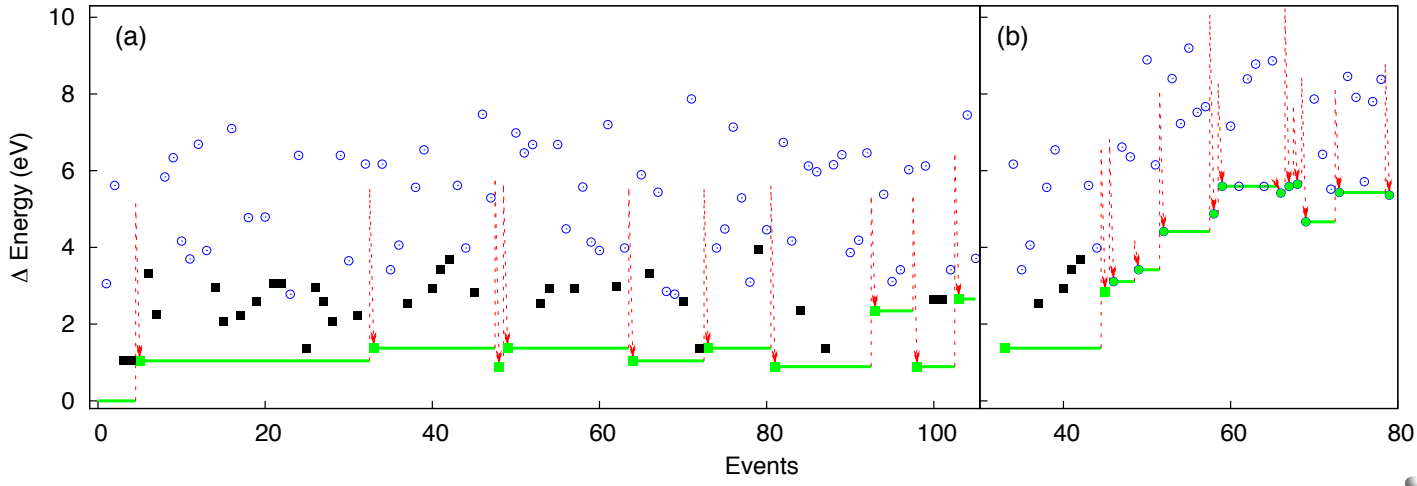
Comparison with other methods

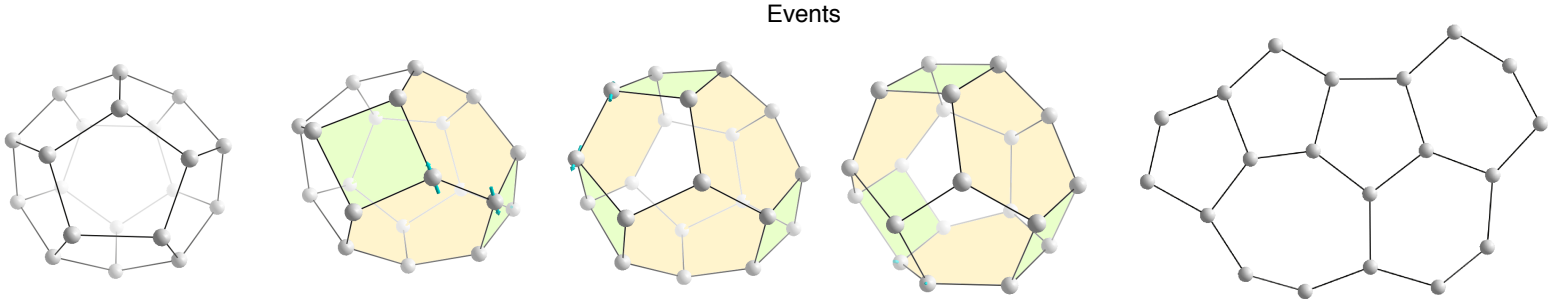
Algo.	ART nouveau				ARTn (Olsen)		Dimer method		Improved dimer		GSM
Ref.					[33]				[34]	[35]	[6]
System	*a-Si*	V_{Si}	C_{20}	SiC	Pt(111)	Pt(111)	Pt(111)	Pt(111)	C_6H_{10}	PHBH/H_2O	VO_x/SiO_2
BC	Bulk	Bulk	Isol.e	Surf.	Surf.	Surf.	Surf.	Surf.	Isol.	Sol.	Isol.
Pot.	SW	DFT	DFT	DFT	Morse	Morse	Morse	Morse	DFT	QM/MM	DFT
Method		PBE	LDA	PBE					B3LYP	AM1	B3LYP
DOF	3000	12[1]	60	222[1]	3	525	3	525	48	144	12[1]
$\langle f \rangle$	235	210	322	262	145	372	204	335	384[2]	425[3]	330
$\langle f \rangle_s$	670	302	718	728	145	2163	204	2148	-	-	-
A/S	2.72	79/78	434/201	134/75	-	-	-	-	-	-	-

E Machado-Charry, LK Béland, D Caliste, L Genovese, NM and P Pochet, J. Chem Phys. **135**, 034102, 11 pp., (2011).

E Cances, F Legoll, M-C Marinica, F Minoukadeh, and F Willaime, J. Chem. Phys. **130**, 114711 (2009).

C20 - BigDFT + ART nouveau





(a)ΔE=0.0 eV (b)ΔE=1.04 eV (c)ΔE=1.37 eV (d)ΔE=0.89 eV (e)ΔE=5.36 eV

E Machado-Charry, LK Béland, D Caliste, L Genovese, NM and P Pochet, J. Chem Phys. **135**, 034102, 11 pp., (2011).

Systematic study of interstitials in Iron

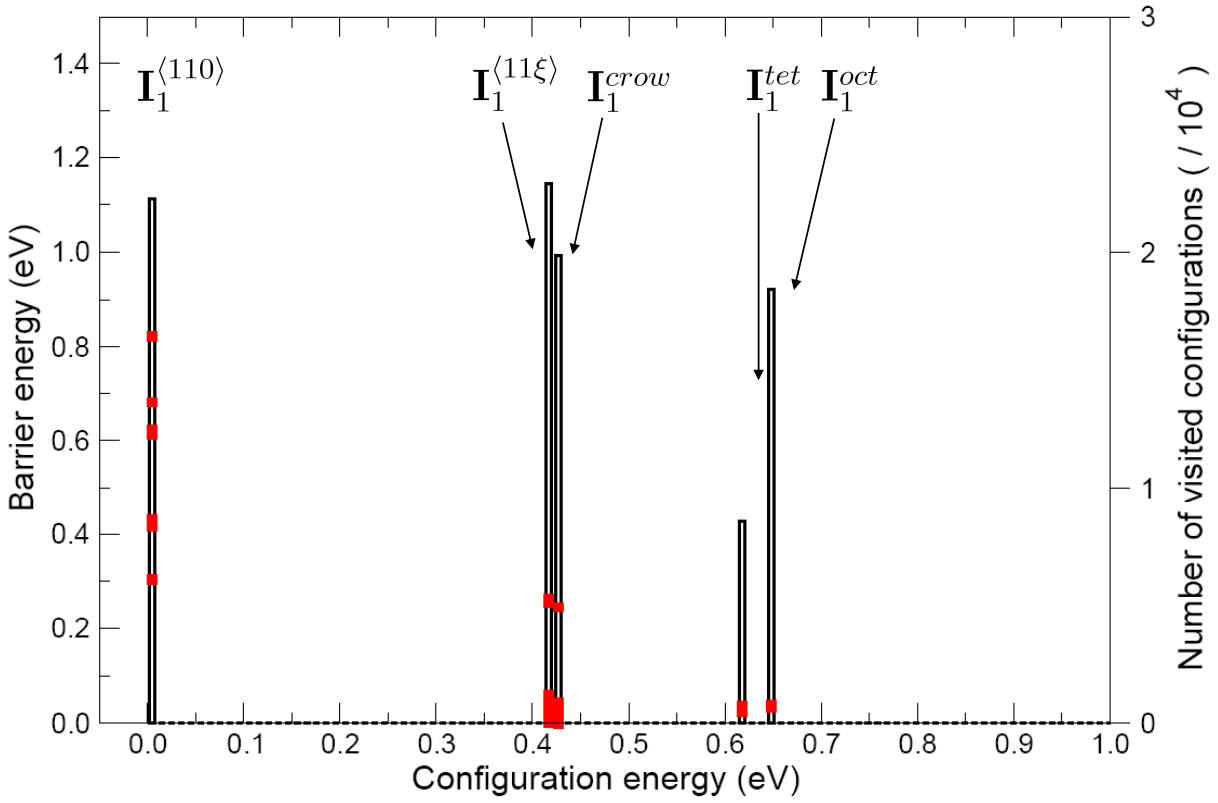
- Interstitial-type defects formed by the clustering of self-interstitials produced under irradiation have rather peculiar properties in α-iron by comparison with other body centered cubic (BCC) metals
- In α-iron isolated self-interstitial atoms (SIA) have a rather large migration energy, about 0.3 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.

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

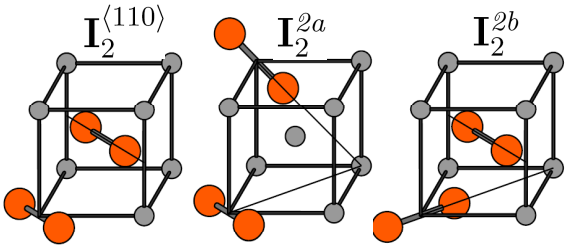
Systematic study of interstitials in Iron

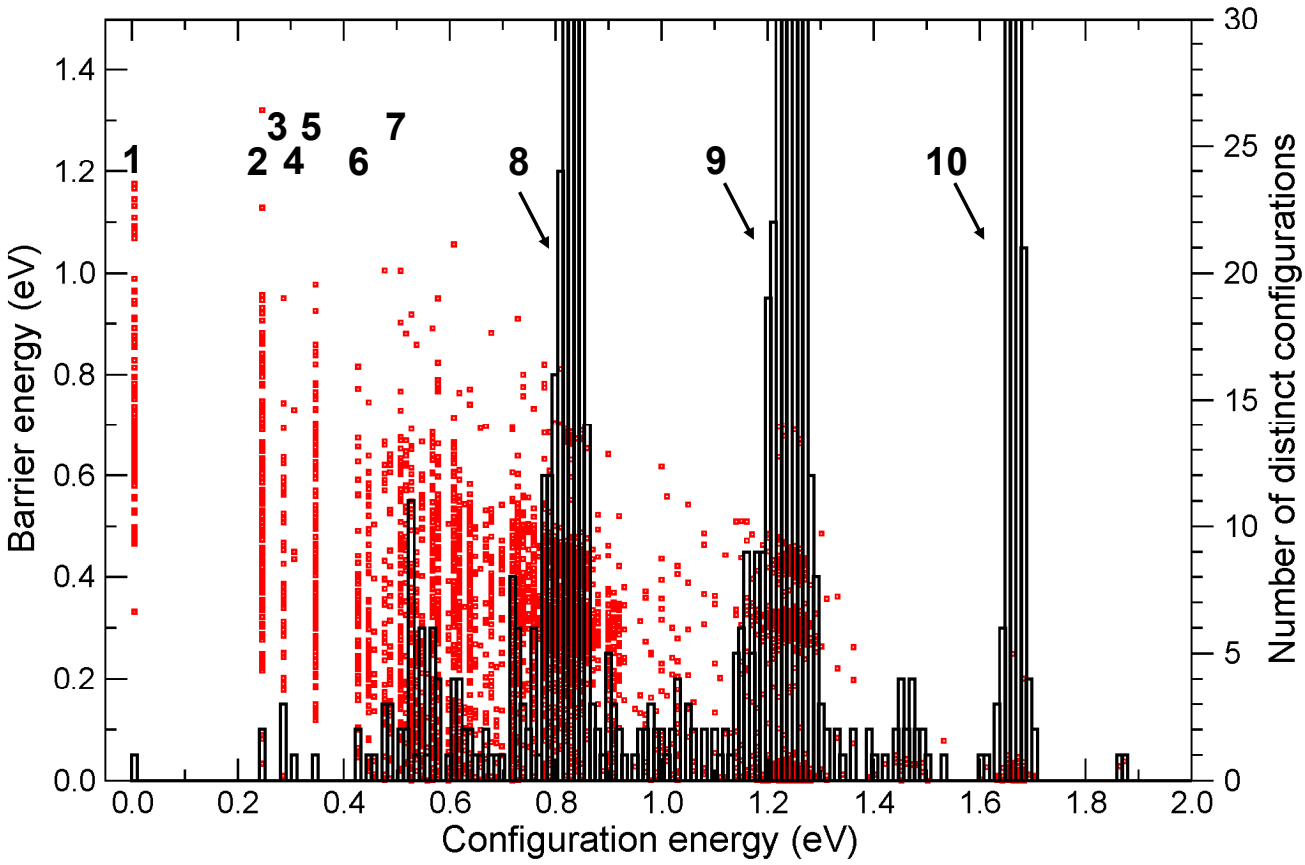
- Ackland-Mendelev potential
- ART nouveau
- 1024 atoms
- 50 trajectories which are stopped after 2000 successful activation events (each taking less than a week)

Mono-interstitials in Iron

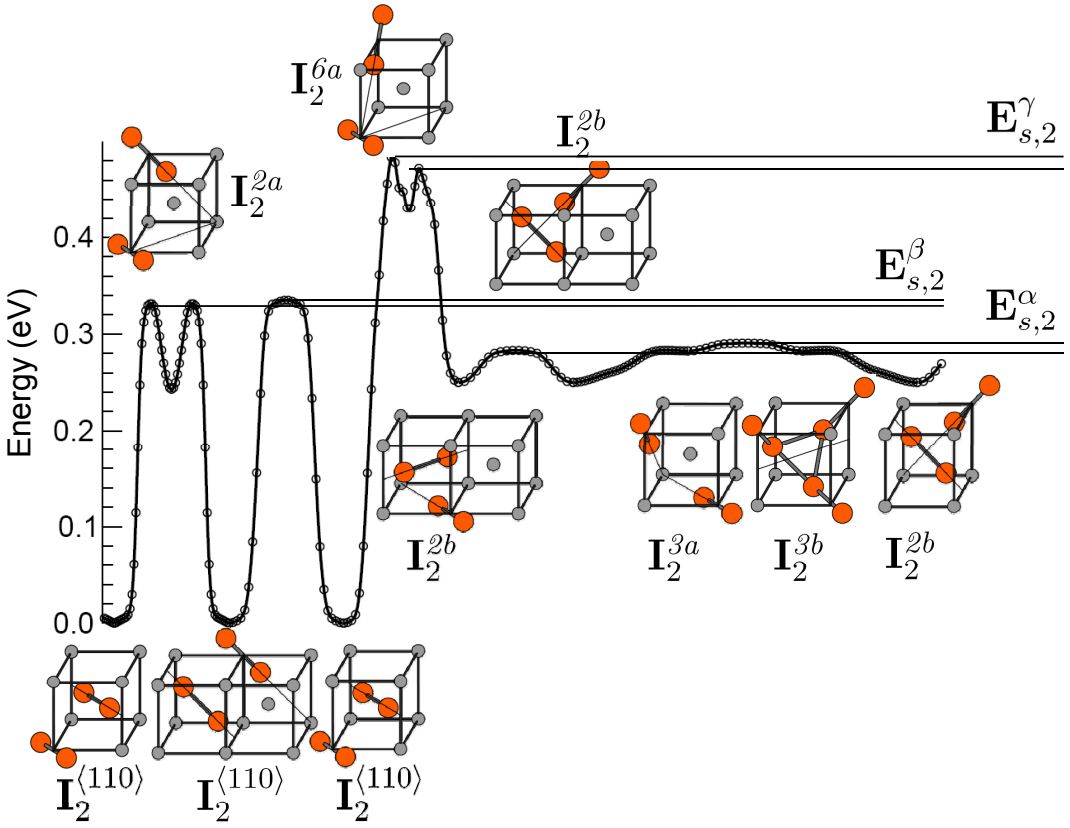


Di-interstitials in Iron

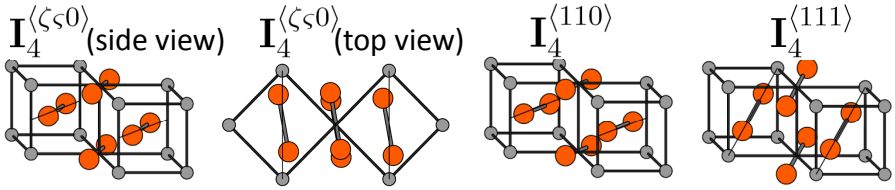


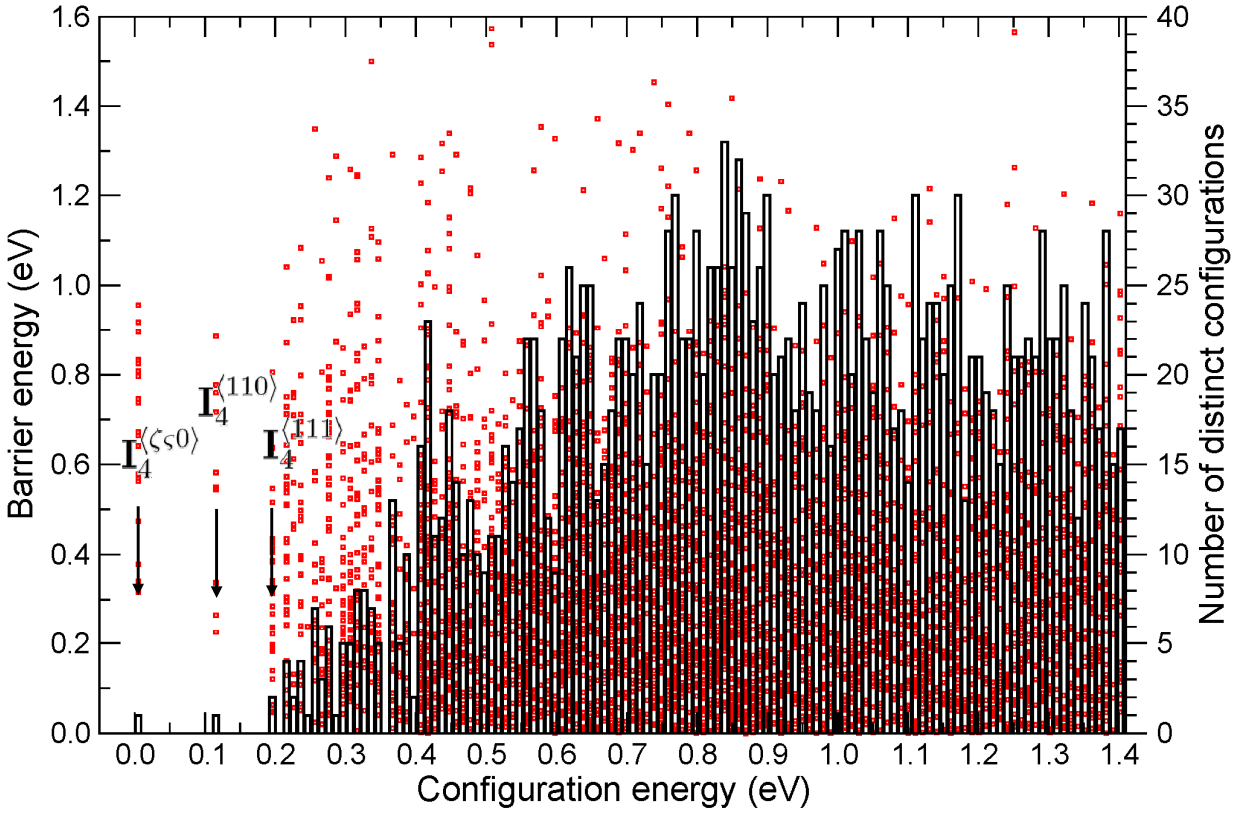


The three lowest-energy saddles for I_2

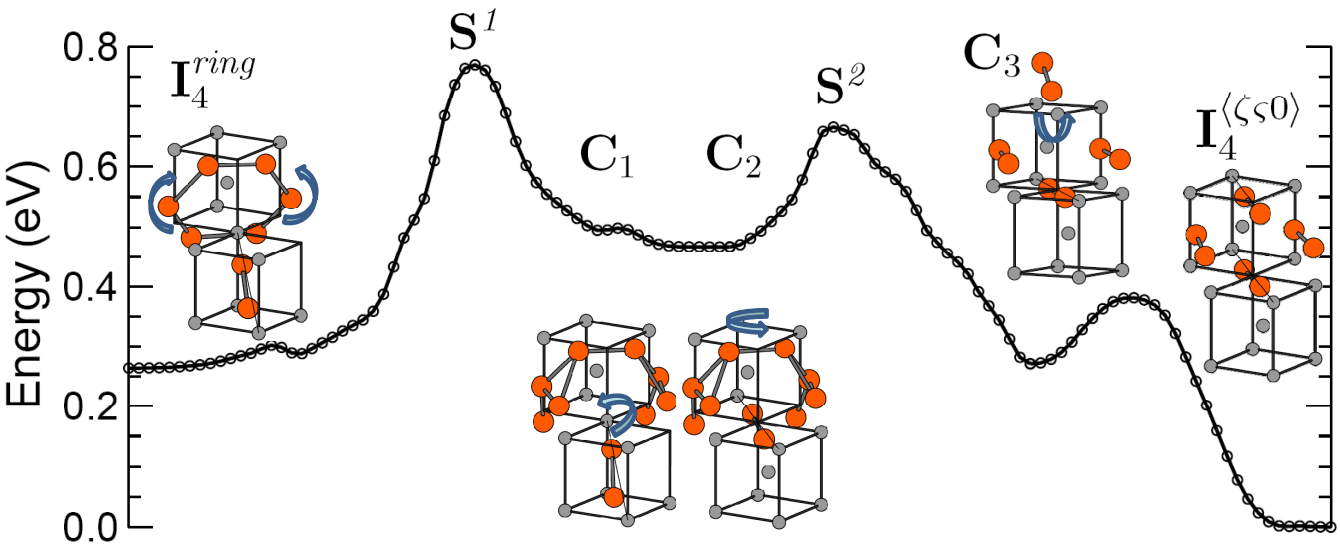


I_4 in Iron


$I_4^{\langle\zeta\varsigma 0\rangle}$ (side view)
$I_4^{\langle\zeta\varsigma 0\rangle}$ (top view)
$I_4^{\langle 110\rangle}$
$I_4^{\langle 111\rangle}$


Barrier energy (eV)
Number of distinct configurations
Configuration energy (eV)
$I_4^{\langle\zeta\varsigma 0\rangle}$
$I_4^{\langle 110\rangle}$
$I_4^{\langle 111\rangle}$
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

Transition pathways for I_4



Transition pathway for the unfaulting mechanism of the ring configuration of the tetra-interstitial, I_{ring}, into the most stable configuration, $I_{\langle\zeta\varsigma 0\rangle}$.

Systematic study of interstitials in Iron

- The number of bound configurations increases rapidly with cluster size, exceeding 400, 1100 and 1500 distinct bound configurations for I_2, I_3 and I_4
- lead to the appearance of a quasi-continuous band of states at relatively low energy above the ground state – at 0.42 eV, 0.23 eV, 0.20 eV for I_2, I_3 and I_4
- For I_3 and I_4, migration is more complicated and takes place via a series of jumps between configurations with relatively energies (0.3 eV or more).

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

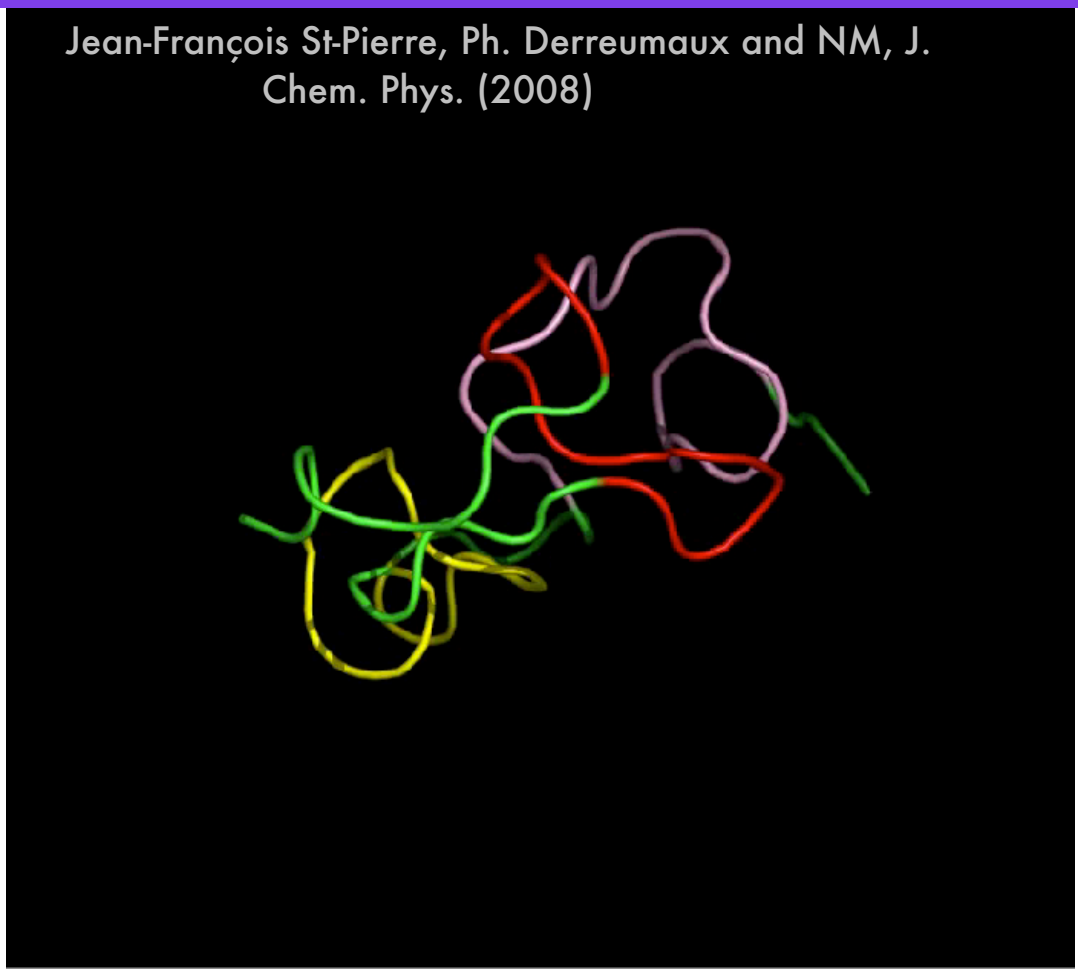
Application to protein folding: B domain of protein A

Jean-François St-Pierre, Ph. Derreumaux and NM, J. Chem. Phys. (2008)

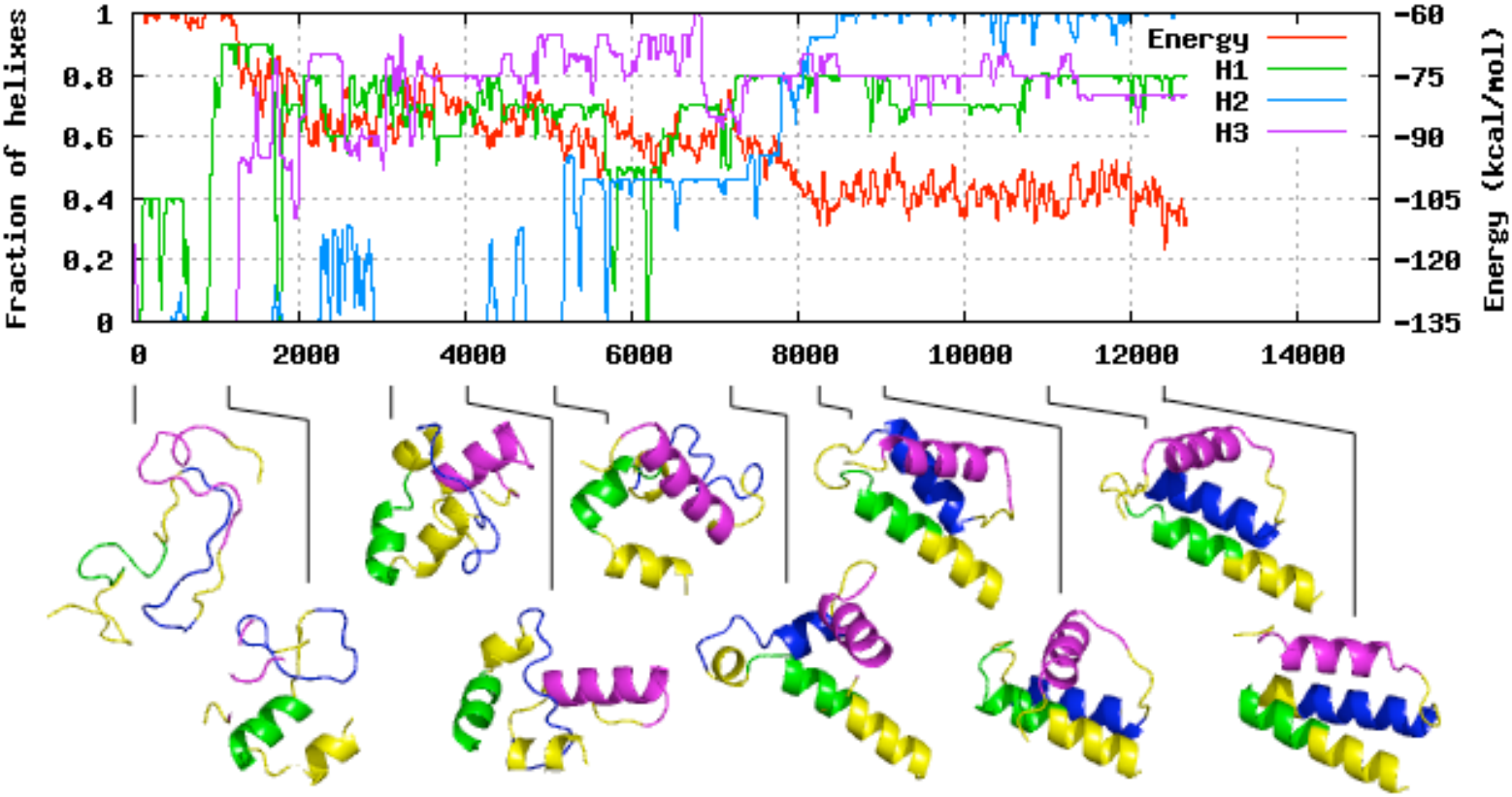
Fast folder - used by Fersht as a way to make contact between simulation and experiment
(Sato *et al*, PNAS 2004)

60 residues

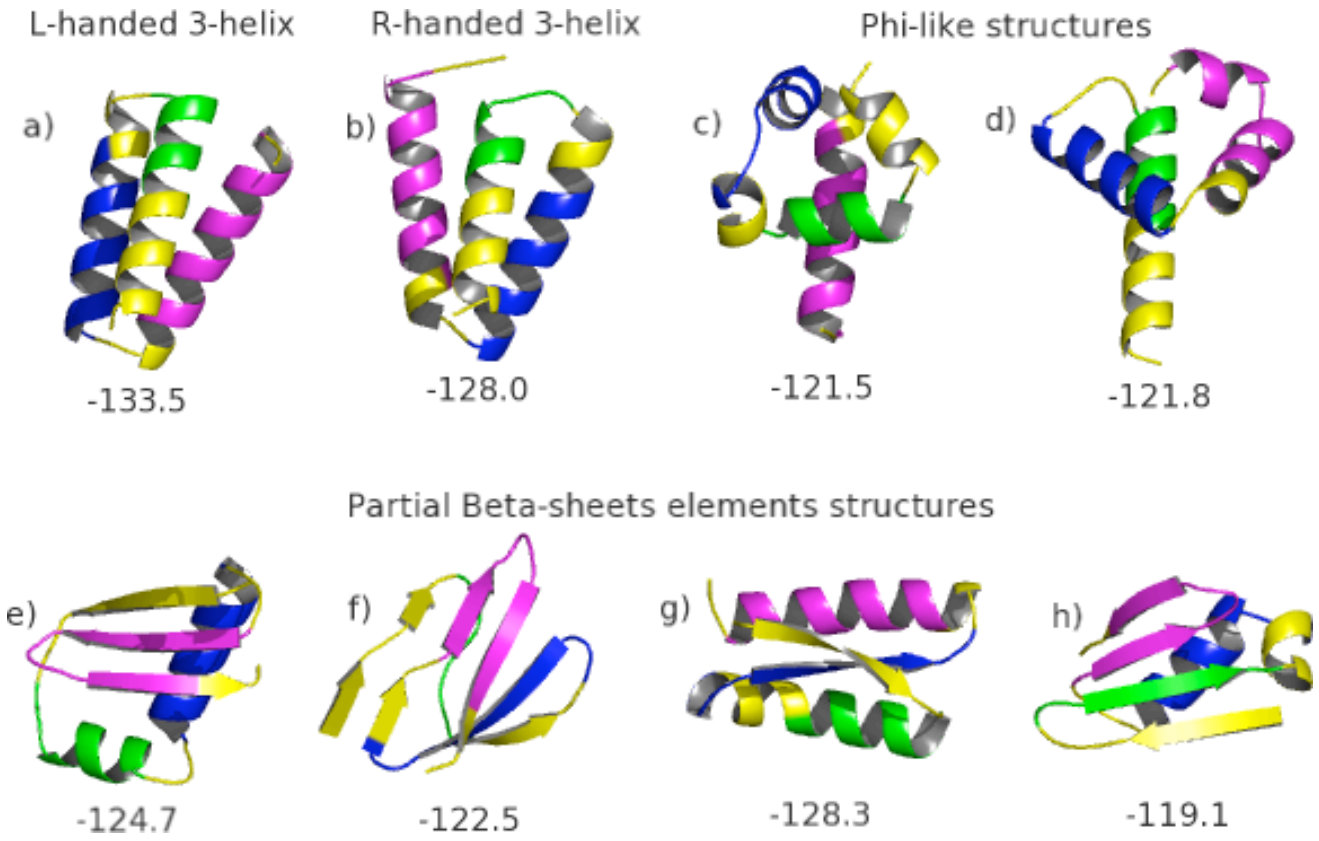
ART-OPEP
600 K
20 000 steps
(5-6 weeks on a single processor)



Two differents folding paths (among many)



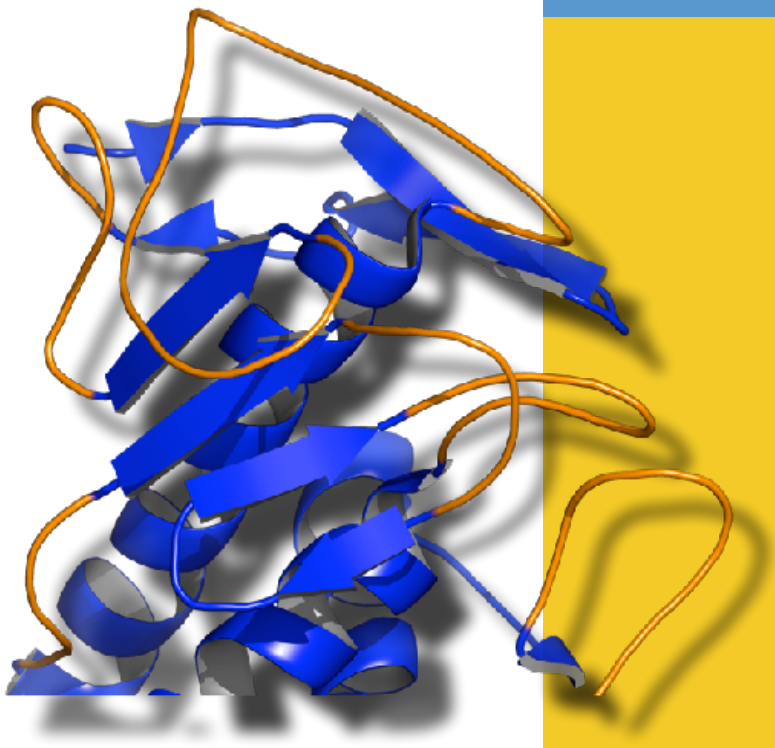
The low-energy structures of protein A



Application to loops

J-F St-Pierre et NM, Proteins: Structure, Function and Bioinformatics (sous presse).

- **Few secondary structure elements**
- **Flexibles**
- **Not conserved between homologous proteins**



Szeltner, Z. and Renner, V. and Polga, L., Protein Science, 2000, 9:353

Loop prediction methods

Based on sequence homology

- Very quick
- Very precise when the homology is good
- Good coverage for short sequences
- (FREAD, ROSETTA)

ab initio Methods

- Based on exhaustive sampling
- Precision limited by the quality of the potential
- Limited to short sequences (~12 a.a.)
- Computation time in $O(e^N)$.
- (MODELLER, PLOP, CCD, RAPPER)

Test models

8 a.a. loops:

- 25 loops from Olson's group
- 3.5 simulations / loop 4000 conformations each

M.A. Olson, M. Feig, and C.L. Brooks, J. Comput. Chem., 29(2008),820

12 a.a. loops:

- 38 loops from Fiser's group
- 2.8 simulations / loop 3000 conformations each

A. Fiser, R. K. G. Do, and A. Sali, Prot. Science, 9 (2000), 1753

19-20 a.a. loops:

- 10 proteins, extracted with the help of PISCES
- 5 simulations / loop small step
- 10 simulations /loop large step

G.L. Wand and R.L. Dunbrack, Bioinformatics, 19 (2003),1589

Results - prediction

8 a.a	ART	Olson Network	Olson REMD
Best RMSD	1.23	2.21	1.57
Top RMSD	3.50	3.89	3.13

M.A. Olson, M. Feig, and C.L. Brooks, J. Comput. Chem., 29(2008),820

12 a.a	ART	ART SCWRL dFire[1]	Rapper[2]	FALCm4[2]	Looper[3]	Rosetta[4]
Best RMSD	1.75	1.75	2.21	1.74		
TOP RMSD	5.60	4.27	4.32	3.84	4.08	2.3

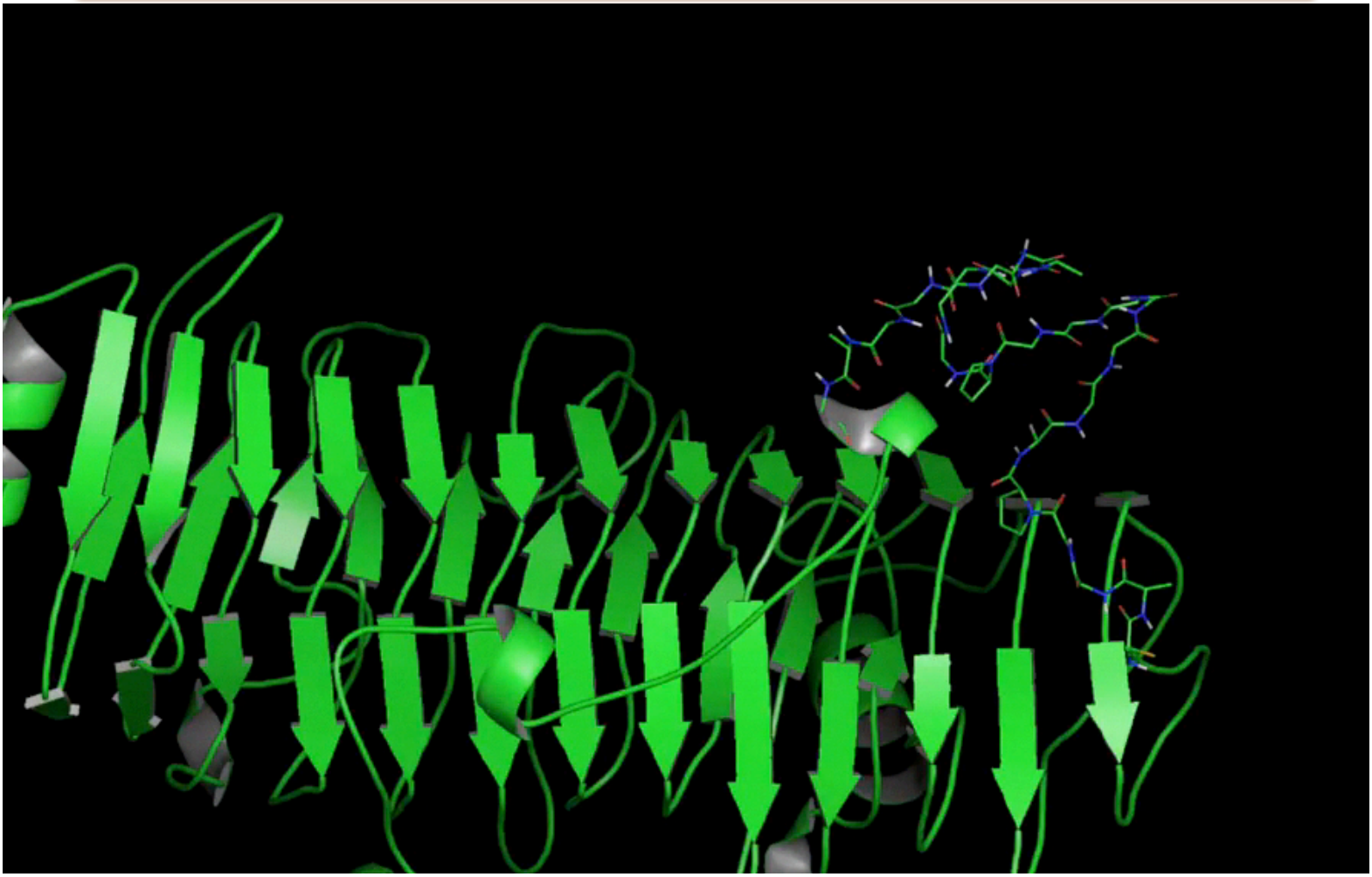
[1]C. Zhang, S. Liu, Y. Zhou, Prot. Science, 2004, 13:391
[2]J. Lee, D. Lee, H. Park, E. Coutsias, C. Seok, Proteins, 2010, 78:3428
[3]S. Spassov, P. Flook, L. Yan, PEDS, 2008, 21:91
[4]D. Mandell, E. Coutsias, T. Kortemme, Nature Methods, 2009, 6:551

Results - prediction

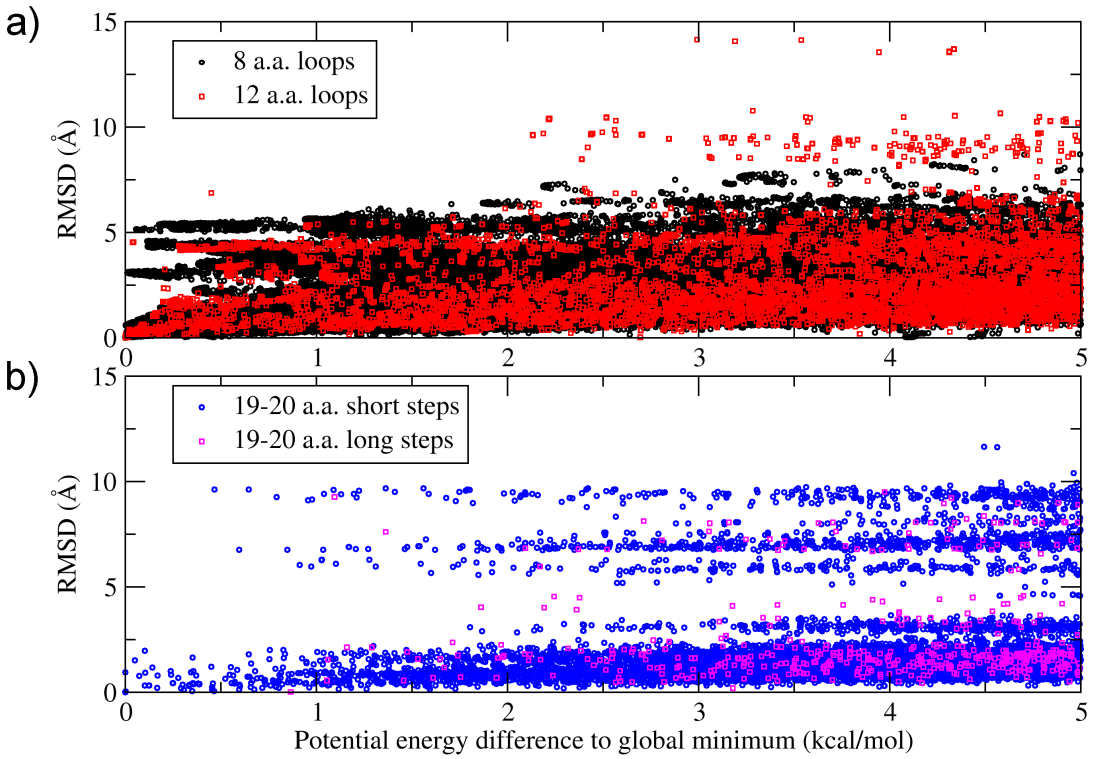
12 a.a	ART	CABS[2]	PLOP[1]	Modeller[1]	Rapper[1]	Rosetta[2]	FREAD[1]
Best RMSD (Å)	2.98	~4	8.43	5.47	5.97	~4	5.20
TOP RMSD (Å)	7.17	~7	11.14	10.49	10.64	~9	7.64

[1]Y. Choi, C.M. Deane, Proteins, 2010, 78:1431
[2]M. Jamroz, A. Kolinski, BMC Struct. Biol., 2010, 10:9

Example: 20 a.a



Minimum degeneresence



Loops can find many low-energy structures

Conclusions : Loops

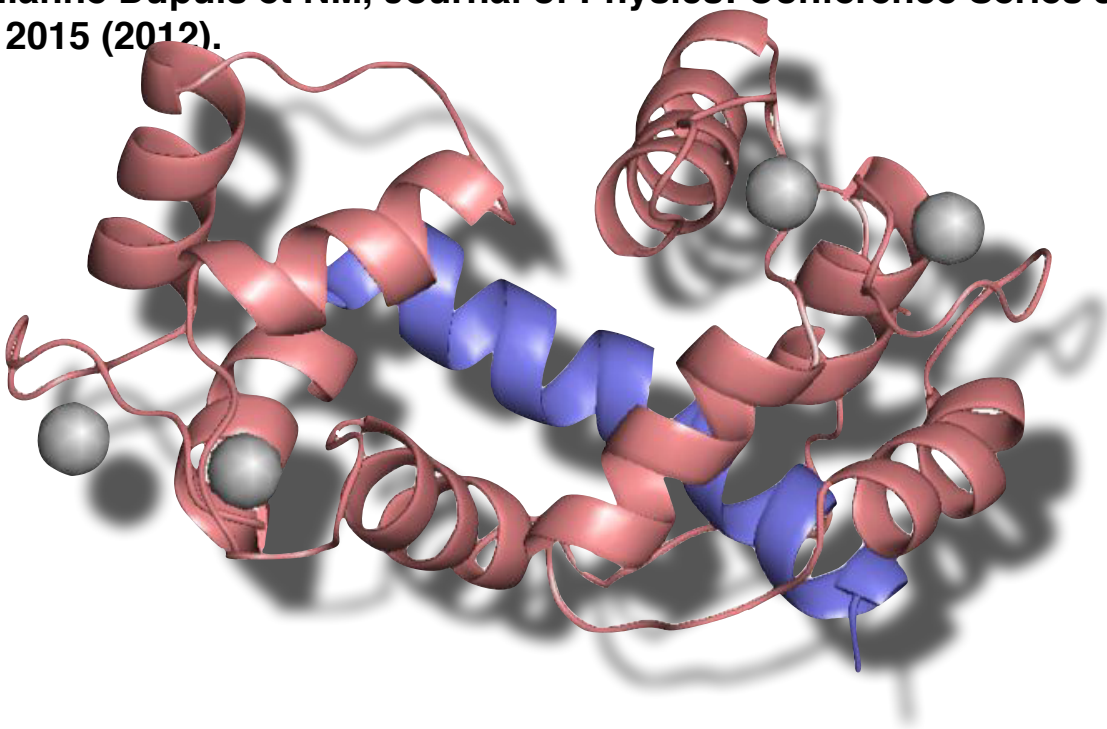
In spite of the potential's limits, results are interesting:

- Execution time is well adapted to long loops
- Prediction level is comparable or superior to other methods (long loops)
- It is possible to improve on the current method

J-F St-Pierre et NM, Proteins: Structure, Function and Bioinformatics (sous presse).

Multiscale simulations

Lilianne Dupuis et NM, Journal of Chemical Physics 136, 035101 (2012)
Lilianne Dupuis et NM, Journal of Physics: Conference Series 341, 012015 (2012).

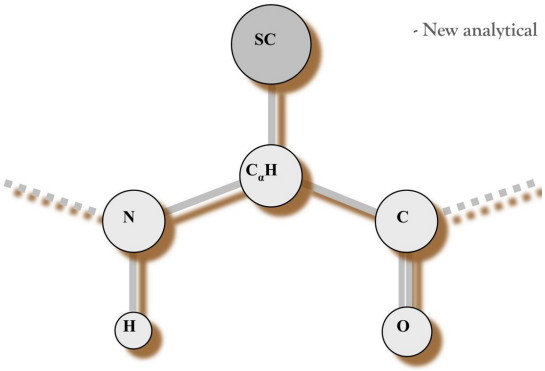


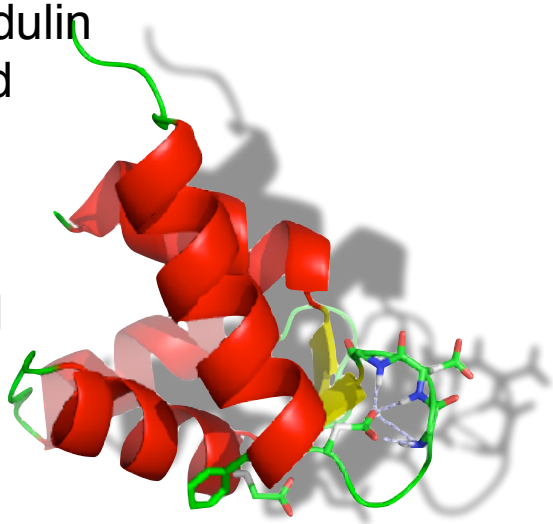
Extended OPEP

- Implicit solvent force field

- **EOPEP Development**
  - hydrogen bonds MC-SC
  - all atom (core: F, M, etc)
  - Calibrated on protein A and Calmodulin
  - Used unmodified on troponin C and protein G
  - TRP : 12b, 18v, 30t

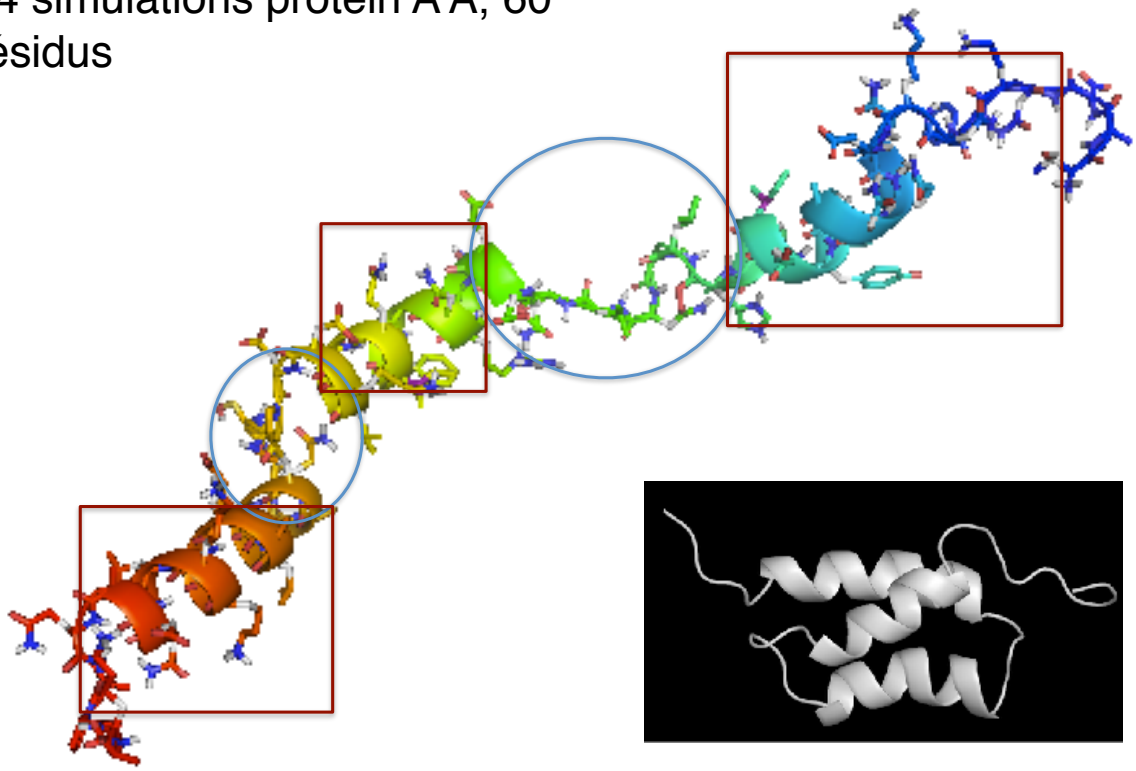
Comparisons with CHARMM19/EEF1





Test : Protein A

24 simulations protein A A, 60 résidus

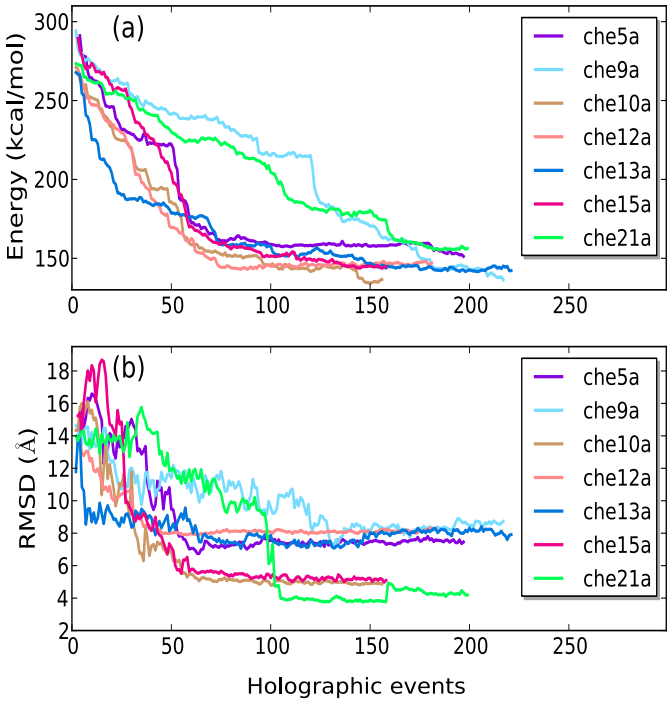


1BDC.pdb

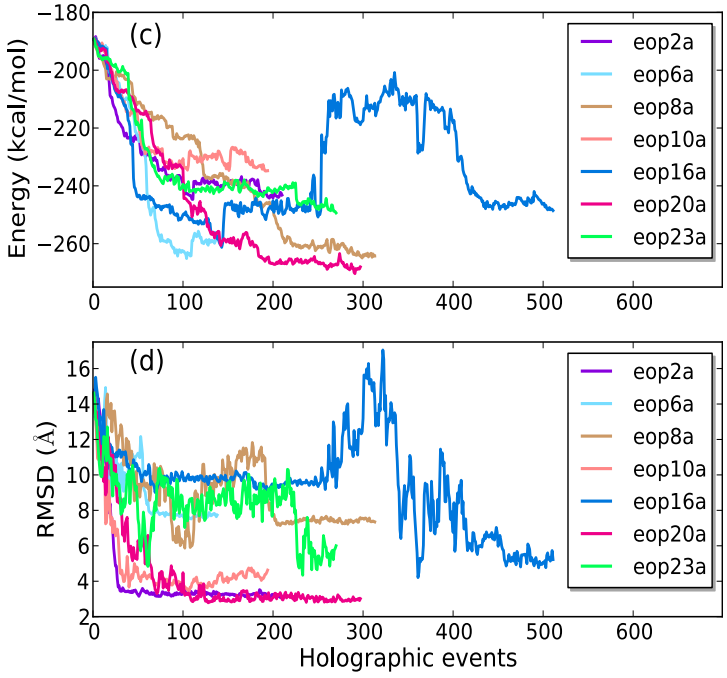
Test : Protein A

Protéine A, 60 résidus

Test : Protein A



Fermeture protéine A avec CHARM19/EEF1



Fermeture protéine A avec EOPEP

Test : Protein A

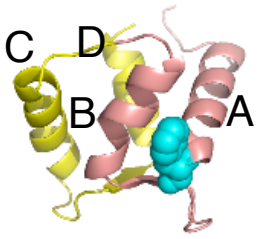
Tableau 4.II – Mean RMSD between events : statistics for a few simulation examples

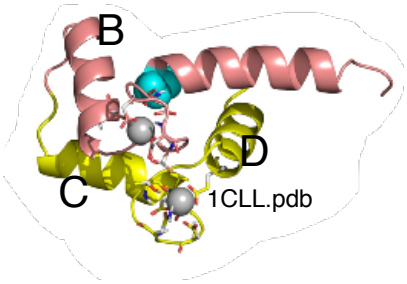
Protein model	Forcefield	Sim	mean RMSD at saddle all events	at min all events	mean RMSD at saddle accepted only	at min accepted only
Protein A	CHARMM19	5	2.29	2.39	1.27	1.28
Protein A	CHARMM19	16	2.93	2.96	0.96	0.77
Protein A	EOPEP	1	4.13	4.38	1.11	1.03
Protein A	EOPEP	20	3.10	3.25	1.16	1.09
Protein G	CHARMM19	2	2.24	2.03	1.26	0.98
Protein G	CHARMM19	11	2.07	1.94	1.12	0.95
Protein G	EOPEP	2	2.74	2.66	1.25	0.83
Protein G	EOPEP	14	1.93	1.52	1.19	0.69

Application to EF-hand proteins

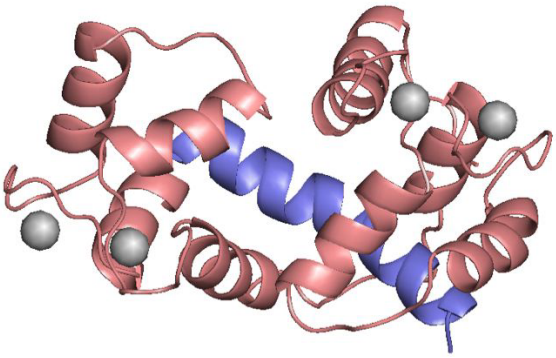
Calmodulin Nt, 76 R

1CFD.pdb





Troponin C bound to its target

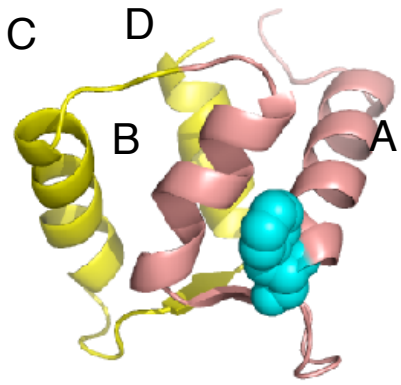


```
CaM NT
EFhand1              ADQLTEEQIAEFKEAFSLFDKDGDGTITTKELGTVMRSL
EFhand2                GQNPTEAELQDMINEVDADGNGTIDFPEFLTMMARKM
TpC NT
EFhand1  ASMTDQQAEARAFLSEEMIAEFKAAFDMFDADGGGDIKSTELGTVMRMLG
EFhand2                QNPTKEELDAIIEEVDEDGSGTIDFEEFLVMMVRQMKEDA
```

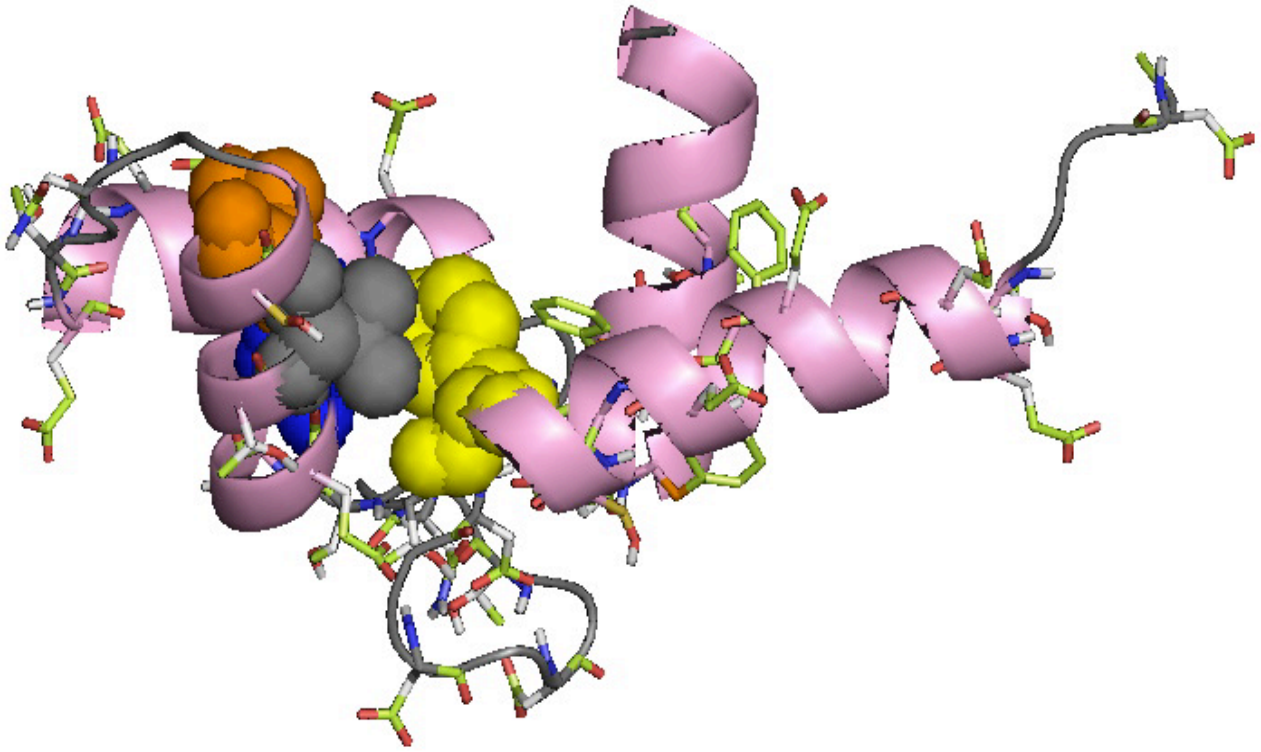
- All previous folding simulations of EF-hand proteins were biased

X. Grabarek's hypothesis

- β-sheet that links the two-loops central zone stabilised the closed structure
- In the loop NT region, oxygen-carrying residues are very flexible and will capture CA^{+2}.
- This restructures the central zone in order to allow helices A & B into a perpendicular position.
- Residu GLU in position 12 moves closed and binds CA^{+2}.

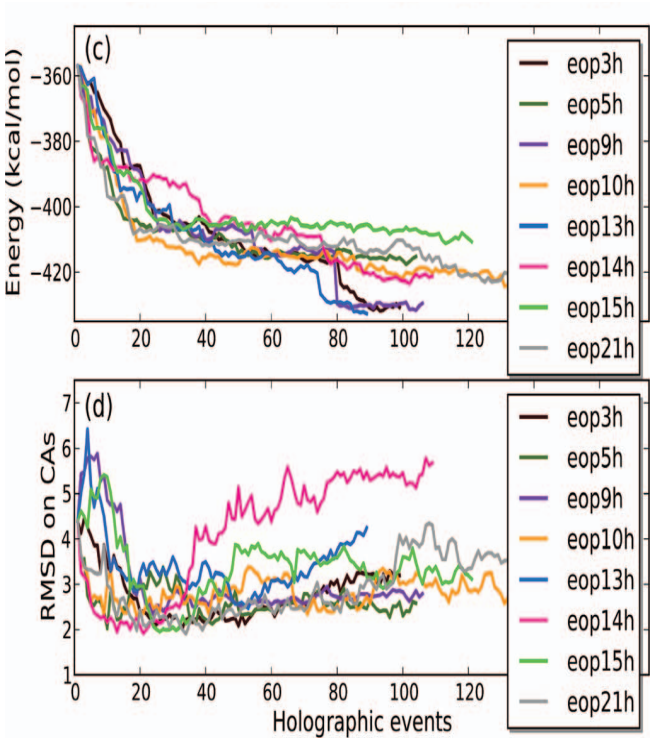


Calmodulin closure

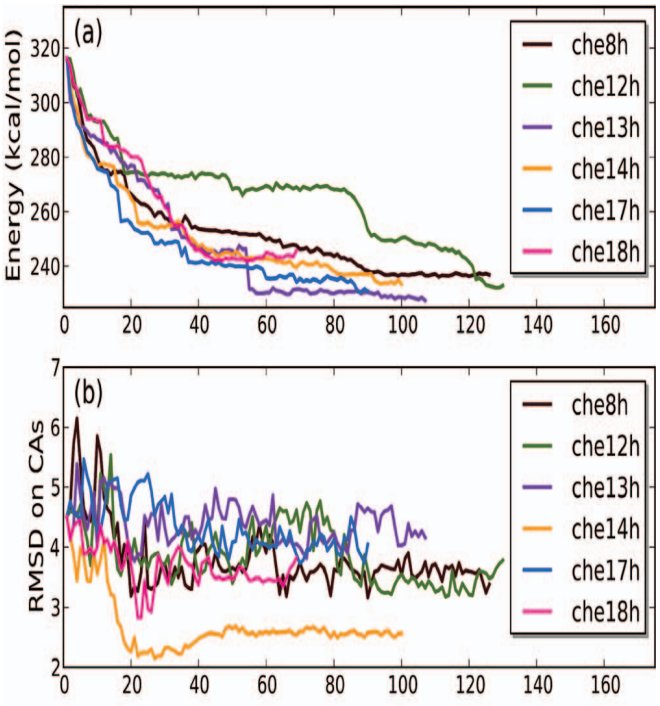


Closing of calmodulin

EOPEP



CHARMM19/EEF1



Closing steps

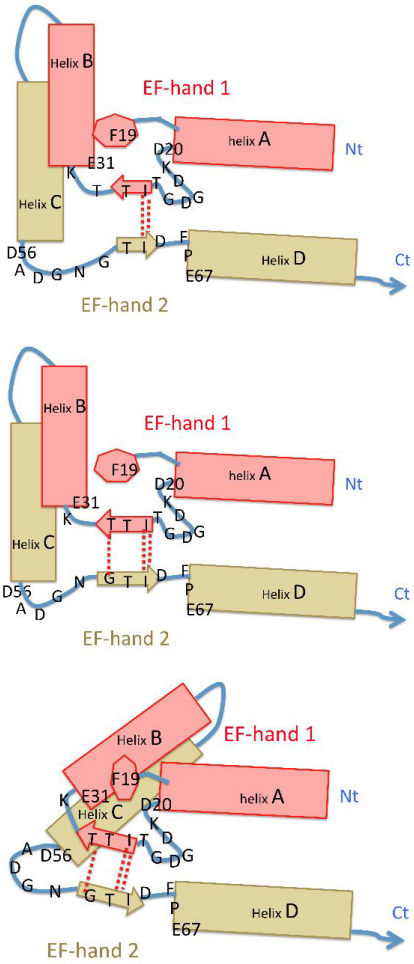
1. Residues bound with CA^{+2} are freed
2. Consolidation/élongation of the loop-binding β-sheet, which increases teh space between helices A and B
3. PHE19 side chains is expelled form the hydrophobic core transiting through VAL35

   CAM: 5, 4 and 5 cas at T_{300k}

   11/24 à ay T_{900k}

   17/24 including intermediate states

   TPC: PHE29, VAL45: 8/24 à 300K



Conclusions : EF-hands

Simulations of the open model for the NT domains of Calmodulin and Tropnonin C have managed to fold into the closed structures allowing us to identify:

- Specific intermediate steps
- the importance of a number of residues
- An intermediate state
- an irreversible sequence that suggests the opening requires the introduction of CA^{+2} ions

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 and NM - PRL (1996,1998), 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)

Available

ART nouveau, version 3.0

http://physique.umontreal.ca/~mousseau/index.php?n=Main.Logiciels

Accelerating time
Part 3

Outline

1. The challenge of simulating over multiple time scales. Energy landscapes. The transition state theory. Overview of various methods for breaching these time scales.

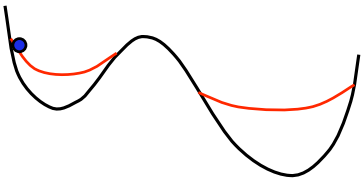
2. Solving the problem for simple systems. The kinetic Monte Carlo approach. Various accelerated molecular dynamics methods.

3. Off-lattice kinetic Monte Carlo methods. The kinetic Activation-Relaxation Technique (part 1). Basic concepts. Searching for saddle points. Toplogical analysis. Constructing an event catalog.

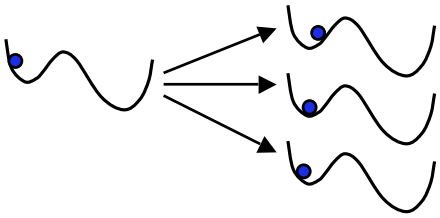
4. The kinetic Activation-Relaxation Technique (part 2). Handling flickers. Limitations of current accelerated methods. Extending to large systems. Coming developments.

Accelerated molecular dynamics

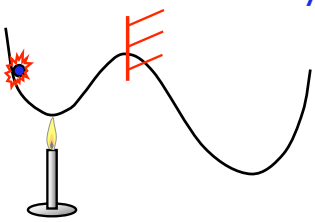
Hyperdynamics (1997)



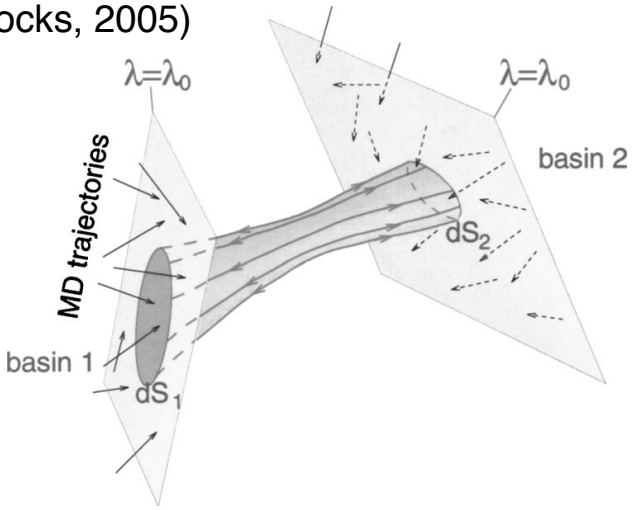
Parallel Replica Dynamics (1998)



Temperature Accelerated Dynamics (2000)



Properly-obeyed probability Activation-Relaxatoin Technique
(Vocks, 2005)

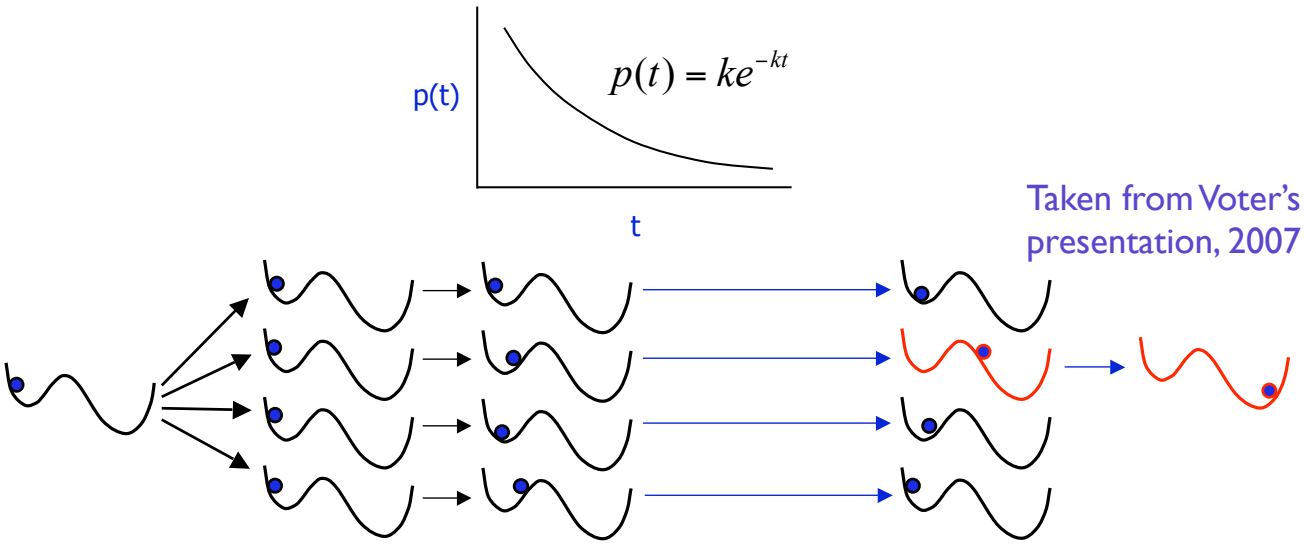


Taken from Voter's presentation

Parallel Replica Dynamics

In a system dominated by rare events, i.e., with: A.F.Voter PRB (1998)

- infrequent and uncorrelated events
- exponential distribution of first-escape time



The total run time, over all copies, follows an exponential distribution and leads to the correct state

Parallel Replica Dynamics: Example

Simulation of Stick–Slip Friction

Martini et al. Tribol Lett (2009)

Applied rate : M*physical rate

M= number of replicas

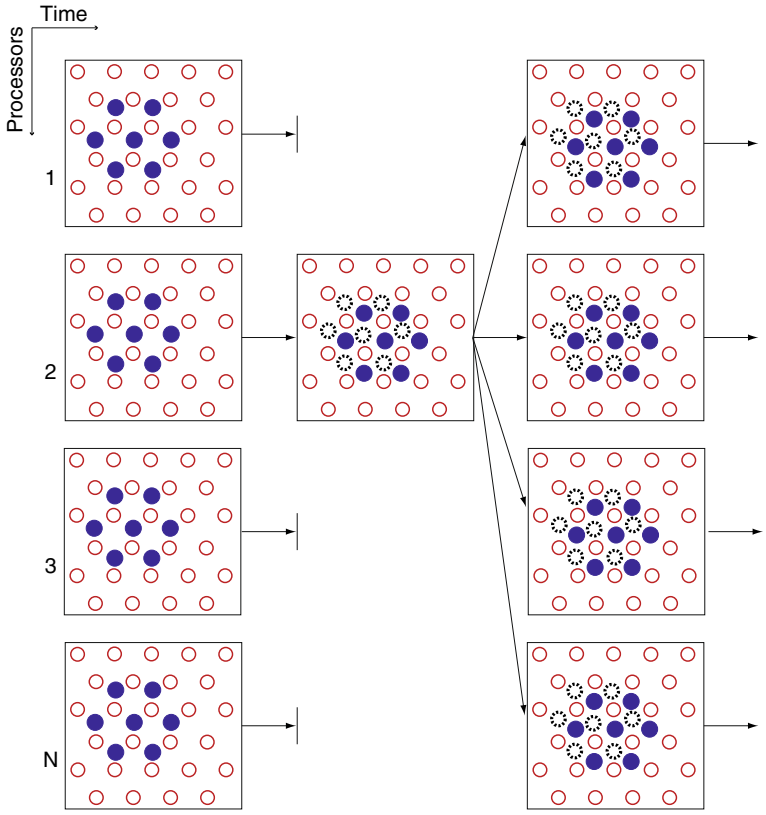
Here: up to 256 cores

Steps:

1- Dephasing/decorrelation

2. MD

3. Minimisation



Parallel Replica Dynamics: Example

Simulation of Stick–Slip Friction

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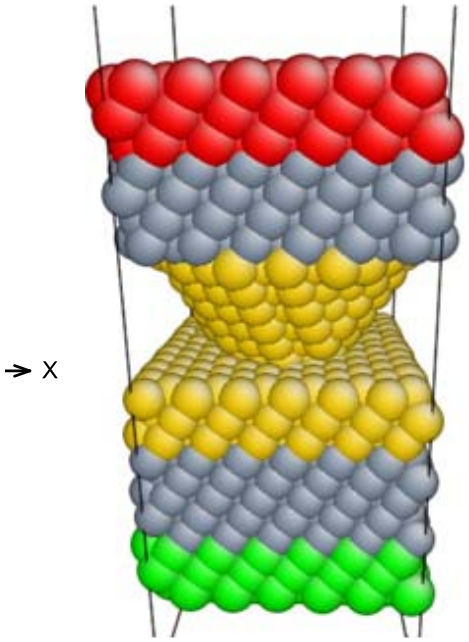
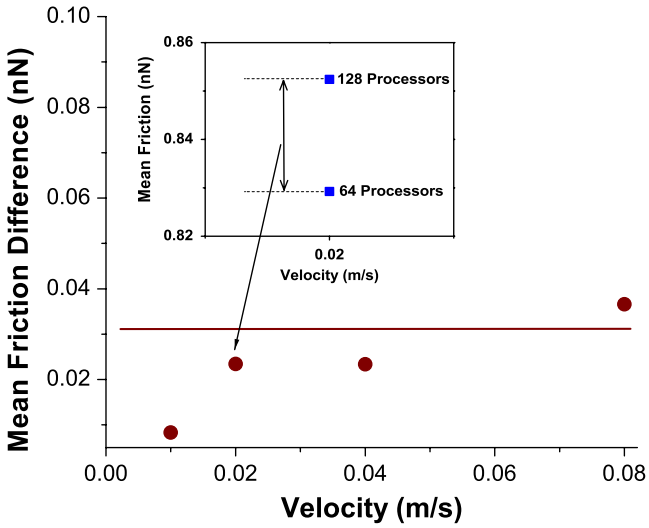
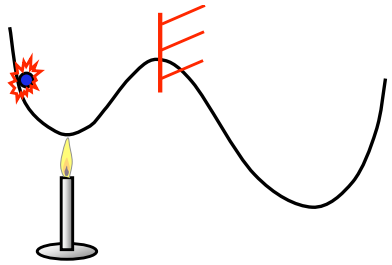




Temperature-accelerated dynamics

- Run MD at elevated temperature (T_{high}) in state A.
- Intercept each attempted escape from basin A
- find saddle point (and hence barrier height)
- extrapolate to predict event time at T_{low}.
- Reflect system back into basin A and continue.
- When safe, accept transition with shortest time at T_{low}.
- Go to new state and repeat.



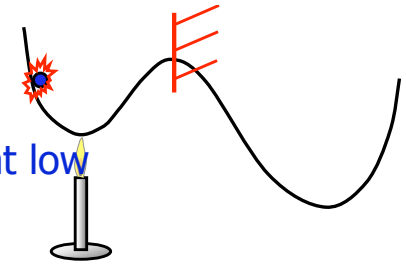
Taken from Voter's presentation

Temperature-accelerated dynamics

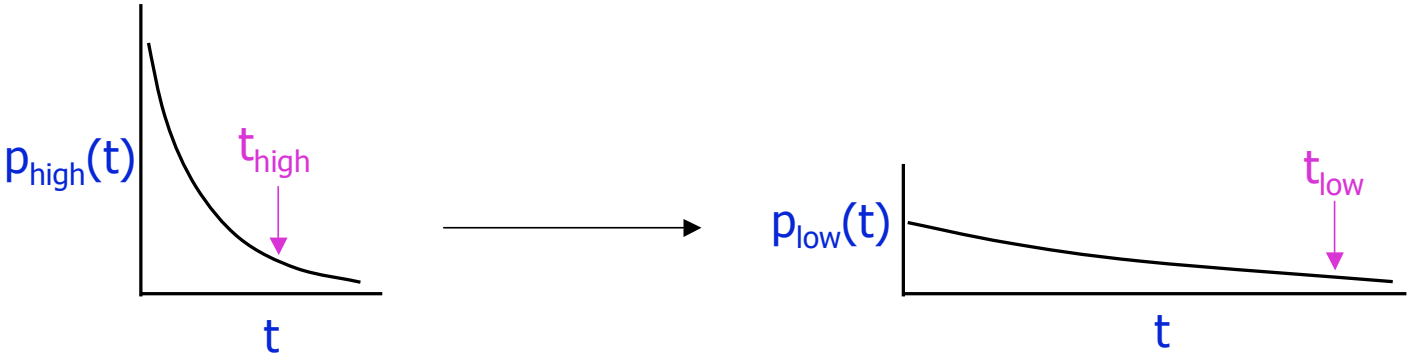
- If each transition follows the Arhenius law:

  $k = \nu_0 \exp[-\Delta E/kBT]$,

- Then it is possible to extrapolate the first-escape time at low temperature from

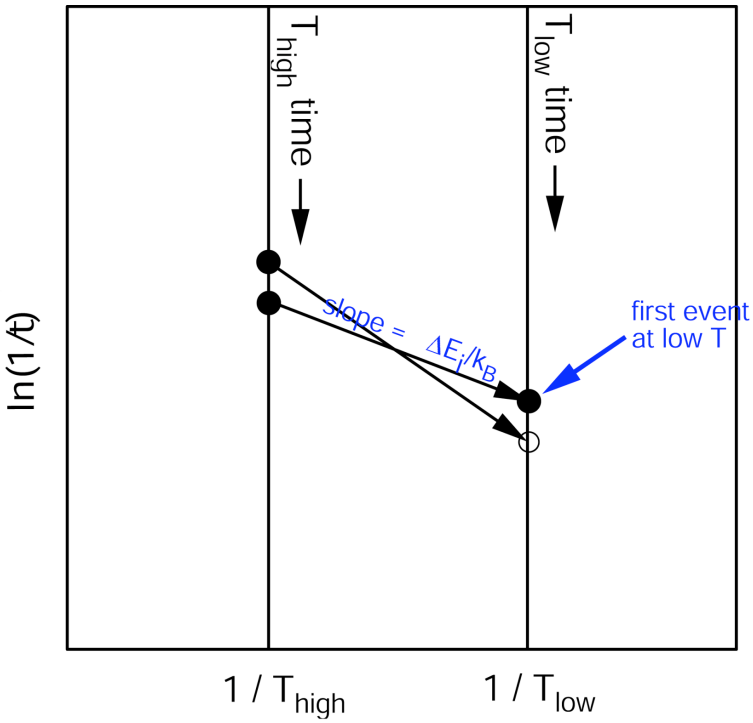


$t_{low} = t_{high} \exp[\Delta E(1/kBT_{low} - 1/kBT_{high})]$



Taken from Voter's presentation

Temperature-accelerated dynamics



Taken from Voter's presentation

Temperature-accelerated dynamics : Example

Vacancy Formation and Strain in Low-Temperature Cu=Cu(100) Growth

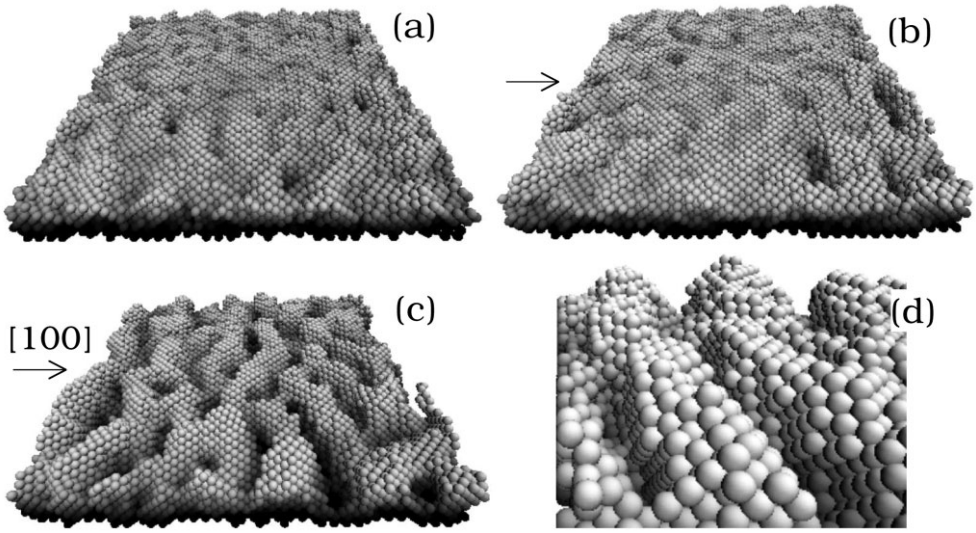
Shim *et al. PRL (2008)*

T_{high} = 200-400 K

T_{low} = 40 K

$\nu_{min} = 10^{12} s^{-1}$

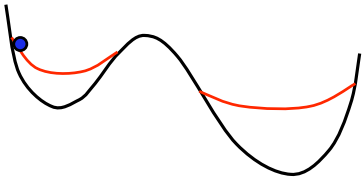
Here: up to 256 cores



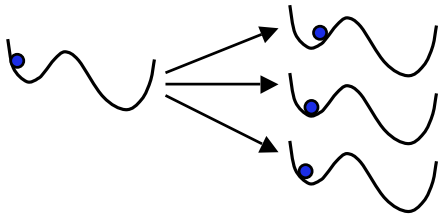
Highest barrier at 40 K : 0.06 eV

Accelerated molecular dynamics

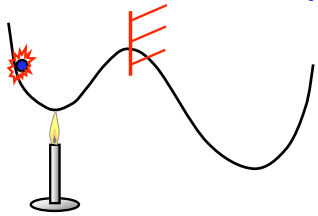
Hyperdynamics (1997)



Parallel Replica Dynamics (1998)

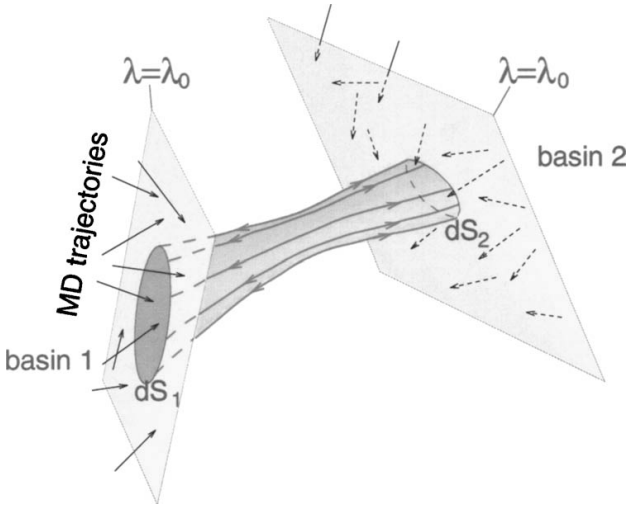


Temperature Accelerated Dynamics (2000)



Taken from Voter's presentation

Properly-obeyed probability Activation-Relaxation Technique
(Vocks, Mousseau et al, 2005)



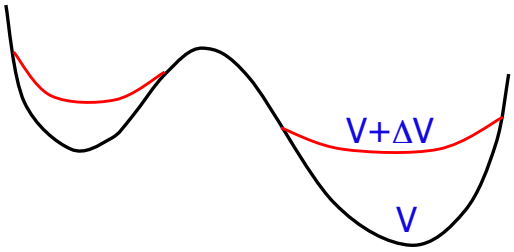
Hyper molecular dynamics

Concept: Fill the basins with a bias potential to increase the rate of escape and renormalize the time accordingly.

Assumptions:

- transition state theory (no recrossings)

Taken from Danny Perez + AF. Voter presentation, 2008



Procedure:

- design bias potential ΔV which is zero at **all** dividing surfaces so as not to bias rates along different pathways.
- run thermostatted trajectory on the biased surface ($V+\Delta V$)
- accumulate hypertime as

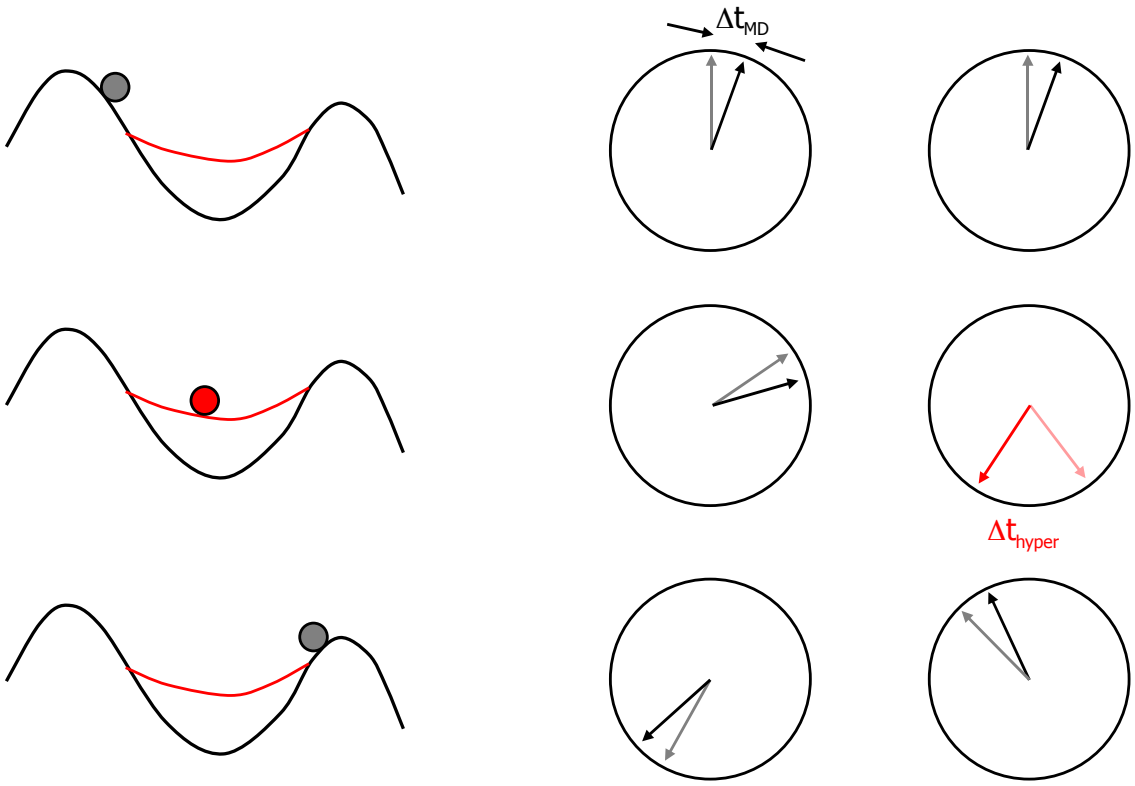
$$t_{hyper} = \Sigma \Delta t_{MD} \exp[\Delta V(R(t))/k_B T]$$

Result:

- state-to-state sequence correct
- time converges on correct value in long-time limit (vanishing relative error)

AFV, J. Chem. Phys. 106, 4665 (1997)

Hyper molecular dynamics : Example



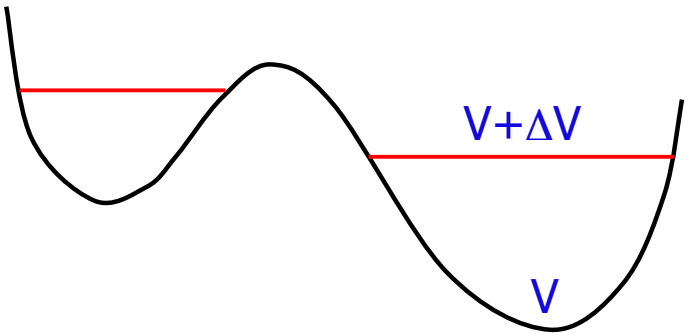
Taken from Danny Perez + AF. Voter presentation, 2008

Boost = hypertime/(MD clock time)

Hyper molecular dynamics : Example

Key challenge is designing a bias potential that meets the requirements of the derivation and is computationally efficient. This is very difficult since we do not have any a priori information about neighboring states nor about the dividing surfaces in between them. Futher, we have to work in very high dimension.

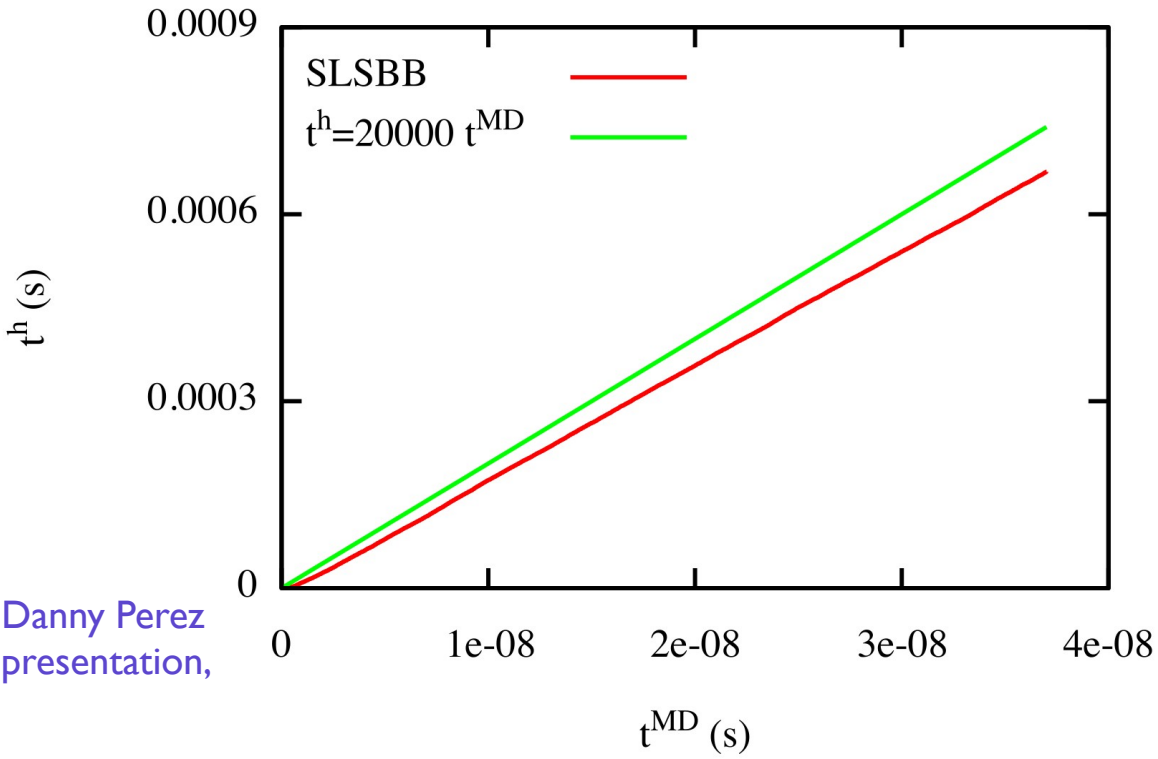
An extremely simple form: flat bias potential



Taken from Danny Perez + AF. Voter presentation, 2008

Hyper molecular dynamics : Example

Ag monomer on Ag (100) at T=300K: long time behavior

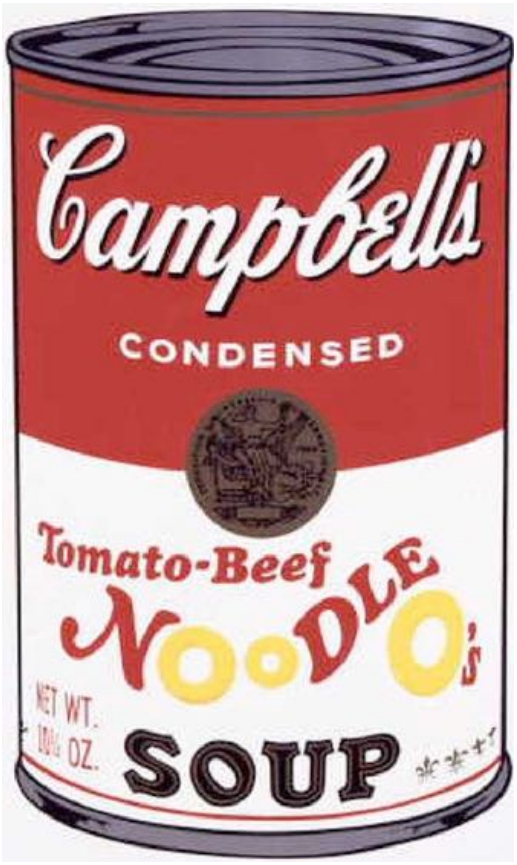


Taken from Danny Perez + AF. Voter presentation, 2008

Properly-obeying-probability activation-relaxation technique

Can we mix ART with a dynamical method to generate a thermodynamically-weighted version of ART ?

POP-ART POP-ART
POP-ART POP-ART



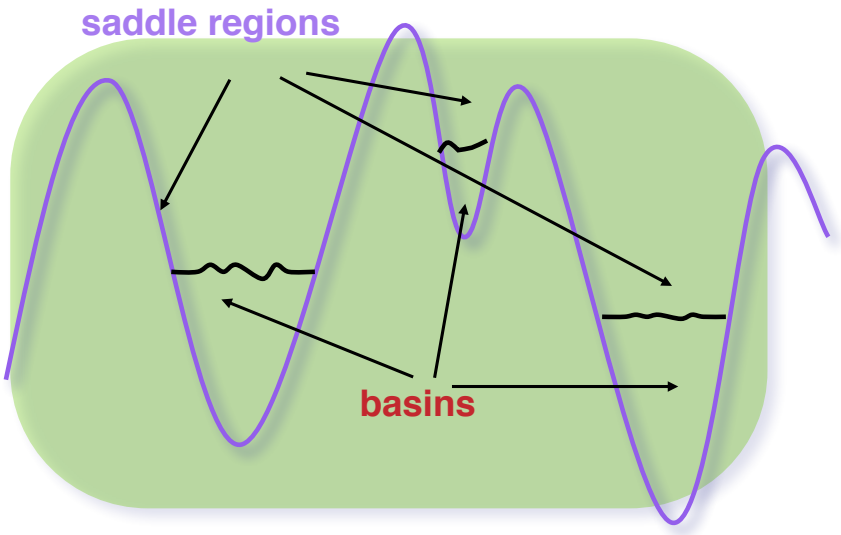
Basic idea

We divide the landscape into two regions :

basins: regions where all the eigenvalues associated with the curvature of the energy landscape are above a give threshold

saddle regions: regions where at least one eigenvalue is below the threshold.

At low temperature, the system samples only the region of phase space associated with the basin regions



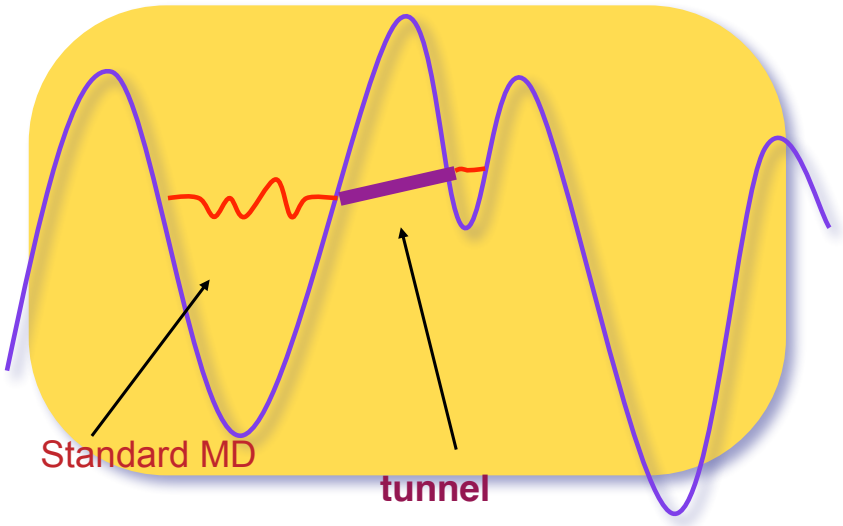
The saddle regions are not visited often and do not contribute significantly to the thermodynamics

Algorithm

Three steps:

1. Standard finite temperature molecular dynamics in a minimum well.

2. As we find a negative eigenvalue, we move on a constant configurational- energy surface following the direction associated with the lowest eigenvalue.

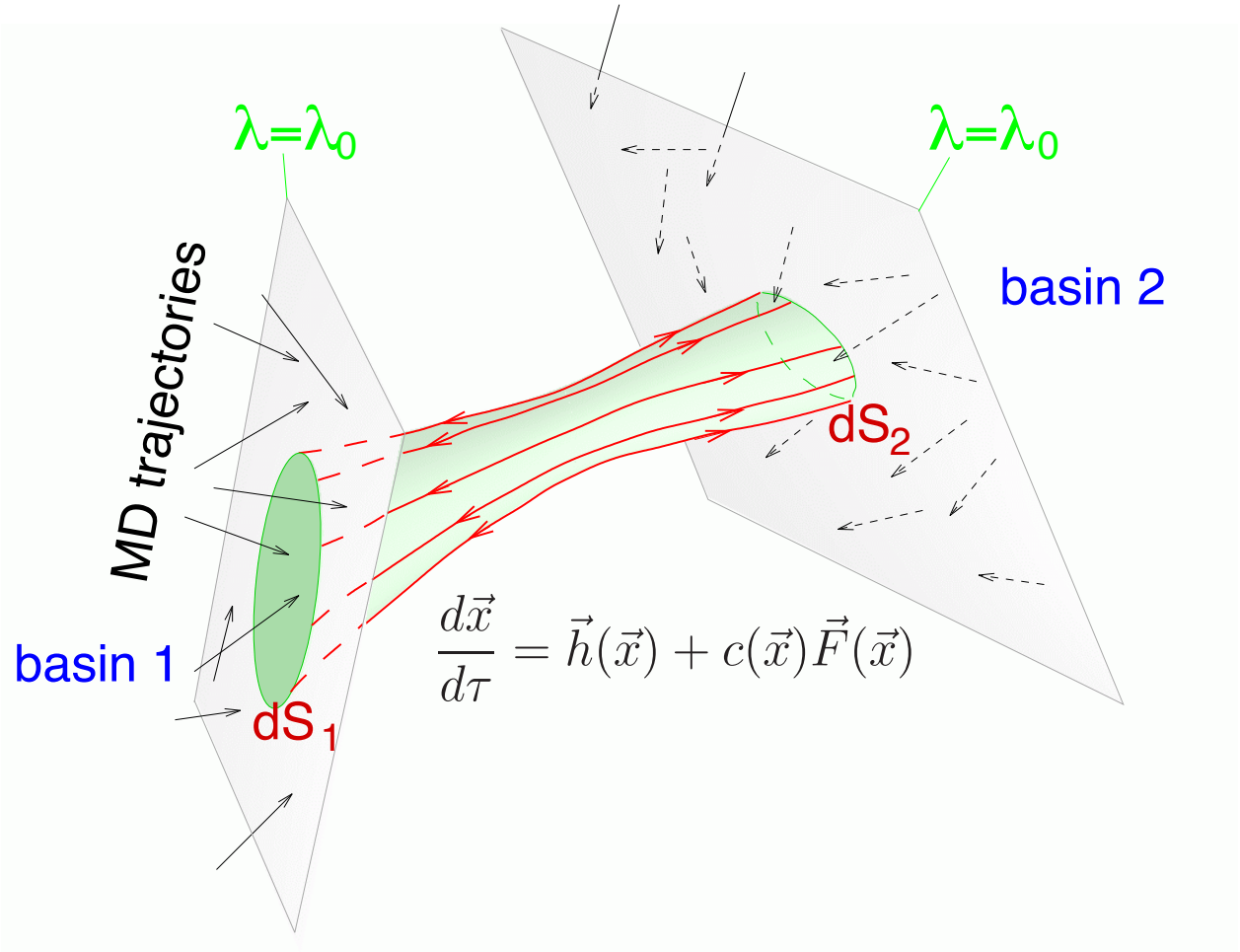


$$\vec{x}_{i+1} = \vec{x}_i + \frac{\Delta\tau}{2}\left(\vec{h}_i + \vec{h}_{i+1}\right) + c\Delta\tau\left(\vec{F}_i + \vec{F}_{i+1}\right)$$

3. We compute the Jacobian of transformation and accept or reject based on this value.

This algorithm respects detailed balance.

Contributions to the Jacobian of transformation



The boundary Jacobian

The correction on the area (entrance and exit) is simply the ratio of the cosine with respect to the normal

$$J_{\mathrm{b}} = \frac{\cos \alpha_1}{\cos \alpha_2}$$

where

$$\cos \alpha_{1,2} = \frac{\vec{h} \cdot \nabla \lambda}{|\nabla \lambda|}$$

and

$$\nabla \lambda(\vec{x}) = \lim_{\delta \to 0} \frac{2\vec{F}(\vec{x}) - \vec{F}(\vec{x} + \delta \cdot \vec{h}) - \vec{F}(\vec{x} - \delta \cdot \vec{h})}{\delta^2}$$

This last quantity is the gradient of the lowest eigenvalue - the direction perpendicular to the surface of constant value

The cross-section Jacobian

The displacement along curve is given by

$$\frac{d\vec{x}}{d\tau} = \vec{f}(\vec{x})$$

With $$\vec{f}(\vec{x}) = \vec{h}(\vec{x}) + c(\vec{x})\vec{F}(\vec{x})$$

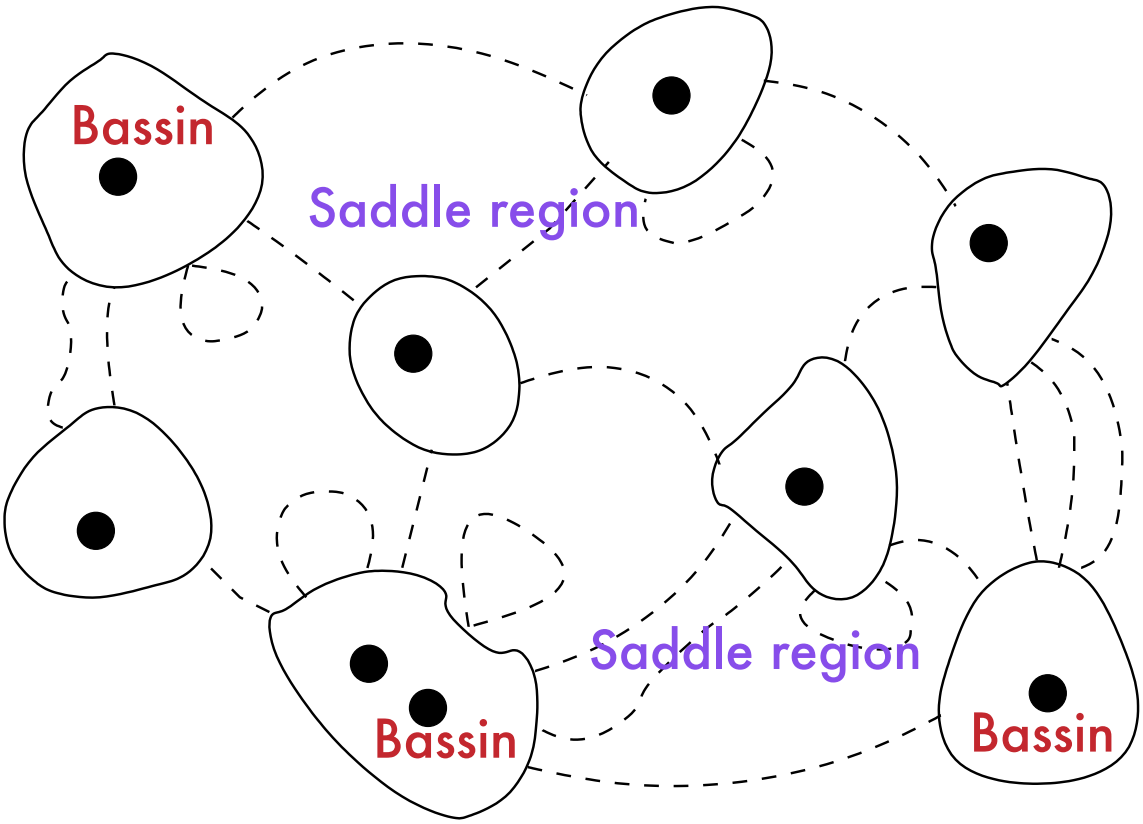
As $\tau \longrightarrow \tau + d\tau$ then $\vec{x} \longrightarrow \vec{x} + \vec{f}(\vec{x})d\tau$

$$\ln J_{\rm xs} = \int_0^\tau j(\vec{x}(\tau'))d\tau'$$

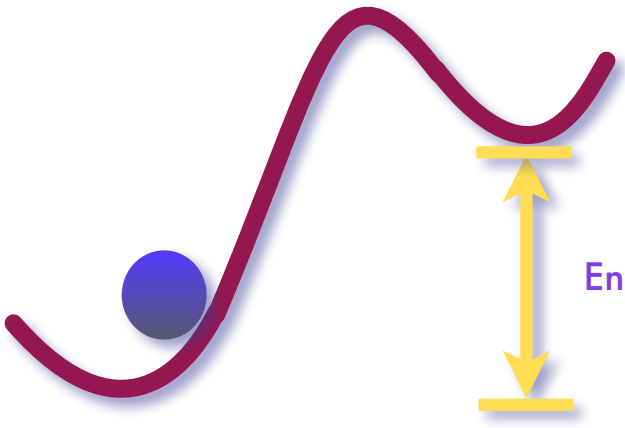
$$j = \mathrm{div}\,\vec{h} + c\,\mathrm{div}\,\vec{F}$$

$$\begin{aligned} J &= \exp(\textstyle\int j(x_0)dx_0) = \exp\left[-(\Delta U_0 - T\Delta S)/k_BT\right] \\ &= \exp[-\Delta\mathcal{F}/k_BT], \end{aligned}$$

POP-ART Trajectories



POP-ART Trajectories



Two energy minima with the same energy (+/- 0.01 eV)

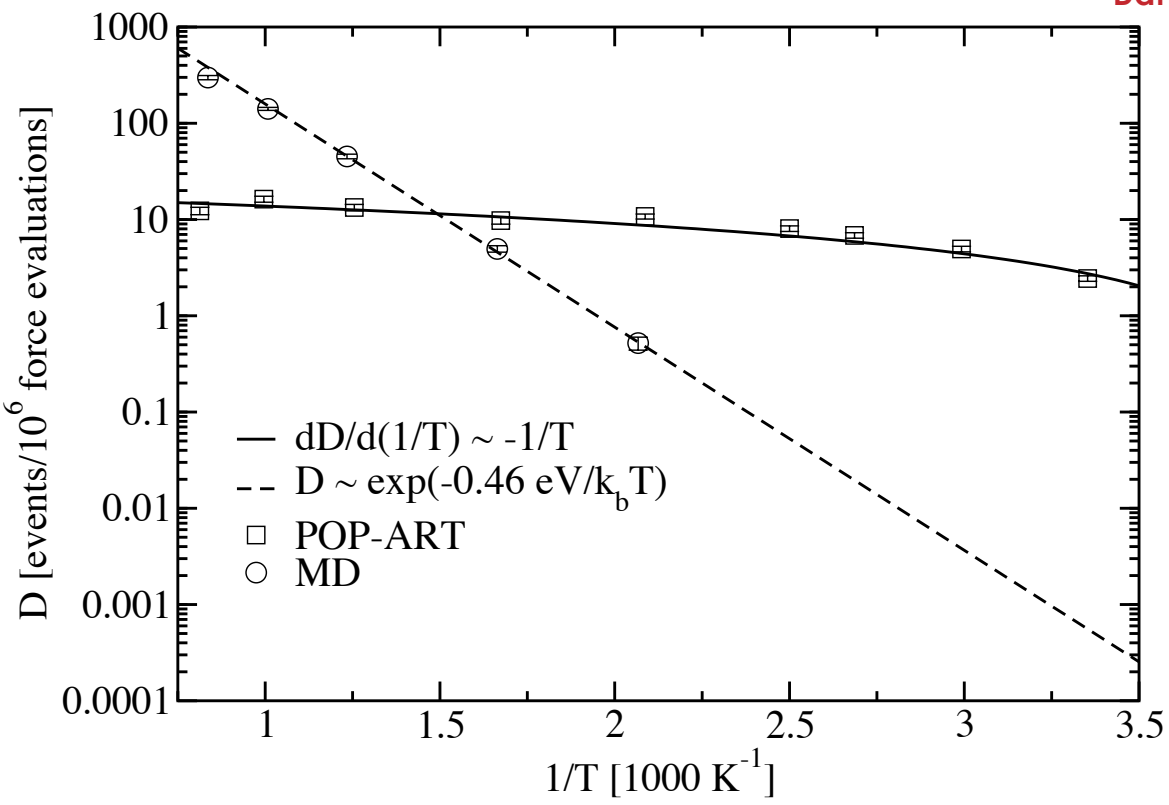
Energy difference: 0.75 eV

To establish the validity of the implementation of POP-ART we compute the probability of begin in the top states vs. the bottom state at 1000 and 1200 K

	MD	POP-ART
Ratio top to bottom at 1000 K	1.6 +/-0.1 %	1.3 +/- 0.3%
Ratio top to bottom at 1200 K	3.6 +/-0.1 %	3.5 +/- 0.3%

Sampling the phase space : vacancy in Si

Barrier: 0.43 eV



At room temperature: POP-ART samples 10000 faster than MD

Conclusions

- POP-ART is a promising method to sample thermodynamically the phase space of complex systems
  - it respects detailed balance
  - it requires only local information
  - it computes exactly the free energy difference (no harmonic approximation)
- POP-ART can be up to 10000 faster than MD even at room temperature
- Suffers from low-barrier - a problem that we did not manage to solve

Standard Kinetic Monte Carlo

We want to solve the evolution of a stochastic system which can be described by the Master's equation:

$$\frac{\partial P_i(t)}{\partial t} = \sum_j \left(P_j(t) R_{j\to i} - P_i(t) R_{i\to j} \right)$$

At any moment, the escape rate from a state is given by :

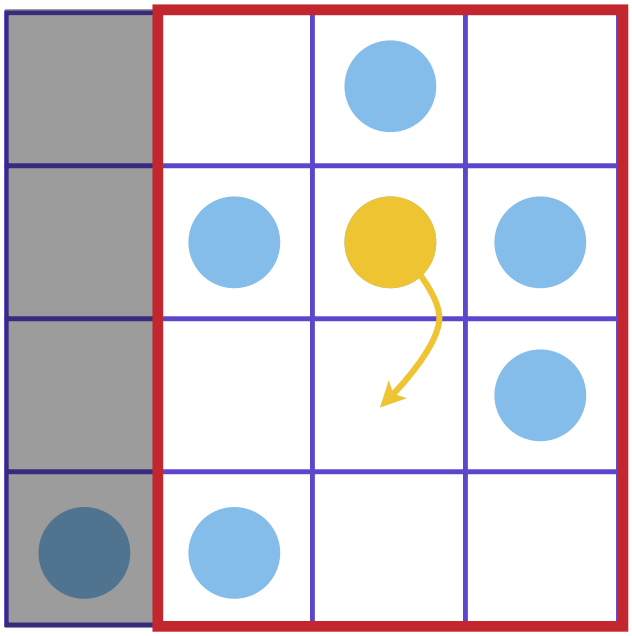
$$r_e^i = \sum_j R_{i\to j}$$

If the first-passage time is given by a Poisson distribution, then the escape time associated with this rate can be written as

$$t_e = -\frac{\ln \mu}{r_e^i} \qquad \text{with the probability} \qquad \mathcal{P}_{i\to j} = \frac{R_{i\to j}}{r_e^i}.$$

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 growth of polycrystalline Cu

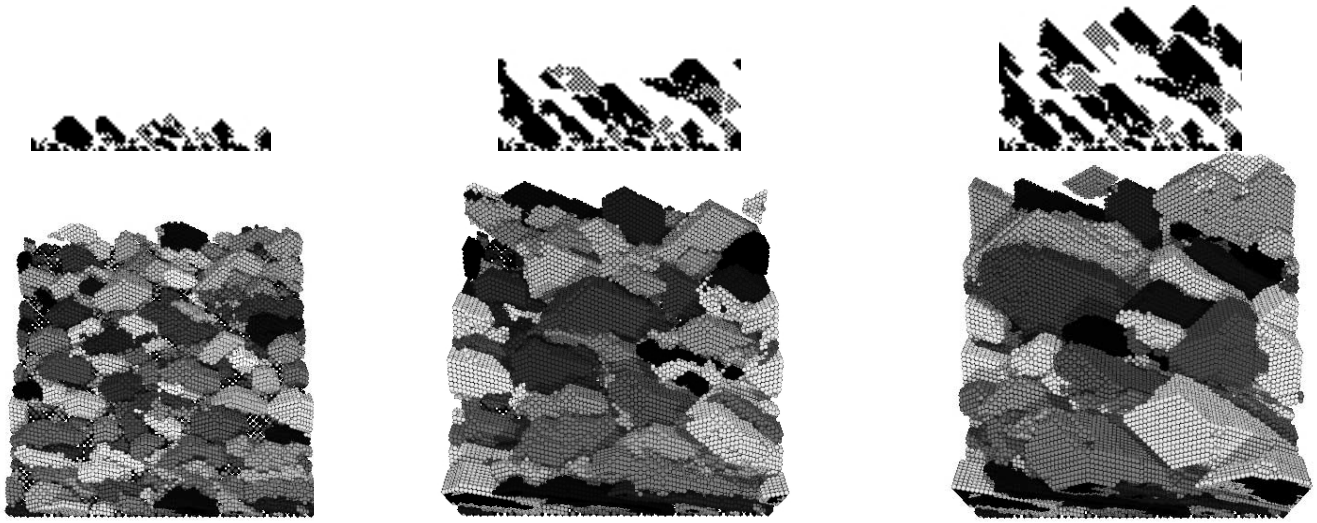
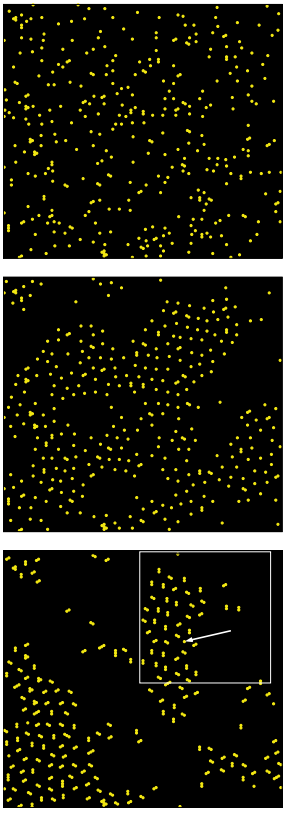
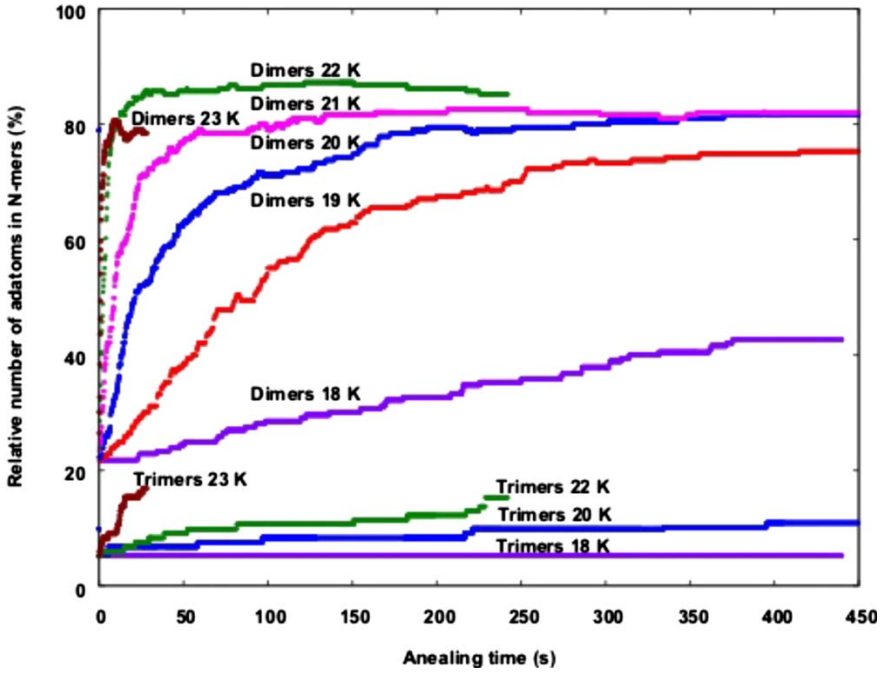


Fig. 1. Three snapshots showing the time evolution of a poly-Cu thin film. Substrate temperature is 150 K, angle of incidence is 75° from normal. Grains of non-bulk-like atoms are indicated by different shades of grey. Bulk-like atoms are shown in black. Images shown from the top to the bottom are top-down (plan) view, a slice through the film (cutaway view), and a perspective view.

Wang and Clancy, Surface Science 473 (2001) 25

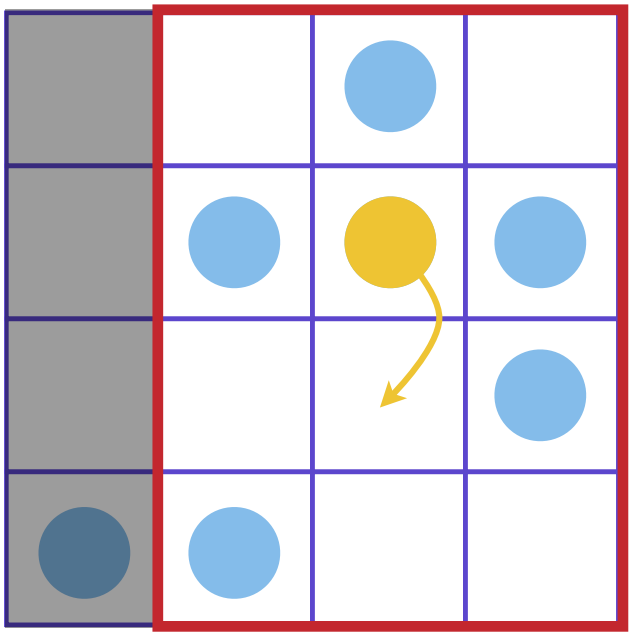
Co growth on Cu(111)





JM Rogowska, PRB (2010)

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

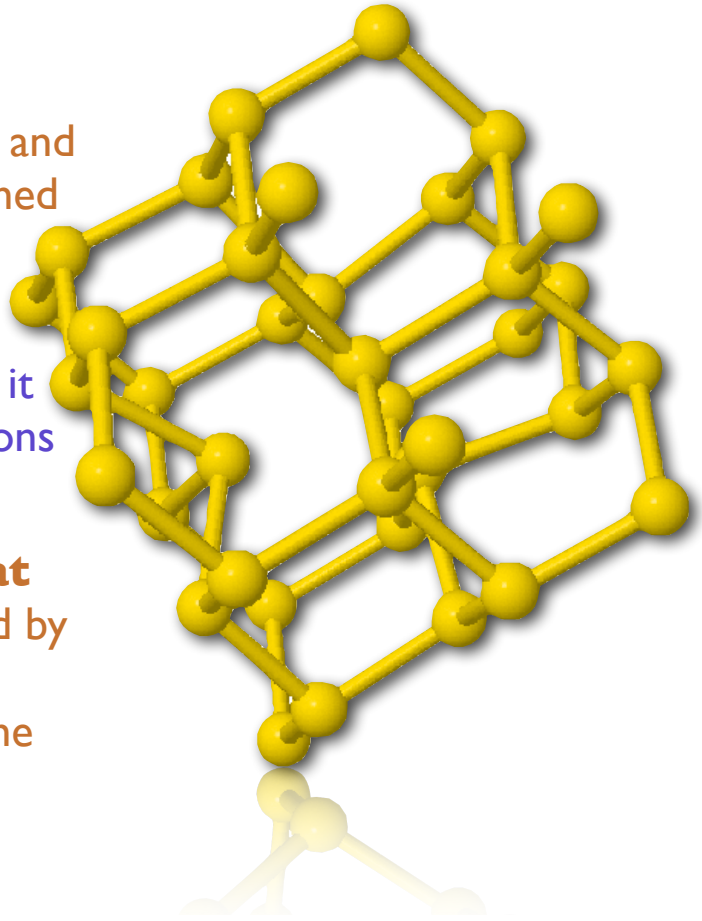
   atoms are not always on lattice

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

   elastic effects can be important

But we know that...

1. Diffusion barriers are affected significantly by the **elastic deformation** around the defect and the event catalogue must be enriched as the system evolves
2. For example, vacancy-vacancy interaction is **long range** and so it should be included in the calculations
3. Off-lattice positions are common, especially in semiconductors and **at high temperature**, as observed by molecular dynamics, for example. These cannot all be predicted at the onset of the simulation.



Overcoming these limitations

Molecular dynamics:

Hyperdynamics (Voter, PRL 1997)

Temperature accelerated dynamics (Sørensen and Voter, JCP 2000)

Parallel MD (Voter, PRB, 1998)

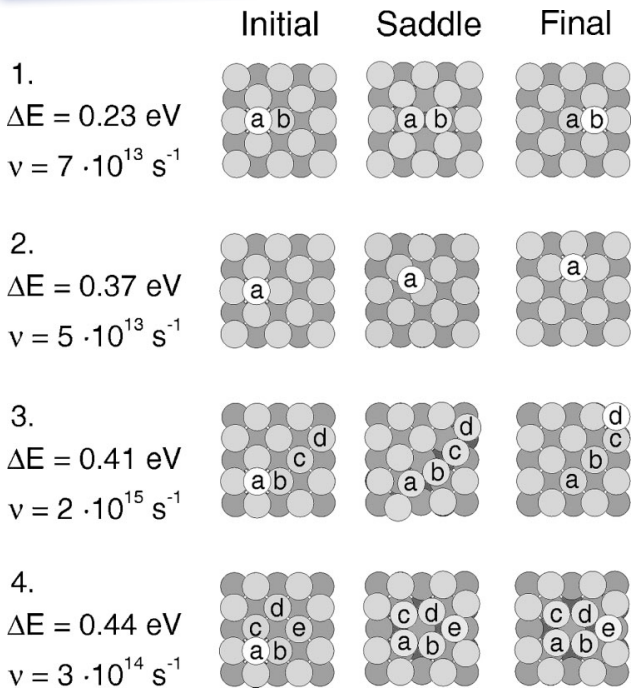
Master equation:

Start a connected network of events (DJ Wales, Mol. Phys. 2002)

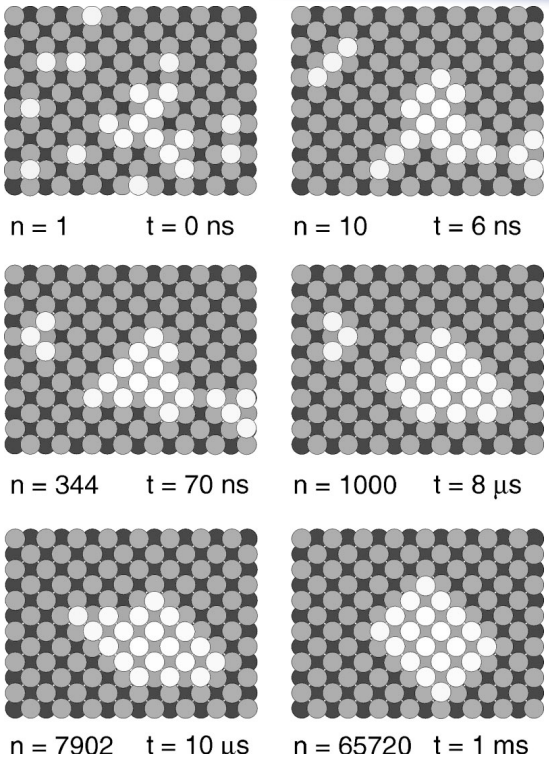
kMC on a precalculated trajectory

Construct a 1D trajectory with autonomous basin climbing method (Fan, Kushima, Yip and Yildiz, PRL 2011)

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

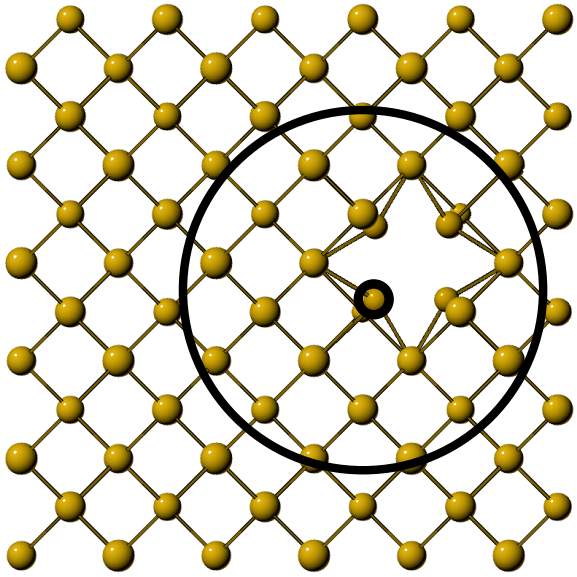
3) Evolves the system with

Kinetic Monte Carlo

A topological classification

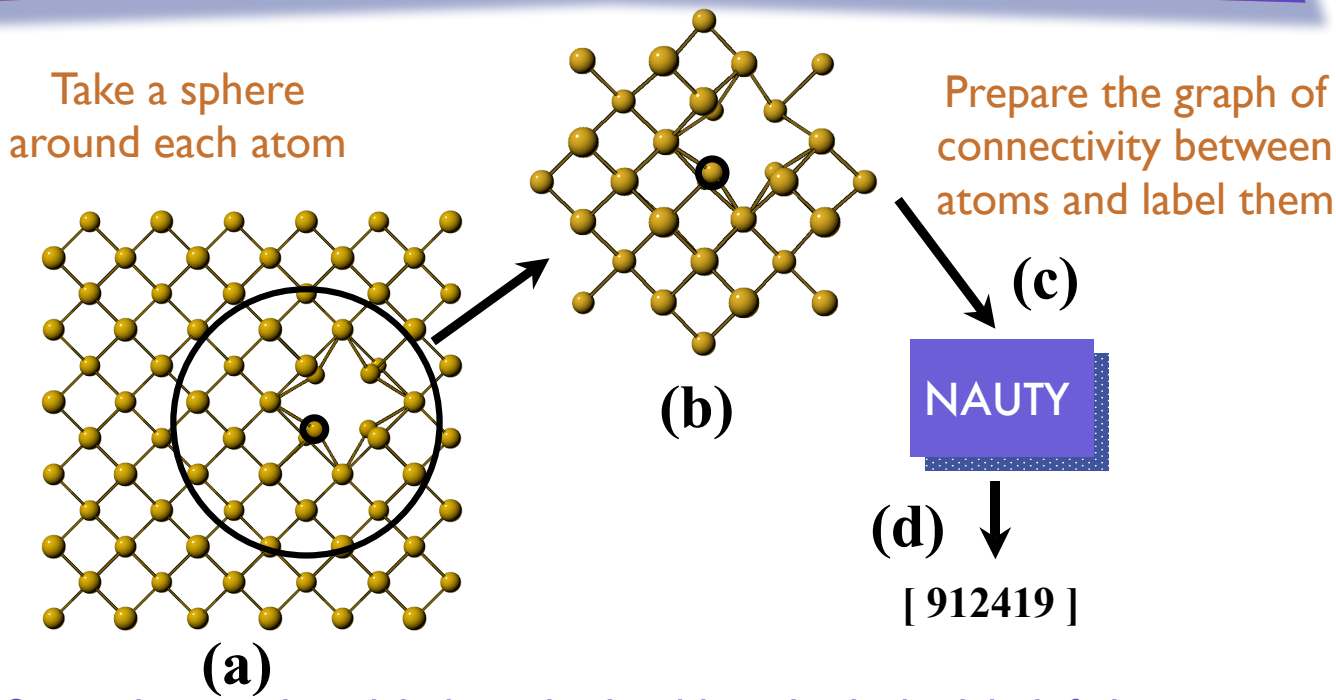
We suppose that all configurations can be classified in terms of their topology and that the events generated will have the same topological evolution.

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).

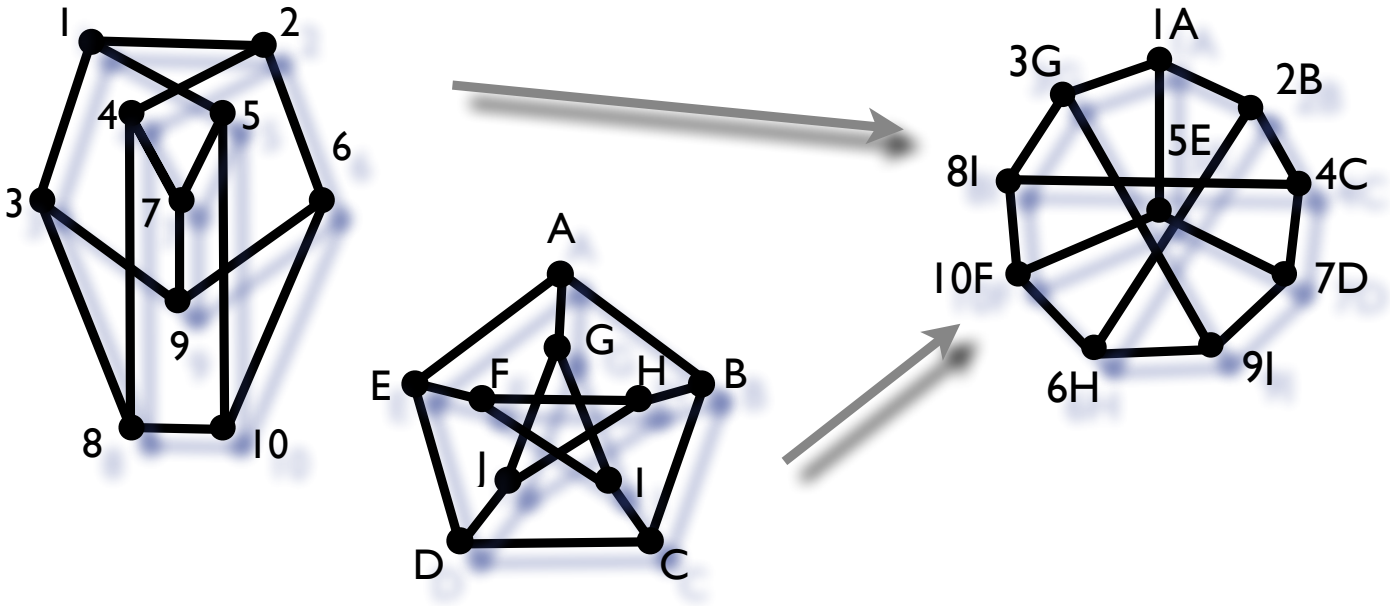
Topological analysis with NAUTY



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.

NAUTY

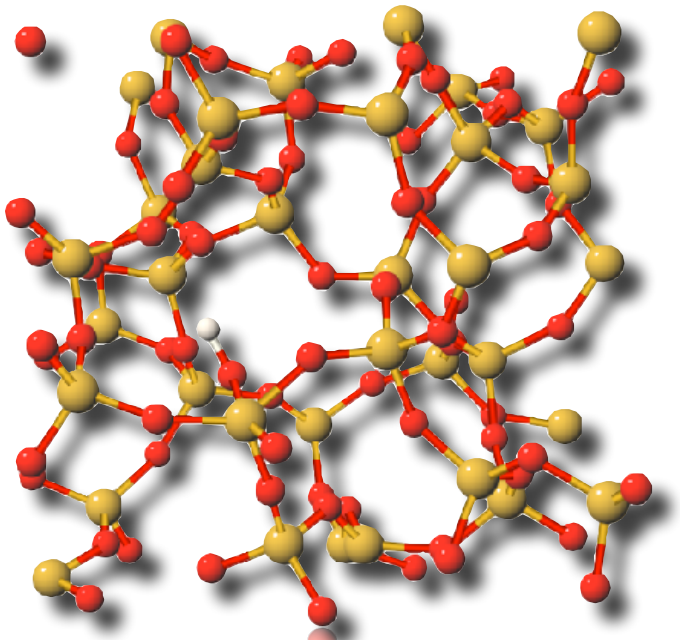
NAUTY is a program for computing automorphic groups of graphs; it can also produce a canonical labelling taking into account symmetry operations of the graph.

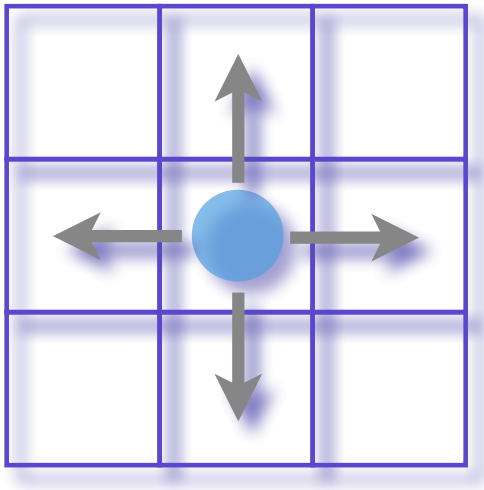


Brendan D. McKay, *Practical Graph Isomorphism*, Congressus Numerantium, **30** (1981) 45-87.
http://cs.anu.edu.au/~bdm/nauty/

NAUTY

Nauty also handles chemical order and distingues same topology with different chemical distribution

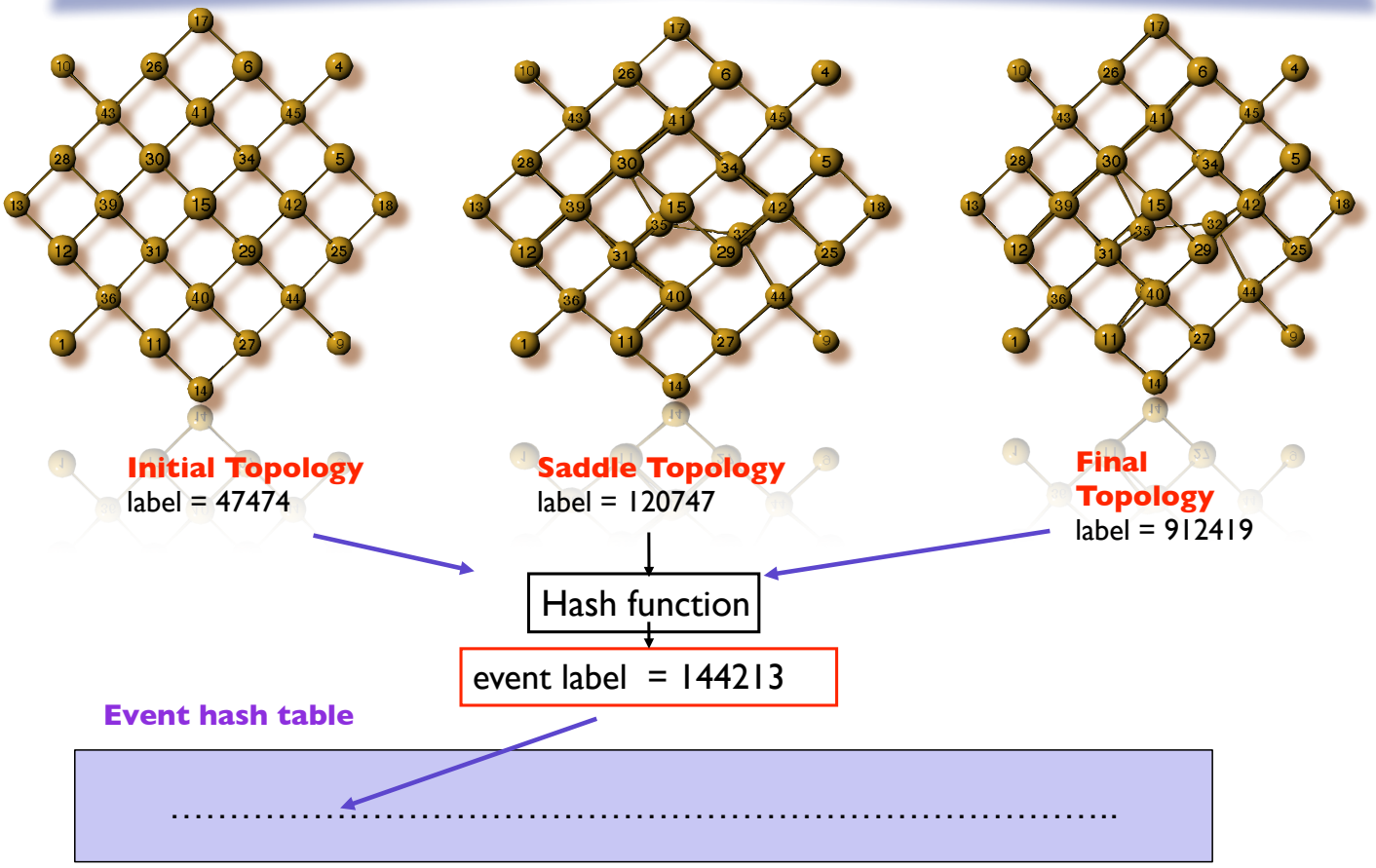




With labels, we can also handle different symmetries with same topology

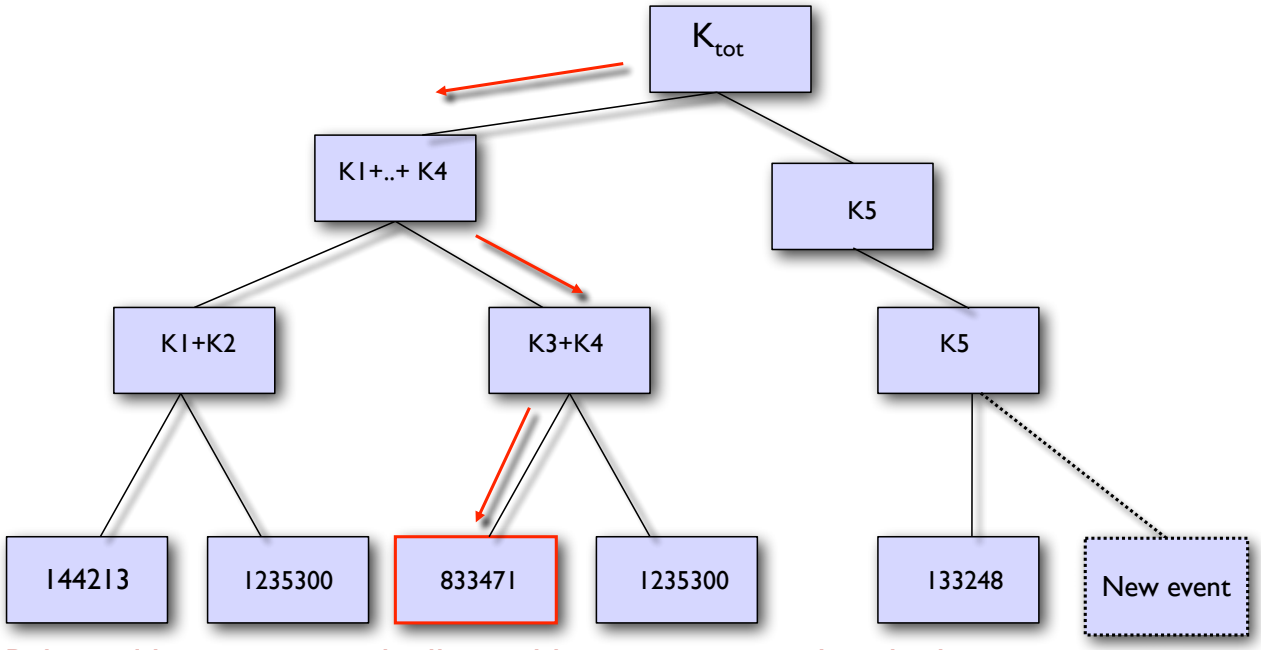
Brendan D. McKay, *Practical Graph Isomorphism*, Congressus Numerantium, **30** (1981) 45-87.
http://cs.anu.edu.au/~bdm/nauty/

A few more details of implementation



Storage of events

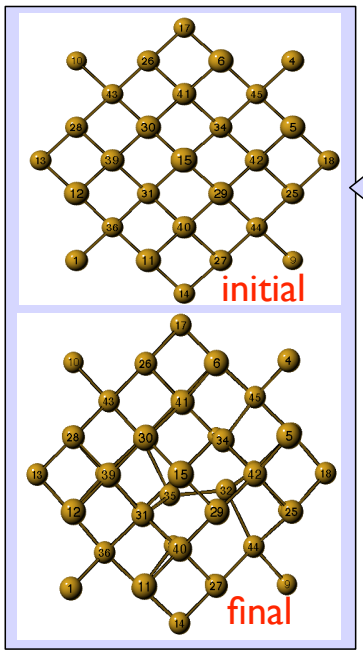
- Generated events are inserted easily to the binary tree;
- Cumulative rates are updated only along one branch;
- Events can be removed easily without unbalancing the tree;
- Event selection requires O(log n) time in the average case.



Balanced binary tree with all possible events inserted at the bottom
The upper nodes contain the cumulative rates.

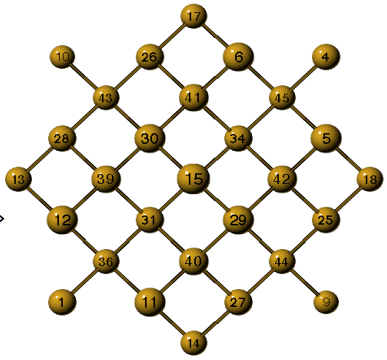
Reconstructing the events

Initial and final atomic positions for event 833471 are stored in the order that conserves the isomorphism group;
The atom that execute this event is randomly chosen from a list of atoms having the same topology label as Initial.

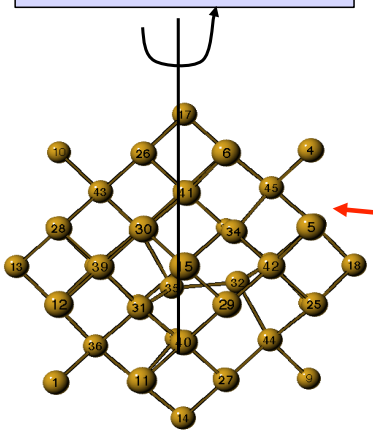


Event 833471

Extract the symmetry operations by comparing atoms order and coordinates



The actual topology around the atom that will execute the move



Finally apply the symmetry operation on final to execute the move correctly

The algorithm

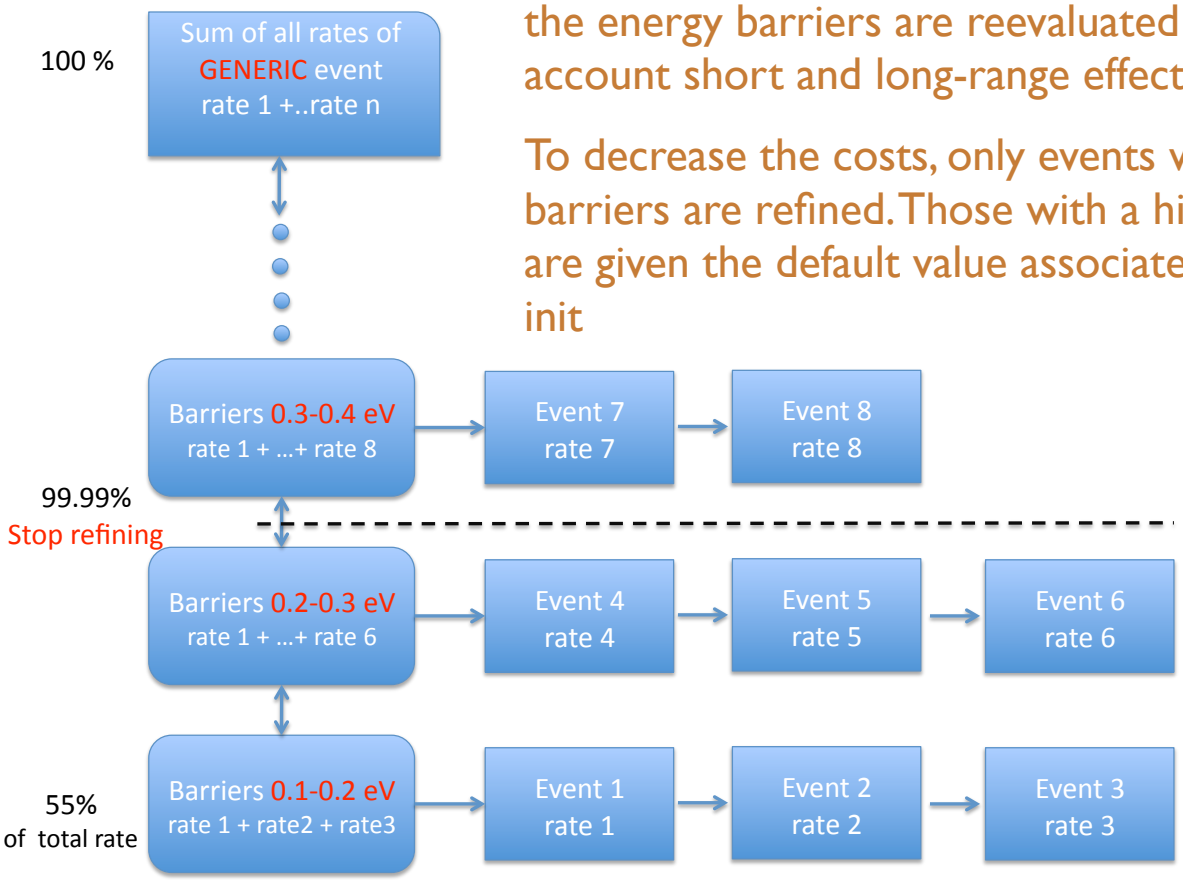
After an event :

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 init



A few implementation details

Economical management of events

All generic events visited **are stored and can be reused**

i. to extend the system's simulation

ii. to use in a new simulation

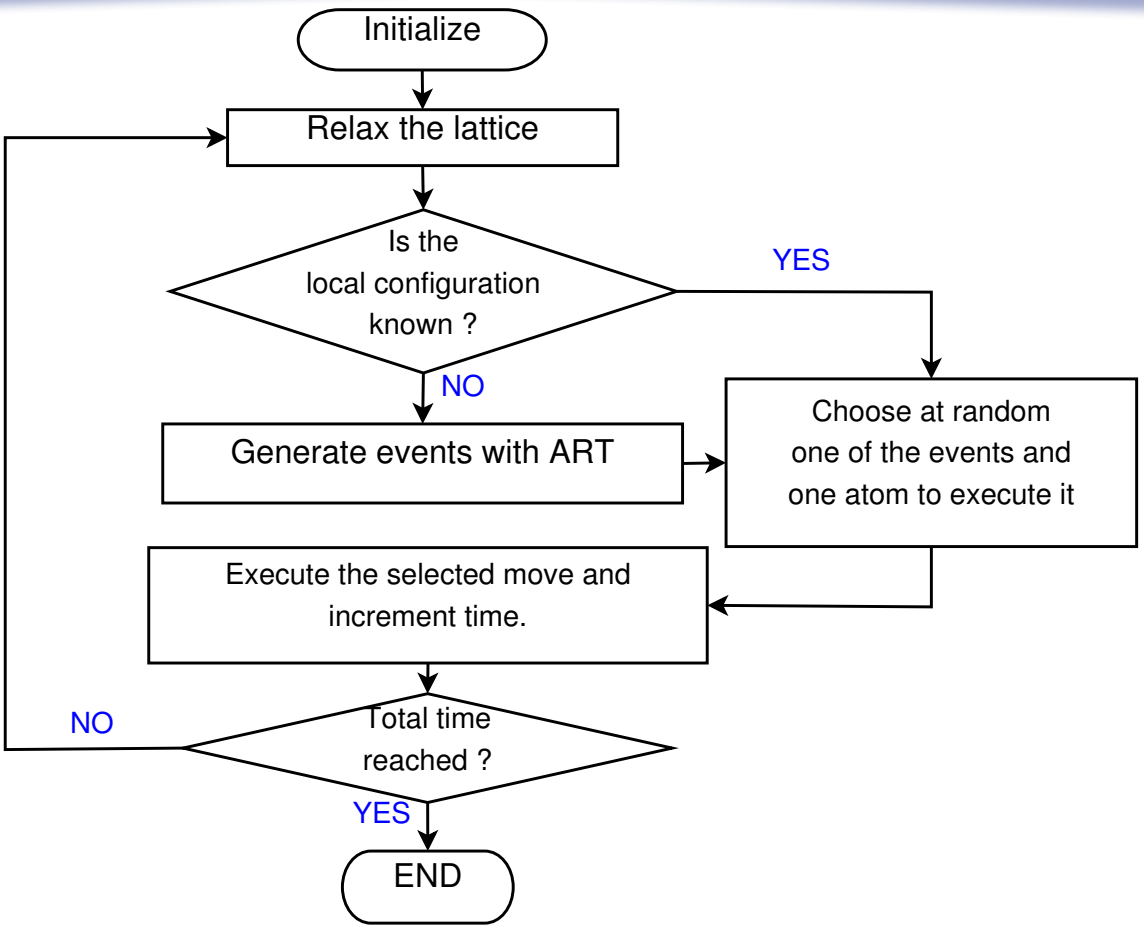
iii. to use with a different system

This can save a tremendous amount of time for example

study of mono-vacancy, di-vacancy can be used for the 10-vacancy problem.

Specific (relaxed) events **are also stored and relaxation starts from the last points**

A flow-chart for kinetic ART



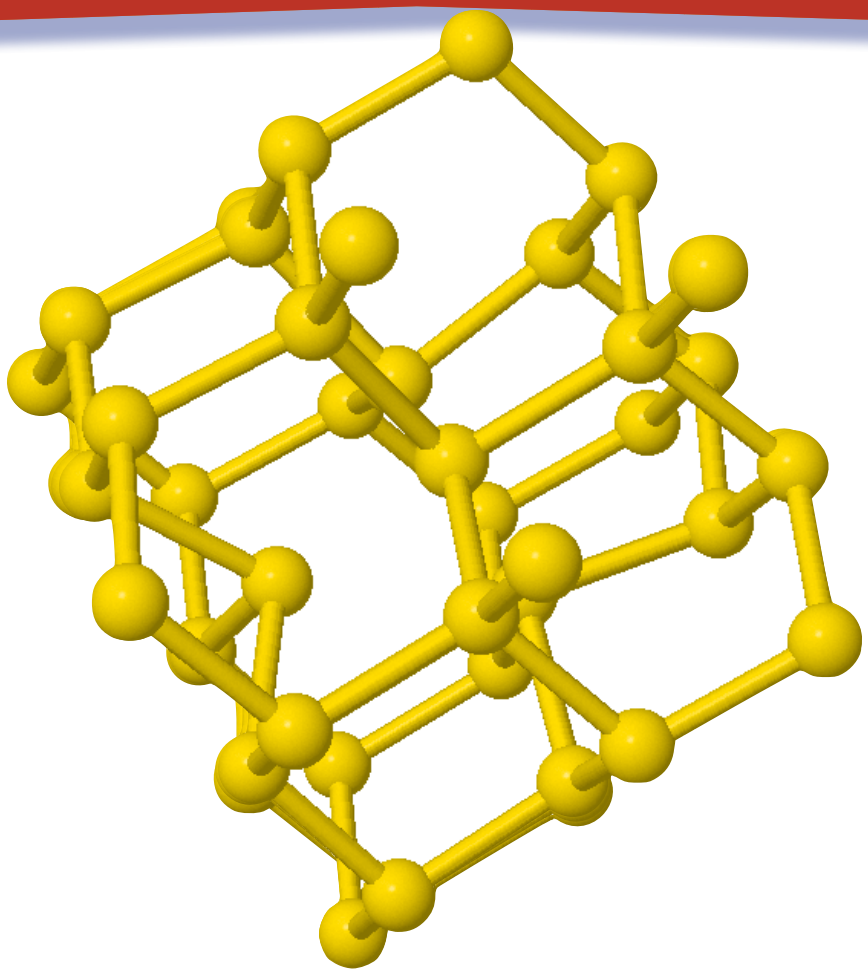
Diffusion of a single vacancy

The five lowest-energy events are:

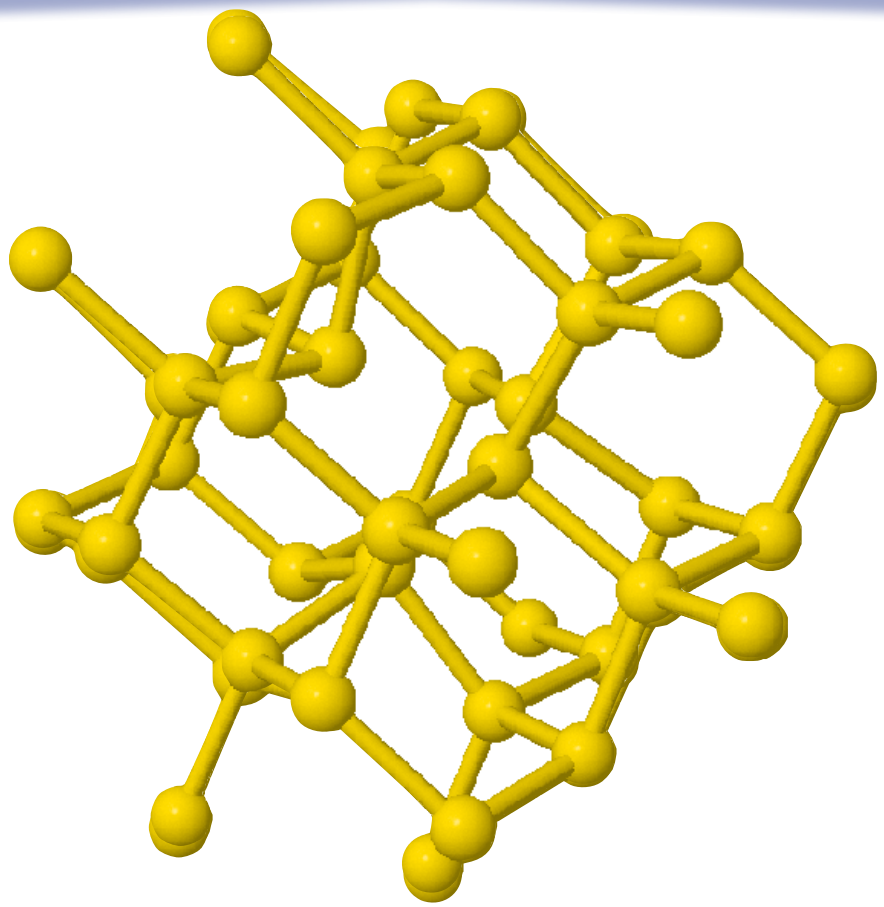
Energy (eV)	Type
0.53	Vacancy hop
0.65	Asymmetric hop
0.90	Asymmetric hop
1.69	WWW + vacancy
2.79	WWW near vacancy
3.43	Isolated WWW

~1000 atoms
Stillinger-Weber potential
1 vacancy

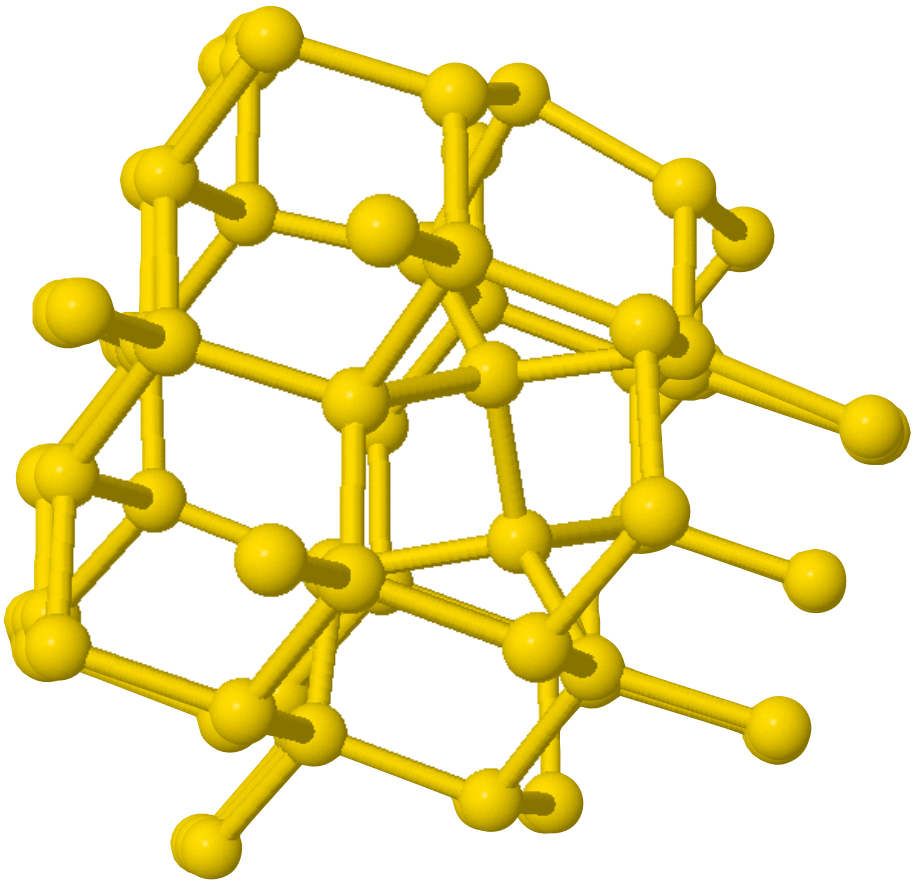
0.53 eV



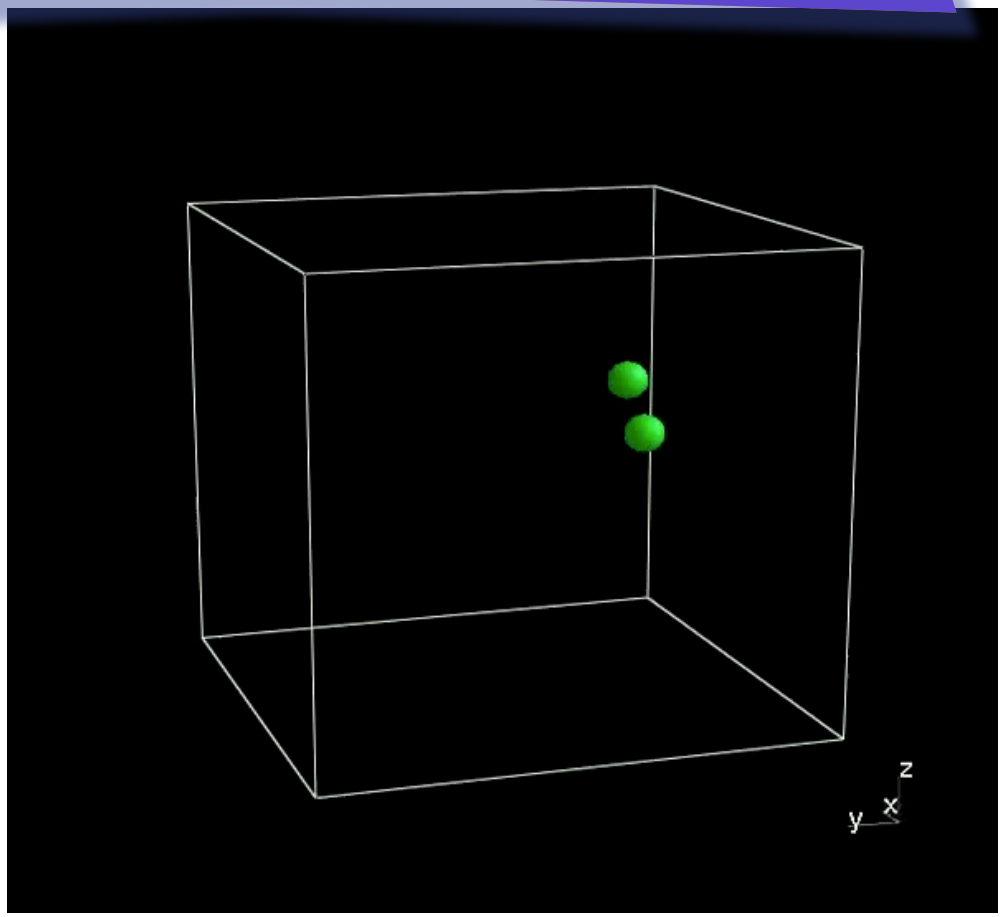
0.9 eV



3.43 eV — Wooten-Winer-Weaire



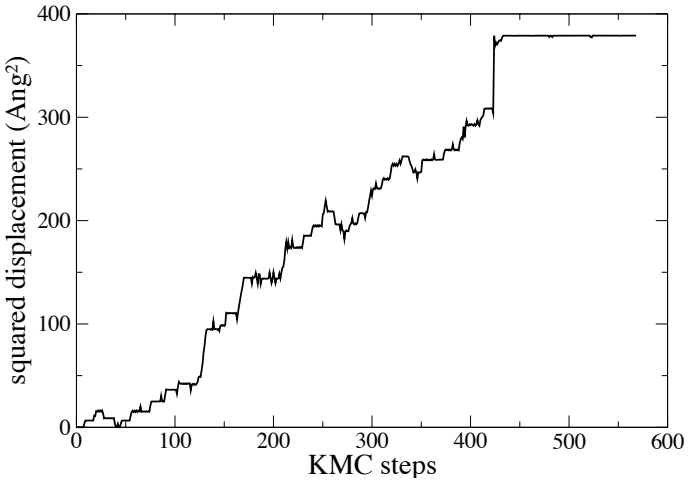
Diffusion of two vacancies

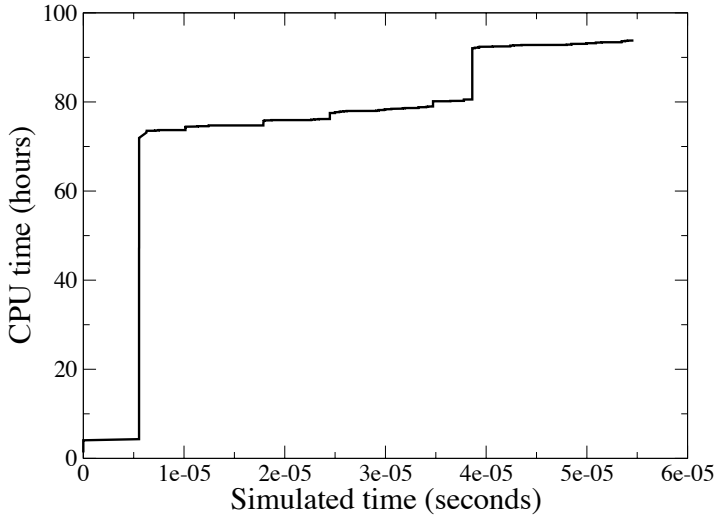


~1000 atoms
Stillinger-Weber potential
2 vacancies
500 K

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

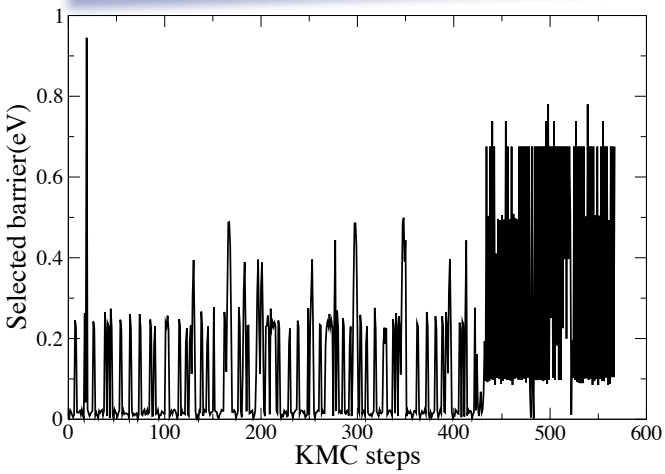
Diffusion of two vacancies — 500 K

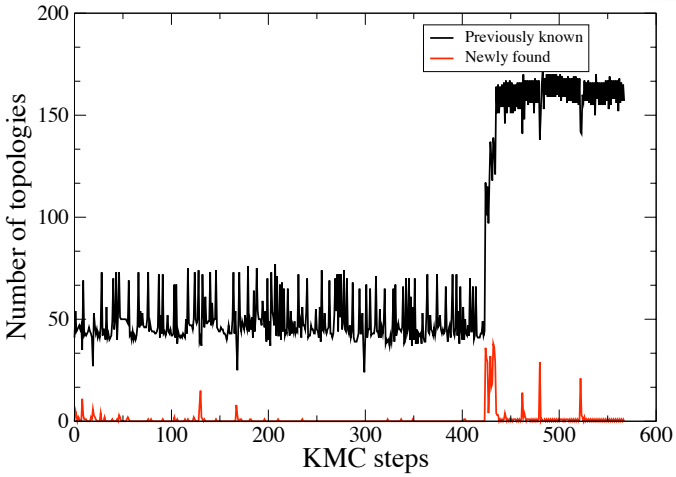




~1000 atoms
Stillinger-Weber potential
2 vacancies
500 K

Diffusion of two vacancies — 500 K





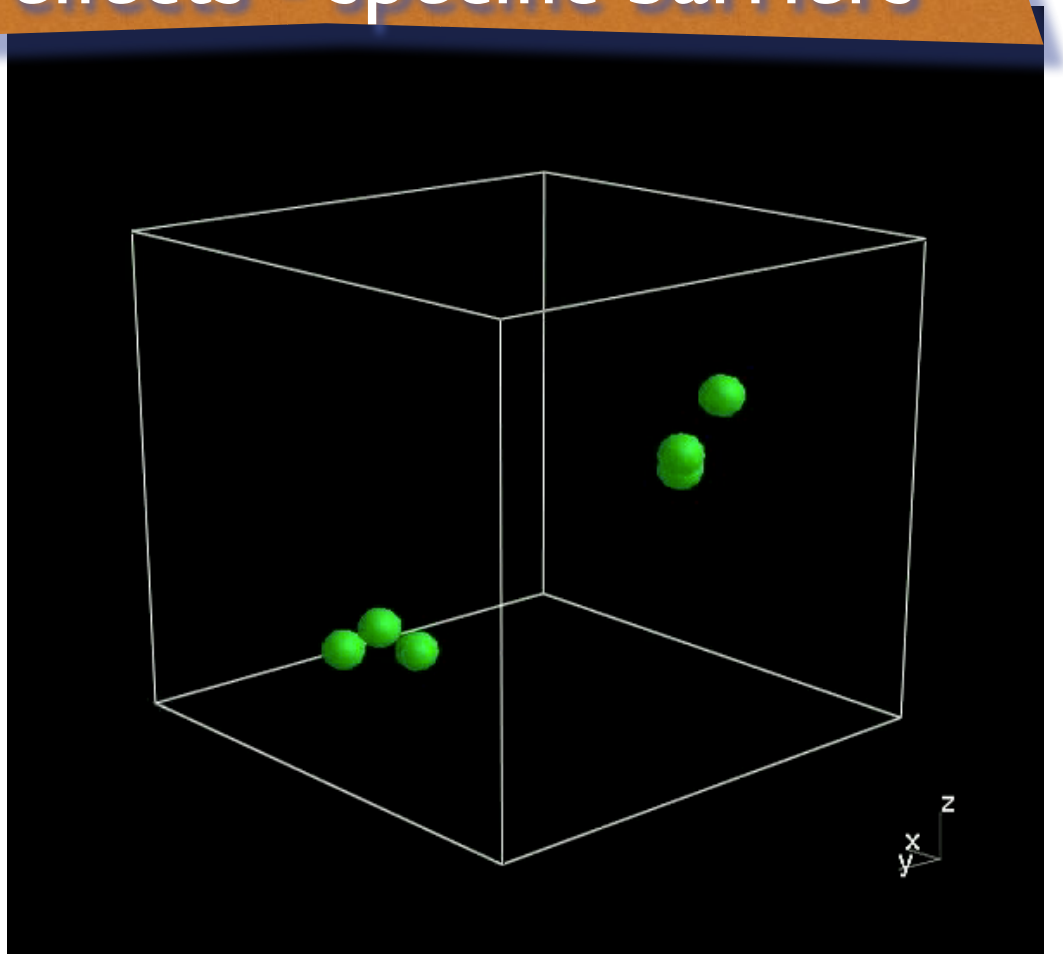
~1000 atoms
Stillinger-Weber potential
2 vacancies
500 K

Elastic effects - specific barriers

~1000 atoms
Stillinger-Weber potential
6 vacancies
500 K

~1200 events

120 μs



Only generic events

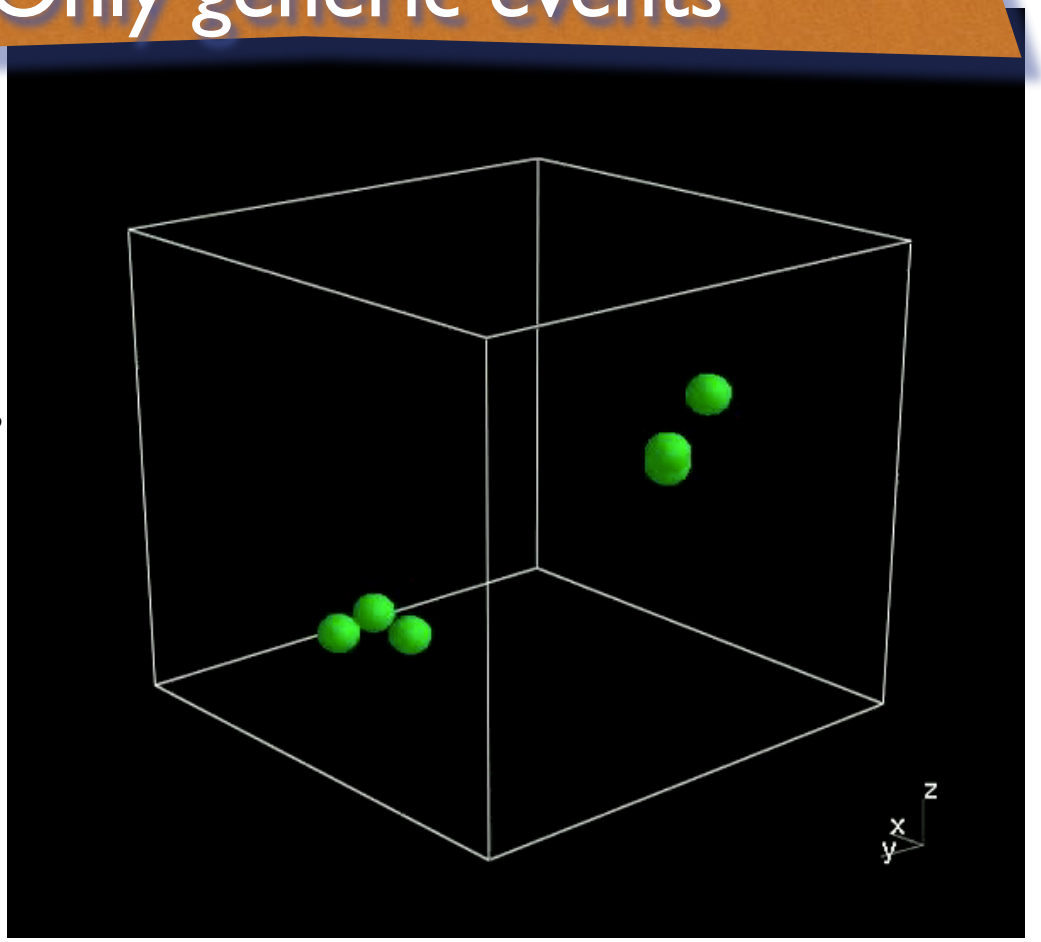
~1000 atoms
Stillinger-Weber potential
6 vacancies

Only generic events, no relaxation for barriers

500 K

~5000 events

0.001 s



Example #1: Interstitials and Vacancies

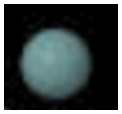
500 K, 8 interstitials and vacancies pairs,

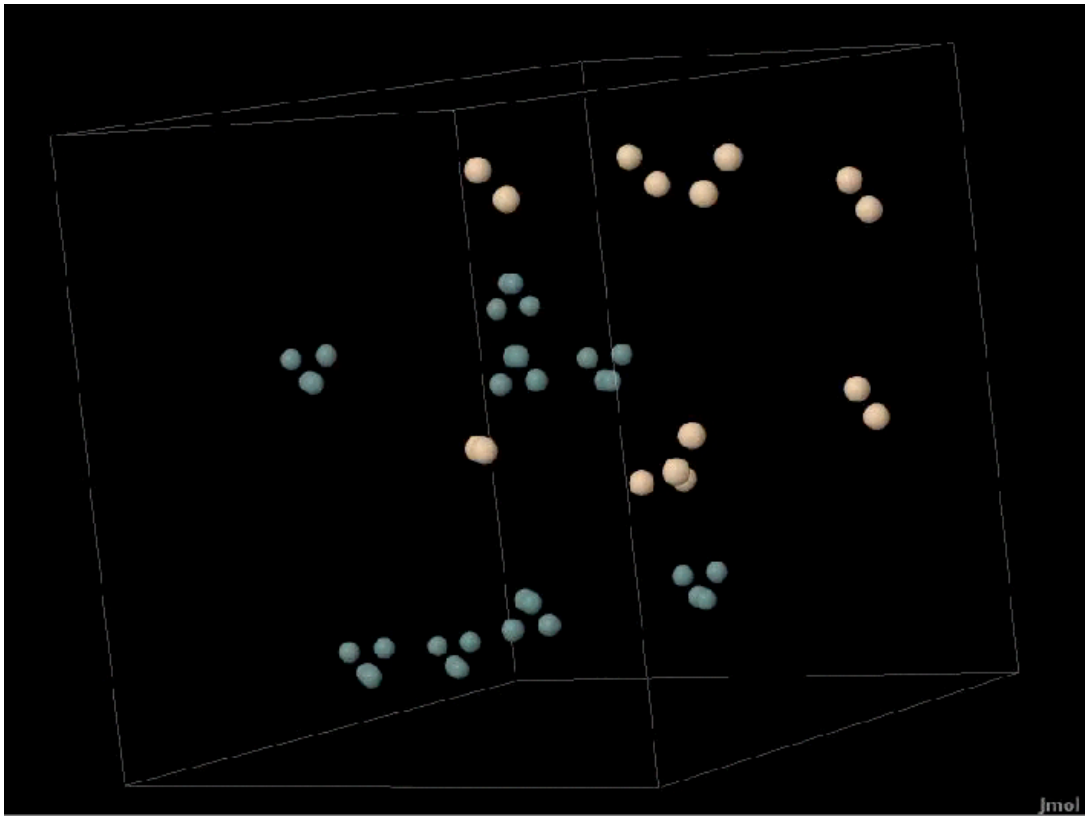
8000 atoms

Stillinger-Weber potential

5-fold coordinated atoms

3-fold coordinated atoms

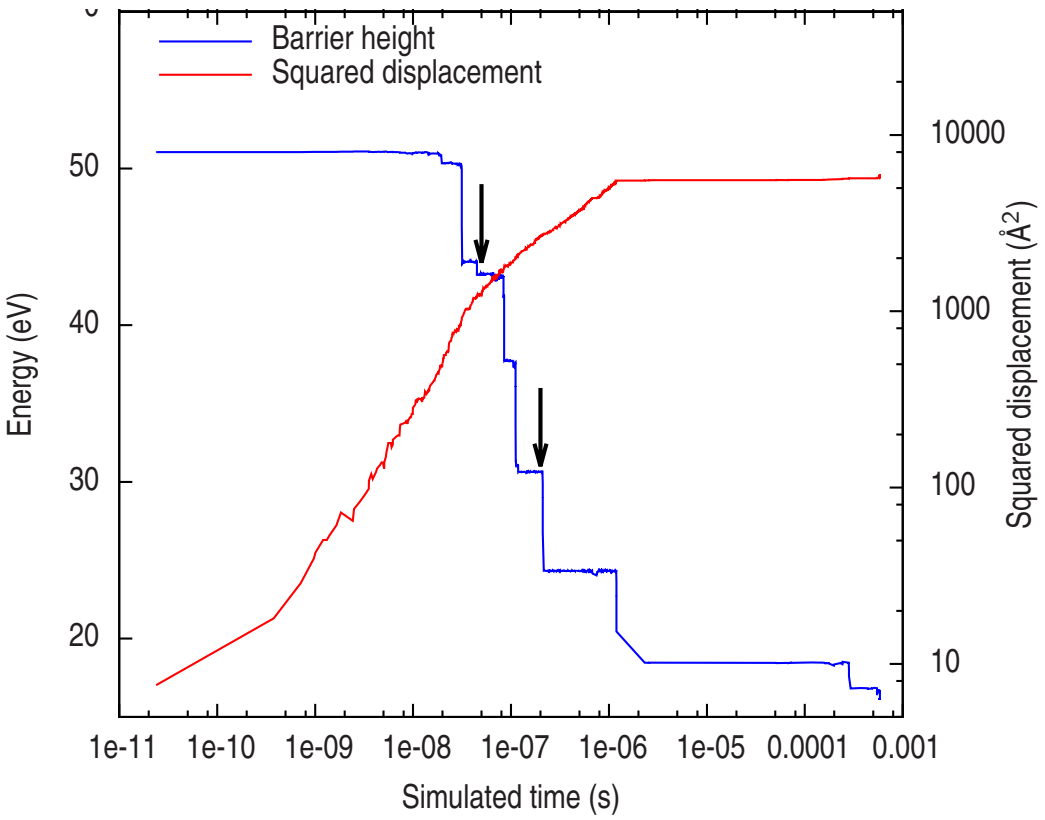




Interstitials and Vacancies

First arrow : we see a metastable oscillatory state within an IV recombination process. kART spends more time when new topologies appear and spends little time for KMC steps

Second arrow : an orthodox IV recombination.

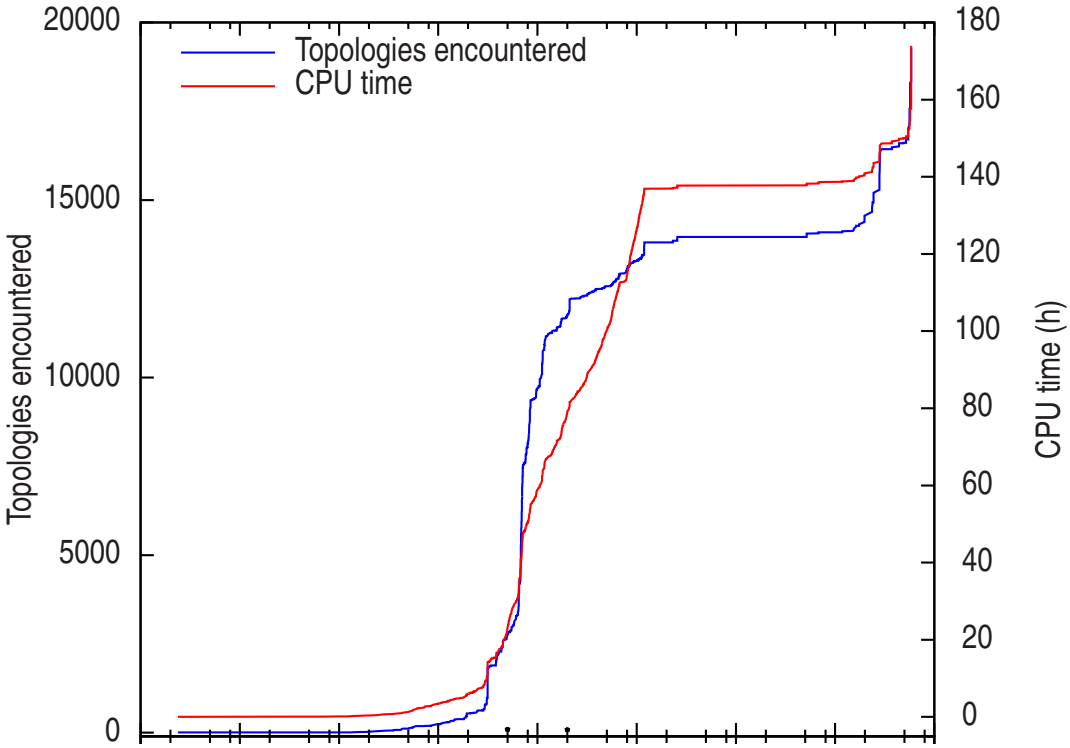


Interstitials and Vacancies

kART spends more time when new topologies appear and spends little time for KMC steps

We reach long time-scales with a rather large system (8000 atoms) at a temperatures comparable to those of experiments (500K).

k-ART analyzes the transitions between configurations autonomously. This is a big advantage compared to other methods.



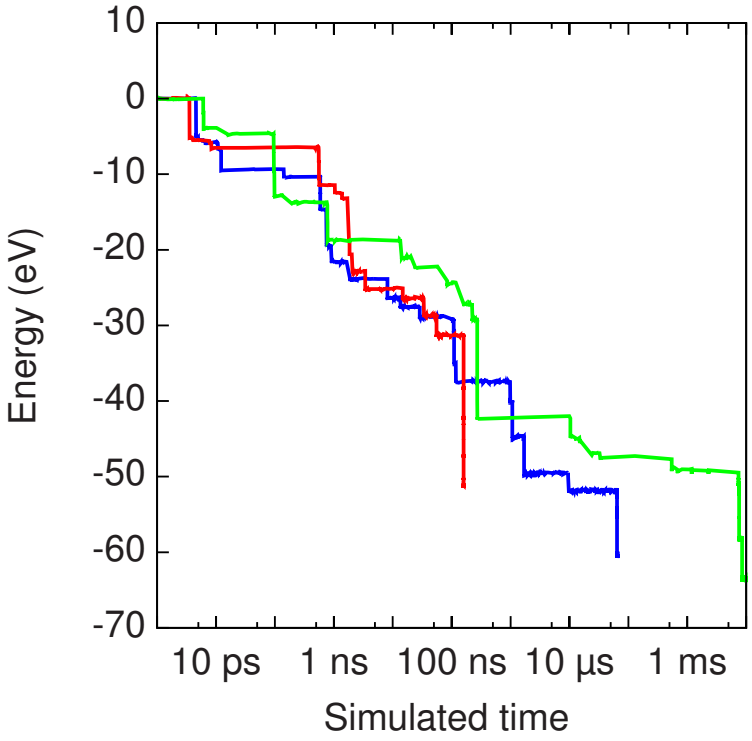
c-Si anneal after ion bombardment

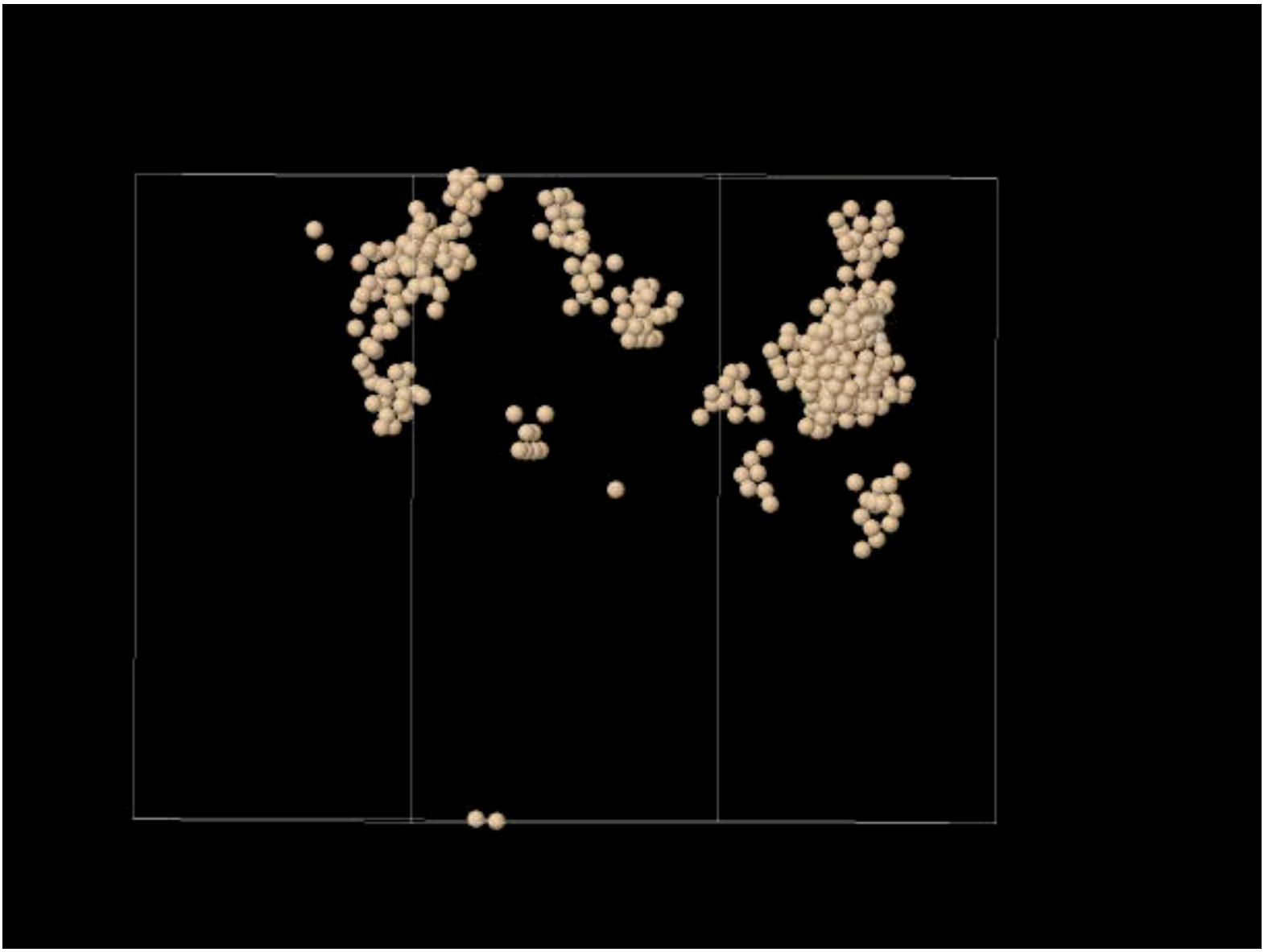
27000 atoms box, 300 K, 1 atom implanted at 3 keV

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



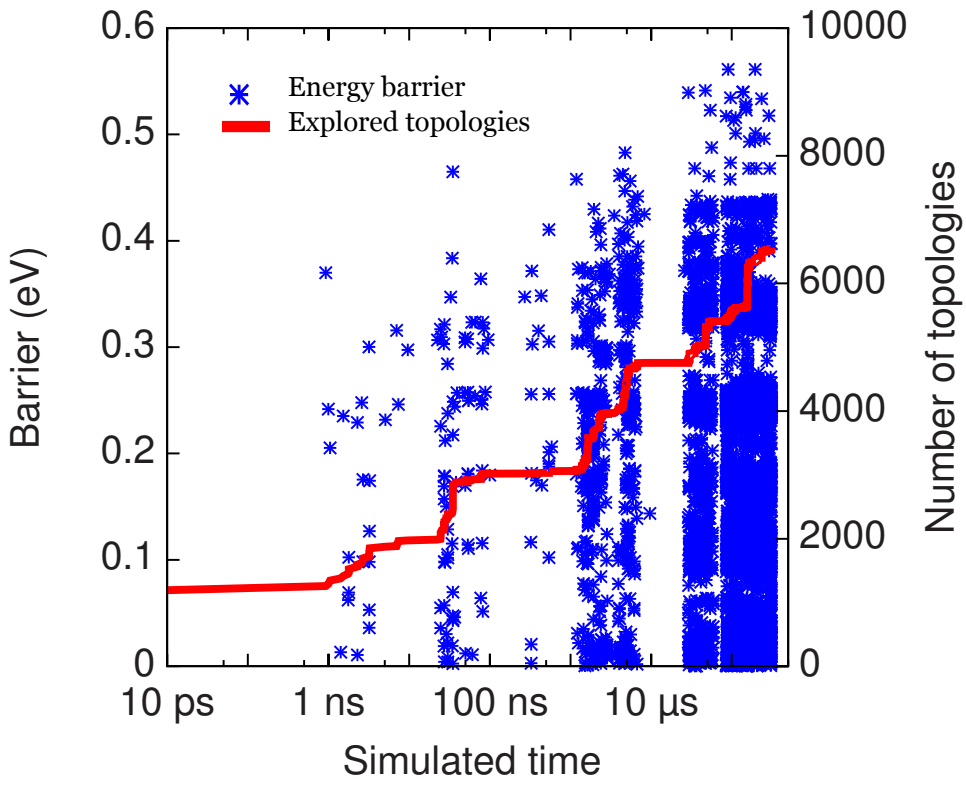


c-Si anneal after ion bombardment

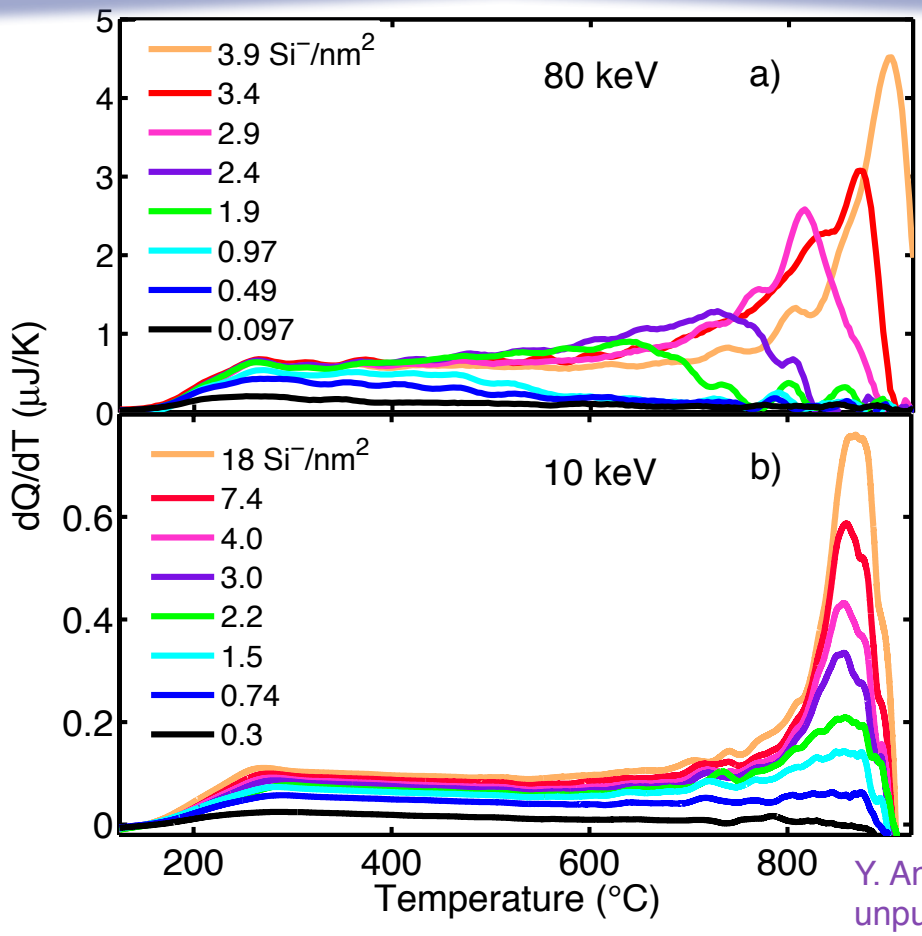
The jumps in time are caused by the basin method acceleration.

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

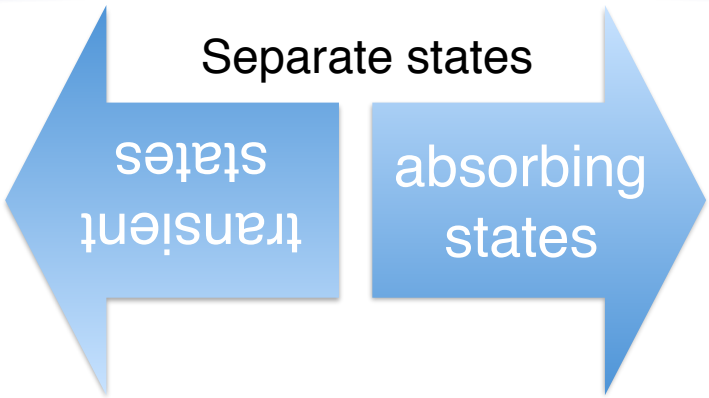


Nanocalorimetry measurements : *c*-Si



Y. Anahory and F. Schiettekatte
unpublished

Taking care of low-energy barriers



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

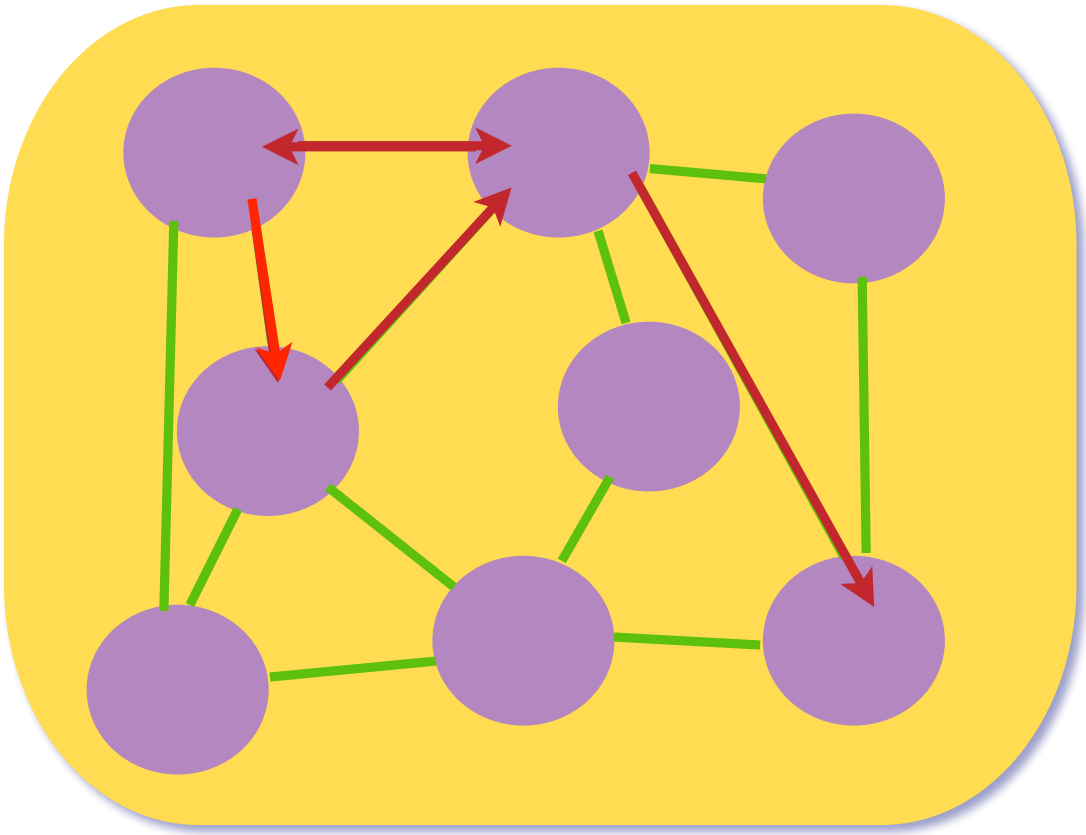
- high-energy barriers

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

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**,

Tabu: Taking care of low-energy barriers

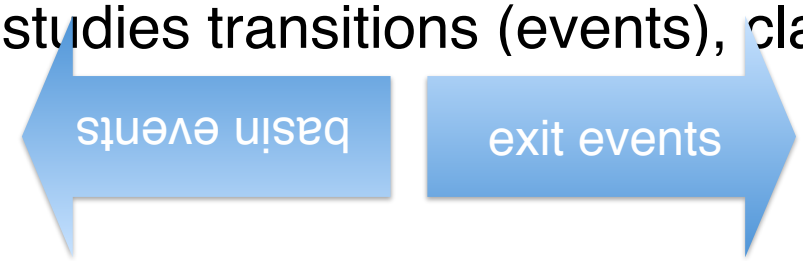


MRM in kART

- Basin exploration is
  - –costly,
  - –even unnecessary (early exit to absorbing state).
- Basins are explored and constructed

on the fly!

- kART studies transitions (events), classifies:



(according to barrier height, reverse barrier height)

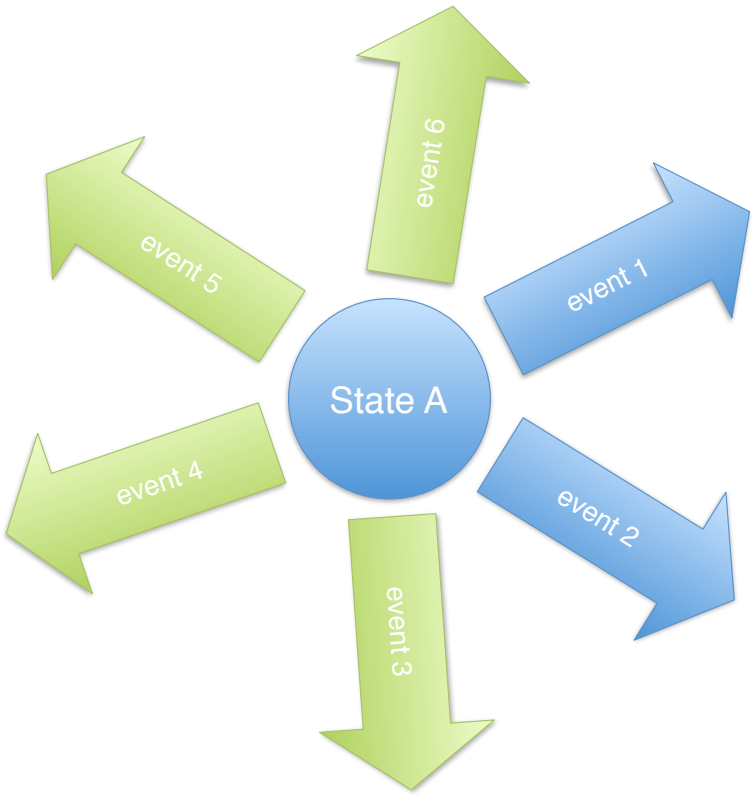
The Basin Mean Rate Method in kART

Starting from state A:

- Identify events.
- If any event could be in basin (low barrier), activate basin search.

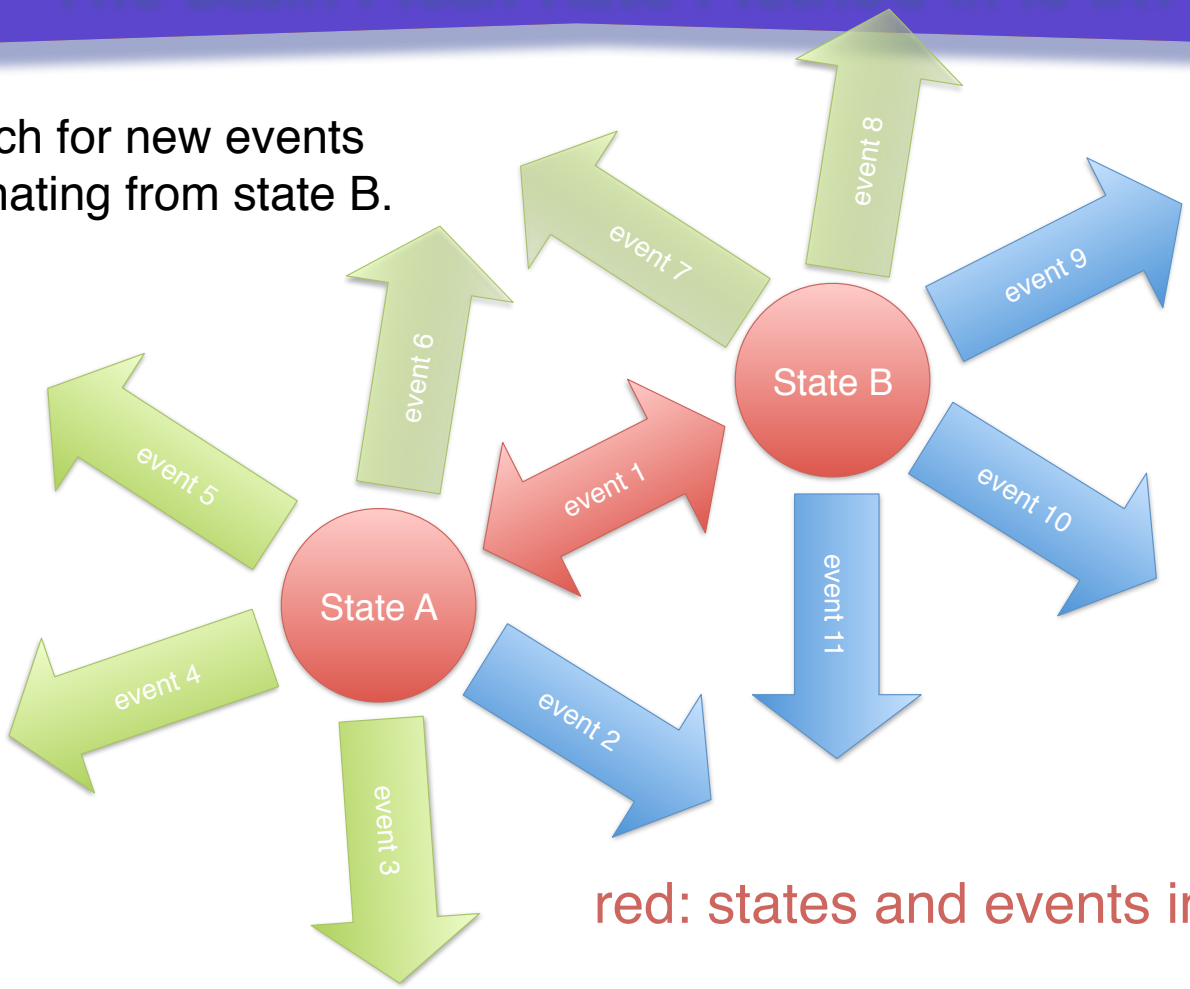
blue: potential basin

green: ordinary event



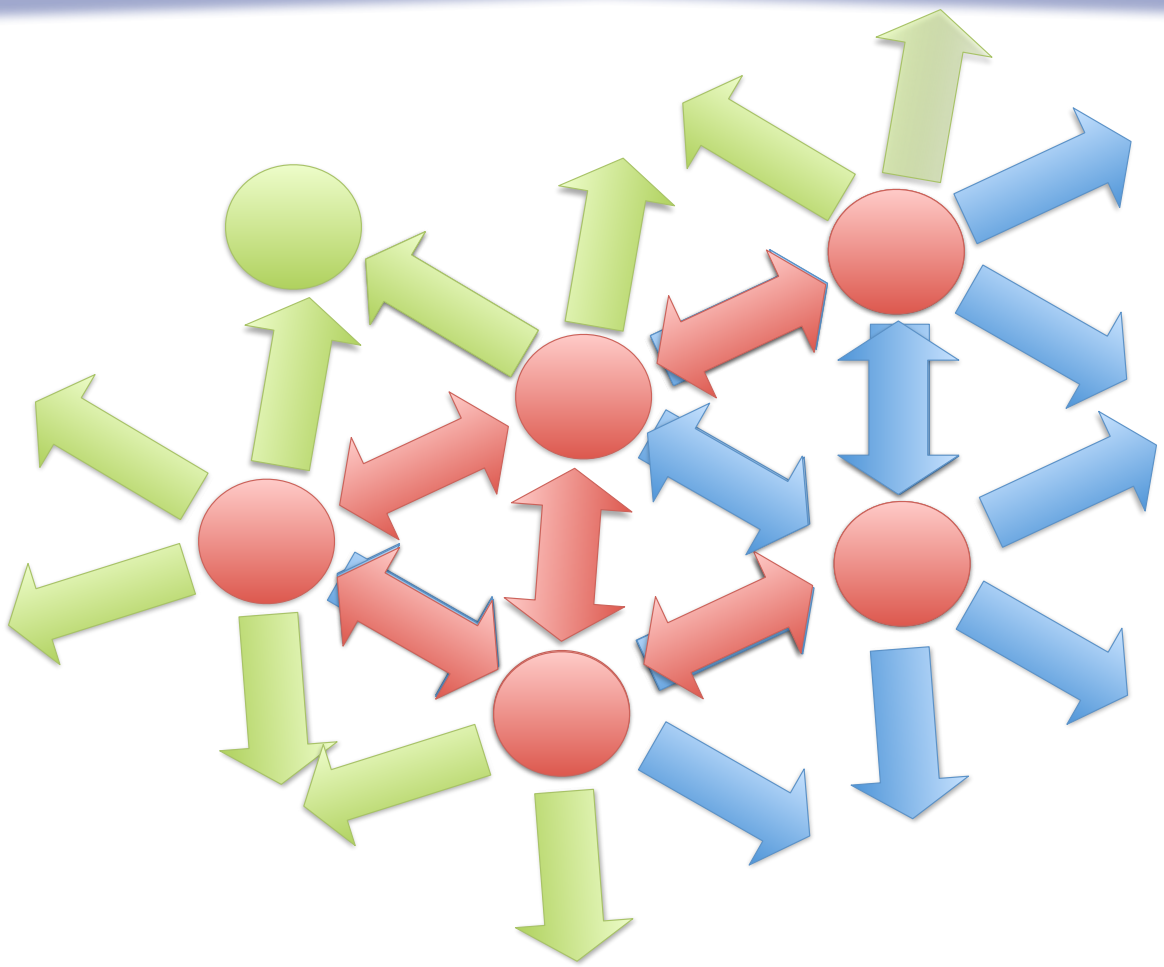
The Basin Mean Rate Method in kART

Search for new events originating from state B.



red: states and events in basin

The Basin Mean Rate Method in kART



The Basin Mean Rate Method in kART

- The transition matrix is computed

$$T_{ji} = \frac{R_{i\to j}}{\sum_k R_{i\to k}} = \tau_i^1 R_{i\to j},$$

- Applying this matrix over the initial state of the basin, computing all possible number of jumps

$$\mathbf{\Theta}^{\text{sum}} = \sum_{m=0}^{\infty} \underline{\mathbf{T}}^m \mathbf{\Theta}(0) = (\mathbb{1} - \underline{\mathbf{T}})^{-1} \mathbf{\Theta}(0)$$

we can compute the average residence time in basin

$$\tau_i = \tau_i^1 \Theta_i^{\text{sum}}$$

state *i* before the system exists the basin

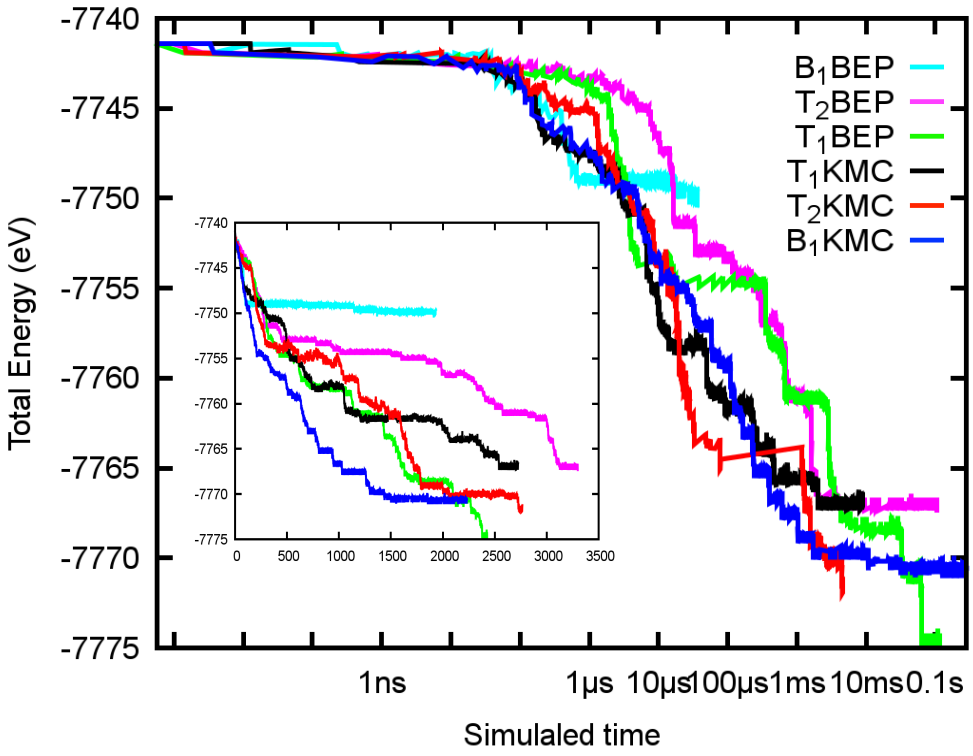
- This allows to compute the rate for leaving the basin (*j* here is an exit state)

$$\langle R_{i\to j} \rangle = \frac{\tau_i}{\sum_k \tau_k} R_{i\to j}$$

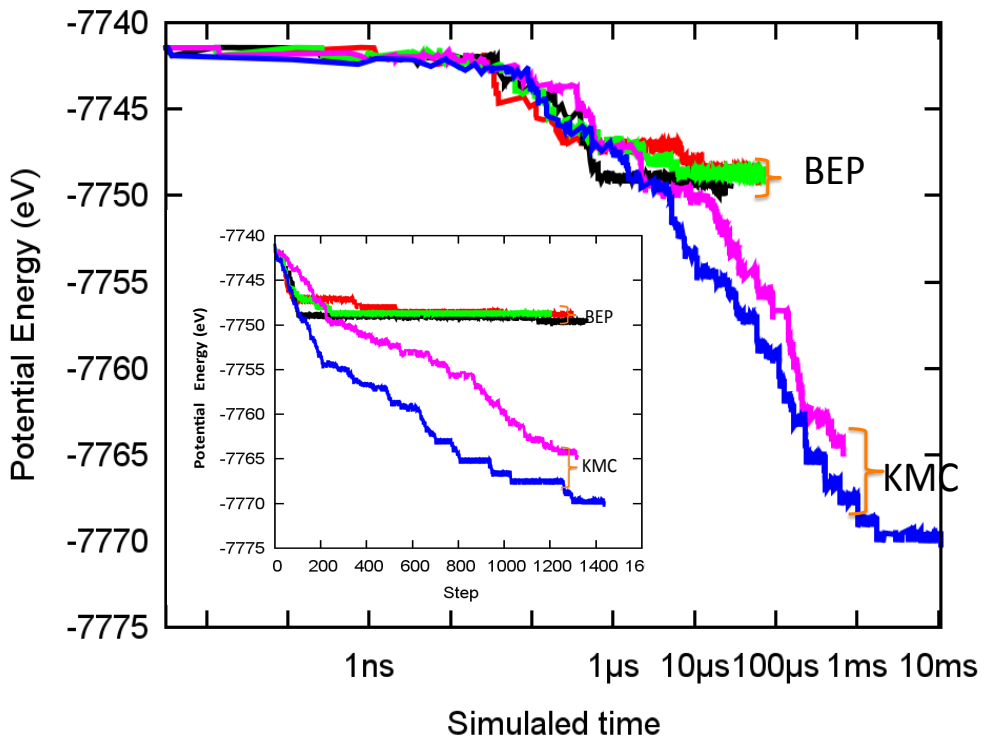
The Basin Mean Rate Method in kART

- Basin is constructed “on the fly” – no unnecessary exploration.
- Realistic distribution of final states.
- If selected event does not originate from current state: Trace system back through shortest path to originating state (burning algorithm).
- Ignores correlation between exit state and

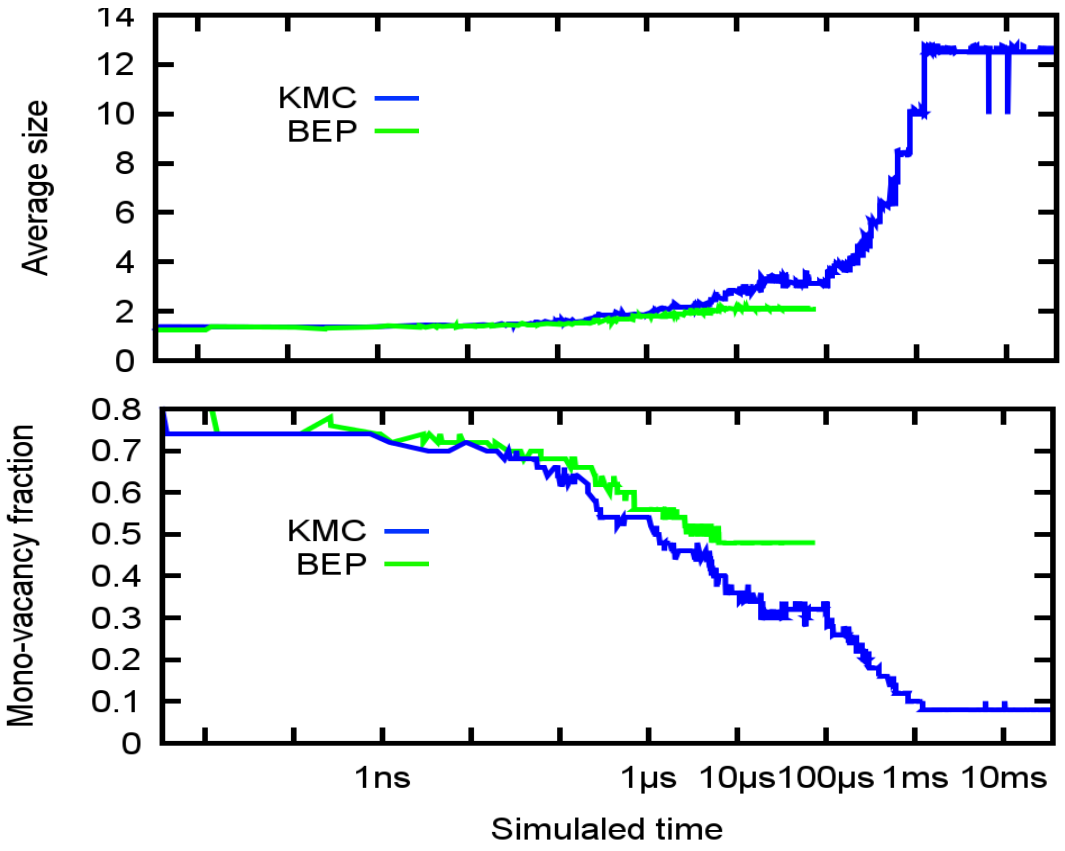
BMRM or Tabu?


-7740
-7745
-7750
-7755
-7760
-7765
-7770
-7775
Total Energy (eV)
1ns
1μs
10μs
100μs
1ms
10ms
0.1s
Simulaled time
B1BEP
T2BEP
T1BEP
T1KMC
T2KMC
B1KMC
0
500
1000
1500
2000
2500
3000
3500

KMC or Bell-Evans-Polanyi



KMC or Bell-Evans-Polanyi



Parallelisation

- Master creates a list of topologies to be searched and distributes the tasks to each node in sequence
- Same approach for refining specific events
  - first a list is constructed
  - tasks are then dispatched to nodes, in sequences
- This ensures maximum flexibility for adapting to the number of available nodes.

Parallelisation

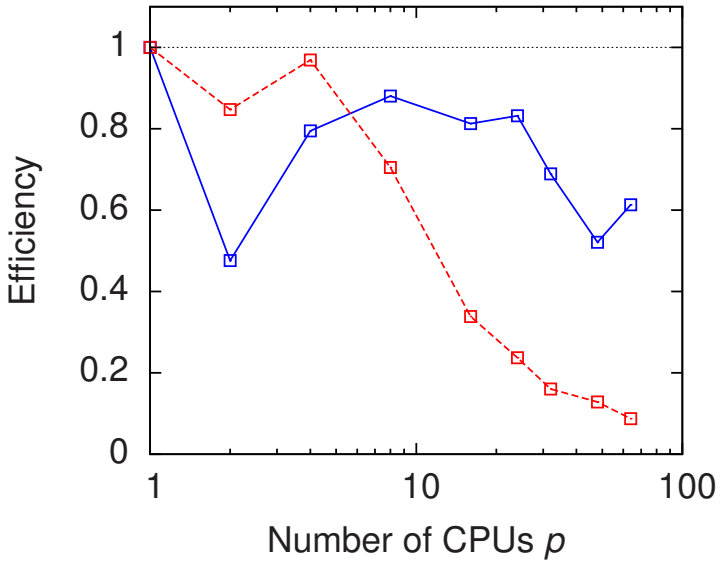


Figure 5. Parallel efficiency of event search. —— generic event search; - - - - specific event search; ····· ideal efficiency.

Parallelisation

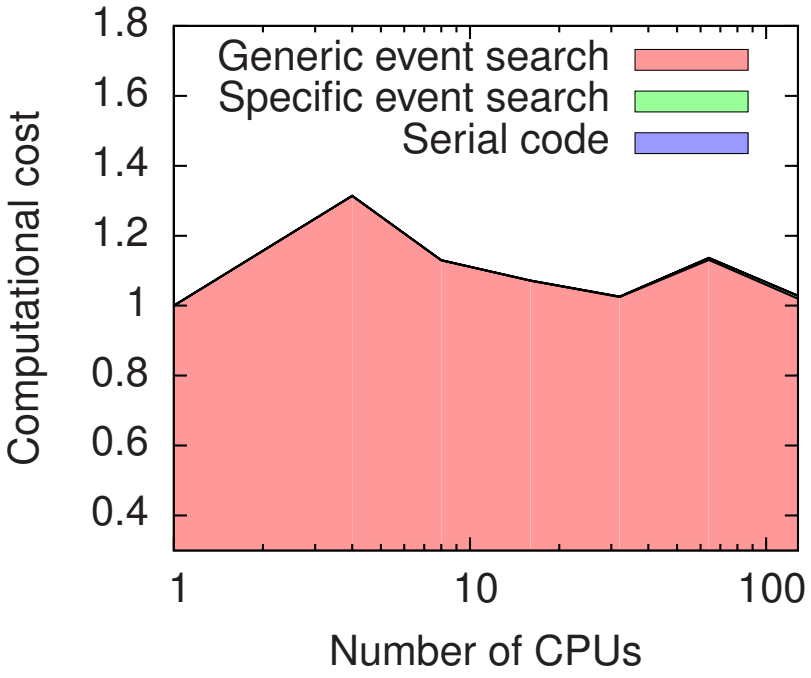


Figure 8. Computational cost to simulate the first KMC step in a-Si without catalog, relative to serial performance.

Parallelisation

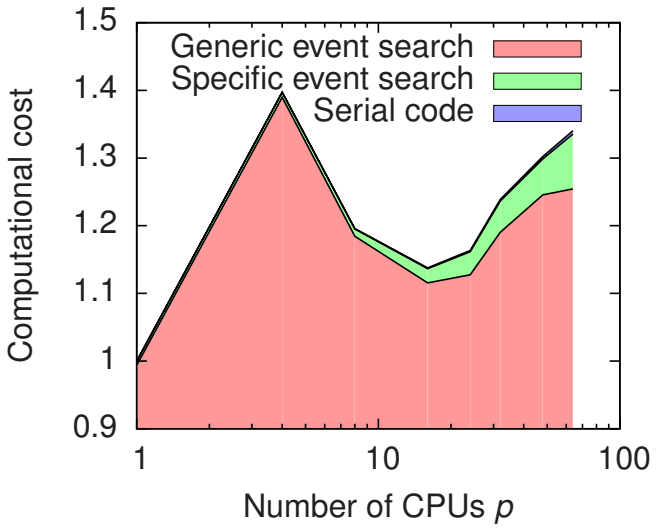


Figure 6. Computational cost (number of CPUs $\times$ per CPU time) to simulate 40 KMC events, relative to single CPU performance. Lower field: generic event search. Central field: specific event search. Top field: serial code. The relative computational cost displayed here is the inverse of the parallel efficiency.

Handling large systems

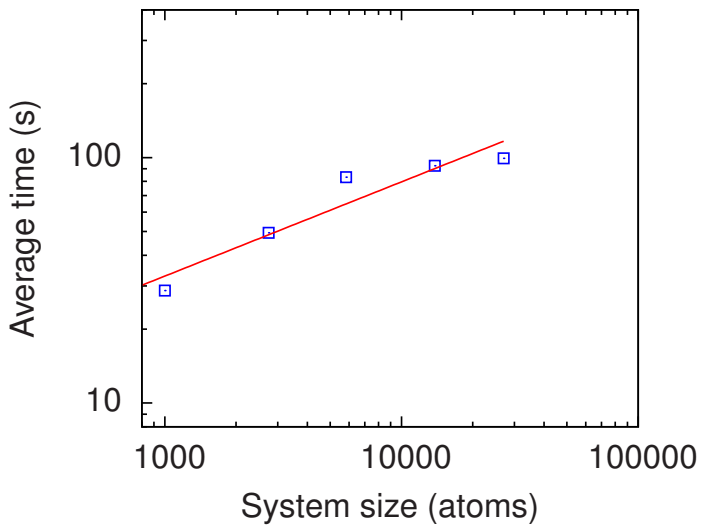
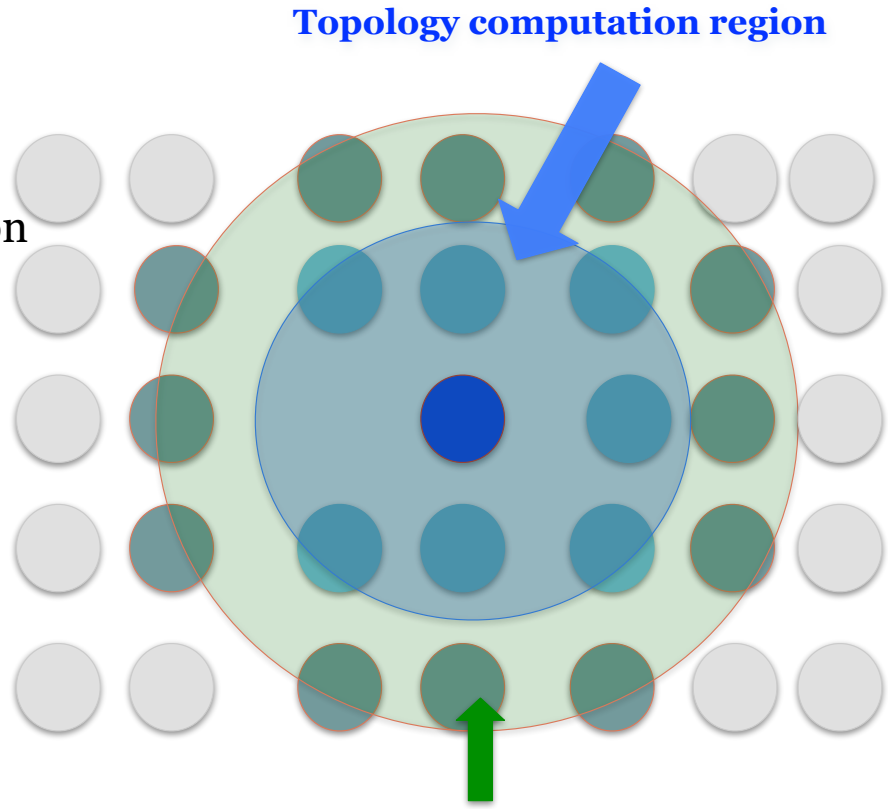


Figure 4. The mean time to attempt a generic event search for systems of various sizes. The initial configuration for each simulation was a c-Si box containing 1000 to 27000 atoms with four vacancies in each. The simulations were performed at 500 K and run on a 2.66 GHz single core on a quad-core Xeon processor. The blue squares correspond to the data, while the green line is a least-square fit of $f(N) = 2.3\,N^{0.4}$

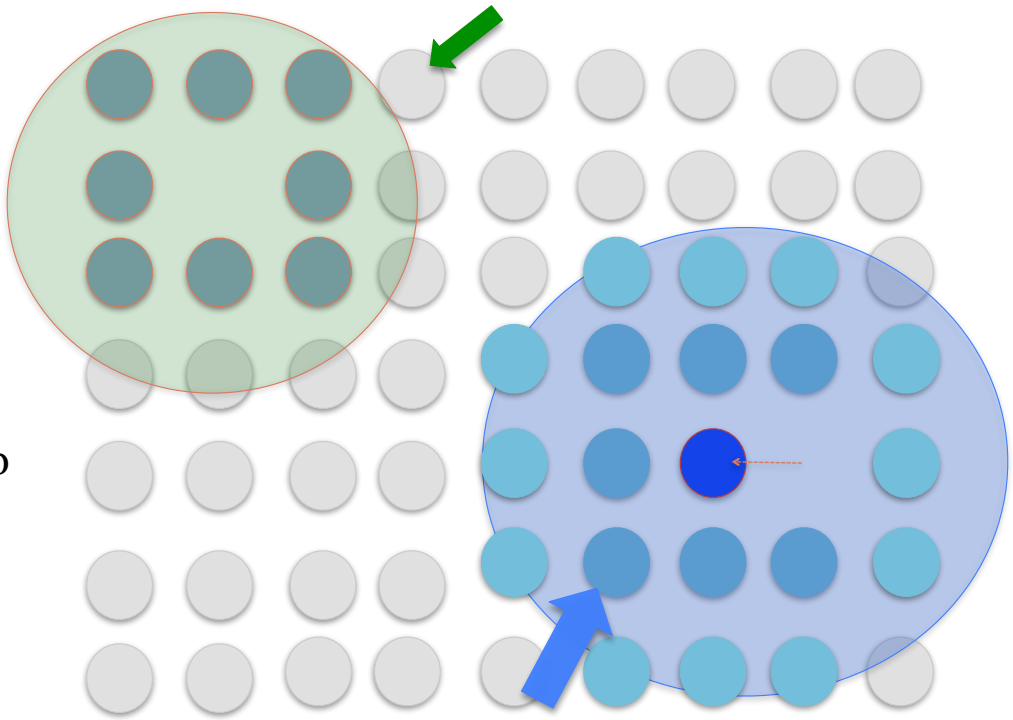
Towards large scale systems

- Local force computation
- Verlet neighbor lists
- Cell lists



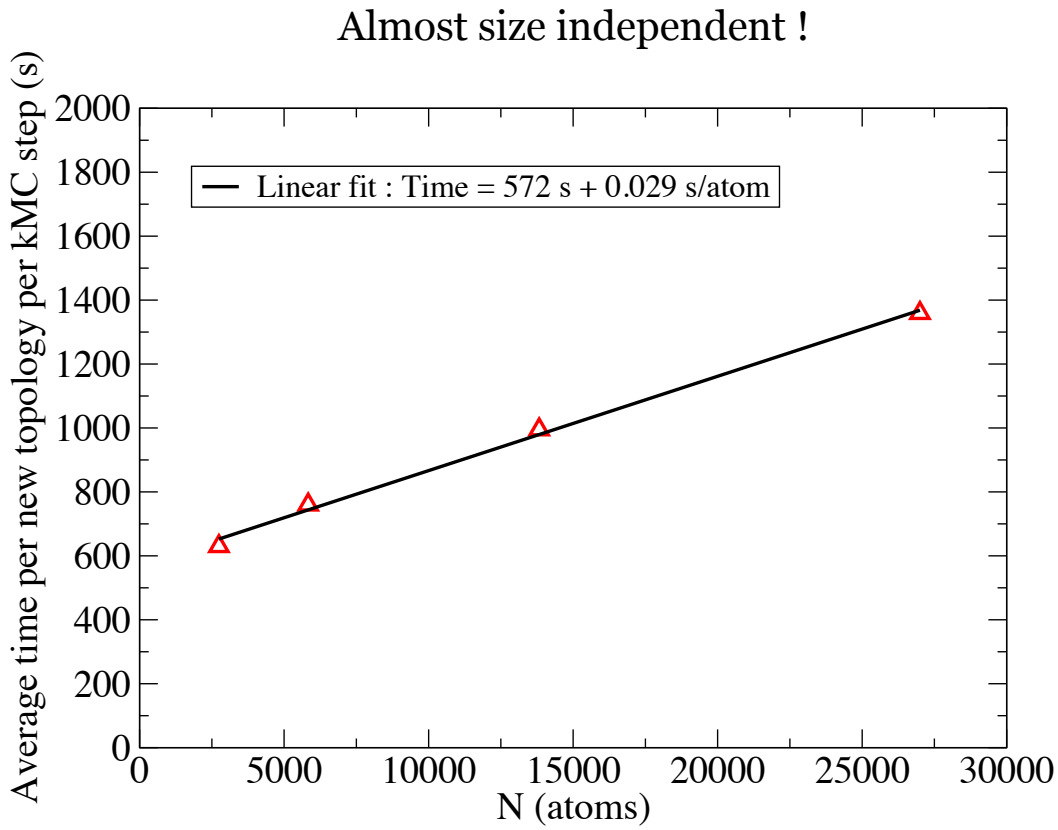
Reusing specific events

- After each kMC step, keep events specific to atoms that have not changed topology.
- Each atom has its own event list
- If an event is in the top 99.9 % of the CDF, reconverge the saddle.



Benchmarking

Almost size independent !



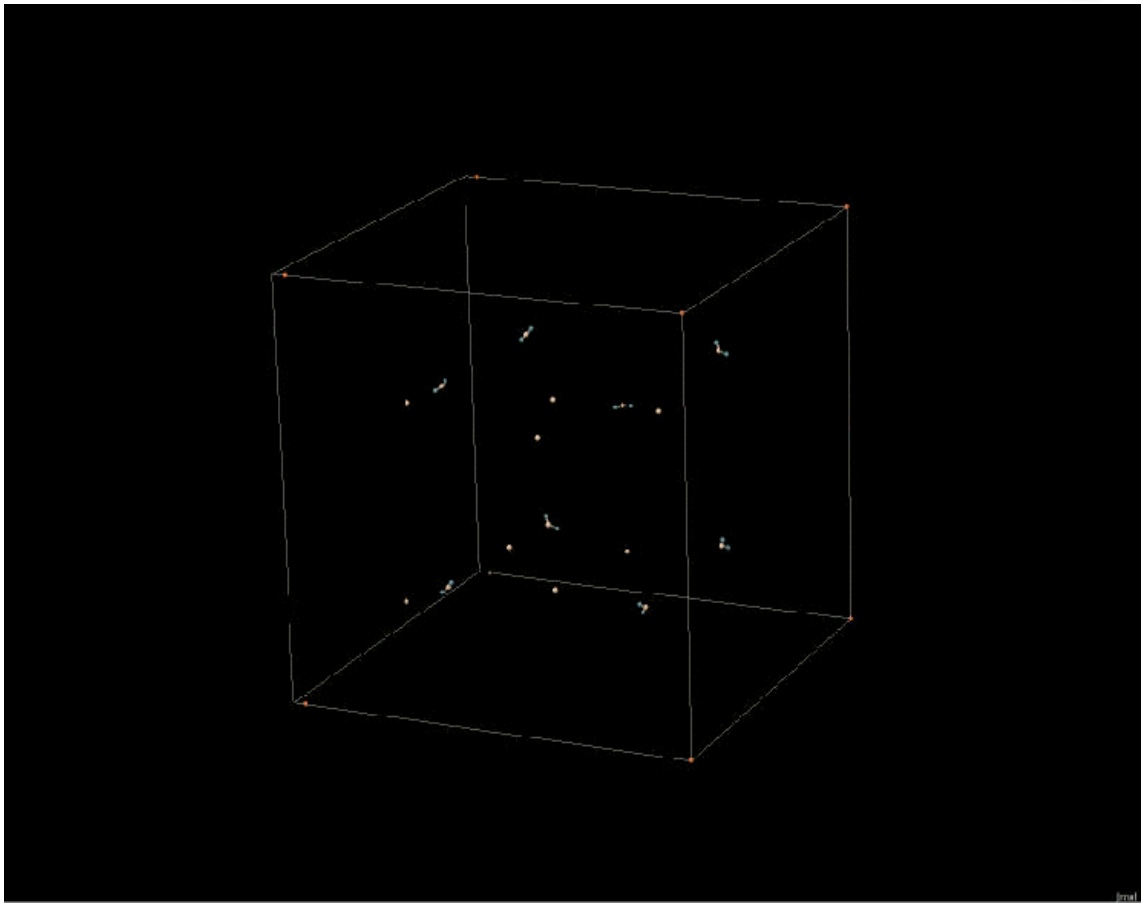
Simulation

27000 atoms
16 defects

« Interstitials » in blue

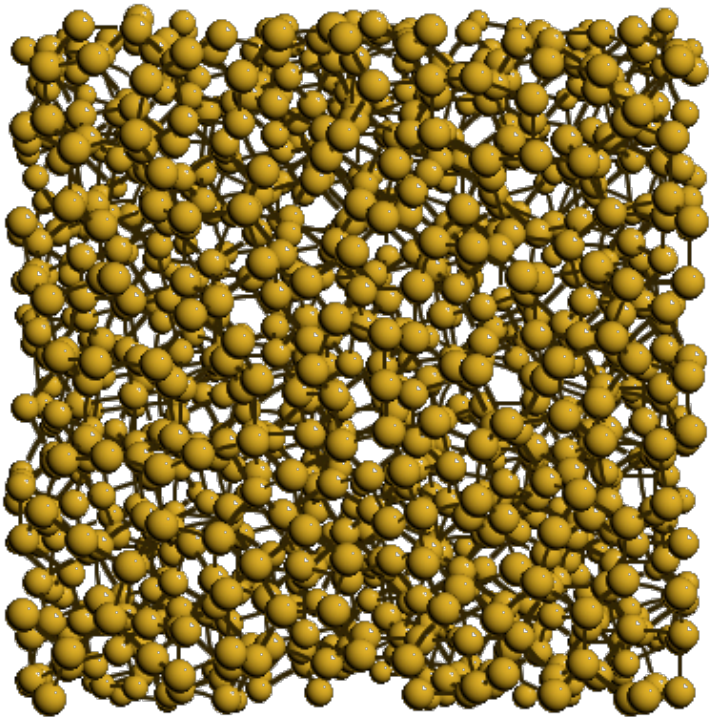
« vacancies » in yellow

A dumbell interstitial is represented as two interstitials and a vacancy



Application to amorphous silicon

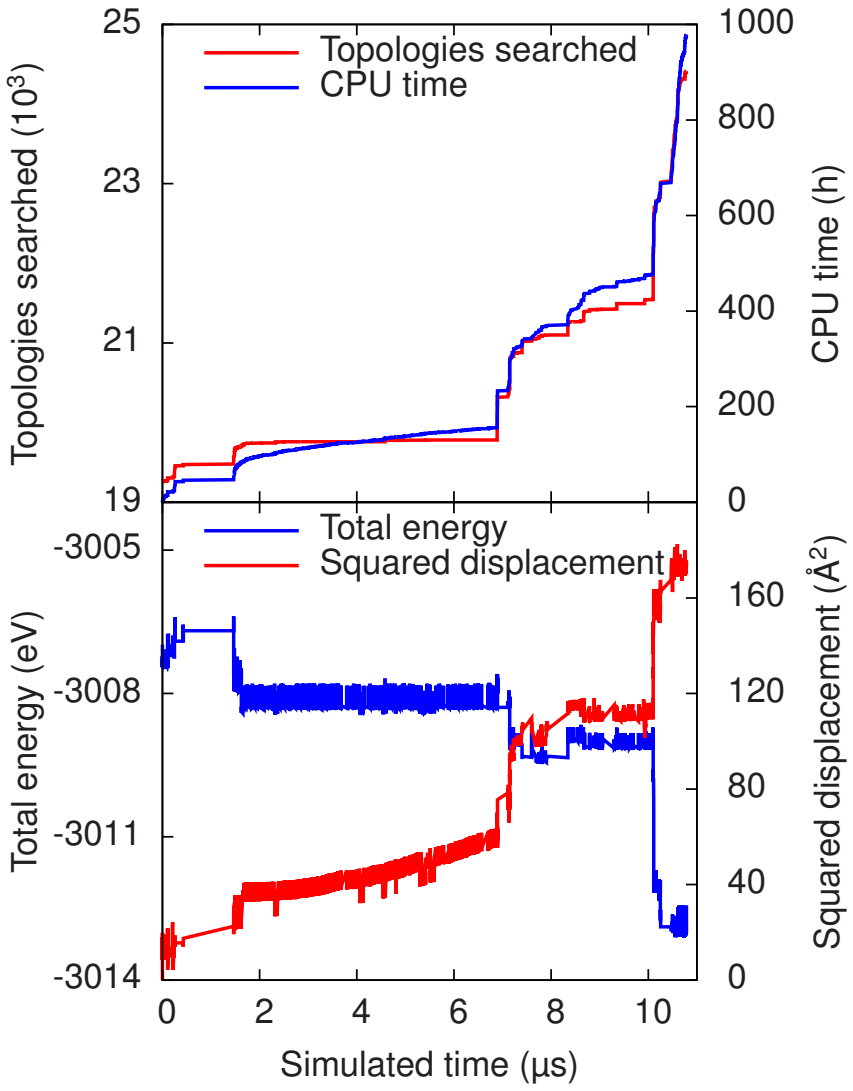
1. What is the relation between average coordination (i.e. defects) and relaxation?
2. How do defects move?
3. No accelerated technique has been applied to these disordered materials



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

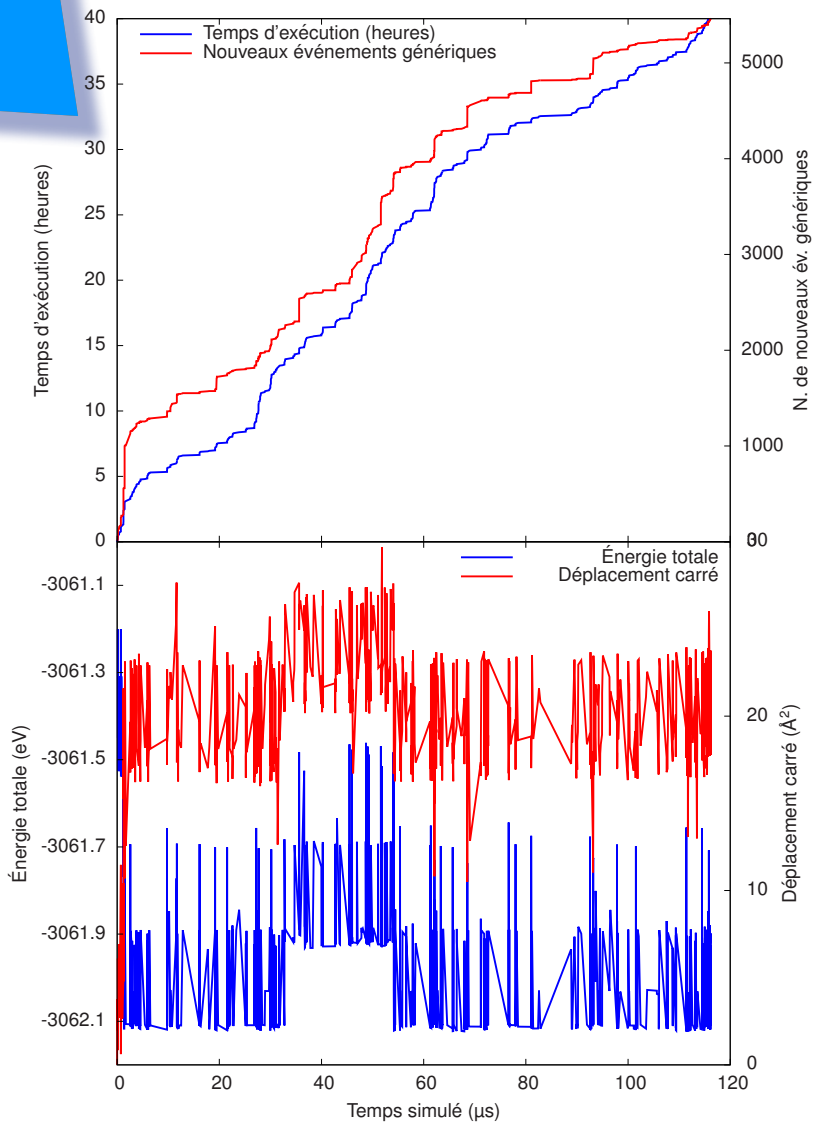
Initial catalog: 32 120 events

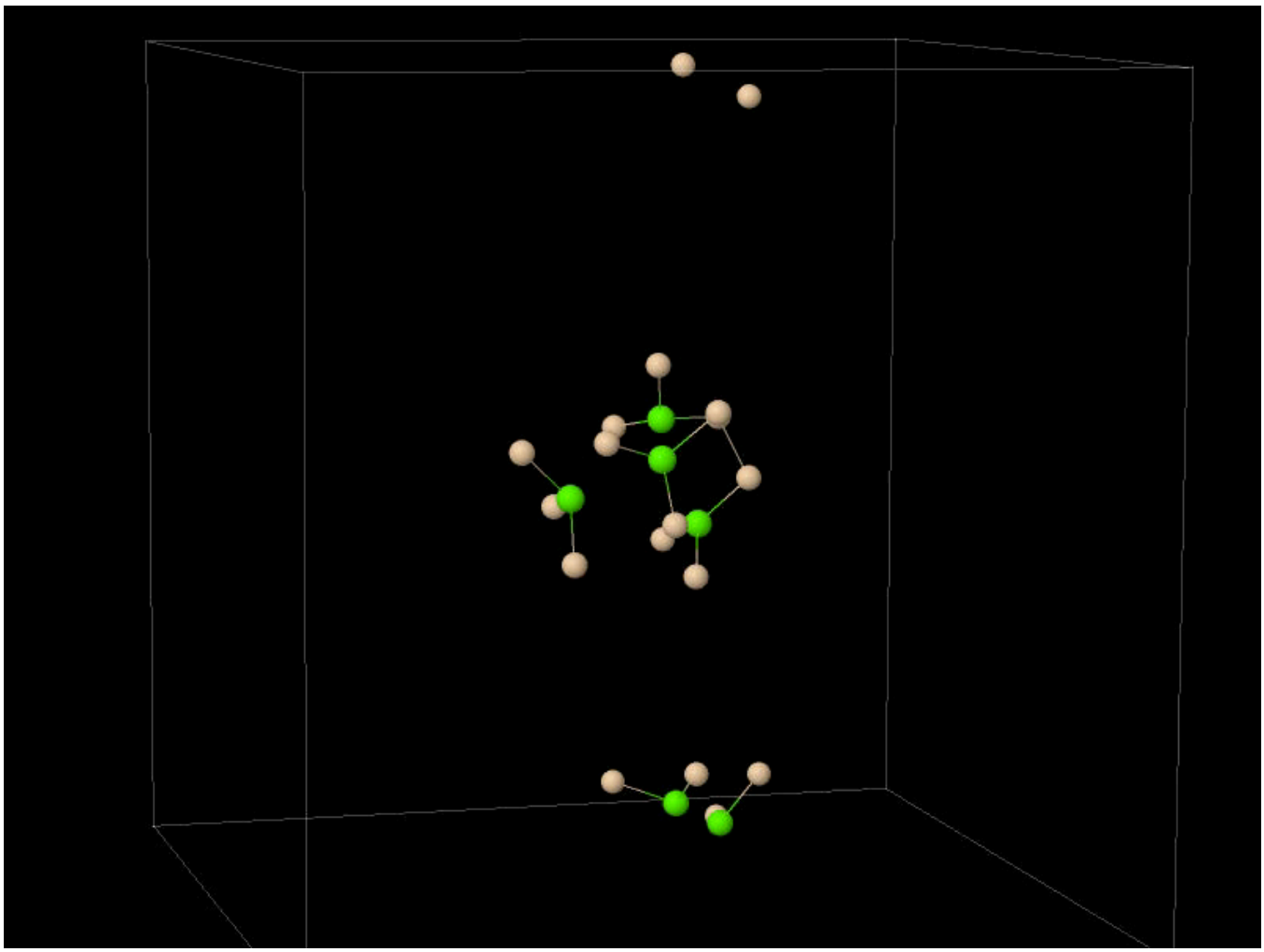
E_{basin} = 0,45 eV

24 processors (Intel Westmere-EP).

Most vacancies disapear within 1 ns

Here, vacancy survives after 120 µs





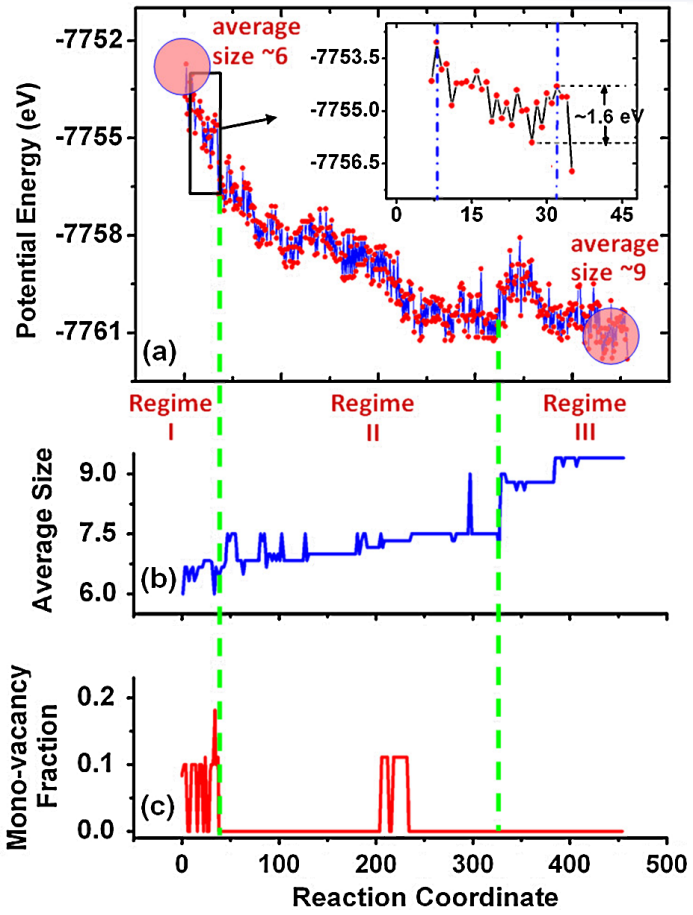
Vacancies in Iron

Fan, Kushima, Yip and Yildiz

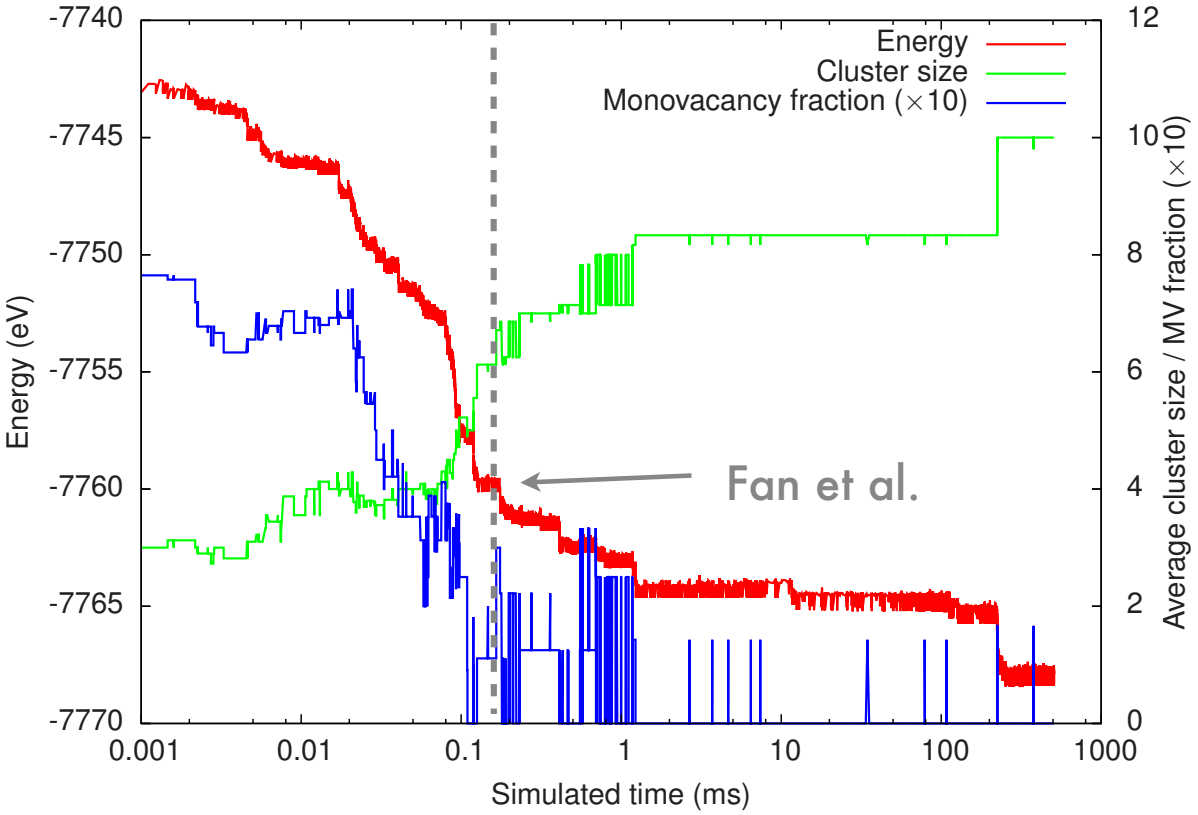
Nanovoid (10-15 vacancies) formation time scale: 20 000 seconds

using KMC + Autonomous climbing basin method

Is it right??

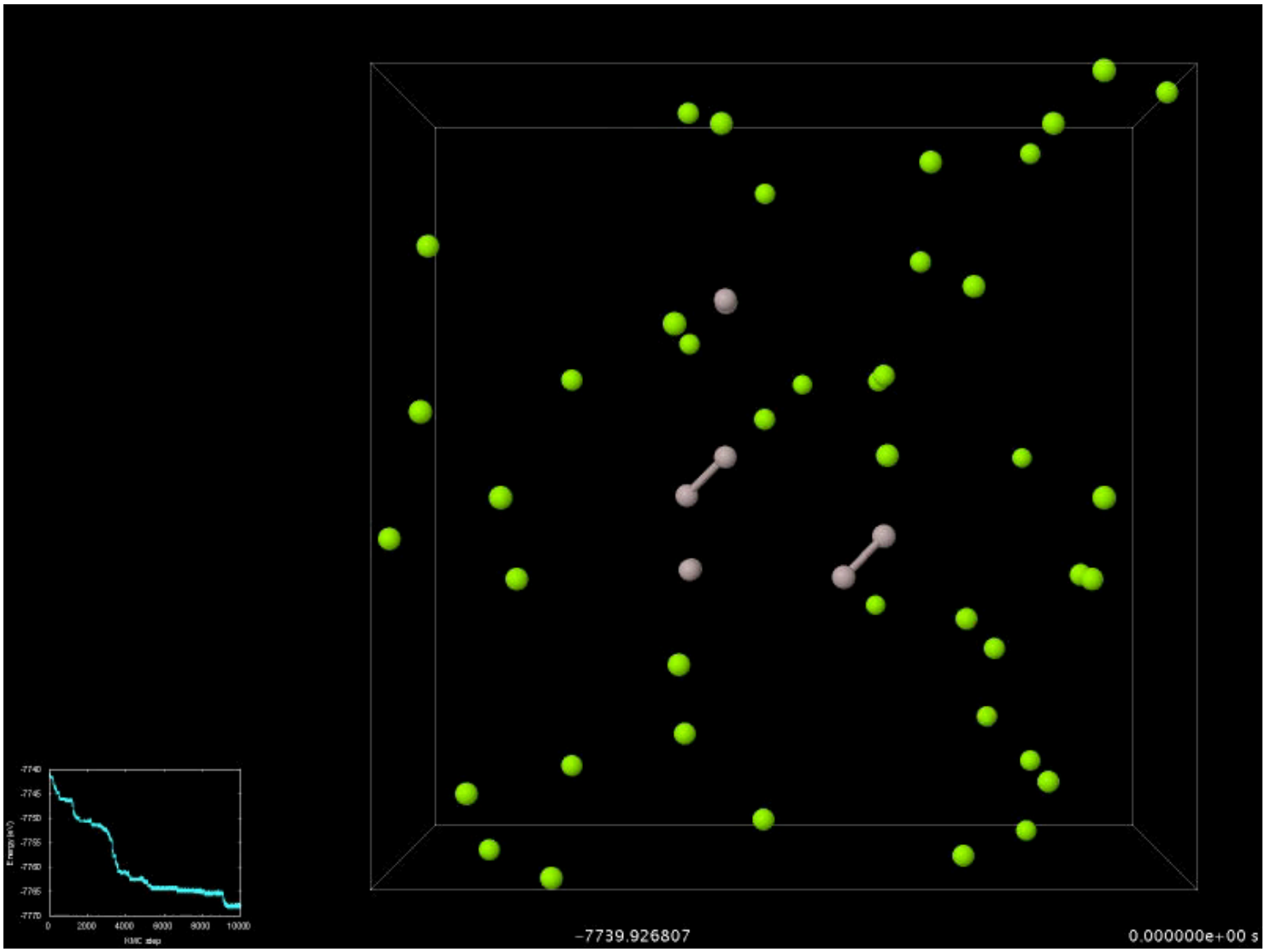


Vacancies in Iron

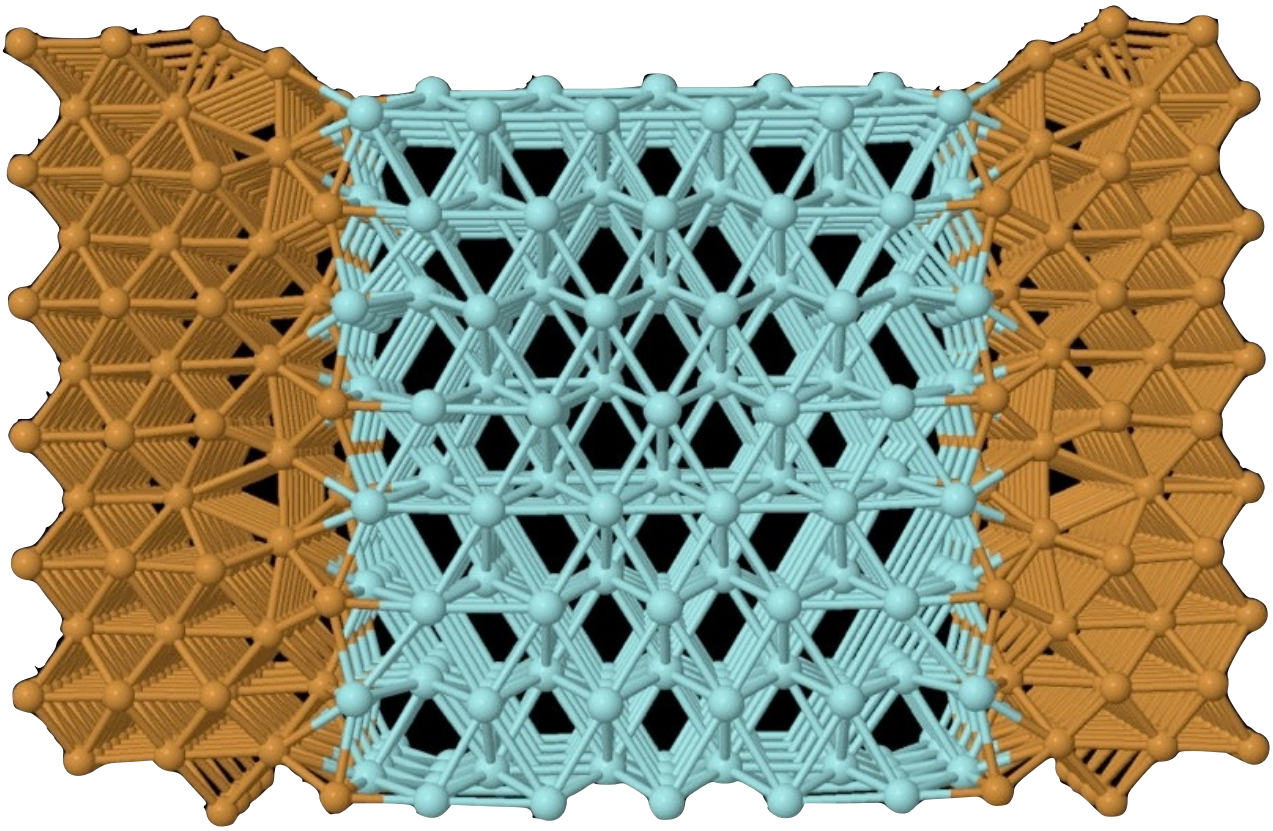


50 randomly placed vacancies in 2000-atom box; Mendeleev Potential.

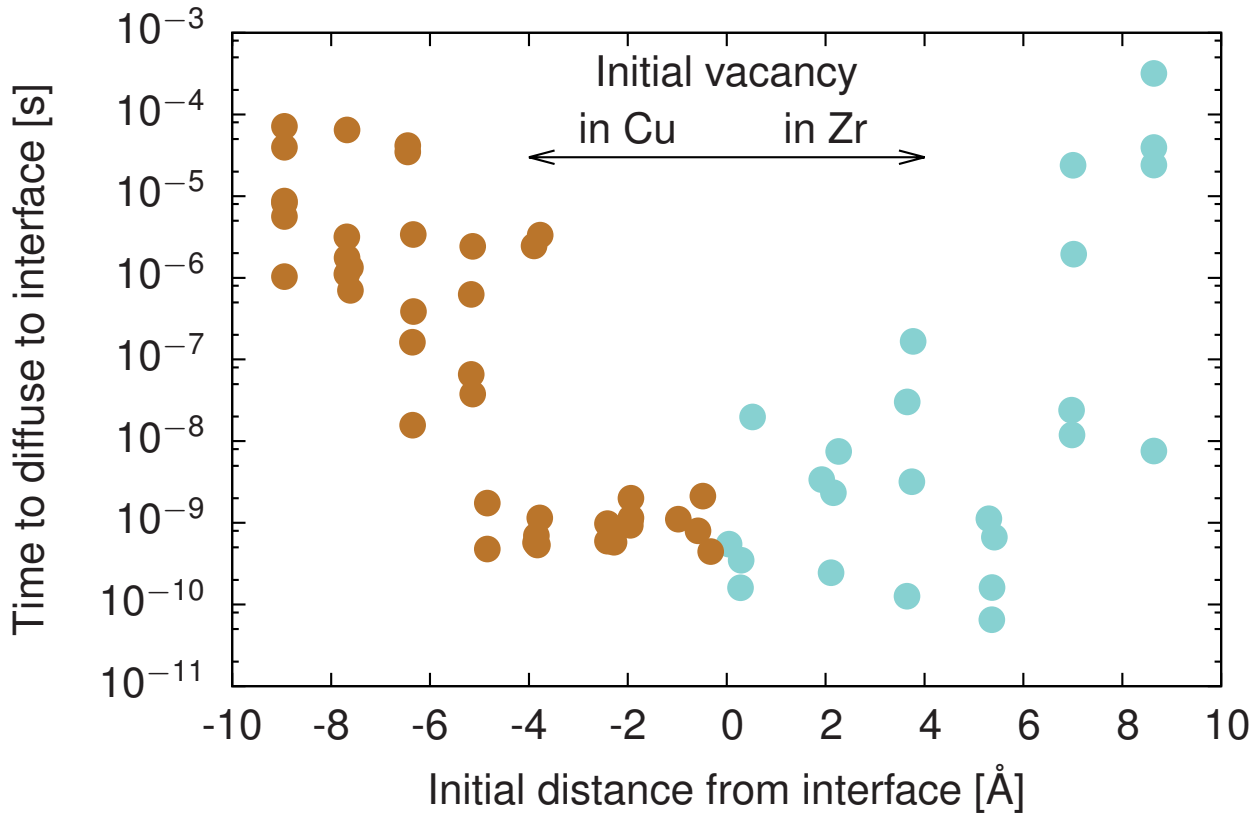
Peter Brommer and NM


-7740
-7745
-7750
-7755
-7760
-7765
-7770
0
2000
4000
6000
8000
10000
HMC step
-7739.926807
0.000000e+00 s

Vacancy at the CuZr interface



Vacancy at the CuZr interface



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

- Kinetic ART should be 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 the type of barriers evolves with time — self-organisation and aggregation phenomena
- A number of details make the method efficient:
  - parallelization
  - recycling of low-energy barriers
  - handling of highly symmetric events
  - handling of blinkers

THANK YOU